Interface structure and strength in model dental resin composites

Nielsen, Mette Skovgaard; Sørensen, Bent F.; Almdal, Kristoffer

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Interface structure and strength in model dental resin composites

Mette Skovgaard Nielsen

DentoFit A/S

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DTU Nanotech, Technical University of Denmark

December 2010

Preface

This thesis entitled “Interface structure and strength in model dental resin composites” was prepared to meet the requirements for receiving the Ph.D. degree at the Technical University of Denmark. The thesis represents the work carried out at DentoFit A/S and DTU Nanotech from January 2008 to December 2010. The work included a one month visit at YKI, Institute for Surface Chemistry in Stockholm, Sweden in April and May 2010 and one week at INM, Leibniz Institut für Neue Materialien in Saarbrücken, Germany. The work in this thesis was financed by DentoFit A/S and is a part of the DentoFit research program in developing a low shrinkage dental resin composite based on an expandable ceramic filler. The hypothesis is that the expansion of the filler is able to counteract the polymerization shrinkage of the polymer matrix.

I would like to thank my supervisors professor Kristoffer Almdal and Dr. Bent F. Sørensen for their direction and support throughout the project. I also want to thank present and former colleagues at DentoFit A/S especially Anne Højer Christensen, Mads Gudik-Sørensen and Tom Weidner for useful discussions, technical support and understanding. The employees at Risø DTU and DTU Nanotech are thanked for technical support and good discussions.

Robert Drum at INM is thanked for good collaboration.

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A special thank to my family and friends for patiently listening and cheering me up, and especially to Anton for his positivity and for always believing in me.

Risø, December 2010

Mette Skovgaard Nielsen

Summery

Most composites for dental restoration are based on a methacrylate polymer matrix and a ceramic filler, often silanized silica or silicate glasses. A problem with these composites is the polymerization shrinkage, which causes the filling to loosen from the tooth under formation of a crack. This will facilitate discoloration by colorants from e.g. coffee and red wine entering the crack, or even worse lead to secondary caries and infection of dental pulp due to bacteria. The aim of this study was to develop a low shrinkage dental composite based on an expandable metastable zirconia filler

A metastable zirconia filler has been developed, which is able to expand in the cured polymer matrix upon water diffusion from saliva and dentin to the filler particles. The tetragonal zirconia will upon exposure to water transform to the monoclinic phase, which has a larger specific volume. This expansion counteracts the polymer shrinkage and reduces the overall shrinkage of the composite. In this thesis the zirconia filler is characterized and tested for the potential as a filler for use in dental composites.

The zirconia powder is composed of highly agglomerated particles of nanosized crystals. The average particle size is 1.5-2 µm and the crystal size is ~6 nm. These crystals are so water sensitive that 65 vol% phase transforms to the monoclinic phase as a result of exposure to the humidity in the air and 84 vol% transforms upon exposure to water. This transformation is very fast and it is impossible to measure the transformation rate with x-ray diffraction. Other molecules are also able to initiate the phase transformation; these are HCl, NH_3, HF, and HBr. Photoacid generators releasing HCl, was tested for their ability to initiate the phase transformation in zirconia crystals imbedded in a dimethacrylate polymer matrix upon radiation with blue light. After 30 min light exposure a monoclinic volume fraction of 0.6 was observed, when using 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine as the photoacid generator.

Surface modification is very important in order to obtain a dental composite with good mechanical properties and high resistance towards hydrolysis. Due to their stabilizing effect on the tetragonal phase, it was, however, not possible to modify the filler surface with silanes or phosphate, which are the most commonly used surfactants in dentistry, and simultaneously preserve the ability to phase transform. Instead it was found possible to bind 3-(acryloyloxy)-2-hydroxy-propyl methacrylate to the surface by reaction with surface carbonates. In this way it might be possible to increase the wetability of the surface and hence increase the mechanical adhesion between polymer matrix and the filler. Reaction between the OH-group of the surfactant and the carbonate furthermore increases the reactivity of the zirconia. This increased reactivity originates from an inhibition of the competing reaction between the surface bound carbonates and water molecules.

As zirconia has a higher refractive index than the polymer matrix, a large particle size will result in a very opaque material. To improve the esthetics of the composite a low particle size of the filler is necessary in order prevent the particles from scattering light. For this reason a particle size below 40-60 nm is desirable. Different deagglomeration methods were tested and it was found possible to deagglomerate almost to the primary crystals with ball milling, but this method causes the zirconia to undergo phase transformation initiated by

shear stresses. Instead ultrasonication was tested and it was found possible to deagglomerate the particles to 300-400 nm without any phase transformation.

Finally the ability of the filler to counteract the polymerization shrinkage was investigated. In this test the phase transformation was initiated by water diffusing in to the composite during water storage at 40˚C. The composite was found to have a monoclinic volume fraction, v_m, of 0.5 after 8 h of water storage. The overall shrinkage of the composites was found to reduce from 3.2 % (initially) to 1.7% (14 days in water).

Danish Summery/ Dansk Resumé

De fleste kompositter til tandfyldninger er baseret på en methacrylat matrix og keramiske fillere, ofte silaniseret silica eller silikat glas. Et problem med disse kompositter er polymerisation skrumpet, der kan forårsage at fyldningen løsner fra tanden under dannelse af en spalte. Spaltedannelse kan resultere i misfarvning eller endnu værre i sekundære caries og infektion af tandroden. Dette tilskrives indsivning af bakterier og farvestoffer fra f.eks. kaffe og rødvin. Formålet med denne afhandling var at udvikle en lavt skrumpende plastkomposit baseret på en metastable zirconia filler, der kan ekspandere.

En metastabil zirconia filler er blevet udviklet. Denne er i stand til at expandere i den hærdede polymermatrix ved diffusion af vand fra spyt og dentin til filler partiklerne. Tetragonal zirconia vil efter eksponering til vand fasetransformere til den monokline fase, som har et større specifik volumen. Denne ekspansion modvirker polymerisationsskrumpet og reducerer det samlede skrump af kompositten. I denne afhandling er zirconia filleren karakteriseret og testet for sit potentiale som filler til fyldningsmaterialer.

Zirconiapulveret består af agglomererede partikler af nano-krystaller. Den gennemsnitlige partikelstørrelse er 1,5-2 µm med en krystalstørrelse på ~6 nm. Disse krystaller er så vandfølsomme, at 65 vol% fasetransformerer til den monokline fase som følge af eksponering til luftens fugtighed og 84 vol% transformerer efter eksponering til vand. Denne transformation er meget hurtig, og det er i praksis umuligt at måle transformationshastigheden med røntgendiffraktion. Også andre molekyler kan initiere fasetransformationen, disse er HCl, NH_3, HF og HBr. Fotosyre generatorer, der frigiver HCl, blev testet for deres evne til at initiere fase transformation i zirconia krystaller i en dimethacrylat polymer matrix ved belysning med blåt lys. Efter 30 min eksponeringstid blev der observeret en monoklin volumenfraktion på 0,6, når 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine anvendes som fotosyre generator.

Overflademodificering er meget vigtigt for at opnå en komposit med gode mekaniske egenskaber og stor modstand mod hydrolyse. Det var imidlertid ikke muligt at behandle overfladen af filleren med silaner eller phosphater, som er nogle af de mest almindeligt anvendte koblingsagenter i tandplejen, pga. deres stabiliserende virkning på den tetragonale fase. I stedet konstateredes det muligt at binde 3-(acryloyloxy) -2-hydroxy-propyl methacrylat til overfladen ved reaktion med karbonater på overfladen. På denne måde er det potentielt muligt at øge dispergeringsevnen af partiklerne og dermed øge den mekaniske adhæsion mellem polymer matrix og filleren. Desuden øger denne reaktion mellem OH-gruppen i det overfladeaktive stof, og karbonat reaktiviteten af zirconia, ved at begrænse den konkurrerende reaktion mellem karbonater og vand molekyler.

Da zirconia har et højere brydningsindeks end polymermatricen vil en stor partikel størrelse resultere i et meget uigennemskinneligt materiale. For at forbedre æstetikken af kompositten er en lav partikelstørrelsen nødvendig, da dette vil forhindre partiklerne i at sprede lyset. Af denne grund er en partikelstørrelse under 40-60 nm ønskelig. Forskellige neddelingsmetoder blev testet og det blev konstateret muligt at deagglomerere næsten til de primære krystaller med kuglemølleformaling. Denne metode medførte desværre at

zirconiakrystallerne fasetransformerede som et resultat af tværspændinger. I stedet blev ultralydsdispergering testet og det blev konstateret muligt at deagglomerere partiklerne ned til 300-400 nm uden nogen fase transformation.

Endelig blev fillerens evne til at modvirke polymerisationsskrump undersøgt. I denne test blev fasetransformation initieret af vand, der diffunderede ind i kompositten under opbevaring i 40˚C varmt vand. Kompositten havde en monoklin volumenfraktion på 0,5 efter 8 timers opbevaring i vand. Det samlede skrump af kompositten reduceredes fra 3,2% (oprindeligt) til 1,7% (14 dage i vand).

List of publications

This thesis is based on the following papers and patents, which are referred to in the text by their roman numerals. The publications can be found in appendix I through IX.

I. Skovgaard, M., Almdal, K. and van Lelieveld, A. (2010). Phase stabilizing effects of phosphates and sulfates on nanocrystalline metastable tetragonal zirconia, J Mater Sci, **45**(22):6271-6274.

II. Skovgaard, M., Almdal, K. and van Lelieveld, A. Inhibition of surface bound carbonate stabilization of tetragonal zirconia, submitted to J Mater Sci on November 29th.

III. Nielsen, M.S. and Van Lelieveld, A. (2010) Dental filling material, useful in dentistry, comprises filler comprising metastable zirconia particles with surface functionalities, in a tetragonal and/or cubic crystalline phase, and a polymerizable resin base. WO2010049522-A2.

IV. Skovgaard, M., Ahniyaz, A., Sørensen, B.F., Almdal, K. and van Lelieveld, A. (2010). Effect of microscale shear stresses on the martensitic phase transformation of nanocrystalline tetragonal zirconia powders, J Eur Ceram Soc, **30**:2749-2755.

V. Skovgaard, M., Almdal, K. and van Lelieveld, A. Light activated phase transformation of metastable tetragonal nanocrystalline zirconia, submitted to J Mater Sci on October 25th.

VI. Van Lelieveld, A., Nielsen, M.S., Almdal, K. and Linderoth, S. (2007) Composite material, useful as dental filling material and for reconstruction of tooth, comprises a filler, a polymerizable resin base, and further water- or acid- releasing agents. WO2007104312-A2; WO2007104312-A3; EP1996144-A2; US2010016465-A1.

VII. Skovgaard, M., Almdal, K., Sørensen, B. F., Linderoth, S. and van Lelieveld, A. Shrinkage reduction of dental composites by addition of an expandable zirconia filler, submitted to J Compos Mater on September 21th.

VIII. Skovgaard, M., Almdal, K. and van Lelieveld, A. Stabilization of metastable tetragonal zirconia nanocrystallites by surface modification, accepted by J Mater Sci.

IX. Skovgaard, M., Stibius, K. B., Sørensen, B. F., Almdal, K. and Negra M. D. Experimental characterization of edges effects in simple adhesion tests, submitted to Int J Adhes Adhes on November 17th.

Paper not included:

X. Goutianos, S., De Souzab, J. A., Skovgaard, M. and Sørensen, B. F. Fracture resistance curves and toughening mechanisms in polymer based dental composites, submitted to J. Mech. Behav. Biomed. Mater in November.

Table of contents

1 Introduction

1.1 Reader instructions

The way to read this thesis is to read the introduction in the beginning of the chapter and then read the associated publications found in the appendixes. After reading the introduction and the associated papers, read the rest of the chapter. For a fast overview; read the introduction in each chapter and proceed to the summery in the end of the chapter. The summery summarizes both the chapter and the publications.

1.2 Dental composites; composition, properties and use

Dental restorations have been known for a long time. Amalgam filling was first reported in china in year 650, but has 'only' been used in Europe and North America for the last ~150 years. These were made of mercury containing materials that are now unwanted due to their environmental effects. The use of amalgam for dental fillings was forbidden in Denmark in 1995, with the exception of fillings in molar teeth, which are exposed to wear. At the moment the only realistic substitute for amalgam is resin composites[1].

The first resin composites were marketed in the 1950's but because of their tendency to discoloration, low resistance to abrasion and high tendency to crack formation, the composites were not very attractive from a practical point of view. In the 60's these materials were improved - especially due to the development of dimethacrylates, and for close to 50 years resin composites have been used as restorative materials to replace missing tooth structure. In the last 15-20 years, resin composites have been the most commonly used dental restorative material. Only in posterior teeth, where esthetics plays little or no role, silver amalgam is still the preferred materials[2].

The term composite refers to a material composed of at least two different phases. In the case of composite restoratives these phases are a filler and a monomer matrix (Figure 1).

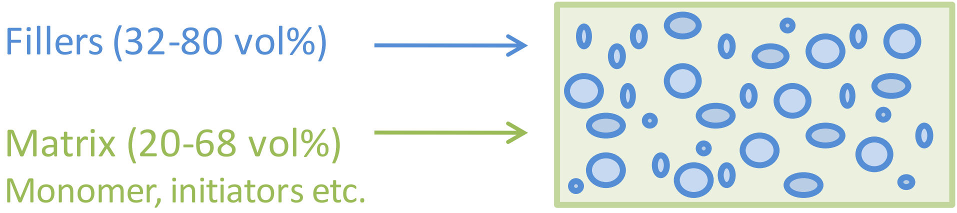


Figure 1 Composition of resin composite restorative materials. The dark blue line around the filler particles symbolizes the coupling agent

The composites can be divided in different categories; hybrid, microfilled and nanofilled composites based on the filler volume fraction and on the size of the filler particles. The characteristics of these categories are listed in Table 1.

Table 1 Characteristics of resin composites[2,3]

Composite type	*Filler size (μm)*	*Volume of filler (%)*	*Handling characteristics and properties*
Nanofilled	0.002-0.075	78.5	High polish, strength and modulus
Hybrid	0.04, 0.2-3.0	60-70	High strength and modulus
Microfilled	0.04-50	32-50	Best polish and esthetics. High shrinkage
Packable microfilled	0.04, 0.4-20	80	Packable, low shrinkage and lower wear
Flowable	0.04, 0.2-3.0	42-62	Syringeable, lower modulus. High wear

Dental resin composites are composed of four important components; an organic polymer matrix, inorganic filler particles, a coupling agent and a light activated initiator/accelerator system. These components are described in section 1.2.1 to 1.2.3.

1.2.1 Monomers

In general, the most optimum combination of monomers to archive composites with the best properties, such as high flexural strength, low watersorbtion and solubility is obtained with methacrylic acid esters called methacrylates. These methacrylates can be obtained with high purity and widely varying structures by relatively simple technical means. Moreover methacrylates demonstrate lower toxicity than acrylates. For this reason most dental resin composites are based on methacrylate chemistry[4,5].

The most important monomers in dental restorative materials are dimethacrylates and some of the most common monomers are represented in Figure 2. The polymerization of these monomers occurs by free-radical polymerization initiated by the photoinitiator system described in Chapter 1.2.3. The viscosities of the two most commonly used monomers, bisphenol A glycidyl methacrylate (Bis-GMA) and Diurethane dimethacrylate (UDMA), are so high that dilution with monomers such as triethylene glycol dimethacrylate (TEGDMA) is necessary to enable compounding of the monomer with sufficient amounts of filler. TEGDMA has a lower molecular weight and its amount should be limited since high amounts will increase the polymerization shrinkage and hydrophilicity of the composite[3].

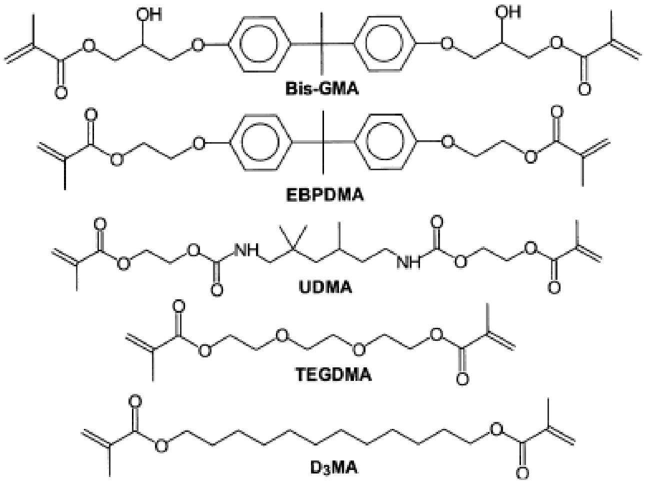


Figure 2 Common monomers for dental resin composites[6]

1.2.2 Fillers and coupling agents

Most composites contain fillers in the form of amorphous silica, Ba-, Sr-, and Zr containing glass, quartz or zirconia particles. The particle sizes vary from 0.002-50 µm. Ba-, Sr-, and Zr containing glass particles are added to increase the radiopacity of the composite. Radiopacity can be useful in resin composites as it makes it possible to distinguish between composite and tooth with x-ray imaging[2,3].

A strong interface between polymer matrix and filler surface is expected to increase the strength of polymeric dental composites. Furthermore, wetting of the filler surface with resin is enhanced by surface modification and consequently the possible filler load in the composite is increased. The resin is normally bonded to the filler surface with a difunctional coupling agent capable of creating a strong bond between the filler surface and the polymer matrix. To get high hydrolysis resistance, the coupling agent should bind the surface either covalently or make strong ionic bonds. For resin composites the functional group is a methacrylate, which is able to react with the methacrylate matrix by copolymerization. Sufficient surface modification of the filler is normally considered vital for achieving high interface strength. This coupling agent also has the function of increasing the water resistance of the polymer/zirconia interface, since surface modification reduces the accessibility of water to the interface and thereby decreases hydrolytic degradation and discoloring of the interface[7]. Hydrolysis of the interface will strongly affect the strength of the composite; this is illustrated in Figure 3. Figure 3b) shows the case with an unsilanized filler; here the interface is hydrolyzed and the crack follows the matrix/filler interface. As no chemical bond exists in the interface, the interface is weaker than the polymer matrix. This will result in a lowering of the fracture resistance. In c) the filler surface is silanized and the interface will be less subjected to hydrolysis. The lower level of hydrolysis will give a composite with higher fracture resistance, as the crack has to go through the polymer matrix.

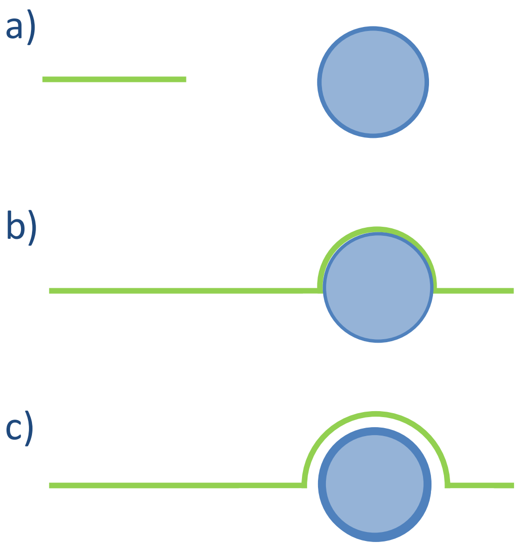


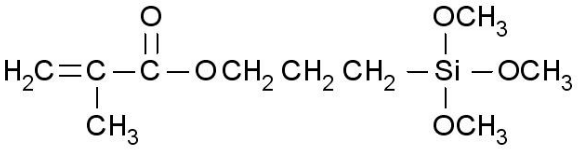
Figure 3 Effect of surface modification on the fracture mechanics of resin composite. The green line symbolizes the crack. (a) Before the crack reaches the filler particle and fracturing of a water stored composite with (b) unsilanized filler and (c) silanized filler (the thick blue line symbolizes the silane layer)

A number of different types of coupling agents are commonly used in dentistry. The most common surfactants in polymer based dental composites are trifunctional silanes ($R'Si(OR)_3$), where R is either $-CH_3$ or $-CH_2CH_3$. The alkoxysilane groups are able to react with OH-groups on silica surfaces and intramolecularly forming covalent bonds. The mechanism proposed by Plueddman[8] is the following:

$$R'Si(OR)_3 + HO\text{-}Si\equiv \rightarrow R'Si(OR)_2OSi\equiv + ROH \tag{1}$$

The OR groups are readily hydrolyzed by reaction with water under formation of $R'Si(OH)_3$. After hydrolysis of the methoxy groups, silanes are able to react with each other under formation of a multilayered interphase. A rule of thumb is that a triple layer of silane is the most optimal for resin composites. When this average is reached the entire surface is expected to be covered.

The most commonly used coupling agent in dental resin composites is γ-methacryloxypropyl trimethoxy silane (MPTMS), which not only increases the strength properties of the composite material but also increases the water resistance of the interface[9]. However, MPTMS is not considered being a good choice of surfactant for zirconia surfaces since the Zr-O-Si bond is not as stable towards hydrolysis as the silicon counterpart, siloxanes and it has been reported that silanes are not always able to bind to zirconia[10]. Several studies have showed that methacrylate-decyl dihydrogenphosphate (MDP) is a better coupling agent than MPTMS for zirconia systems[11,12,13].



$$H_2C=\underset{\displaystyle CH_3}{\underset{|}{C}}-\overset{\displaystyle O}{\overset{||}{C}}-OCH_2\,CH_2\,CH_2-\overset{\displaystyle OCH_3}{\overset{|}{\underset{\displaystyle OCH_3}{\underset{|}{Si}}}}-OCH_3$$

Figure 4 γ-methacryloxypropyl trimethoxy silane (MPTMS)

In this thesis, a wide range of surfactants have been tested to improve the filler surface properties – with the big challenge of achieving this without reducing the ability of the crystals to undergo a phase transformation later.

1.2.3 Initiators and inhibitors

Photoinitiation is very common in dentistry as the degree of conversion with photoinitiation ranges from 65 to 80 %, but only from 60 to 75 % with chemical initiation[14]. The most popular initiator system is a combination of camphorquinone (CQ) and a tertiary amine such as ethyl 4-dimethylamino benzoate (DABE). Camphorquinone is a yellowish substance, which absorbs visible light in the wave length range of 400-500 nm ($\lambda_{max} \approx 465$). Addition of CQ gives the composite a slight yellow tint, which disappears or faints during cure[3]. DABE is added to accelerate the radical formation from CQ and acts as co-initiator or accelerator. The radical formation occurs when the carbonyl groups of CQ are activated by light. In this process an intermediate is formed, which abstracts one H atom from DABE. The formed α-amino alkyl radical initiates the polymerization reaction (Figure 5). The used amounts of CQ and DABE ranges from 0.2 to 0.3 % by mass of the monomer matrix[2,3].

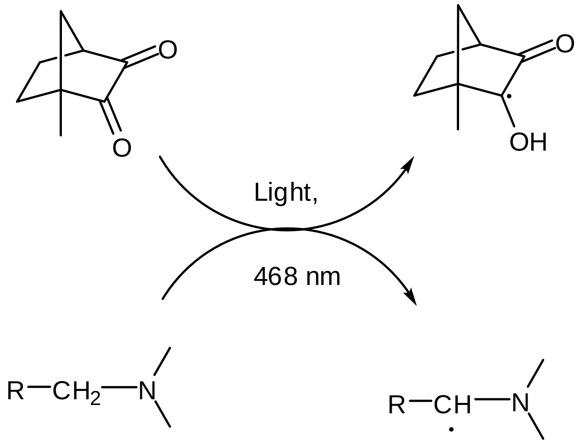


Figure 5 Reaction of camphorquinone by exposure to blue light.

Inhibitors are added to all monomers as these have a tendency to spontaneously polymerize. These inhibitors are often phenols such as hydroquinone monomethyl ether. These aerobic inhibitors interact with oxygen and are only fully affective in the presence of oxygen. Oxygen from the atmosphere dissolves in the monomer matrix and prevents premature polymerization. During storage dissolved oxygen will be used up and the packing should allow diffusion of oxygen from the atmosphere to elongate shelf life. Inhibitors are added in range of 0.001-0.1 wt% of the monomer. Oxygen is able to react with the radical of polymer chain ends[2]:

$$\text{R-M-M-M-M}\bullet + O_2 \rightarrow \text{R-M-M-M-M-O-O}\bullet \qquad (2)$$

This is a chemical equilibrium, which is shifted to the right. The formed peroxy radical has a low reactivity and hence reduces the polymerization rate. These peroxy radicals can also react with the phenol inhibitors (ρ-OH)[2]:

$$\rho\text{-OH} + \text{R-M-M-M-M-O-O}\bullet \rightarrow \rho\text{-O}\bullet + \text{R-M-M-M-M-O-O-H} \qquad (3)$$

The formed radical, ρ-O•, is not able to initiate polymerization but can contribute to termination[2].

1.3 Durability of resin composite fillings

During the last couple of decades great effort has been spend on improving resin composites. Especially problems with polymerization shrinkage, water sorption, discoloring and abrasion have gained attention. After many years of research the abrasion of commercial composites is acceptable. This is a result of development of hybrid and nanofilled composites where the mean distance between the filler particles are lower than in microfilled composites. The smaller distance lowers the abrasion of the polymer matrix and reduces the loss of filler particles from the abraded composite surface[2]. Also silanization of the filler particles reduces the abrasion of the composite surface[15].

Internal discoloration is a darkening of the composite material as a result of oxidation processes. These are mainly observed in two-component systems because of the relatively high concentration of tertiary and aromatic amines. The amines will as a result of oxidation turn yellowish, reddish and brownish. After the development of the photoinitiator system internal discoloration of the filling is no longer a problem, as two-component composites are no longer used as filling material[2].

The polymerization shrinkage, however, has only been reduced, and can be minimized by the use of varies techniques. In large fillings however, the result is not always acceptable[2]. So optimization of the composites with regard to polymerization shrinkage is still needed in order to make better fillings and to ease the preparation techniques. In this thesis focus is on reduction of polymerization shrinkage.

1.3.1 Polymerization shrinkage in resin composite restoratives

Shrinkage is inherent in all resins. Most resin composites give a wall-to-wall contraction (linear strain)of 0.3-0.5 % and an overall volume contraction of 2-3 %[2]. This shrinkage creates polymerization stress as high as 13 MPa between the cavity walls and the composite filling. This stress severely strain the tooth/filling interface and will in a cavity cause the formation of cracks. The crack may result in loss of the filling, secondary caries, discoloration or even infection of the dental pulp and if the formed polymerization stress exceeds the tensile strength of the enamel, the stress can cause stress cracking and enamel fractures along the interface[2,3]. The crack formation is illustrated in Figure 6.

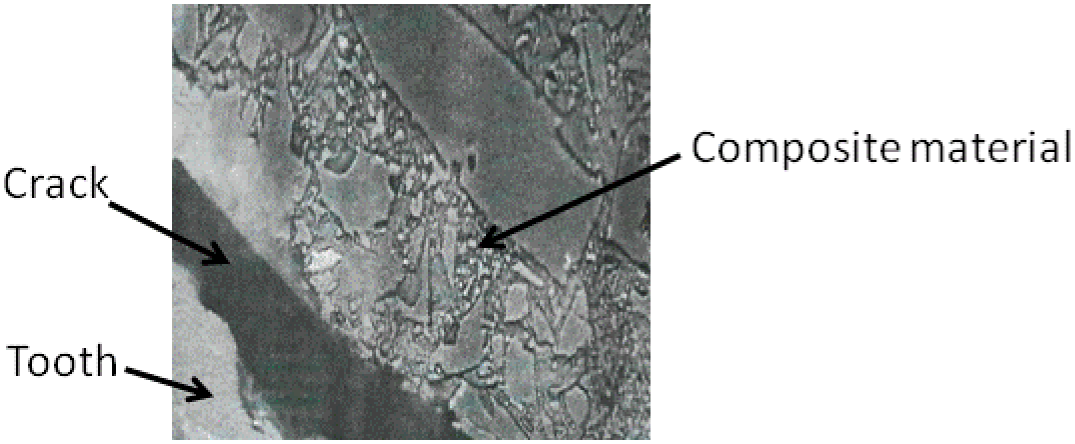


Figure 6 SEM picture of the formed crack between the tooth and the composite filling. The width of the crack is ~15 µm

Techniques to minimize crack formation involves building up the filling by inclined layers of composite and cure these layers separately[2]. This is, however, time consuming and the possibility to make complete bulk fillings in one operation is preferable for the dentist to reduce chair time. Bulk fillings set demands to the polymerization shrinkage as well as to the depth of cure of the composite. To prepare bulk fillings the light from the light probe should be able to penetrate all the way through the material. For this reason the opacity of the material is a crucial parameter.

1.3.2 Central hypothesis of this study

The chosen path to lower the composite contraction is to ad an expandable zirconia filler[16]. The working hypothesis is that the expantion of the filler in the cured or semicured organic matrix can counteract the overall polymerization shrinkage of the composite.

1.4 Zirconia in prosthetic dentistry

Ceramic materials are used in a wide range of dental applications, such as inlays, onlays, implants, crowns and fixed partial dentures, because of its biocompatibility, wear resistance and esthetics. They are, however, subject to brittle failure. Yttria stabilized zirconia (YSZ) is a durable and tough dental material, which has esthetical advantages over metals. Compared to other ceramics YSZ has superior strength and rising fracture resistance (R-curve behaviour)[17,18,19]. The mechanical properties of YSZ are mainly due to transformation toughening when loaded above the fracture resistance. The transformation toughening originates from stress induced tetragonal to monoclinic (t→m) phase transformation, which causes the zirconia to expand ~4 vol%[20].

Zirconia has attracted interest both as catalyst support and as catalyst in varies reactions such as isomerization of n-butane[21], synthesis of derivatives of 1,5-benzodiazepine and diaryl sulfoxides[22], and benzylation of toluene[23]. This is the reason the surface properties of zirconia have been intensively studied. High surface area[24] and thermal stability as well as controllable crystal size and density of OH-groups on the surface are desirable properties[25]. Control of surface area, crystal size and OH-density are also very important properties when a high activity of zirconia and easily initiated phase transformation is desired.

At room temperature (RT) and atmospheric pressure, the thermodynamic stable phase for pure zirconia is the monoclinic. As the temperature is raised, zirconia undergoes the following change in crystal phases:

$$\text{Monoclinic} \rightarrow \text{tetragonal} \rightarrow \text{cubic} \rightarrow \text{melt} \qquad (4)$$

At RT, a metastable tetragonal phase is often seen, but it easily transforms to the stable monoclinic phase. Ruff and Ebert first documented the existence of metastable tetragonal zirconia[26]. Since the discovery of metastable tetragonal zirconia the tetragonal to monoclinic phase transformation at RT has been studied intensively, due to the excellent mechanical properties of zirconia, which are associated with this phase transformation. The known triggers for this transformation are: Chemical reaction with e.g. water[27], annealing[28] and mechanical stress[29]. However, mostly the effect of water and humidity on the crystal phase has gained attention. Murase and Kato[30] found in 1979, that presence of water molecules on the zirconia surface caused phase transformation in metastable tetragonal zirconia crystals during milling. In contrast the tetragonal phase was stabile, when milled in water free argon atmosphere. Since then a number of publications concerning the effect of water on the phase stability of tetragonal zirconia at RT have been published. Different transformation mechanisms of the tetragonal phase have been proposed, ranging from hydrolysis of Zr-O-Zr bonds in the surface[31], water reacting with Y_2O_3 under formation of $Y(OH)_3$[32] to the most current perception; that the phase transformation is a result of reaction between OH^- and oxygen vacancies under formation of hydrogen defects in the crystal lattice[33,34].

The tetragonal phase is metastable at RT and atmospheric pressure and an activation barrier must be overcome before transformation from the tetragonal phase (high energy state) to the monoclinic phase (low energy state) can proceed. Thus, the phase transformation cannot proceed spontaneously (Figure 7).

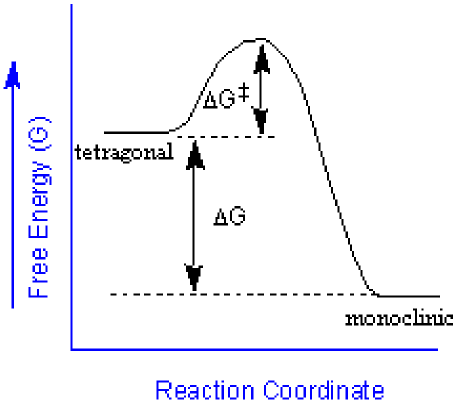


Figure 7 Free energy in tetragonal and monoclinic zirconia

The phase transformation is martensitic, which by definition means that the transformation is diffusionless[35] - the crystal structure needs no extra atoms to undergo the transformation. Thus, the transformation can be very fast, almost instantaneous and can be controlled. The transformation mechanism has to have a free energy high enough to overcome the activation energy needed to go from the metastable tetragonal phase to the stable monoclinic phase (see Figure 7).

1.5 Zirconia in dental composite restoratives

In the dental clinic zirconia ceramics is used in bridges, crowns, veneers, and for other applications where high strength and low solubility is crucial for the life time of the material. Also in composite restorative materials, zirconia is used, again because of its mechanical properties but also to increase the radiopacity, which is important to distinguish the filling from the tooth with x-ray imaging. The use of zirconia is already marketed in products, such as Filtek supreme and Filtek Z250 both produced by 3M. These two products have good mechanical properties, such as high flexural strength and fracture toughness[36].

The use of zirconia in resin composites sets high demands to the particle size because of the high refractive index of zirconia. Zirconia has a refractive index of 2.1-2.2 depending on the crystal phase, but the refractive index of the polymer matrix is 1.45-1.55. This means that in order to get a good esthetic composite the particle size has to be well below the wavelength of visible light, and preferable below 40 nm to prevent light from scattering from the particles giving the material an opaque appearance[37]. Opacity is a property of the materials that prevents the passage of light. When all the colors of the spectrum from a white light source is rejected at the same intensity as received, the object appears white. Opacity is represented by a constrast ratio, which is the difference in the daylight apperent reflection ratio of a sample, when backed by a white and a black standard. The constrast ratio for a dental composite should lie between 0.55 and 0.7[68].

The reason for opaque appearance is the increased light scattering with increasing particle diameter as described by Rayleighs law[38]:

$$\frac{I}{\mathrm{I}_0} = \left[\frac{3\phi_p x r^3}{4\lambda^4}\left(\frac{n_p}{n_m} - 1\right)\right] \tag{5}$$

Where I_0 is the intensity of the incoming and I of the transmitted light, ϕ_p is the volume fraction of the particles, x is the optical path length, r the radius of spherical particles, λ is the wavelength of the light and n_p and n_m are the refractive index of the particles and the matrix respectively. High scattering will make the composite opaque due to multiple scattering. The necessary particle size is, however, also dependent upon the differences between the refractive indices of the particles and the matrix. If these are equal the scattering intensity is independent of the particle size[38]. Glass and resin has the same refractive index, which allows addition of large glass particles to the composite.

1.6 The aims of this study

The aim of this project is to develop a low shrinkage dental composite based on an expanding metastable zirconia filler. In order to achieve this, a better understanding of the zirconia particles is needed in order to reduce polymerization shrinkage in dental composites. The key questions are: What triggers the phase transformation? Is it possible to increase the transformation rate? High transformation rate of the zirconia is attractive as it enables phase transformation during the fast polymerization of the dimethacrylate matrix. Furthermore, detailed knowledge of the effect of surface modification and deagglomeration on the zirconia filler is required to improve the mechanical and esthetic properties of the resin composite.

The main tasks of this study are:

- To find molecules, which enable light initiated phase transformation of the zirconia filler dispersed in a dimethacrylate matrix simultaneous with curing of the resin.
- To surface modify the zirconia particles without losing reactivity.
- To deagglomerate the zirconia particle in order to obtain particle sizes below 40 nm.
- To test the material properties of the final material.

Chapter 2 contains descriptions of the used experiment procedures and characterization methods. In chapter 3, the zirconia powder is described in regards to properties and morphology. The phase transformation and how the transformation rate can be increased are described in chapter 4. Possible ways to induce phase transformation as a result of exposing the composite to blue light during polymerization of the composite are also described in this chapter. Chapter 5 deals with surface modification of the zirconia particles including the effect of surface modification on the transformation rate and on the fracture energy of the filler/matrix interface. Surface modification is very important for improving the interface strength and water resistance of the composite. Methods to deagglomerate the zirconia powder are described in chapter 6. Surface modification is also essential to stabilize zirconia particles in water free suspension and prevent the particles from flocking after deagglomeration. In chapter 7, the shrinkage reduction properties of the expanding zirconia filler are described along with results from mechanical testing of prepared test composites. The last chapter gives a summery and future prospects of the result presented in this thesis. In the end of every chapter a short summery is given of the chapter and the associated publications to ease the overview for the reader.

2 Experimental methods

2.1 Experimental

All chemicals were supplied by Sigma-Aldrich (St. Louis, MO, USA) and used as received. Except for zirconium oxychloride, which is purchased from Bröste AB (Mölndal, Sweden) and ammonium hydroxide purchased from Borup Kemi I/S (Borup, Denmark).

2.1.1 Synthesis of $ZrO(OH)_2$

Amorphous zirconia is prepared according to the following general procedure:

1. Precipitation of amorphous zirconia. The reaction is:

$$ZrOCl_2 + 2\ NH_3 + 2\ H_2O \rightarrow ZrO(OH)_2 + 2\ NH_4Cl \qquad (6)$$

Aqueous solutions of 0.5 M $ZrOCl_2$ and 5 M NH_3 are prepared. The two solutions are added together at a ratio of approx. 2.8 times as much 5 M NH_3 as 0.5 M $ZrOCl_2$ by volume and the pH is monitored during this mixing. The pH should be close to 10, never above, and at best at 9.8-10. If pH drops below 9.6 only ammonia is added to the reaction mixture until pH reaches ~ 9.9 at room temperature and with stirring. $ZrO(OH)_2$ gel precipitates during the mixing.

2. Washing

The precipitate is filtered at 1100 rpm and washed with water at room temperature in a basket centrifuge in order to exclude chlorine and ammonium ions. Water is added until a chloride test of the centrifugate is negative (no AgCl precipitate (white) can be detected when drops of 0.5 M $AgNO_3$-solution is added to a sample of washing water). Then the filter cake is centrifuged at 1600 rpm for 15 minutes. The filter is removed from the basket of the centrifuge and the $ZrO(OH)_2$ cake is gently and quantitatively released from the filter.

3. Conditioning

The $ZrO(OH)_2$-cake from the centrifuge is transferred to a blender and mixed with 15 L of water pr. 9 L zirconium oxychloride original solution used. The mixture is blended to a uniform slurry. The slurry is transferred to a flask, and fitted with condenser and stirrer. With stirring the slurry is heated to the boiling point and kept boiling for 10 hours.

4. Washing

The conditioned precipitate is then filtered and washed with 100 L water as in step 2.

5. Azeotropic distillation

The amorphous $ZrO(OH)_2$ cake is transferred in portions to a blender and mixed with isopropanol to a homogeneous dispersion. The dispersion is transferred to the round bottom flask for the pilot plant sized rotary evaporator. The product is dried when a fresh sample of distillate gives no precipitation when adding zirconium(IV) butoxide, 80 wt% solution in 1-butanol. A white precipitate in this test indicated that the water content was higher than 0.7 % in the distillate. For a full portion (9 L $ZrOCl_2$ solution) expect 35-40 L isopropanol to be required. When a negative water test is obtained, the remaining isopropanol is evaporated. The dried powder is transferred to a glass oven pan, and dried at 60°C for at least 48 hours.

2.1.2 Calcination

The amorphous $ZrO(OH)_2$ is grinded in a coffee mill (OBH Nordica) until no detectable grains are remaining, usually one minute (determined by rubbing a small sample between the fingers, wear thin nitrile protective gloves). Keep the milled amorphous $ZrO(OH)_2$ in an airtight container prior to use. 80 g milled amorphous $ZrO(OH)_2$ is placed in the glass dish. The material is heated to 130°C overnight under vacuum. After vacuum drying, it is beneficial to carefully agitate the powder, as the powder may sink during vacuum drying. The glass dish with amorphous $ZrO(OH)_2$ is placed in the retort. The sample is calcined for 3 hours at 475°C under dry air with an airflow of 9-11 L/min. The reaction for the calcination is:

$$ZrO(OH)_2 \rightarrow ZrO_2 + H_2O \qquad (7)$$

When the retort is cold the air inlet valve is closed. The retort is immediately after placed in the glovebox antechamber. The antechamber with the retort is evacuated twice, and refilled with nitrogen. The retort is moved into the glovebox and the glass dish is taken from the retort. The tetragonal zirconia is placed in an aluminum laminate bag, which is sealed.

2.1.3 Surface modification

2.1.3.1 Surface modification of zirconia powder

In inert atmosphere in a glovebox, the zirconia powder was stirred overnight with 6 ml anhydrous methanol and 1 ml surfactant for each 1 g zirconia. The surface modified particles were filtered and washed three times with anhydrous methanol. After washing the samples were dried in the filter inside the glove box

2.1.3.2 Surface modification of silicon wafers

Silicon wafers were surface modified with hexamethyl disiloxane (HMDS) in a YES 6112 oven (Yield Engineering Systems, San Jose, US) at 150°C. Modification of the surfaces with γ-methacryloxypropyl trimethoxy silane (MPTMS) and (3-Aminopropyl)trimethoxysilane (APS) were obtained by covering the specimens with a mixture of 10:1 dry methanol : surfactant for 2 hours. Subsequently the samples were washed three times with methanol and dried under an air flow. Reference samples were prepared with clean silicon wafers.

2.1.4 Preparation of dimethacrylate monomer mixture

40 g (20 wt%) triethylene glycol dimethacrylate (TEGDMA) is poured into a glass beaker, then 88 g (44 wt%) Diurethane dimethacrylate (UDMA) is added and then 72 g (36 wt%) Bisphenol A glycidyl methacrylate (Bis-GMA). Before addition, Bis-GMA is taken out of the refrigerator and heated in an oven at 60°C until it is pourable. The mixture is stirred by hand until homogeneous. 0.5 wt% camphorquinone (CQ) and 0.5 wt% ethyl 4-dimethylaminobenzoate (DABE) are added. The mixture is stirred by hand until DABE and CQ are dissolved in the resin. After addition of the photoinitiator system the resin has to be stored at maximum 5°C in aluminum coated bottles in order to prevent premature polymerization.

2.1.5 Preparation of matrix dispersed zirconia samples for XRD

The zirconia powder for analysis is mixed, in the glovebox, with the dimethacrylate monomer mixture from section 2.1.4. A sample of this is placed between two glass plates and cured for 2 min using blue light (1100 mW) from a Bluephase® (Ivoclar Vivadent, Liechtenstein). Such samples are called matrix dispersed zirconia. The samples are subjected directly to XRD measurement for phase analysis.

2.1.6 Spray drying

Dispersions of amorphous zirconia in water were spray dried in a MOBILE MINOR™ Pilot Plant with an overall chamber diameter of 0.8 m, a cylindrical height of 0.83 m and a 60˚ cone. The drying gas, air (once through), is heated by an electrical heater and enters the drying chamber through a ceiling gas disperser. At drying temperatures 275/145˚C (inlet/outlet), dry looking powders were obtained.

Other spray dried particles were produced in a lab scale spray-drying reactor, which consists of a spraying chamber combined with a tube furnace and a filter[39]. Droplets of the precursor solution were generated in the spraying chamber using a two-flow spray-nozzle with a replaceable orifice with a diameter of 1.5 mm. The liquid flow and gas flow was set to 1.76 ml/min and 16,000 ml/min, respectively. Own temperature was 280°C and dry-looking white spherical powders were collected in both cases.

2.2 Characterization

2.2.1 X-ray diffraction (XRD)

One of the main uses of x-ray is in the determination of structures of materials using x-ray diffraction. When an x-ray beam strikes a crystal the beam will diffract in many specific directions. It is possible to identify the chemical composition and crystal phase of a material by analyzing the angle and the intensity of the diffraction pattern[40,41].

An x-ray diffractometer comprises an x-ray source, a detector and data collection and processing systems (Figure 8). In the x-ray source x-rays are generated by accelerating an electron beam onto a metal target in a vacuum tube, most often copper. The high energy electrons hit the metal target. In the hit atoms electrons are ejected from the ground-state. This ejection of electrons creates holes and x-rays are emitted during the refilling of the ground-states[41].

In powder diffraction, which is the used technique in this thesis, every possible crystalline orientation will be represented equally in the diffractogram[41]. Some powders can have a tendency to align in the sample holder, this leads to an over representation of one specific crystal orientation. This, however, seems not to be the case for the zirconia particles studied in this thesis, but to be safe the sample holder is rotated during analysis.

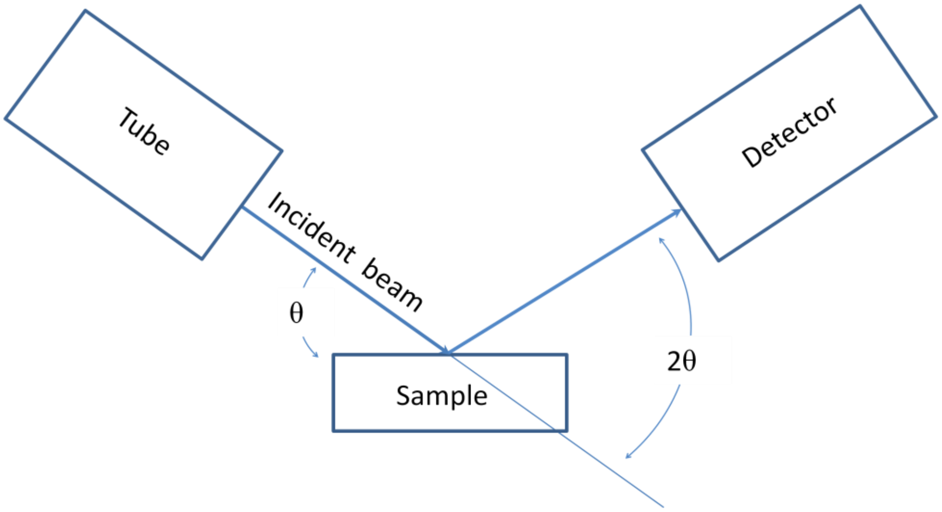


Figure 8 schematic drawing of XRD

The crystal phases of zirconia can be identified with the use of powder XRD as seen in Figure 9. Tetragonal zirconia gives a diffractogram with a high intensity reflection (101) at 30.2° (2θ angle) suitable for comparison with monoclinic zirconia. Monoclinic zirconia gives a diffractogram with two high intensity reflections (-111) and (111) at 28.2° and 31.5° (2θ angle) suitable for comparison with tetragonal zirconia.

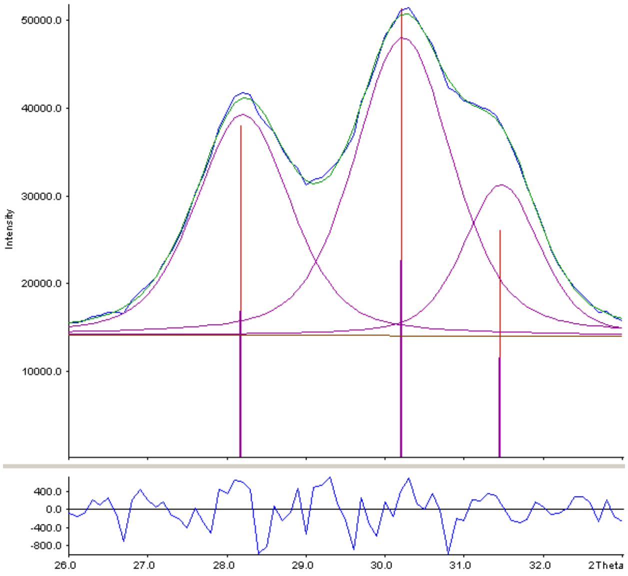


Figure 9 Screen dump from WinX$^{\text{POW}}$, analysis of a sample containing both tetragonal and monoclinic crystals.

The volume fraction of monoclinic zirconia (v_m) can be determined from the following relationships[42]:

$$v_m = \frac{1.34 * x_m}{1 + (1.340 - 1) * x_m} \tag{8}$$

where 1.34 is the intensity of reflection *hkl*, from the surface of a thick layer of the crystal powder and the integrated intensity ratio (x_m) is:

$$x_m = \frac{I_m(111) + I_m(-111)}{I_m(111) + I_m(-111) + I_t(101)} \tag{9}$$

where I_m(111) and I_m(-111) are the integrated intensities of the (111) and (-111) reflections for monoclinic zirconia and I_t(101) is the integrated intensity of the (101) reflection for tetragonal zirconia. Intensities were integrated using STOE WinX^{POW} (ver.2.07) software, as seen in Figure 9. The method is generally good and gives valid results - integration may however not give a precise ratio of the phase transformation, when one or two of the reflections are small and overlaps with a greater reflection. To reduce this problem with overlapping reflections, the full width at half maximum intensity is fixed when analyzing the raw data. This gives a better fitting of the reflections.

The crystal size can be calculated from XRD patterns by the Scherrer equation[43]:

$$\tau = \frac{K\lambda}{\beta cos\theta} \tag{10}$$

where τ is the mean crystallite dimension, K is the shape factor, λ is the x-ray wavelength (1.54 Å for Cu K_α), β is the full width at half maximum intensity (FWHM) in radians, and θ is the Bragg angle. The dimensionless shape factor varies with the shape of the crystallite, but has typically a value about 0.9. XRD cannot be used to analyze thick zirconia containing composite samples due to absorption. This can cause a problem when testing phase transformation initiated by diffusion of water. For that reason the samples are prepared with a thickness of 1 mm. The attenuation in a material is dependent on the element number of the atoms the sample. The attenuation increases with Z^4. In the analyzed composites the x-rays will reach zirconia particles hundreds of µm down in the sample. There can however be some gradient differences through the sample, but this is not possible to test, because if the sample is split in two the dispersed zirconia will be exposed to humidity in the air and phase transform.

2.2.2 Scanning Electron Microscopy (SEM)

A scanning electron microscope uses a focused electron beam to image the surface. The image is obtained by scanning the focused electron probe across the surface and collecting the resulting image signal from the surface. The signal is collected from the specimen surface and the electron beam loses energy by inelastic scattering as the electrons penetrate beneath the sample surface. Most of the electron current from an excited sample is due to release of secondary electrons from the sample surface[44]. Changes in the local curvature will change the probability that a secondary electron can escape. A region with a positive radius of curvature increases the chances of the secondary electron to escape and vice versa will regions with negative radius of curvature reduce the secondary electron current. The scanning electron microscope provides images that closely approximate what the eye and brain expect. As the intensity of the image will depend upon the number of secondary electrons reaching the detector, secondary electron imaging provides topographic images of rough surfaces[45].

2.2.3 Transmission Electron Microscopy (TEM)

The transmission electron microscope uses a focused electron beam, just like the SEM. In TEM the detector is, however detecting electrons transmitted through the sample. This sets limitations on the specimen thickness, which should be less than 0.1 µm to allow most of the high energy electrons to pass without serious energy loss. This setup gives high resolution in two dimensions, but does not provide topographic images as SEM does[44].

Both SEM and TEM needs vacuum to operate. The high energy electron beam has limited path length in air, so the whole microscope column should be kept under a vacuum better than 10^{-6} Torr and for the highest resolution 10^{-7} Torr is desirable[44].

2.2.4 Atomic force microscopy (AFM)

In atomic force microscopy a cantilever with a very fine needle (typical tip radii is 20-60 nm) is scanned across the sample surface, which registers the changes in height or stiffness in the surface. AFM can be operated in two ways; (i) in contact mode where the tip is lowered to the surface until a surface repulsion is detected as a positive deflection of the cantilever. Under atmospheric conditions a film of moisture on the surface can result in capillary forces. Also electrostatic charging of nonconducting surfaces can result in either attraction or repulsion of the probe tip. These effects can be limited by the use of contact mode, if the deflection of the tip is positive. (ii) In tapping mode the cantilever oscillate vertically at its resonance frequency. The tip-surface force interaction causes a change in the amplitude, the phase and the resonance frequency of the vibrating cantilever. This technique is used to overcome the limitations of contact mode in studying soft materials. AFM gives a topographic image of the surface in an area ranging from 1 µm x 1 µm to 50 µm x 50 µm[46].

2.2.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is also known as electron spectroscopy for chemical analysis (ESCA) and is frequently used to characterize surfaces. The technique is used to probe most of the energy levels in the surface atoms, but does not have any spatial resolution. XPS uses x-rays to generate photoelectrons from the atoms in the surface. The kinetic energy (E_{kin}) of these photoelectrons is detected and the binding energy (E_b) of the exited electron can be calculated:

$$E_b = h\upsilon - (E_{kin} + \phi) \qquad (11)$$

where $h\upsilon$ is the energy of the x-ray and ϕ is the orientation-dependent workfunction that is required to bring the electron from the Fermi level into the vacuum just outside the surface. The workfunction is specific for each particular spectrometer. The binding energy of an electron depends on the atom the electron originates from, on the orbital where it was placed and on the binding of the atom to other atoms. The last effect is called chemical shift and is much smaller, than the first two. The binding energy in the atom increases as the energy of the photoelectron decreases[47].

In practice the quantification is done by integrating the specific peak of all detectible elements in the sample correcting the areas for instrumental factors and dividing with relative photoelectron cross sections for each peak to give the relative concentration of elements. XPS cannot detect hydrogen or helium atoms. In this thesis whenever an atom composition percentage is presented, it is the percent of electrons detected from a specific atom species compared with the total number of electrons from all detected atoms.

2.2.6 Dynamic light scattering (DLS)

Dynamic light scattering, also known as photon correlation spectroscopy is used to find the size distribution of particles in suspension. This is done by monitoring the temporal fluctuations in the intensity of the scattered light. From monitored Brownian motions the particles the particle size can be calculated from the Stokes-Einstein relation, when the viscosity of the solvent and the temperature are known[48].

2.2.7 Differential scanning calorimetry (DSC)

Differential scanning calorimetry is a thermoanalytical technique used to find the difference in the amount of heat needed to increase the temperature in a sample and a reference sample. In DSC a sample and a reference is subjected to a controlled temperature program and the difference in energy input into the sample and the reference is measured as a function of temperature. The reference sample should have a well defined heat capacity in the measured temperature range[49].

2.3 Mechanical tests

2.3.1 Peel test

The so-called peel test is a simple method for qualitative assesment of the fracture toughness of bimaterial interfaces. The method is used to measure the fracture resistance of a thin layer bonded on a thick substrate or of two layers bonded together. The force needed for tearing an adherent layer from a substrate or for tearing two adherent layers from one another is measured. The peel test is well suited for fracture mechanical charaterization of thin layers. Furthermore the failure mode of peel tests generally is adhesive i.e., cracking along the film/substrate interface[50]. The energy release rate is calculated according to the equation[51]:

$$G = \frac{P}{b}(1 - \cos(\varphi)) \qquad (12)$$

where G is the energy release rate, P is the value of the peel force during separation, φ is the peel angle and b is the width of the flexible adherent. This equation applies if the adherent is flexible in bending, but inextensible[51]. During an experiment, the force increases. When the force reaches a critical value, crack propagation occurs along the film/substrate interface. Through (12), the critical value of the force can be used to calculate the critical energy release, G_c, also called the fracture energy. A picture of the experimental setup is seen in Figure 10.

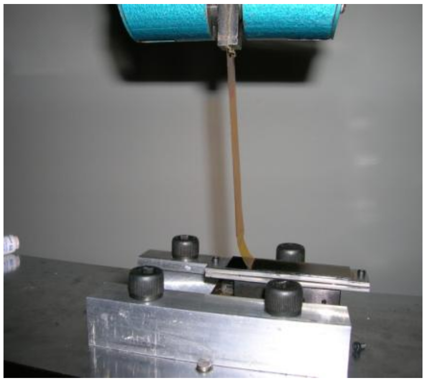


Figure 10 photo of the peel test set up (the test specimen is 20 x 60 mm)

For a constant fracture energy and width of the sample the peel force will decrease with increasing peel angle for angles between 0° and 180°. The fracture occurs under a combination of peel and shear (Mixed Mode), but the mode mixety is fairly insensitive to the peel angle[52].

2.3.2 Three point bend test

The three point bending test is used to characterize the strength of materials such as dental composites and ceramics. In this test method, a beam of the material, supported at each end, is applied a load on the middle and the maximum stress in the beam is calculated. The highest stress measured during the bending test is called the flexural strength. The maximum stress in the specimen can be calculated from the equation[15].

$$\sigma = \frac{3Fl}{2bh^2} \qquad (13)$$

Where F is the load (in newtons), l is the distance between the supports and b and h are the specimen width and height respectively. The flexural strength is found when the maximum value F_{max}, corresponding to the breakage of the specimen, is inserted into (13)[15].

All flexural strength tests were performed according to ISO 4049:2000(E). Test composites were prepared by mixing zirconia powders with the monomer mixture described in section 2.1.4. The mixing was done in a 60°C warm mortar, to increase the viscosity of the monomer mixture. For each mixture, a total of 8 specimens were prepared. Six specimens were tested with 3-point bending test and two specimens were use for determination of the filler content according to DS/EN 12880:2001. In the 3-point bending test surface defects are dominating over bulk defects. For this reason, the specimen preparation is very important for the measured strengths and the sample surfaces have to be polished prior to testing. For brittle materials, the strength is controlled by the size of the defects in the specimens. Such materials can show a large variation in strength due to variation in defect size from specimen to specimen. The strength variation can be described in terms of the Weibull distribution[53]. Polymers, however, usually show smaller strength variations.

2.4 Deagglomeration

2.4.1 Ultrasonication

Ultrasonication is the act of applying ultrasound to agitate particles in a sample. It is a soft nonimpact method to deagglomerate particles or to speed dissolution, by breaking intermolecular interactions. The deagglomerating effect derives primarily from acoustic cavitation (the formation, growth and collapse of bubbles). Near a solid surface the implosion of the cavitation bubbles results in micro-turbulences and micro-jets of liquid into the surface of up to 1000 m/sec. Large particles of brittle materials are subject to surface damage and fragmentation[54].

3 Zirconia powder – Surface and Morphology

3.1 Introduction

Resin composites are highly affected by the filler load. A high filler load will result in a composite with lower shrinkage and wear, but also a composite with higher strength[2]. To obtain these high filler loads it is important to have well characterized filler particles in regards to size, porosity and particle size. In this case, where the filler is expected to phase transform from one crystal phase to another, crystal phase analysis is an extra parameter of concern.

In this chapter morphology, crystal phase and surface chemistry are described for the synthesized zirconia powder.

3.2 Particles

The synthesized zirconia powder was analyzed with SEM and the particles were found to have a highly porous structure (Figure 11), where the zirconia particles appear as small “clouds”. The large particles in the picture are agglomerates of zirconia. It was tried to separate those with a spatula resulting in the smaller particles with a diameter of ~1-2 µm. This was also the result confirmed by DLS where the particle size was determined to 1.8 µm.

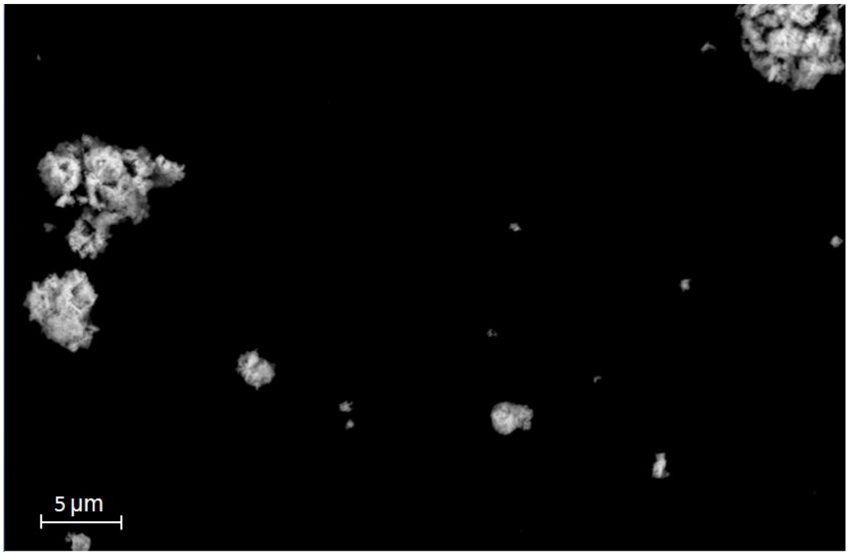


Figure 11 SEM picture of zirconia powder. The large agglomerates were separated with a spatula

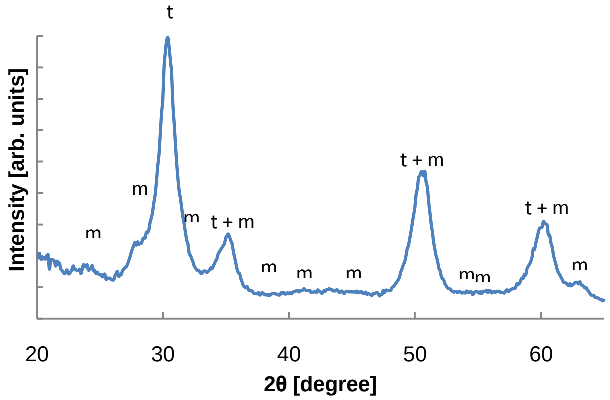


Figure 12 XRD patterns of the calcined zirconia powder (in resin) t=tetragonal reflection, m=monoclinic reflection

It was confirmed with XRD that the zirconia is tetragonal and only contains traces of monoclinic crystals (Figure 12). The crystal size was calculated to ~6 nm from the XRD patterns by the Scherrer equation[43]. This crystal size was confirmed by transmission electron microscope analysis. The analysis showed that the zirconia powder indeed are composed of very small 6-8 nm nanocrystallites, which are interconnected and make three dimensional porous networks of about 1.5-2.0 micrometers (Figure 13). The structure of highly agglomerated nanocrystals gives rise to a high surface area and the specific surface area was determined by nitrogen adsorption to ~150 m^2/g.

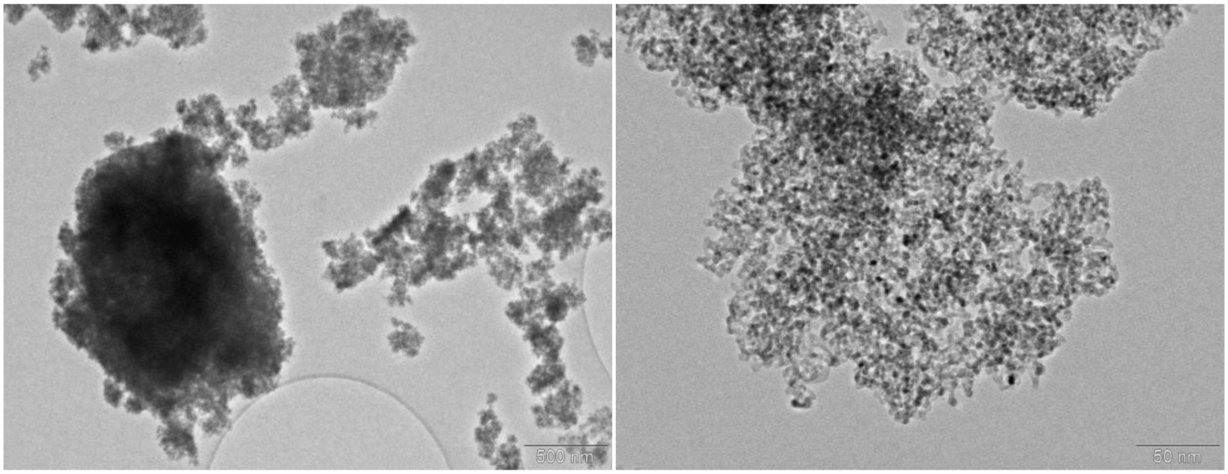


Figure 13 TEM pictures of zirconia powder

3.3 Surface

From infrared spectroscopy of the zirconia only two kinds of hydroxyl groups on zirconia can be determined; isolated hydroxyl group and the bi-bridged zirconia at 3766 and 3686 cm^{-1} respectively. The number of OH-groups on the surface was determined, by $LiAlH_4$ titration, to 3-4 groups per nm^2. Other species on the surface of zirconia are carbonates (15 atom% carbon was found) which are described in section 4.1. The production method does, however, not leave ions adsorbed on the surface as it was found that the electrolytic conductivity do not change in de-ionized water when 1 wt% zirconia is added.

On the surface of m-ZrO_2 was furthermore a water layer, the amount of adsorbed water on the monoclinic zirconia surface is found to be 5.5 wt%. 5.1 wt% is deadsorbed below 110˚C, this means that only a small fraction of the water molecules are chemically bound.

3.4 Summary of Chapter 3

A primarily tetragonal zirconia powder was obtained, which consist of heavily agglomerated nanocrystals, with a size of ~6 nm. The sizes of these agglomerates are 1.5-2 µm and they have a very large surface area in the range of 150 m^2/g. On the surface is found 3-4 OH-groups per nm^2 and 15 atom% carbon found as carbonates.

4 Phase transformation

4.1 Introduction

As described in Chapter 1 tetragonal zirconia is used in many applications. For this reason the phase transformation mechanism is widely studied. Mostly the effect of water and humidity on the crystal phase has gained attention.

The synthesized zirconia powder is very reactive towards water and starts to transform when the water content in the atmosphere gets above 150 ppm (dewpoint = -40˚C). At room temperature in ambient atmosphere the degree of phase transformation of the zirconia powder is approximately 65 vol% (see figure 1 in Appendix I). The phase transformation is very fast and it is not possible to measure the transformation rate with XRD. This high transformation rate is also reported by Xie et al[55]. They measured a phase transformation time of 10 seconds as a result of exposure to ambient atmosphere.

It is important that the zirconia filler is very sensitive towards water, as the activity of water in the composite is low due to the hydrophobicity of the resin. Because of this low water content all unwanted side reactions should be minimized. It is known from literature that carbonates on the zirconia surface react with water molecules. This will hinder water from initiating the phase transformation[56]. It was investigated how this competing reaction could be hindered. The results of this study is presented in Appendix II and in the patent presented in Appendix III.

Chemical reaction is, however, not the only way to initiate phase transformation. Also application of mechanical stress and annealing can induce phase transformation. It was tested how sensitive the produced zirconia was towards uniaxial stress and the results of this study is presented in the first part of Appendix IV. The effect of annealing was also tested and the produced $ZrO(OH)_2$ was calcined at different temperatures. It was observed that the zirconia turns monoclinic when the temperature is increased above 550°C. But because chemically initiated phase transformation is the only possibility in dental resin composites this is the initiation mechanism, which has gained attention in this thesis.

In this chapter the sensitivity and reactivity of the produced zirconia filler is described. Also different molecules able to initiate the tetragonal to monoclinic phase transformation are identified. In this study water and other molecules were tested for their ability to initiate phase transformation in metastable tetragonal zirconia at RT. This investigation is performed to find molecules, which on exposure to the curing light are able to phase transform the zirconia. The results are described in Appendix V and Appendix VI. Furthermore the ability of zirconia to phase transform when dispersed in a dimethacrylate matrix was investigated (see Appendix VII). As presented above, water is one of the most important initiator molecules for inducing phase transformation of the zirconia filler.

4.2 Photoacid generators

During the study of the phase transformation in water, it was proven possible to phase transform the zirconia in a dimethacrylate matrix by diffusion of water to the zirconia surface (see Appendix VII). The most desirable scenario, however, is to initiate the phase transformation during curing, while the resin is in the gel state. One way to do this is by light initiated release of initiator molecules. Water and HCl releasing photoacid generators (PAG) and photoacid generator systems were identified and tested (see Appendix V). The best candidate was found to be the commercially available 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine. But this HCl releasing PAG leads to a discoloration of the polymer matrix and absorbs at a low wavelength (λ_{max} =379 nm). The light probe used by dentists has an emission peak at 430-490 nm. For this reason the merocyanine dye linked bis(trichloromethyl)-1,3,5-triazine (MT1), described by Kawamura[57], was synthesized. The synthesis route is illustrated in Figure 14 and Figure 15. MT1 has λ_{max} =430 nm and is known to bleach upon irradiation[57]. These properties make MT1 a very interesting candidate.

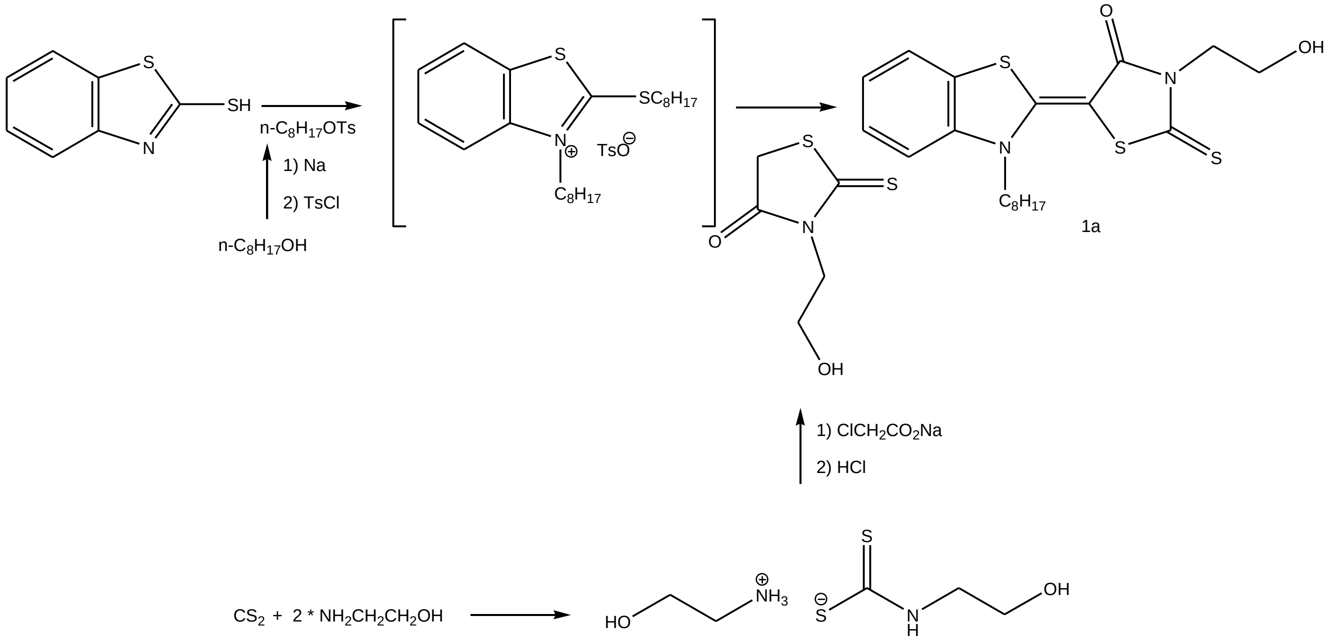


Figure 14 Synthesis of the merocyanine dye (3-(2-hydroxyethyl)-5-(3-octyl-3H-benzothiazol-2-ylidene)-2-thioxo-thiazolidin-4-one)

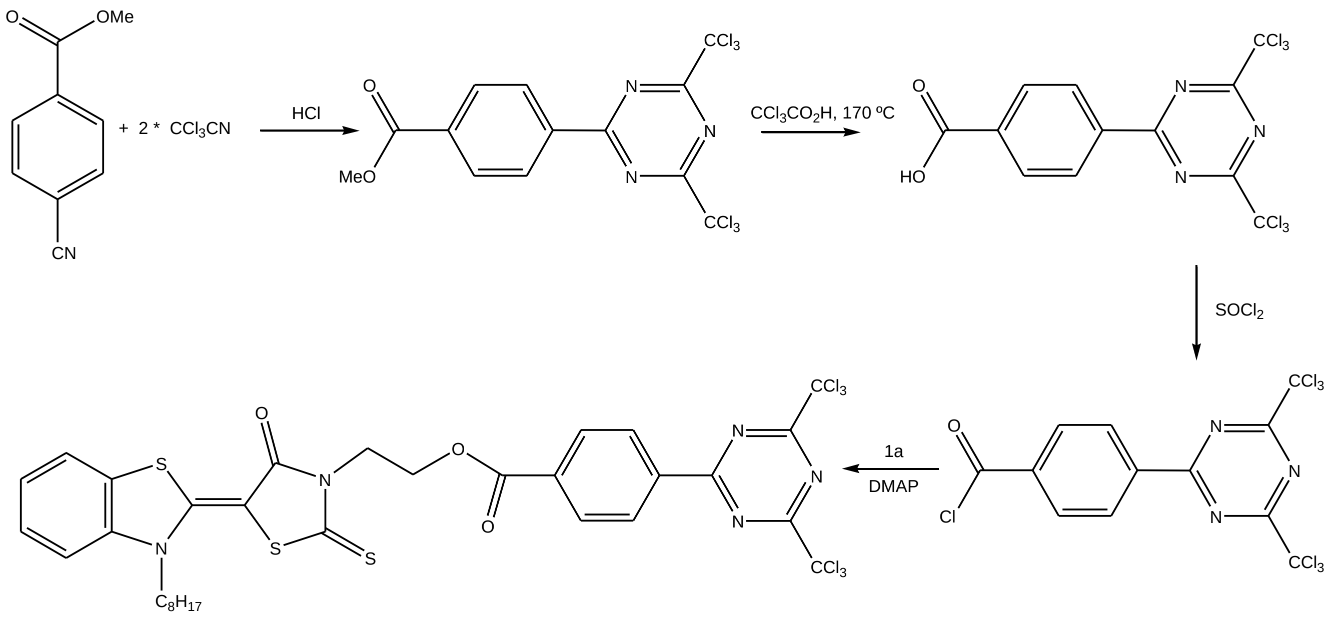


Figure 15 Synthesis of 4-(4-chlorocarbonylphenyl)-2,6-bis-(trichloromethyl)-*s*-triazine and coupling with the merocyanine dye

The HCl yield of the merocyanine dye linked bis(trichloromethyl)-1,3,5-triazine was determined by exposure to blue light in methanol and the formed HCl was precipitated with a 0.5 M $AgNO_3$ solution. The yield of HCl, with respect to molar amount of the PAG, was found to 5.6 % after 20 min of irradiation at max. intensity. This is almost twice as much as the HCl yield of 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (see Appendix V), which proves that the merocyanine dye linked bis(trichloromethyl)-1,3,5-triazine is more effective in the given emission range. Another advantage is that the merocyanine dye linked bis(trichloromethyl)-1,3,5-triazine actually bleaches at low concentrations such as 0.5-1 wt% in the resin leading to removal of the yellow color.

4.3 Summary of Chapter 4 and Appendixes I through VII

The tetragonal to monoclinic phase transformation can be induced by chemical initiator molecules. Molecules known to initiate phase transformation are water, HF, HCl, HBr and NH_3 – with water as the most efficient. The zirconia is sensitive towards shear stress and phase transforms in uniaxial strain tests with applied pressures as low as 60 MPa. Also annealing initiates the phase transformation and at temperatures above 550°C the crystals turn monoclinic

Chemically initiated phase transformation is a very quick reaction. When the zirconia powder reacts with water vapor in air, the reported transformation time down is as low as 10 s. It is possible to phase transform 60 - 70 vol% of the zirconia crystals in air and up till 84 vol% in water. A phase transformation of ~60 vol% is obtained for zirconia in a water stored composite material. The phase transformation happens in the water stored composite over 2 days after curing – most within the first 8 h.

It was also shown possible to phase transform matrix dispersed zirconia crystals by light initiated formation of HCl, by exposing 2-(4-Methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine in the compound to blue light. A phase transformation of 60 vol% was reached after 30 min exposure. The synthesized merocyanine dye linked bis(trichloromethyl)-1,3,5-triazine (MT1) gave a HCl yield of 5.6 % and were able to photobleach in the matrix upon exposure to blue light.

It was found that carbonates on the zirconia surface reduce the transformation rate in the composite due to competing reactions with water. This inhibition of the phase transformation can be suppressed by addition of alcohols , thiols and molecules with other functional groups, which react with the carbonates and hence hinder the carbonates from reacting with water – and thus works as activators making the phase transformation faster. Polyalcohols and dialcohols, however, which have the possibility to coordinate bi-dentate, hinder phase transformation.

5 Surface Modification

5.1 Introduction

A strong surface modification is very important for the properties of the final composite, as described in section 1.2.2. Different surfactants were tested for their ability to bind to the zirconia surface. In this thesis it was found possible to silanize the zirconia particles in a water free atmosphere without any phase transformation (see Appendix VIII), but because of the absence of water and hence absence of hydrolysis of the methoxy groups, it is only possible to obtain one monolayer of silane regardless of solvent, temperature and the use of an amine catalyst[8]. In the same way it was possible to modify the surface with phosphates, sulfonic acids and carboxylic acids, but these caused some phase transformation due to water formed by condensation with OH-groups on the zirconia surface (see Appendix VIII). The surfactants were also tested for their ability to prevent hydrolytic degradation of the matrix/filler interface and it was found that MPTMS gave the highest interlaminar fracture energy both in the dry and in the water aged samples (see Appendix IX).

In this chapter, the effect of surface modification on the interface strength and resistance to hydrolysis is tested. Also the stabilizing effect of surfactants on the tetragonal crystals is analyzed. To overcome the stabilizing effect of these surfactants a new surfactant had to be identified. This study is described at the end of the chapter.

5.2 Effect of surface modification on strength

Appendix IX describes how peel tests can be used to evaluate the effect of different surfactants on the interface fracture toughness of the zirconia/dimethacrylate interface (see also section 2.3.1). The same study was conducted on adhesives bonded to silicon surfaces. The tested surfactants were hexamethyl disiloxane (HMDS), (3-Aminopropyl)trimethoxysilane (APS) and 3 γ-methacryloxypropyl trimethoxy silane (MPTMS). These results were compared with the results found for an untreated surface. The tested specimens are 2 x 6 cm silica samples covered with a methacrylate film with the thickness of 100 µm. Polymers can possess rate-dependant properties[58,59]. Therefore, it was first necessary to identify the most optimal peel speed. Two experiments were conducted. First, the tape/dimethacrylate interface was tested in order to ensure that this interface was stronger than the Si/dimethacrylate interface. Otherwise it would be difficult to test the right interface. Tests of the interface between the kapton tape and the dimethacrylate film showed that the peel force increased for speeds between 0.5 mm/min and 50 mm/min and the results of this study are plotted in Figure 16. Then a similar peel experiment was performed for a dimethacrylate resin cured on a clean Si wafer. This interface was significantly weaker than that of the kapton tape, however the load and thus the fracture energy was seen to increase with peel speeds between 0.5 mm/min and 20 mm/min (Figure 17).

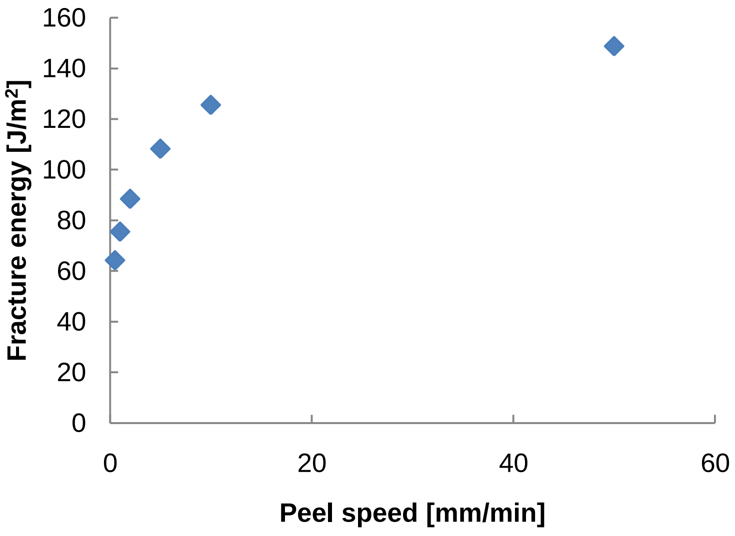


Figure 16 Peel speed dependency on the fracture energy for kapton tape on a dimethacrylate surface

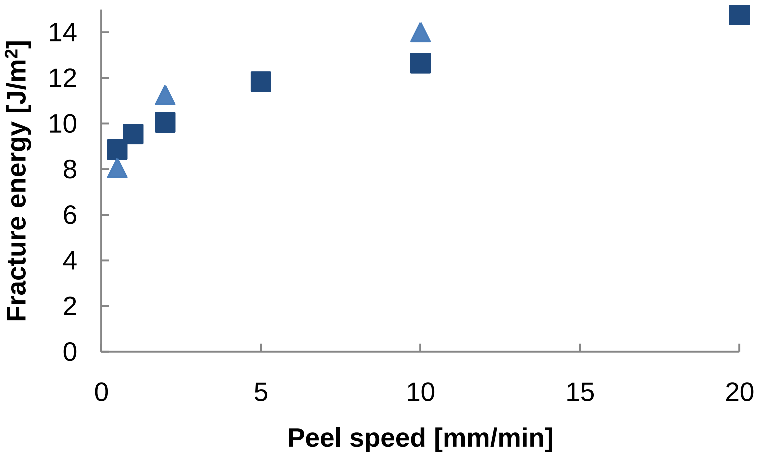


Figure 17 Peel speed dependency on the peel force for a dimethacrylate film on a silicon wafer. The plotted data are originating from 2 equivalent samples.

Furthermore stick-slip failures are observed at higher speeds. Slip-stick behavior is characterized by a saw-tooth shaped load profile for a peel test specimen[60] (see Figure 18). Initially the specimen is loaded until the fracture propagates. As the velocity of the crack decreases and stops, an arrest load is reached. This type of behavior is repeated several times as the crack moves down the specimen length. The load required for initiating the fracture is greater than that required for stable crack growth and part of the energy is dissipated as kinetic energy[61].

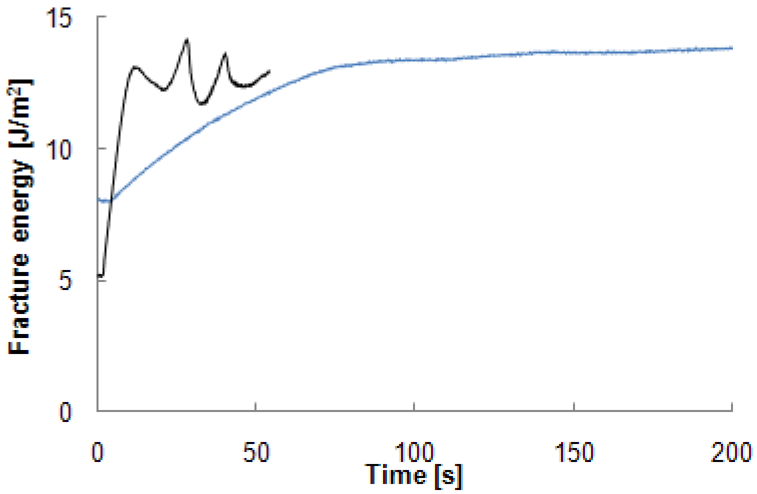


Figure 18 Plot of the measured fracture energies of silicon/methacrylate interfaces measured at different peel speed; (blue) 1mm/min and (black) 10 mm/min; the latter shows slip-stick behavior

It is observed that the fracture energy increases with increasing peel speed. This can be due to two different phenomena or a combination of these, 1) the fracturing is rate dependent[62] or 2) the bulk plasticity is rate dependent and absorbs more energy at higher peel speed[59].

From these results it was decided to use a peel speed of 1 mm/min so that slip-stick fracture is avoided. Next, the effect of different surfactants on the fracture energy of the interface was analyzed. The results of this test are represented in Table 2. Just as for the zirconia surfaces studied in Appendix IX, MPTMS gave the highest fracture energy and again the test specimens surface modified with HMDS were so weak, that they were impossible to test - they cracked during handling. APS did not increase the fracture energy significantly compared with the untreated surfaces. This is not surprising since APS is unable to bond the resin and it is known from literature that a coupling agent has to connect to both the surface and the resin covalently in order to secure sufficient high interface toughness[63].

Table 2 Mean (standard deviation) of fracture energy (J/m^2) recorded using peel-test

Surface treatment	*Fracture energy*
HMDS	NA
Reference	15.0 (5.7)
APS	20.4 (2.3)
MPTMS	36.2 (11.8)

NA; not analyzed

5.3 Mechanically induced phase transformation

It was readily observed that many of the tested surfactants stabilized the tetragonal phase and hence prevented the zirconia filler from undergoing phase transformation. Thorough studies were conducted and this lead to the articles presented in Appendix I and Appendix VIII.

As described above, surface modification of tetragonal zirconia often leads to a stabilization of the crystal phase, e.g., silanes stabilize the tetragonal phase so strongly, that not even boiling in water is sufficient to initiate phase transformation. The reason for such behavior is not understood. Therefore, the ability of surfactants to stabilize the tetragonal zirconia crystal from undergoing phase transformation as a result of applied shear stress was investigated. Mechanical compression tests were performed for both the surface modified the untreated samples as described in the article “Effect of microscale shear stresses on the martensitic phase transformation of nanocrystalline tetragonal zirconia powders” in Appendix IV.

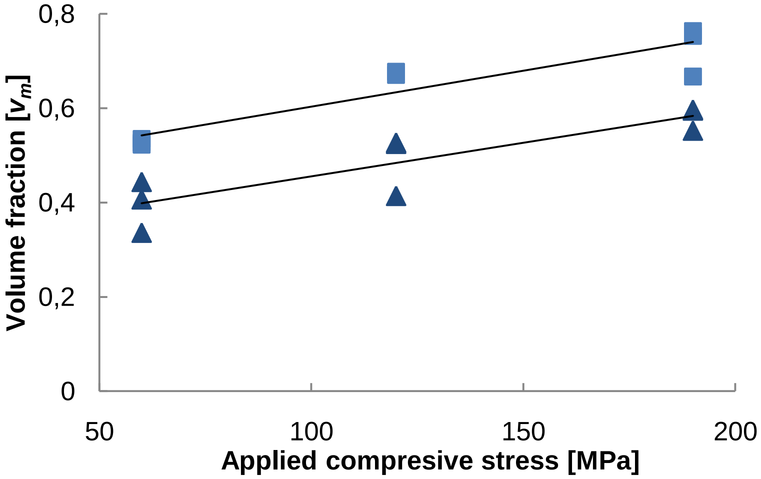


Figure 19 Volume fraction of monoclinic zirconia as a function of applied pressure to silanized samples (■) and an unmodified zirconia sample (▲) results from Figure 3 in Appendix IV

It is observed that the silanized zirconia phase transforms, just as it is observed with untreated zirconia when macroscopic compression is applied (Figure 19). As for the unsilanized sample, microscale shear stresses cause the zirconia to undergo a t→m phase transformation. So surface modification only stabilizes the tetragonal phase towards chemically initiated phase transformation and does not hinder a phase transformation due to mechanical stress. It is observed in Figure 19 that application of a pressure to the surface modified zirconia seems to induce a higher amount of phase transformation than the unmodified zirconia. But as the curves in both experiments have similar slopes, it is more likely that the increase originates from water initiated phase transformation during the silanization.

5.4 Promoting wetting of the surface

Even though many of the tested surfactants stabilize the tetragonal phase, it was necessary to find one surfactant, which is able to bind to the surface in order to improve the wettability of the surface. It is a well known fact that surface modification of ceramic fillers for resin composites is necessary to wet the surface in order to gain higher filler loads in the final composite[9]. As described in section 1.2.2 silanes are commonly used as coupling agents in dental materials and MDP is used to bond resin to zirconia surfaces. But silanes or phosphates are not an option due to problems with phase stabilization and unwanted phase transformation. A number of alternatives were evaluated (see Appendix VIII).

The carbonates on the surface react with alcohols as described in section 4.1 and it was found that addition of a methacrylate or acrylate with an alcohol group, such as 3-(acryloyloxy)-2-hydroxy-propyl methacrylate (Figure 20), increases the wettability of the surface and the surfactant also works as an activator. Better wetting of the surface will result in a stronger mechanical adhesion of the resin to the highly porous zirconia particles and in higher strength of the composite. Because the surfactant has two double bonds able to bind into the resin during the curing, the surfactant will not work as a softener, but become a part of the polymer matrix. The bond of the surfactant to the surface is not stable towards hydrolytic degradation, its purposes are to enhance wetting of the surface and hence increase the filler load and to work as an activator. At the same time the surfactant ensures a good and deep penetration of the resin into the porous material – securing the maximal mechanical bonding between the particles and the polymer matrix.

To enable the reaction between the surfactant and the carbonates, it is important to make the dispersion in a solvent free of functional groups, which can compete with the surfactant for reaction with the carbonates on the zirconia surface. Acetonitrile was chosen for its ability to dissolve the resin.

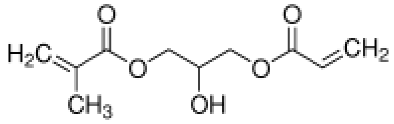


Figure 20 3-(acryloyloxy)-2-hydroxy-propyl methacrylate.

5.4.1 The ability of 3-(acryloyloxy)-2-hydroxy-propyl methacrylate to work as an activator

20 g zirconia, 16 g monomer mixture (without photoinitiator system), 1 g 3-(acryloyloxy)-2-hydroxy-propyl methacrylate and 60 g acetonitrile were dispersed 20 min with a high speed dissolver. 20 ml acetonitrile was added and the mixture was dispersed 5 min more. The dispersion was transferred with 20 ml acetonitrile to the sonication chamber. The mixture was sonicated 45 min at maximum intensity with a 1000W ultrasound device (UIP1000hd from Hielcher, Teltow, Germany). A small sample was dried in vacuum and mixed with a dimethacrylate monomer system (with initiator system). The sample was cured between two glass plates for 1 min on each side and stored in water at 40 °C for three days. The sample was subjected to XRD analysis after water storage.

5.4.2 Results

The dispersion was fairly stable but not transparent and the particle size of the zirconia dispersion was determined with DLS to 300-400 nm. The XRD patterns of the reference sample and the water stored samples are illustrated in Figure 21. It is observed that the zirconia is able to phase transform as a result of water aging. From this it is concluded that 3-(acryloyloxy)-2-hydroxy-propyl methacrylate is able to react with the carbonates on the surface and hence work as an activator.

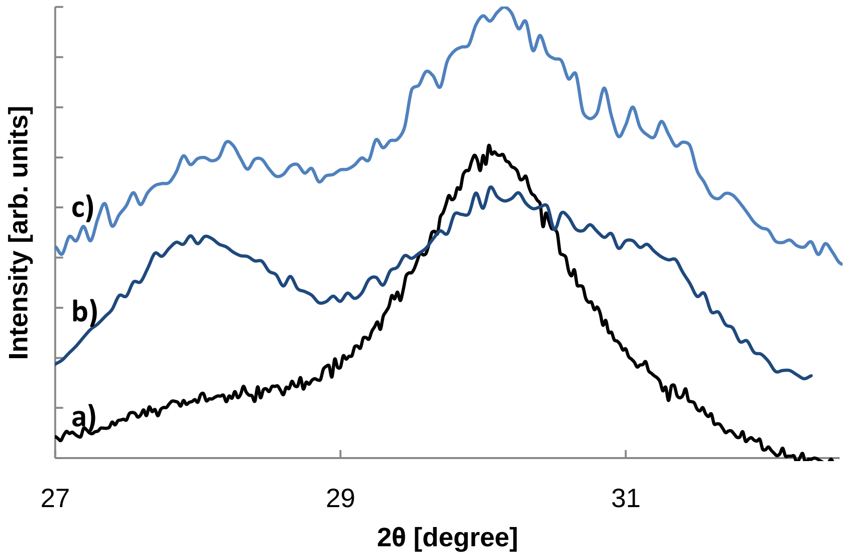


Figure 21 XRD patterns of a) reference sample and b) sample water stored for 3 days at 40 °C c) reference sample without surfactant stored in water for 21 day

5.5 Summary of Chapter 5 and Appendixes VIII and IX

In peel tests of zirconia/methacrylate and Si/methacrylate interfaces, the surface modification with MPTMS was found to result in the highest fracture energy (higher than the untreated silicon wafer, HMDS and APS modified silicon wafers). But surface modification of the zirconia particles with conventional surfactants is not a possibility due to stabilization of the tetragonal phase or phase transformation due to water from condensation reactions between surfactant and OH-groups on the zirconia surface. The surfactants, however, only cause stabilization towards chemical initiation and not towards mechanically initiated transformation. But mechanical initiation of the order of this stress level (190 MPa) is of cause not a possible way to induce phase transformation in a dental composite.

It was found possible to modify the zirconia surface by addition of 3-(acryloyloxy)-2-hydroxy-propyl methacrylate to the compound. This surfactant binds into the resin system and secures a good penetration of the porous material securing a high degree of mechanical adhesion of the polymer matrix to the filler particle. It was also concluded that the surfactant was able to inhibit surface bound carbonate stabilization.

6 Deagglomeration

6.1 Introduction

For zirconia particles in dental composites a low particle size is very important because of the high refractive index of zirconia (n = 2.2). The importance of low particle size is due to a desire of gaining low opacity and the resulting high depth of cure in the dental composite. This is described in section 1.5.

After the calcination step, the zirconia powder consists of large agglomerated particles with a diameter of 1-2 µm. To reduce the particle size, deagglomeration is needed. Ball milling, spray drying and ultrasound were tested for their ability to deagglomerate the zirconia particles. The results of the investigations with ball milling can be found in Appendix IV. In order to obtain a stable dispersion of the deagglomerated zirconia particles, a dispersant, is needed. This dispersant should neither stabilize nor induce phase transformation of the zirconia Furthermore the dispersant should be able to stabilize the deagglomerated particles in water free solvent in order to prevent reagglomeration. The surfactant should either be able to stabilize the zirconia dispersion in low concentration or be able to bind into the polymer matrix, to prevent softening of the polymer matrix by the dispersing agent.

This chapter describes the screening for the most optimal surfactant. But also the deagglomeration techniques ball milling, ultrasonication and a couple of spray drying methods are described.

6.2 Screening of dispersants

A screening of possible dispersants was performed at INM (Leibniz Institut für Neue Materialien) in Saarbrücken and at YKI (Ytkemiska Institutet) in Stockholm. Many chemical groups were tested for their ability to stabilize zirconia in suspension and for their ability not to induce or hinder phase transformation of the particles. Also several solvents were included in the test.

6.2.1 Experimental

Screening experiments were conducted to find suitable dispersing agents, which prevents agglomeration of the hydrophilic zirconia particles in the partial hydrophobic monomer mixture. In order to save time and material, the screening was done in small volume experiments.

In small bottles (20 ml) 1 g ZrO_2 and 0.2 g of dispersant were added to three solvents (Butyl glycol, 2-Butanone, Xylol). Sedimentation and agglomeration behavior were observed for the samples. The tested dispersants are listed in Table 3. Additional testing on the ability to stabilize the suspension was performed on: phosphates, polyamines, soluble polymers/emulgators, complex builders, glycols and derivates of glycols and combinations of the above.

Table 3 Most important dispersants tested for their ability to stabilize zirconia in suspension. The compositions of the commercial surfactants are unknown

Acids	*Commercial surfactants*
Oleic acid	Disperplast 1142
Phthalic acid	Disperplast 1150
Benzoic acid	Disperbyk 106
Glycolic acid ethoxylatelaurylether	Disperbyk 180
3,4,5 Trihydroxybenzoeacid	Disperbyk 9076
Decanoic acid	Disperbyk 108
Polyethylenglycol(600)dioic acid	Disperbyk 111
3,6,9-Trioxadecanoic acid (TODS)	Disperplast I
Stearic acid	Ilco Lube 5500
Hydroxybenzoic acid	Dapral AKZO GE 202
Benzilicacid	Tegin OV
Sorbic acid	Jeffamine D 230
Levulinic acid	Jeffamine M 600
Gluconic acid	Ultrasil CA 2
Citric acid	Octacare DSP OL 300
	Dispex A 40

6.2.2 Results

Neither of the tested dispersants nor combinations of dispersants worked optimally giving the desired stabilization of the suspension. Some of the carboxylic acids looked promising seen from a stabilizing point of view, e.g., TODS, but the acids had a tendency of causing phase transformation due to water formation from condensation reactions on the zirconia surface. The lack of stabilization is probably due to the low dispersant concentration. It is not possible to add unlimited amounts of dispersant to the suspension as this will compromise the mechanical properties of the final composite.

6.3 Milling with Polyethylenimine (PEI)

High concentrations of PEI were found to prevent reagglomeration of the deagglomerated zirconia particles. So PEI was used for initial ball milling and separation studies of zirconia despite the need for high concentrations.

250 ml Si_3N_4 coated stainless steel grinding bowl was filled with a mixture of about 10 g of ZrO_2 powder and 145 g of PEI solution (a mixture of 20 g of PEI (Mw=1800) and 125 g IPA) and 150 g of 0.5 mm $ZrSiO_4$ in the Ar atmosphere in the glove box and after sealed carefully with tape It was milled with a P6 planetary mill at 500 rpm for 20 h.

After milling, the suspension was cooled for several hours and the product was moved into anhydrous IPA in a N_2 atmosphere (plastic glove box). The milled product was stirred slightly with a spatula in order to recover the part that stuck to the bowl. Otherwise, it was easily poured into the glass bottle. The $ZrSiO_4$ balls remained in the grinding bowl. The milled ZrO_2 suspension in isopropanol was separated by centrifugation. First, it was separated at 4000 rpm, 30 min with a Rotina 420 centrifuge. The precipitate was washed with IPA and the resulting suspension was marked S4. The supernant was subjected to further separation with a Beckman Ultracentrifuge. A polyallomer (ethylene-propylene copolymer) tube with 25 ml capacity was used, and separation was carried out at 25,000 rpm for 0.5 h. The supernant had a clear upper part, but was translucent at the lower part (marked S5 - translucent and slightly white in colour). The bottom precipitate was washed with IPA and marked S6. As the sample S5 was not transparent, 2/3 of this sample was further separated with ultracentrifuge again at 25,000 rpm, for 2h. The supernant was totally clear and marked S7 (Figure 22).

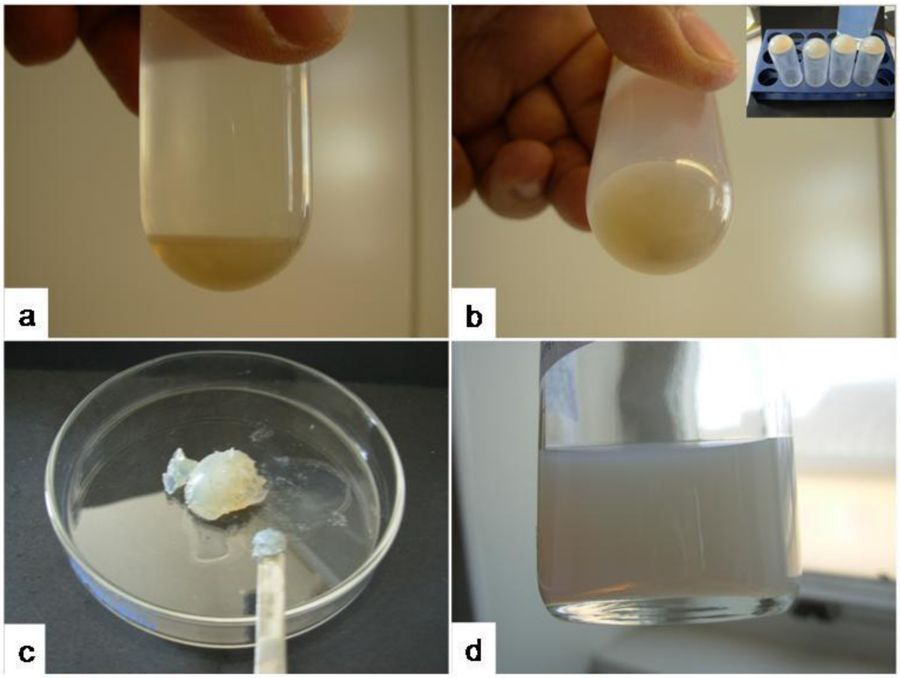


Figure 22 Side view of centrifuged sample in the 25 ml polyallomer tube after separation of sample S5 at 25000 rpm, 2 hrs; (b) Bottom view of sample S8 (precipitate) after the supernant was removed. (c) Appearance of wet-cake (sample S8) in a Petri dish; (d) Appearance of wet-cake dispersion (S8-1) in anhydrous IPA (2,2g wet cake dissolved in 50 ml IPA).

~ 8.6 g precipitate (slightly yellowish transparent cake) was collected and it was divided in two. 6.4 g (¾ of it) collected in a glass bottle and kept in 30 ml IPA solution. It was not totally suspendable in isopropanol - not transparent. 2.2 g (¼) of it was dispersed in 50 ml isopropanol by hard shaking and marked S8-1 (not transparent either) (see Figure 22). An overview of the separation experiment is found in Figure 23. Size distribution was analyzed by diluting the samples with isopropanol.

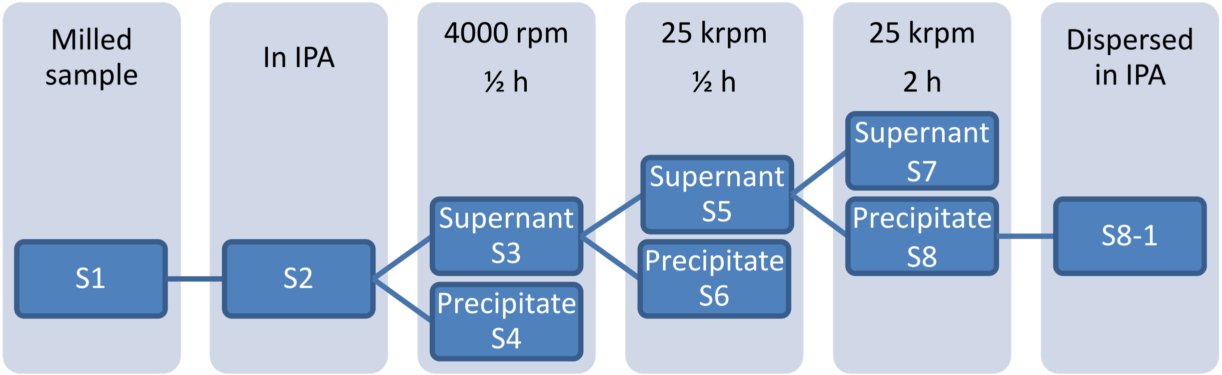


Figure 23 Overview of the separation test

The particle sizes of the collected samples were analyzed with DLS. The measured particle sizes are given in Table 4. The precipitate from the separation at 4000 rpm had an average size of 190 nm and had of course the largest measured particle sizes. It is shown that the particle size in the supernant is dependent upon the separation time and for 2½ h at 25000 rpm a particle size of 16 nm is reached. The collected samples were also analyzed with TEM and the particle sizes were confirmed. Progression of the particle size and morphology during the experiment is shown in Figure 24.

Table 4 measured particle sizes

Sample	*Particle size (nm)*
S4	190
S5	40
S6	90
S7	16
S8-1	45

PEI seems to work and no further settling was observed after stabilization with this polymer. Milling at 500 rpm, for 20 h with 0.5 mm $ZrSiO_4$ balls effectively reduce the size of ZrO_2 particles to below 200 nm. To collect nanosized portion (which is lower than 40 nm) milled ZrO_2, it seems that centrifugation between 25000 rpm for 30 min and 25000 rpm for 150 min is necessary. In this case transparent precipitate can be collected and this precipitate can be used for dental composites. Particle sizes in the supernant depend on the centrifugation time, which is logical. 30 min separation at 25000 rpm, leaves particle below 90 nm in the supernant, while 150 min separation leaves the particle size below 16 nm in the supernant.

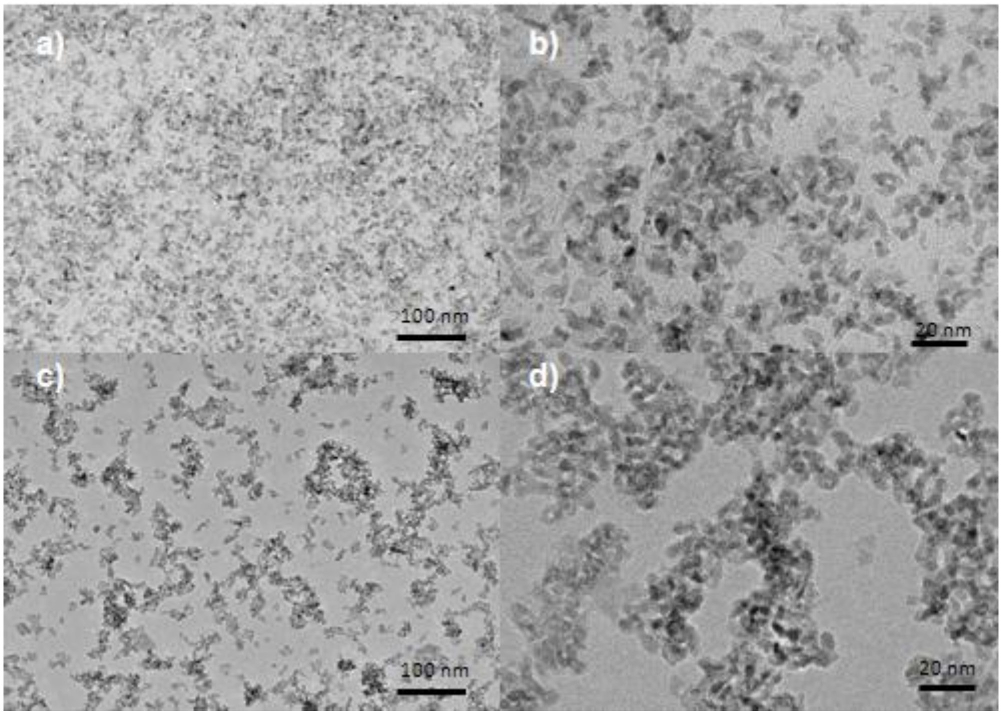


Figure 24 TEM images of (a & b) the supernant after 25,000 rpm for 2h (S7) and (c & d) the precipitate (S8-01)

PEI was found to only stabilize zirconia in suspension to a certain extend when added in high concentration. Addition of surfactants in that high concentration to the final composite will compromise the mechanical properties due to a lowering of the degree of polymerization. For this reason it was decided to change surfactant and instead focus on dimethacrylate monomers and 3-(acryloyloxy)-2-hydroxy-propyl methacrylate. These surfactants can be added in higher concentration, without working as softeners, as they are able to copolymerize with the monomer mixture.

It was found possible to deagglomerate the zirconia particles to a particle size of 190 nm. But after XRD analysis it was observed that the powder had phase transformed during milling in the same way as the powder in the article ‘Effect of Microscale Shear Stresses on the Martensitic Phase Transformation of Nanocrystalline Tetragonal Zirconia Powders’ in Appendix IV. As stated in section 4 the zirconia is sensitive towards shear stresses and phase transforms even with relatively low applied pressure. Applied pressures as low as 60 MPa are enough to initiate the phase transformation (see Appendix IV). A similar experiment was performed with commercial tetragonal zirconia stabilized with 3% yttria, and no sign of phase transformation were observed even when exposed to 188 MPa. Because of this high sensitivity, processing such as ball milling could potentially cause a problem when deagglomerating the particles. Through the experiments with milling of the zirconia it was concluded that it in fact is impossible to mill the particle as even low milling speeds, such as 120 rpm induces phase transformation. In recognition of this, ultrasonication was evaluated as an alternative way of deagglomerating the particles.

6.4 Ultrasonication

Zirconia is known from literature to phase transform upon ultrasonication[64]. For this reason the effect of the available ultrasound equipment (Vibracell CV 33 VCX 750 (750 watts), Sonics & Materials Inc., Newtown, CT , USA) was tested at high amplitude for its ability to initiate phase transformation.

6.4.1 Effect of ultrasonication on phase transformation of zirconia

~100 g of ZrO_2 in IPA (35 wt%) was ultrasonicated in nitrogen atmosphere at 75% amplitude for 1 h. To identify the effect of exposure to the atmosphere in the ultrasonication chamber a reference sample was kept in the ultrasonication chamber while the experiment was ongoing. This sample was not sonicated, but only exposed to the atmosphere in the chamber.

Another sample of ZrO_2 in IPA (35 wt%) was ultrasonicated for ~25 min at 95% amplitude at pulsed mode (1 sec. on - 1 sec. off). Stopped due to overload of the ultrasonication equipment.

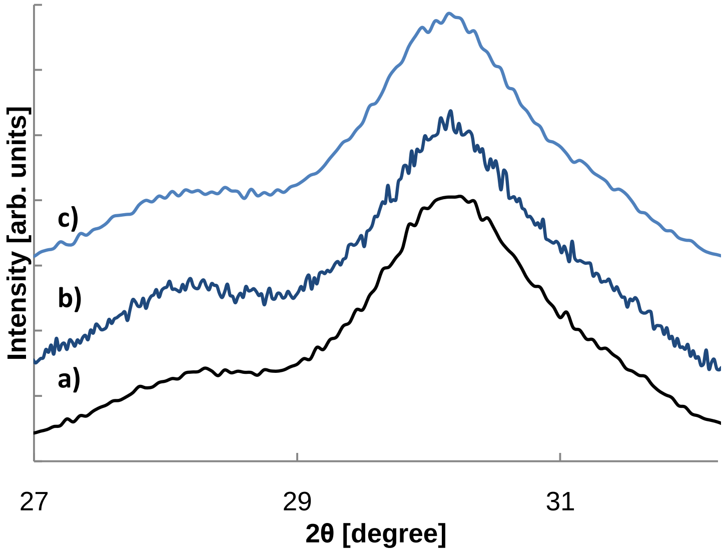


Figure 25 XRD patterns of (a) reference sample, (b) zirconia sonicated at 75 % amplitude for 1h and (c) zirconia sonicated at 95 % amplitude for ~25 min at pulsed mode

The XRD patterns from these experiments are illustrated in Figure 25. It is observed that the three samples have the same monoclinic volume fraction. This means that it is possible to ultrasonicate the zirconia powder without initiating phase transformation. Because of this result ultrasonication experiments were performed with different dispersing agents.

6.4.2 Ultrasonication in isopropanol

First PEI was tested because it was known to stabilize the zirconia particles in suspension.

Three samples were prepared. 10 g PEI, with different molecular weight, were mixed with 40 g of ZrO_2 in IPA (35 wt.-%) and the mixtures were ultrasonicated for 20 min at 38 % amplitude with a Vibracell CV33 VCX 750 (750 watts), Sonics & Materials Inc., Newtown, CT , USA.

Table 5 Measured particle sizes for the ultrasonicated PEI/zirconia dispersions

Sample	*Particle size (µm)*
Reference	1.8
M600	0.4
M1800	0.3
M10000	0.35

It is observed that it is possible to deagglomerate the zirconia particles down to a size of 0.3-0.4 µm with some variations in the particle size for the three different suspensions (Table 5). This might be a result of PEI M1800 being the best surfactant or it could be a result of deviations in the test. The reproducibility of these results was not tested, as the most important result was that deagglomeration was possible with ultrasonication.

6.4.3 Ultrasonication in acetonitrile

As described in section 5.4, 3-(acryloyloxy)-2-hydroxy-propyl methacrylate is able to stabilize zirconia in suspension in acetonitrile. Acetonitrile is used instead of isopropanol in order to prevent a competition between the isopropanol and 3-(acryloyloxy)-2-hydroxy-propyl methacrylate in reacting with the carbonates on the zirconia surface. Other dispersing agents were tested as well in acetonitrile and in lower concentration than in the ultrasonication experiments with PEI's above.

20 g of ZrO_2 in acetonitrile (47 wt%) and 0.7 g surfactant was ultrasonicated 30 min at 38% amplitude with a Vibracell CV33 VCX 750 (Sonics & Materials Inc., Newtown, CT). The results are listed in Table 6With these studies it was found possible to deagglomerate to a particle size of 300-400 nm with the ultra sound system with no phase transformation observed.

Table 6. For the stable suspensions the particle size distribution was determined. All the samples had precipitate of large zirconia agglomerates, because the ultrasound equipment not was strong enough to deagglomerate all the particles. These precipitates of large agglomerates are not observed after ultrasonication with a 20 kHz, 1000W ultrasound device (see section 5.4). But this equipment was first purchased after this experiment was conducted.

With these studies it was found possible to deagglomerate to a particle size of 300-400 nm with the ultra sound system with no phase transformation observed.

Table 6 The effect of different dispersing agents on the stability of dispersions of zirconia in acetonitrile

Dispersing agent	*Stabile*
PEI M600	Yes
Pentaethylene hexaamine	No
3-(acryloyloxy)-2-hydroxy-propyl methacrylate	Yes
Pluronic 1231	Yes
Monomer mixture	No

6.5 Salt assisted spray drying

Another way to obtain small zirconia particles are by modifying the preparation route. Salt assisted spray drying was tested as a possible way. It is known from literature that salt assisted spray drying and salt assisted spray pyrolysis can be used to produce nanosized ceramic particles[65].

In this study different ways to prepare nanosized zirconia particles were investigated. The tested preparation routes are azeotropic distillation, spray drying of pure $ZrO(OH)_2$ and spray drying in combination with either CsCl or NH_4NO_3. An overview of the tested methods is illustrated in Figure 26. The effect on particle size, crystal size, surface area, crystallization temperature and crystal phase of the formed zirconia is studied.

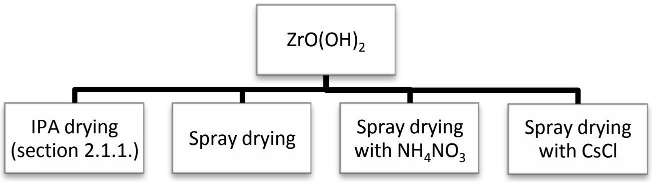


Figure 26 the tested preparation routes

6.5.1 Spray drying of neutral, aqueous dispersions

An suspension of amorphous $ZrO(OH)_2$ was prepared as described in section 2.1.1 (step 1-3). From this three different aqueous dispersions of $ZrO(OH)_2$ were prepared by stirring, with non, low ($lCsZrO_2$) and high ($hCsZrO_2$) CsCl concentration. The pure ZrO_2 precursor was spray dried without further preparation. The $lCsZrO_2$ precursor solution was prepared by stirring 4 L 5.0 wt% $ZrO(OH)_2$ water suspension with 100 g CsCl until the salt was dissolved. The $hCsZrO_2$ precursor solution was prepared by stirring 4 L 5.0 wt% $ZrO(OH)_2$ aqueous suspension with 200 g CsCl until the salt was dissolved. The dispersions were spray dried at pilot plant scale (see section 2.1.6) and the produced powder was calcined at varies temperatures.

Originally it was expected to be possible to washout the salt with anhydrous methanol. But the solubility of the salt was too low and the salt was instead removed with water to facilitate characterization of the particles.

6.5.2 Spray drying of acidic, aqueous dispersions

Dispersions containing high ($hNZrO_2$) and low ($lNZrO_2$) concentrations of NH_4NO_3 were prepared. The $hNZrO_2$ precursor solution was prepared by mixing 200 g 5.0 wt% $ZrO(OH)_2$ water suspension, 200 ml ethanol (99.7%), 10 g acetic acid, 100 g ammonium nitrate and 8 g of 2.0 M HCl. The resultant suspension was sonicated 30 minutes with Vibracell before spray drying.

The $lNZrO_2$ precursor solution was prepared by mixing 200 g 5.0 wt% $ZrO(OH)_2$ water suspension, 200 ml ethanol (99.7%), 10 g acetic acid, 5 g ammonium nitrate and 5 g of 2.0 M HCl. The resultant suspension was sonicated 30 minutes with Vibracell before spray drying. The precursor solutions were spray dried in lab scale (see section 2.1.6) and the produced powder was calcined at various temperatures.

6.5.3 Results

The effects of preparation methods and the presence of either salts or isopropanol during calcination are listed in Table 7. It is observed that the different methods result in zirconia powders with very different properties. This means that the preparation route has a large effect on the properties of the produced zirconia powders, especially the crystal phase and crystal size are influenced. For the CsCl containing samples also the crystallization temperature is influenced.

Table 7 Crystal size in nanometers, calcination temperature, monoclinic volume fraction (v_m) of the spray dried samples and crystallization temperature (from DSC)

Sample	*Crystal size (nm)*	*Calcination temp. (°C)*	v_m	*Crystallization temp. (°C)*
Reference sample	5.5	450	0.68	433
Spray dried ZrO_2	7.2	450	0.69	435
$hCsZrO_2$	7.1	550	0.23	525
$lCsZrO_2$	7.5	550	0.27	525
$hNZrO_2$	11.6	450	0.10	437
$lNZrO_2$	13.7	450	0.65	437

The XRD patterns for the samples calcined at 450°C are illustrated in Figure 27. It is observed that the (101) tetragonal reflection at $2\vartheta = 30.2°$ is more dominating for $hNZrO_2$ comparing with $lNZrO_2$ and the two pure samples, which have more dominating (-111) and (111) monoclinic reflections. The difference in peak width is a result of different crystal sizes. This difference is most pronounced when comparing the XRD patterns of the alcohol dried sample and $lNZrO_2$ (Figure 27c & 27e). The alcohol dried sample has the broadest peaks because it has the smallest crystal size. It is, furthermore, found that while both the pure zirconia samples and the two samples spray dried with NH_4NO_3 are crystalline at 450°C, this is not the case for the two CsCl containing samples, which still are amorphous at this temperature. For this reason these two samples were calcined at 550°C and subjected to XRD. The results are illustrated in Figure 28. It is observed that the tetragonal reflection is dominating for both samples.

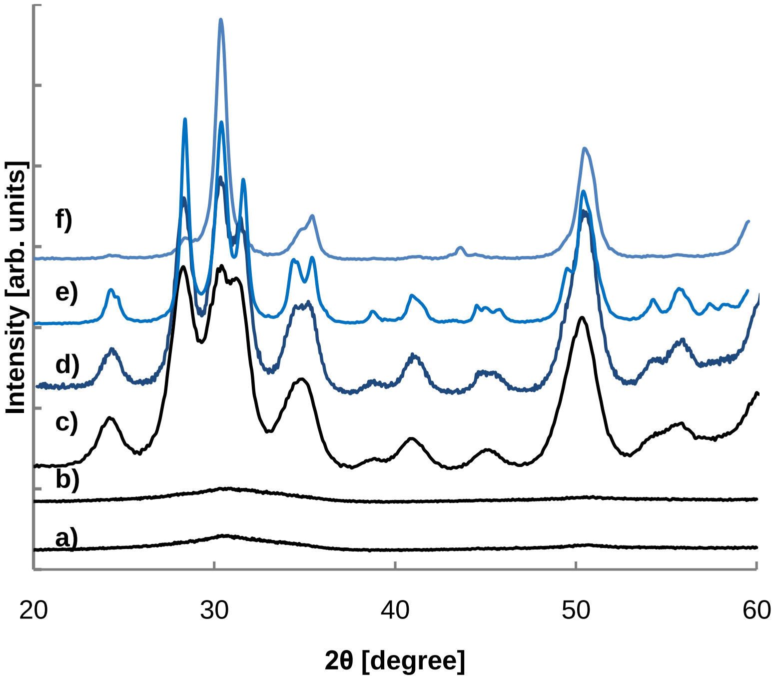


Figure 27 XRD patterns of powders calcined at 450°C; (a) lCsZrO2, (b) hCsZrO2, (c) alcohol dried zirconia, (d) spray dried pure zirconia, (e) lNZrO2 and (f) hNZrO2

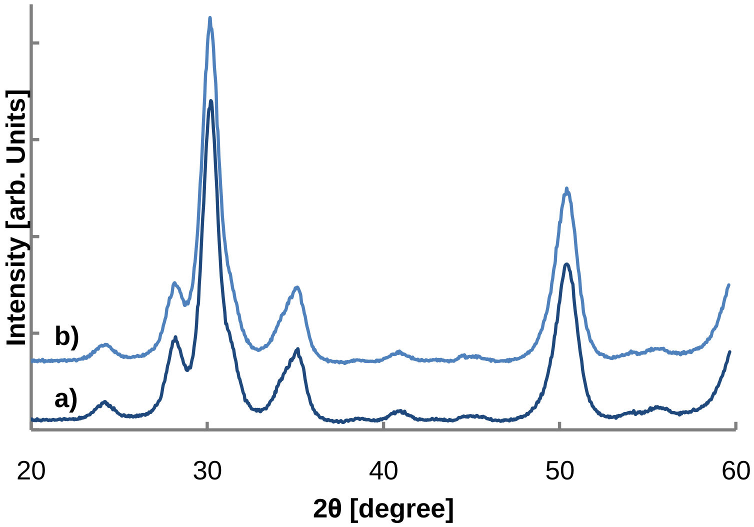


Figure 28 XRD patterns of zirconia spray dried with CsCl calcined at 550°C; (a) l CsZrO2 and (b) hCsZrO2

The XRD patterns of the powders prepared with salt assisted spray drying show only the existence of zirconia peaks and none of the peaks corresponding to CsCl or NH_4NO_3 are observed. This result indicates that all the salt is removed during washing.

All the samples were analyzed with SEM and TEM. The azeotropic distillation (section 2.1.1) resulted in particles with a diffuse morphology (Figure 13), whereas spray drying resulted for all samples in spherical particles with a diameter in the range of 1-2 µm for the pure sample and for the samples spray dried with CsCl (Figure 29 and Figure 30a-d). For the two samples spray dried with NH_4NO_3 the particle sizes were in the range of <0.5 µm (Figure 30e-i). The two NH_4NO_3 containing samples gave the widest particle size distributions. Except for the size differences, no changes in morphology were observed with either SEM or TEM in any of the spray dried samples.

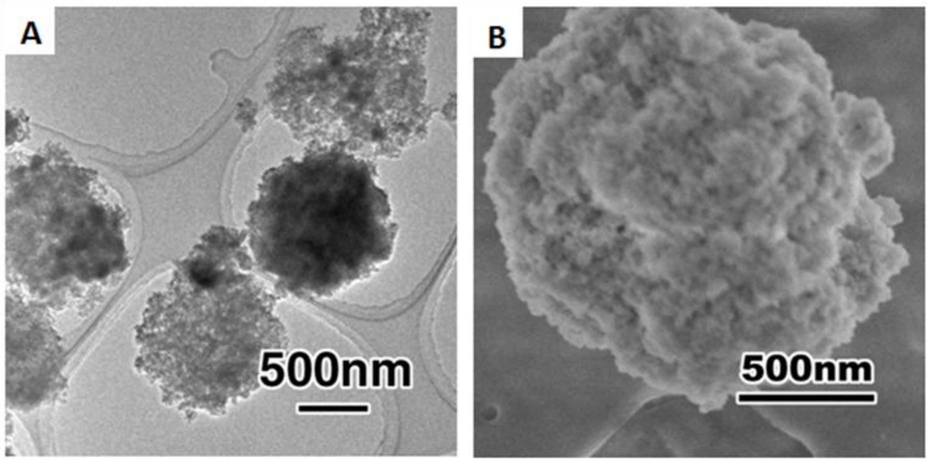


Figure 29 TEM and SEM images of spray dried pure ZrO_2

All the tested methods resulted in crystalline nanoporous zirconia powders with particle sizes up to 2 µm. This is in contrast to the very large and hard agglomerates of zirconia obtained by just calcining the air dried $ZrO(OH)_2$ dispersion.

The two pure zirconia samples have quite equal properties, but azeotropic drying gives the smallest crystals and micron sized particles with a more diffuse structure. Spray drying, however, gives micron sized spherical zirconia. Both methods give pure zirconia with primarily the monoclinic phase and the samples contain only 30 vol% tetragonal crystals. From the DSC analyses the crystallization temperature is found for the samples and it is observed that both the pure zirconia samples crystallize at ~435°C.

Salt assisted spray drying with CsCl lowers the monoclinic volume fraction in the zirconia samples. Both CsCl containing samples have lower v_m than the pure zirconia sample (see Table 7). The crystallization temperatures are however increased and the two CsCl containing samples crystallize at 525°C. Calcination at 550°C was expected to increase the sintering of the zirconia samples and hence increase the crystal size, but the crystal size does not increase significantly in any of the two samples and does not differ significantly from the spray dried pure zirconia sample. The decrease in v_m is probably a result of anionic stabilization origination from incorporation of Cl^- in the tetragon crystal lattice. The stabilizing effect is among others described by Gutzov et al[66]. Furthermore does chloride ions adsorb strongly on zirconia and is difficult to remove completely from the surface[67].

In contrast to the CsCl containing samples, the presence of NH_4NO_3 during calcination causes no increase of the crystallization temperature, as both the samples crystallizes at ~435°C. For the two NH_4NO_3 containing samples a significant difference is observed. h$NZrO_2$ has a volume fraction of monoclinic crystals (v_m) of 0.10 and l$NZrO_2$ has a v_m of 0.65. The later is close to the v_m of the two pure zirconia samples (Table 7). Also the crystal sizes vary in these two samples and h$NZrO_2$ has a crystal size of 11.6 nm and l$NZrO_2$ a size of 13.7 nm. These crystal sizes were confirmed by TEM. Both samples show increased crystal sizes comparing with all the other samples. Especially the sample containing the lowest content of NH_4NO_3 has increased crystal size.

h$NZrO_2$ gives the lowest v_m, but has larger crystals, than the pure zirconia samples. This indicates a stabilization of the tetragonal phase, which most likely originates from ammonium ions working as mineralizers, in the same way, as chlorine ions stabilize the samples calcined in the presence of CsCl. The stabilizing effect of ammonium ions counteracts the size effect and increases the critical size of the tetragonal crystals. Normally when the crystal size increases the v_m will increase as well. This is not the case in this study and supports the presence of ammonium stabilization. Surprisingly l$NZrO_2$ is not stabilized to the same extend and is the one of all the salt containing samples with the highest v_m. l$NZrO_2$ and l$CsZrO_2$ have the same zirconia concentration and the fact that only the CsCl is able to stabilize the tetragonal phase in the crystals underlines the stabilization potential of chlorine ions.

In contrast to the diffuse particle structure of the samples dried with azeotropic distillation, all the spray dried samples are spherical, but with different sizes depending on the production process. This indicates that the morphology and size are more a result of processing parameters, than a result of the properties and concentrations of the salts. Also the fact that the two NH_4NO_3 containing samples gave a wider particle size distribution supports this conclusion.

It was expected possible to produce nanosized particles. This was, however not the case. Furthermore either a stabilization of the tetragonal phase or phase transformation were observed. For these reasons the project with salt assisted spray drying was terminated.

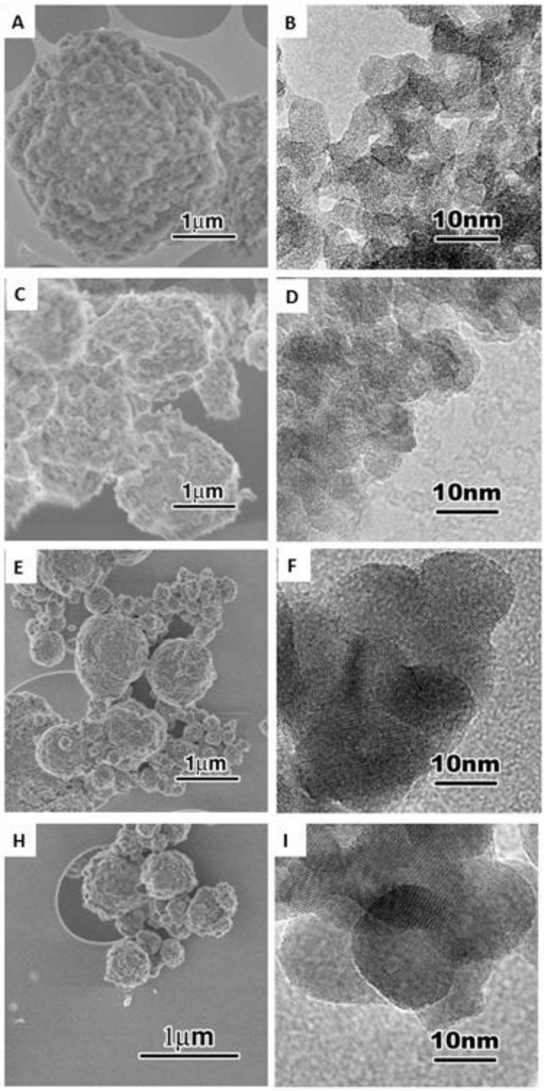


Figure 30 SEM and TEM of salt-assisted spray dried ZrO_2 (a & b) $hCsZrO_2$, (c & d) $lCsZrO_2$, (e & f) $hNZrO_2$ and (h & i) $lNZrO_2$

6.6 Zirconia-silica samples

Another idea is to add silica to the amorphous zirconia in order to lower the refractive index of the particles. This method is, e.g., used in the zirconia contain composite materials Filtek Z100 and Z250 (3M, MN, USA).

Zirconia-silica particles were produced in an effort to lower the refractive index of the resulting particles. In this study two different approaches to produce zirconia-silica powders were investigated; (i) Spray drying of a dispersion of amorphous $ZrO(OH)_2$ and silica nano-particles (as section 6.5.1). (ii) Precipitation amorphous $ZrO(OH)_2$ from a solution zirconium oxychloride containing silica nanoparticles.

6.6.1 Spray drying of neutral, aqueous dispersions

An aqueous dispersions of $ZrO(OH)_2$ and silica nanoparticles were prepared by adding Ludox® TMA colloidal silica (34 wt%, suspension in deionized water) to the amorphous $ZrO(OH)_2$ dispersion described in section 2.1.1 (step 1-3). The silica suspension was added in such amounts that the calcined product will contain 20 wt% silica. The dispersion was spray dried in pilot plant scale (see section 2.1.6) and the produced powder was calcined at varies temperatures

6.6.2 Precipitation with nano-silica

$ZrO(OH)_2$ were prepared according to the previously described method in section 2.1.1, but with addition of Ludox® TMA colloidal silica (34 wt%, suspension in deionized water) to the zirconium oxychloride solution, so the calcined product will contain 20 wt% SiO_2. Before calcination the $ZrO(OH)_2$ sample was dried by azeotropic distillation with isopropanol. The sample were dried until no reaction was detected between the distillate and $Zr(OBu)_4$.

6.6.3 Results

The XRD patterns of the zirconia-silica samples are illustrated in Figure 31. It is observed that none of the two samples are crystalline after calcination at 450°C. The spray dried sample, however, contains small amounts of tetragonal crystals (the reflection at 44° originates from the sample holder). When the samples are calcined at 850°C both the samples turn crystalline. They are primarily tetragonal also after exposure to humidity. More information on the calcined samples are listed in Table 8. It is observed that there are some variations in the two samples such as crystal size and crystallization temperature.

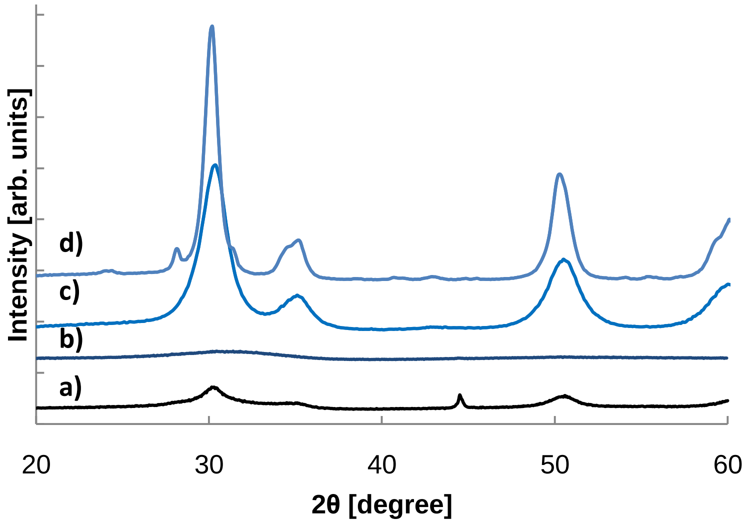


Figure 31 XRD patterns of zirconia spray dried with silica (a) calcined at 450°C and (c) calcined at 850°C. Zirconia precipitated with SiO_2 (b) calcined at 450°C and (d) calcined at 850°C

Table 8 crystal size in nanometers, monoclinic volume fraction and the crystallization temperature (from DSC) of the spray dried samples

Sample	*Crystal size (nm)*	*Calcination temp. (°C)*	v_m	*Crystallization temp. (°C)*
SiO_2 spray dried	8.8	850	0	435 and 671
SiO_2 precipitated	4.5	850	0.07	811

To understand the difference in crystallization temperature in the zirconia-silica samples the calcined samples were analyzed using TEM to produce elemental mapping of the samples. The TEM images of the precipitated sample showed very homogeneous samples and the silica particles are evenly distributed throughout the sample (Figure 32). This is in contrast to the more inhomogeneous spray dried sample (Figure 33). Here it was found that the silica particles had a tendency of clustering and the particles had large areas without silica particles. The zirconia was, however equally distributed throughout the sample. This can also explain the fact that some of the zirconia in the spray dried sample crystallized at 435°C and the rest of the sample need calcination at 671°C to get crystalline. For the precipitated sample nothing happened even at 600°C. This indicates that when the zirconia particles are not in direct contact with the silica particles, they behave as pure zirconia. But when the zirconia is in contact with the silica particles crystallization is inhibited.

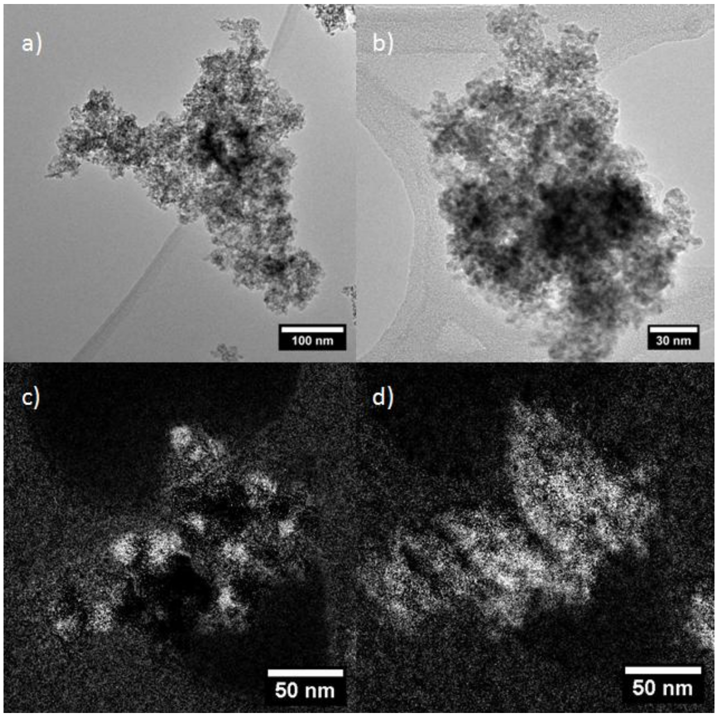


Figure 32 TEM of zirconia precipitated with silica and (a & b) calcined at 850°C, (c) Si map and (d) Zr map of the same particle

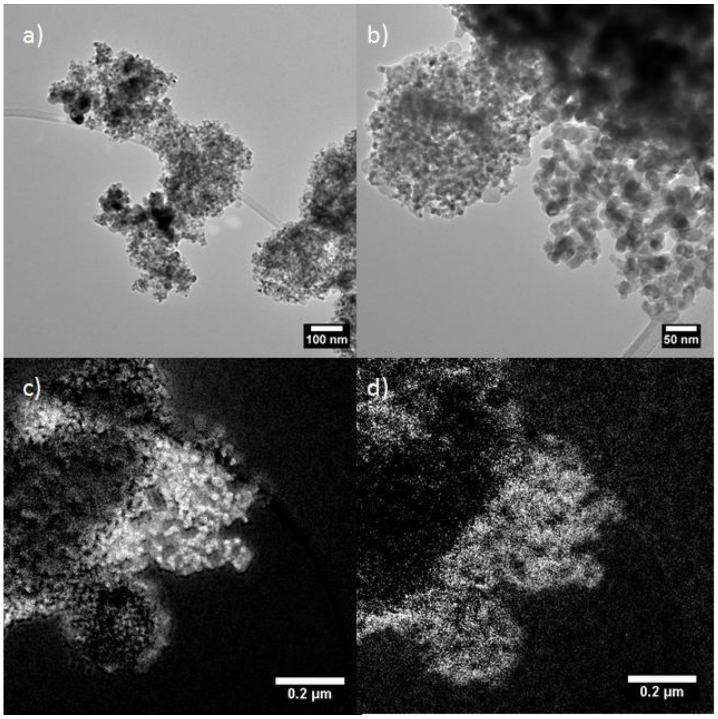


Figure 33 TEM of zirconia spray dried with silica and (a & b) calcined at 850°C, (c) Si map and (d) Zr map of the same particle

Addition of silica to the amorphous zirconia lead to an increase of the crystallization temperature, which was increased from 435°C to 671°C and 811°C for the two samples. Furthermore silica stabilizes the tetragonal phase. From these results it was concluded that none of the two techniques described above were possible solutions to the problem with the high opacity of the composites.

6.7 Summary of Chapter 6 and Appendix IV

It was found possible to deagglomerate zirconia almost to the primary crystals, but deagglomeration in media mills is not a possibility as it, even at low milling speeds, causes the zirconia to phase transform. Ultrasonication deagglomerates zirconia down to 300-400 nm without any observed phase transformation.

Because this thorough screening of surfactants did not lead to any solution, it was decided to deagglomerate in a mixture of 3-(acryloyloxy)-2-hydroxy-propyl methacrylate and the monomer mixture. This worked fairly well as dispersion agent and got past the problems with dispersants softening the polymer matrix. This surfactant was chosen from a number of available commercial monomers due to its relative size and properties.

Separation condition for smaller particles (less than 100 nm) should be identified. Based on previous experiment, higher speed than 4000 rpm and at least 30 minutes is necessary to leave only the smaller particles in suspension. Then, the smaller size ZrO_2 particles in the suspension should be further separated with ultracentrifuge at 25,000 rpm for up to 2½ h in order to obtain a suspension with a particle size less than 40 nm.

Four different preparation routes were tested to prepare nanoporous zirconia powders; azeotropic distillation with isopropanol, spray drying and salt assisted spray drying with NH_4NO_3 or CsCl (two different concentrations in both cases). From the results of this study it is concluded that addition of high amounts of NH_4NO_3 gives the crystals with the lowest monoclinic volume fraction and particles having a spherical shape. Spray drying of a precursor solution containing 1:1 ZrO_2:CsCl results in almost the same properties, but have a little higher monoclinic volume fraction and a little smaller crystal size. None of the tested preparation resulted in nanosized zirconia particles and the project was terminated.

It was also tested if it was possible to lower the refractive index by addition of silica nanoparticles to the zirconia. Both spray drying and precipitation were tested as possible preparation routs to silica-zirconia powders. It was, however observed that addition of silica increased the crystallization temperature of the zirconia and stabilized the tetragonal phase.

From the experiments described above it was concluded to use ultrasonication to deagglomerate the zirconia particles even though this method gave to large particles, it was the only method, which did not result in phase transformation or stabilization of the tetragonal crystal phase.

7 Composite properties

7.1 Introduction

The durability of a dental composite depends on the mechanical, the chemical and the physical properties of the composite. These properties could be compromised by addition of an unsilanized, highly porous zirconia filler and for this reason the flexural strength of different test composites were tested. However in this thesis, the focus is on the polymerization shrinkage. So, firstly, it was tested whether the zirconia filler was able to counteract the polymerization shrinkage of dental composites. In this study the phase transformation was initiated by water diffusing into the polymer matrix (see Appendix VII). It was found that the overall shrinkage of a composite containing 42 wt% zirconia stored in water at 40˚C was reduced with 44 % within the first 7 days in comparison with an equivalent sample stored in air.

The ability of the produced zirconia filler to reduce the overall curing shrinkage of a test composite is described in this chapter. This test is the most important test at all because if the addition of the zirconia filler does not change the overall shrinkage the hypothesis (section 1.3.2) falls. Also the effect on the mechanical properties is described for test composites.

7.2 Mechanical properties

The effect of addition of the porous filler on the flexural strength was investigated by three point bending tests. First, composites with various amounts of the unsilanized zirconia or MPTMS modified zirconia were tested. The results are plotted in Figure 34. A weak tendency of increasing flexural strength with increasing filler load is observed. It is also observed that the composites containing silanized zirconia have higher flexural strength.

An experiment with the Silquest® A-1230 modified monoclinic zirconia showed strongly decreased flexural strength for the test composites – even lower than the results from the tests with unmodified monoclinic zirconia. The low flexural strength of this sample indicates that Silquest® A-1230 (polyethylene glycol trimethoxy silane) works as a softener of the system and it proves how important it is to identify the most optimal surfactant for the system to prevent this lowering of the flexural strength.

Composites containing tetragonal zirconia were also tested. These composites were prepared according to the procedure described in section 2.3.1, but in water free air in a glove box to prevent premature phase transformation. As mentioned in section 1.2.3, oxygen works in conjugation with the phenol inhibitors and it is not possible to handle the monomer in an oxygen free atmosphere for longer periods of time. For this reason the samples were prepared in dry air and not in the normally-used nitrogen atmosphere.

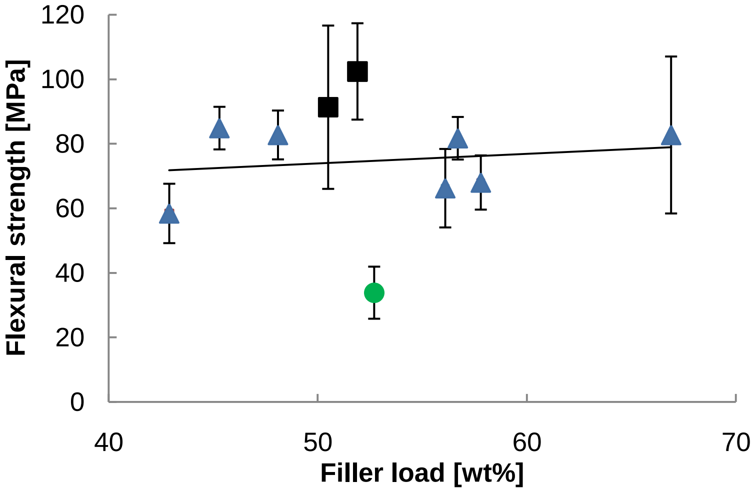


Figure 34 Flexural strength as function of filler load for test composites containing unsilanized, monoclinic zirconia (▲), for MPTMS modified monoclinic zirconia (■) and for Silquest® A-1230 modified monoclinic zirconia (●).

Six test series were conducted with three MPTMS modified zirconia samples and three with unsilanized zirconia. Different specimens were tested under three different conditions: dry, after boiling in water for 48h and after water storage for a month at 37°C. The results are plotted in Figure 35. It seems that silanization has a tendency to increase the flexural strength, but it is not statistically significant. It is also observed that water aging reduces the flexural strength of the test composites. From the three point bending tests of different zirconia containing test composites, it is concluded that silanization of the zirconia particles prior to mixing do not have a statistically measurable effect on the flexural strength of the resulting composites. This could be due to the fact that the particles are highly porous, which result in a strong mechanical adhesion between filler and polymer matrix.

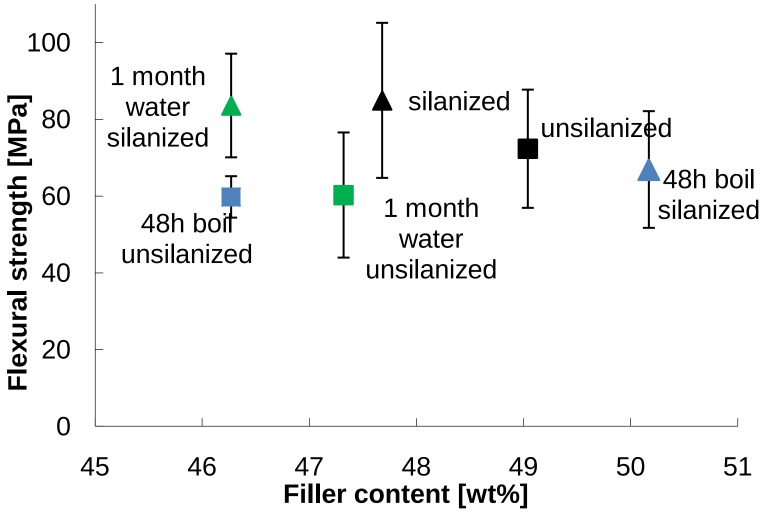


Figure 35 Flexural strength as function of filler load for test composites containing silanized (■) or unsilanized (▲), tetragonal zirconia. (black) reference sample, (green) stored in water for 1 month and (blue) boiled in water for 48h.

Also, the composites described in Appendix VII were tested. The results are listed in Table 9. It is observed that the compounds have higher filler loads and flexural strength. All the composites have flexural strength above 80 MPa, which is the requirement for a dental resin composite according to the ISO standard (ISO 4049:2000 (E)); composites 2 and 3 have flexural strength comparable with commercial materials. The problem with these composites is the opacity. The samples are opaque and have an opacity close to 1. This is a result of the large particles, which prevents passage of light through the composite and hence reduces the depth of cure[68].

Table 9 Zirconia content, crystal phase, filler load and flexural strength of three test composites

Sample	*Zirconia content (wt%)*	*Crystal phase*	*Filler content (wt%)*	*Flexural strength (MPa)*
Composite 1	42	Tetragonal	63	96
Composite 2	32	Tetragonal	65	113
Composite 3	32	Monoclinic	65	121

7.3 Summary of Chapter 7 and Appendix VII

Test composites were prepared and it was found possible to decrease the polymerization shrinkage of resin composites by addition of metastable tetragonal zirconia filler particles, which are able to expand upon exposure to water molecules. The overall shrinkage of the composite (42 wt% zirconia) sample stored in water at 40˚C was reduced with 44 % within the first 7 days compared with an equivalent sample stored in air at 40˚C. For the composite containing 32 wt% metastable zirconia the shrinkage was reduced with 29%. It was shown that the reduced shrinkage of the composite was not a result of water up take, as the composite containing the stable monoclinic zirconia filler did not show the same reduction in shrinkage (11% reduction). The flexural strength of the tested composites were all acceptable and in the range of values for commercial dental resin composites.

From the three point bending test it was concluded that silanes do not have a large effect on the flexural strength of the tested composites. This could be due to the high porosity of the zirconia filler, which gives a good mechanical adhesion of the resin.

8 Conclusions and outlook

The aim of this study was to produce a low shrinkage dental composite based on an expandable zirconia filler. This filler was characterized in regards to crystal phase, surface chemistry and morphology. It was found to consist of 1.5-2 µm large highly porous agglomerates of 6 nm tetragonal zirconia crystals. It was found possible to initiate the martensitic tetragonal to monoclinic phase transformation by annealing above 550°C, by application of stresses and by reaction with water, HCl, HF, NH_3 and HBr. The crystals are more sensitive towards these initiators than YSZ powders.

Photoacid generators were tested for their ability to induce phase transformation upon exposure to the light of a curing probe and phase transformation was observed. The reaction speed was, however, to slow and the light activated reaction led to a discoloration of the polymer matrix. So, water diffusing into the composite was used as an initiator resulting in a monoclinic volume fraction of 0.6.

Various ways to surface modify the zirconia were analyzed and it was quickly found that many of the commercial surfactants either stabilizes the tetragonal crystal phase or induces phase transformation as a result of water formation on the zirconia surface. A surfactant was, however, identified. 3-(acryloyloxy)-2-hydroxy-propyl methacrylate is able to bind carbonates on the surface under formation of a carboxylic ester. This enables stabilization of the deagglomerated particles in acetonitrile and works as an activator of the zirconia crystals.

Methods to deagglomerate the zirconia particles were investigated and it was found possible to ball mill the particles almost down to the primary crystals. This, however, caused the crystals to undergo the t→m phase transformation. Instead ultrasonication was tested and it was found possible to reach particle sizes of 300-400 nm without any phase transformation. This is, however, not small enough to produce a transparent composite material.

Finally the ability of the produced zirconia filler to counteract the polymerization shrinkage was investigated and a number of composites were prepared. The volume change over time was measured using Archimedes method. From these experiments it was shown that the addition of the metastable zirconia filler actually reduced the polymerization shrinkage with up to 44% after a week in comparison with and equivalent sample stored in air.

It was also concluded that it is possible to produce a low shrinking dental composite containing a metastable tetragonal zirconia filler with acceptable mechanical properties. But the large particle size of the filler causes problems with high opacity and a small depth of cure.

In order to optimize this composite the following three areas has to be addressed: Reduction of compound opacity, acceleration of phase transformation in matrix dispersed zirconia and increase of filler load.

8.1 Reduction of opacity

Dental resin composite materials need a low opacity to imitate the natural dentine of the tooth, especially when used for visible fillings. Besides the esthetic aspect, a low opacity of the composite material will also insure a high depth of cure.

The produced test composite materials have shown a high opacity, in the order of 99%, resulting in a rather low depth of cure. This is possibly caused by a combination of reagglomeration of particles during evaporation of solvent as part of the compounding process and the particle size in itself.

Based on the initial development work, it has been possible to deagglomerate zirconia to a particle size of 300–400 nm by use of ultrasonication, without causing undesired phase transformation of the particles. Furthermore, a reduction in particle size ultimately to a size below 100 nm is expected to improve the opacity dramatically. A decrease in particle size can in principle be met by optimizing the deagglomeration of existing particles or by modifying the existing production process making particles easier to deagglomerate. Alternatively, it might be possible to produce nano sized particles by an alternative process.

8.2 Acceleration of the transformation rate

The shrinkage of dental resins occurs when the resin starts to cure and continue for a couple of weeks until the polymerization is completed at ~70 % polymerization. Around 85 % of this shrinkage takes place within the first 15 minutes after the resin is exposed to curing light.

At present, the zirconia particles phase transform by water diffusing into the resin, a process which takes place over a couple of days with about 50 vol% of the particles transforming within the first 8 hours. The optimal situation would be to have a phase transformation rate closer to the curing rate of the resin – at least for a part of the zirconia. A faster transformation could be reached by the following routes; optimization of a photoacid generator, which do not discolor the composite, or making the particles more sensitive to water or other initiators.

8.3 Increasing filler load

The initial compounding trials have proved it possible to add up to 42 wt% zirconia and in total 63 wt% filler, with the remaining being silanized glass. This is a rather low number compared to traditional resin composites.

The zirconia powder is characterized by a very large surface area. This requires a lot of resin to fully wet the surface. Initial tests were done with a 3-(acryloyloxy)-2-hydroxy-propyl methacrylate. However the system has never been optimized. A higher filler load can be reached by optimization of the compounding process and of the surfactant.

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10 List of abbreviations

AFM	atomic force microscopy
APS	(3-aminopropyl)trimethoxysilane
Bis-GMA	bisphenol A glycidyl methacrylate
CQ	camphorquinone
DABE	ethyl 4-dimethylamino benzoate
D_3MA	decane-1,10-diol dimethacrylate
DMAP	dimethylaminopyridine
DSC	differential scanning calorimetry
DLS	dynamic light scattering
EBPDMA	ethoxylated bisphenol A glycol dimethacrylate
FWHM	full width at half maximum intensity
HMDS	hexamethyl disiloxane
IPA	isopropanol
MDP	methacrylate-decyl dihydrogenphosphate
MPTMS	3 γ-methacryloxypropyl trimethoxy silane
MT1	merocyanine dye linked bis(trichloromethyl)-1,3,5-triazine
m-ZrO_2	monoclinic zirconia
PAG	photoacid generator
PEI	polyethylenimine
RT	room temperature
SEM	scanning electron microscopy
TEGDMA	triethylene glycol dimethacrylate
TEM	transmission electron microscopy
TODS	3,6,9-trioxadecanoic acid
Ts	tosyl group
t-ZrO_2	tetragonal zirconia
UDMA	diurethane dimethacrylate
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
YSZ	yttria stabilized zirconia

11 List of symbols

b	width
E_b	binding energy
E_{kin}	kinetic energy
F	max load
G	energy release rate
G_c	critical energy release rate
h	height
$h\upsilon$	photon energy
I	intensity of transmitted light
I_0	intensity of incoming light
I_m	integrated intensities of monoclinic reflections
I_t	integrated intensities of tetragonal reflections
K	shape factor
l	distance between supports
m	monoclinic
n_m	refractive index of polymer matrix
n_p	refractive index of particles
P	peel force during separation
r	radius of spherical particles
t	tetragonal
v_m	monoclinic volume fraction
vol%	volume percent
wt%	weight percent
x	optical path length
X_m	integrated intensity ratio
β	full width at half maximum
ΔG	change in Gibb's free energy
Θ	Bragg angle
λ	wavelength
λ_{max}	wavelength at absorption maximum
ρ	phenyl group
σ	stress
τ	crystal size
φ	peel angle
Φ	workfunction
ϕ_p	volume fraction of particles

12 Appendixes

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LETTER

Phase stabilizing effects of phosphates and sulfates on nanocrystalline metastable tetragonal zirconia

M. Skovgaard · K. Almdal · A. van Lelieveld

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Introduction

Sulfated zirconia has gained a lot of interest due to the ability to catalyze a wide range of organic reactions such as isomerization of *n*-butane [1], synthesis of derivatives of 1,5-benzodiazepine and diaryl sulfoxides [2], and benzylation of toluene [3]. The catalytic properties of phosphated zirconia are likewise well-known [4–6]. Phosphates and sulfates are known to stabilize the tetragonal and cubic phase in zirconia, but the effect is not yet fully understood. Several authors have proposed that the stabilization is a crystal size effect, where the surface free energy difference between the tetragonal and monoclinic phase for sufficiently small crystals exceed the bulk free energy difference between the two phases [7, 8]. Other authors ascribe the stabilization to the presence of anionic impurities such as SO_4^{2-}, PO_4^{3-} and Cl^- [9–11]. The theory based on anionic stabilization of the tetragonal phase is the most commonly accepted. This investigation specifically addresses the surface effect of the stabilization by sulfate and phosphate on tetragonal zirconia, by experimental removal of the crystal size effect.

Experimental

All chemicals were supplied by Sigma–Aldrich Inc. (St. Louis, MO, USA) and used as received. Highly porous nanocrystalline tetragonal zirconia powders were synthesized as previously described [12] by controlled hydrolysis of $ZrOCl_2$ followed by careful calcination. The t-ZrO_2 powders are extremely porous and have specific surface area of $\sim 150\ m^2/g$. The synthesized t-ZrO_2 powders were kept in water-free environment for further treatment.

Surface modification

In the inert atmosphere of a glovebox, 1 g metastable tetragonal zirconia was stirred for 150 min with 10 mL anhydrous methanol and 1 mL of either 99.99% phosphoric acid or concentrated sulfuric acid. The mixture was filtered and the zirconia powder was washed twice with anhydrous methanol and dried at RT in the glovebox. Four samples were prepared with tetragonal zirconia, originating from two different batches. For reference a small sample of the surface modified zirconia was mixed with a methacrylic monomer mixture (bisphenol-A diglycidyl ether dimethacrylate, urethane dimethacrylate, and triethylene glycol dimethacrylate—Bis-GMA/UDMA/TEGDMA, 36/44/20 wt%) and a photo polymerization system (champhorquinone and ethyl 4-dimethylamino benzoate—CQ/DABE both 0.5 wt%). A sample was placed between two glass plates and cured for 2 min using blue light (1,100 mW) from a Bluephase® light probe (Ivoclar Vivadent, Liechtenstein). The polymer matrix prevents the tetragonal crystals from undergoing phase transformation. Such samples are termed matrix dispersed zirconia. The cured samples were then subjected directly to the X-ray diffraction (XRD) measurement for phase analysis.

M. Skovgaard (✉) · A. van Lelieveld
DentoFit A/S, Frederiksborgvej 399, 4000 Roskilde, Denmark
e-mail: ms@dentofit.com

A. van Lelieveld
e-mail: avl@aneedle.net

M. Skovgaard · K. Almdal
Department of Micro- and Nanotechnology,
Technical University of Denmark, Frederiksborgvej 399,
4000 Roskilde, Denmark
e-mail: kral@nanotech.dtu.dk

Results and discussion

The phosphor and sulfur content in the phosphated and the sulfated samples were by XPS (K-alpha Monochromated, XPS spectrometer, Thermo Fisher Scientific Inc., Waltham, MA United States) analysis determined to ~5 and ~4 atom%, respectively. Due to the careful washing in the preparation step, it is assumed that measured amounts represent ionic binding of SO_4^{2-} and PO_4^{3-} to the surface. The reference sample did not contain either phosphor or sulfur.

The recorded X-ray diffraction (XRD) patterns (STOE & Cie GmbH, Darmstadt, Germany) for the reference sample, the phosphated and the sulfated samples are illustrated in Figs. 1, 2, and 3. For all three samples the XRD patterns are recorded in air and in water. Furthermore matrix dispersed zirconia samples were analyzed using XRD. From Fig. 1 it is seen that the reference sample only contains traces of the monoclinic phase prior to exposure to humidity and the tetragonal 101 reflection of zirconia at $30.2° = 2\theta$ is dominating. Broad peaks in the XRD patterns are a result of small crystal sizes. The powder is very moisture sensitive and a few seconds of air exposure induces the martensitic tetragonal to monoclinic (t → m) phase transformation [13]. After air exposure the two monoclinic reflections (−111 and 111) grows in intensity and the (101) reflection decreases, indicating a t → m transformation. The monoclinic volume fraction (v_m) is calculated following a procedure proposed by Toraya et al. [14] to ~0.68. After addition of a drop of water to the XRD sample the monoclinic reflections becomes even more dominating ($v_m \approx 0.84$). For both the phosphated and the sulfated samples no change in XRD patterns are observed even with water addition and v_m is calculated to ~0.5 both before and after exposure to humidity. Thus, phase transformation does not occur in any of the samples. However, it also shows phase transformation of some of the zirconia crystals during the surface modification procedure. This is presumably due to water in the phosphoric and sulfuric acids or condensation reactions of the two acids with OH groups on the zirconia surface.

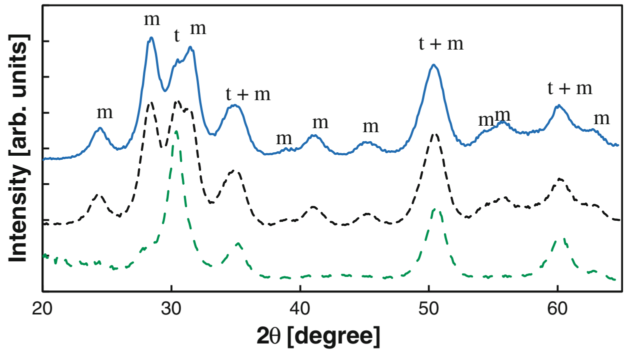

Fig. 1 Unmodified zirconia in resin (*dashed green*), exposed to ambient atmosphere (*dotted black*) and water (*blue*)

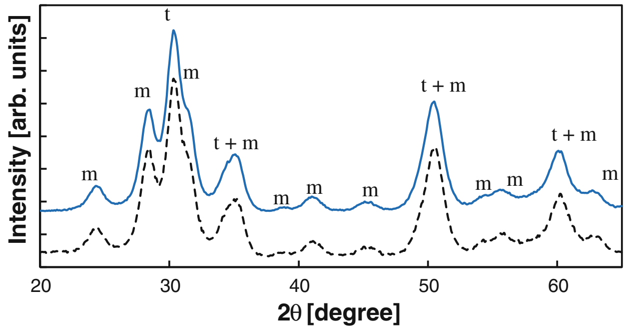

Fig. 2 Phosphated zirconia exposed to ambient atmosphere (*dotted black*) and water (*blue*)

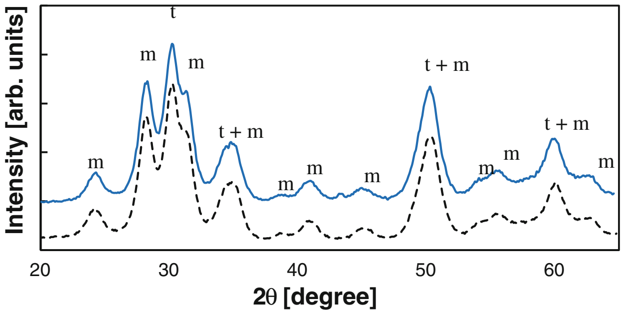

Fig. 3 Sulfated zirconia exposed to ambient atmosphere (*dotted black*) and water (*blue*)

It has been speculated that the stabilizing effect of sulfate and phosphate on the tetragonal phase at RT is due to a retardation of particle growth during the calcination [15]. However, in the present study the zirconia is sulfated or phosphated after calcination and thus the crystal size is the same for neat and surface treated specimens. The crystal size of the reference sample was calculated by the use of Scherrer equation [16] to ~6 nm which, as expected, did not change as a result of the modification with phosphoric or sulfuric acid in any of the samples. The crystal size was confirmed by the transmission electron microscope analysis (FEI Technai, FEI Company, Hillsboro, OR USA)—showing that all the samples indeed are composed of very small, heavily agglomerated 6–8 nm nanocrystallites, which are interconnected and make three dimensional porous networks of up to 1.5–2.0 μm. From the TEM images could further be concluded that the morphology of the zirconia powder does not change as a result of modification with either phosphoric or sulfuric acid (see Fig. 4).

The results support that the phase stabilization is an anionic stabilization effect and not crystal size effect. Mekhmer and Ismail [10] found that calcination of phosphated monoclinic zirconia does not influence the crystal

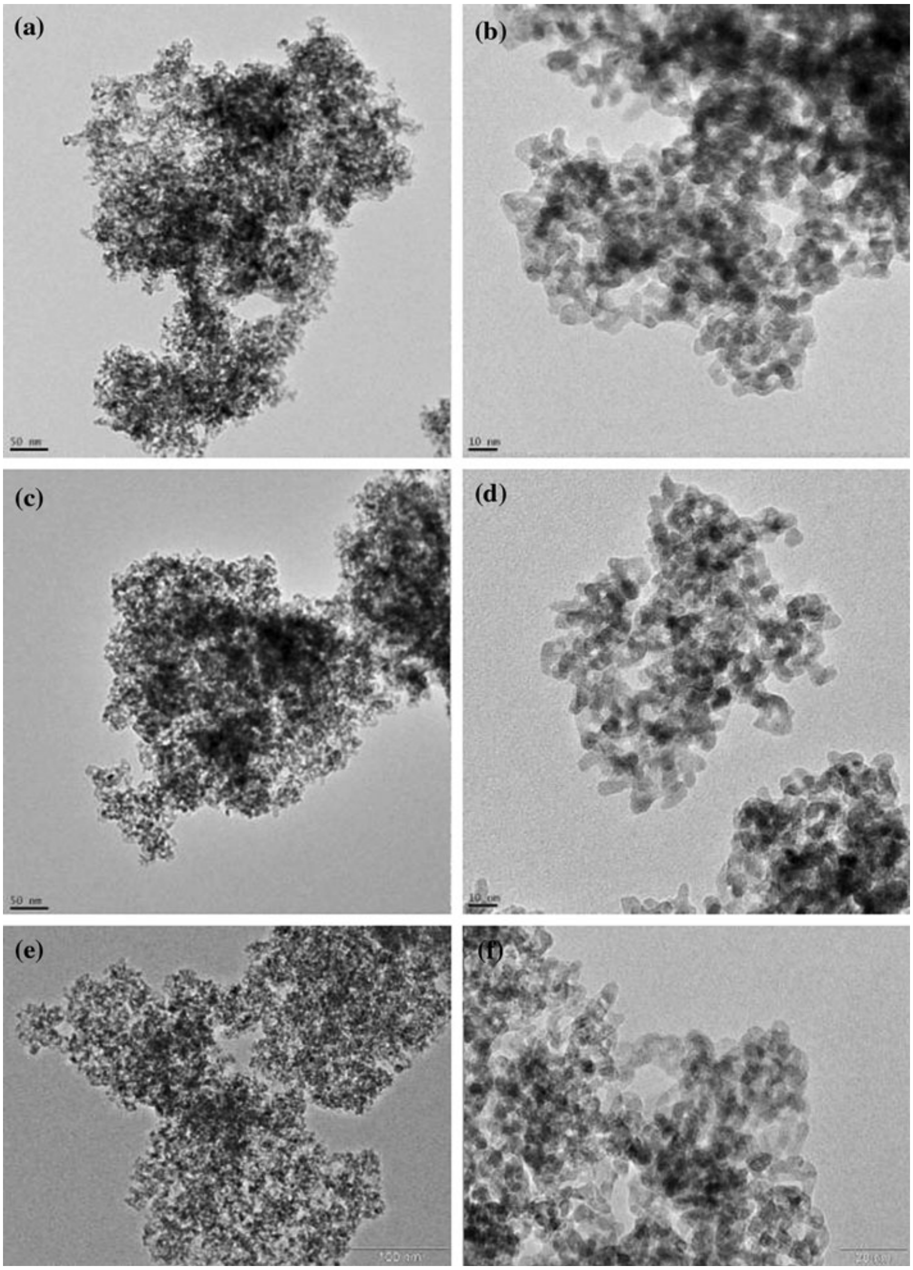

Fig. 4 TEM images of **a**–**b** phosphated sample, **c**–**d** sulphated sample, and **e**–**f** reference sample

phase and furthermore that the zirconia remained monoclinic upon calcination, similarly to the unmodified zirconia sample. Thus, PO_4^{3-} ions are capable of hindering phase transformation but are not capable of inducing a monoclinic to tetragonal phase transition.

Different mechanisms are proposed for the t → m phase transformation. A number of these are based on reaction with water on the crystal surface. Today, it is commonly accepted that the existence of metastable tetragonal zirconia at RT is due to the stabilizing effect of oxygen vacancies in the crystal lattice and that the phase transformation of pure tetragonal zirconia can be initiated by reaction with water [17]. Within this framework SO_4^{2-} and PO_4^{3-} ions prevents water molecules from reacting with the zirconia surface and/or retards the migration of OH^- ions into the oxygen vacancies and thereby prevents the hydrolytic degradation of tetragonal zirconia. Alternatively SO_4^{2-} and PO_4^{3-} ions both change the surface energy and thereby retard the transformation. It has been proposed that water adsorbed on the tetragonal zirconia surface reduces the surface energy difference between the tetragonal and the monoclinic phases [18, 19]. Such a surface energy reduction will reduce the critical size of the tetragonal crystals and thereby induce the t → m phase transformation. An eventual change of the surface energy through sulfate and phosphate treatment can be sufficient to prevent phase transformation caused by adsorption of water on the surface.

Conclusion

The effect of phosphates and sulfates on the stability of metastable tetragonal zirconia in water and ambient atmosphere at RT was studied. Due to experimental setup—calcination followed by surface treatment with either phosphoric or sulfuric acid—crystal size difference between native and surface treated specimens are neither expected nor observed. Hence retardation of crystal growth cannot be the reason for the observed stabilization. Instead the stabilization of tetragonal zirconia by phosphate and sulfate is caused by anionic interactions with sulfate and phosphate ions on the zirconia surface. The stabilization is either a result of hindered reaction of water on the surface or a result of change in surface energy, which favors the tetragonal phase. Further investigations have to be conducted to understand the stabilizing effect of SO_4^{2-} and PO_4^{3-} ions on tetragonal zirconia at RT.

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II

Inhibition of surface bound carbonate stabilization of tetragonal zirconia

M. Skovgaard

DentoFit A/S, Frederiksborgvej 399, 4000 Roskilde, Denmark

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Department of Micro- and Nanotechnology, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark

ms@dentofit.com, direct: +45 46 77 42 84, fax: +45 46 77 47 91

K. Almdal

Department of Micro- and Nanotechnology, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark

kral@nanotech.dtu.dk

A. van Lelieveld

DentoFit A/S, Frederiksborgvej 399, 4000 Roskilde, Denmark

avl@aneedle.net

Abstract

Water is known to initiate a tetragonal to monoclinic phase transformation in zirconia particles. Carbonates on the zirconia surface react with water molecules and hence reduces the transformation rate. This study investigates the possibility of inhibition of the reaction between surface carbonates and water in order to increase the transformation rate in the zirconia crystals. It was found possible to limit the reaction by reacting the surface carbonates with alcohols, a thiol and a primary amide prior to reaction with water. It was also concluded that di- and trialcohols are able to stabilize the tetragonal phase, probably as a results of induced lattice strain.

Keywords: zirconia, surface carbonates, phase transformation

Introduction

A problem with dental resin composites is the polymerization shrinkage, which results in loosening of the filling from the tooth or induced crack formation. The formation of a crack can give raise to discoloration due to colorants from *e.g.* coffee and red wine entering the crack or - worse - to secondary caries and infections of the dental pulp due to bacteria [1].

We have developed an expandable metastable tetragonal zirconia filler, which transforms into the lower density monoclinic phase upon reaction with water or HCl, and thereby, seen for the composite as a whole, is able to counteract the polymerization shrinkage of the monomer matrix. The tetragonal to monoclinic (t→m) phase transformation is accompanied by a 4% decrease in density. This expansion is for instance used in transformation toughening of ceramic materials [2].

In previous work we have tested the potential of the filler to counteract the polymerization shrinkage by initiating the phase transformation by water diffusing into the polymer matrix [3] and found that the overall shrinkage of a composite containing 42 wt-% zirconia stored in water at 40˚C was reduced with 44 % within the first 7 days comparing with an equivalent sample stored in air. However, the most desirable scenario is to initiate phase transformation of the tetragonal zirconia filler during polymerization of the organic matrix. We envisage that simultaneous phase transformation initiation and curing can be achieved by adding a photoacid generator, which releases HCl or water upon illumination [4].

Water is known for the ability to induce phase transformation of tetragonal zirconia [5]. High sensitivity of the zirconia filler towards water is however important as the activity of water in the composite is low due to the hydrophobicity of the resin. It is known from literature, that carbonates on the zirconia surface react with water molecules [6]. This limits the water availability for phase transformation initiation. In this study we investigate how this undesirable side reaction can be inhibited in order to increase the sensitivity of the metastable tetragonal zirconia filler towards water and HCl and hence increase the phase transformation rate.

Experimental

All chemicals were supplied by Sigma-Aldrich (St. Louis, MO, USA) and used as received. Highly porous (specific surface area of ~150 m^2 /g) nanocrystalline tetragonal zirconia powders were synthesized as previously described [7, 8] by controlled hydrolysis of $ZrOCl_2$ followed by careful calcination. The synthesized t-ZrO_2 powders were kept in water-free environment for further treatment to prevent the t→m phase transformation which is induced by exposure to water vapor [9, 10].

Test of different activators

1 mmol of the potential activators (as described in Tab. 1) was mixed with 500 mg of a dimethacrylate monomer mixture (bisphenol-A diglycidyl ether dimethacrylate, urethane dimethacrylate, and triethylene glycol dimethacrylate - Bis-GMA/UDMA/TEGDMA, 36/44/20 wt%) and a photo polymerization system

(camphorquinone and ethyl 4-dimethylamino benzoate - CQ/DABE both 0.5 wt%). In a glove box 200 mg of the metastable tetragonal zirconia powder and 100 mg of 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine were added. Tested solid activators were dissolved in the dimethacrylate matrix prior to mixing with the zirconia powder.

A sample of this mixture was placed between two glass plates and cured for 30 min using blue light (1,100 mW) from a Bluephase® light probe (Ivoclar Vivadent, Liechtenstein). The phase transformation is initiated during curing. The cured samples were then subjected directly to the X-ray diffraction (XRD) measurement for phase analysis. The polymer matrix prevents the tetragonal crystals from undergoing phase transformation initiated by humidity.

Also a reference sample without addition of any potential activator were prepared

Samples for water aging

In inert atmosphere a sample of 1 g tetragonal zirconia was suspended in anhydrous methanol. The suspension was filtered and left to dry in the filter overnight in inert atmosphere. 200 mg of this methanol treated zirconia were matrix dispersed (as described above) and cured. Furthermore, equivalent samples were prepared containing 200 mg unmodified zirconia and 500 mg dimethacrylate mixture. Such samples are termed matrix dispersed zirconia. The matrix dispersed samples were stored in water at 40 °C and following subjected directly to the X-ray diffraction (XRD) measurement for phase analysis.

Characterization

X-Ray Diffraction (XRD) evaluation

XRD patterns were scanned in 0.1 steps (2θ), in the 2θ range from 27° to 33°. The XRD patterns were analyzed using WinX^{POW} software. The tetragonal and monoclinic volume fractions (v_t and v_m) were calculated from the integral intensities of the monoclinic diffraction lines (-1 1 1) and (1 1 1) and the tetragonal diffraction line (1 0 1), following the procedure proposed by Toraya et al [11].

Fourier transform infrared spectroscopy

Fourier transform infrared spectrometry (FTIR) was performed using a PerkinElmer Spectrum one FTIR spectrometer. The samples for analysis were prepared by pressing a pellet with a diameter of 1 cm of 30 mg zirconia and placing it between two CaF_2 windows in an airtight holder. All handling was done in a glove box (<10 ppm water). Spectra were collected within the range from 900 to 4000 cm^{-1} with averaging over 32 scans.

Autosorbtion: determination of water adsorption

The amount of water adsorbed on the zirconia surface at a given partial pressure can be determined using a Quantachrome XT autosorb analyzer, (Quantachrome Instruments, Florida, US). A sample of the zirconia powder is kept at 0°C (ice bath) during the experiment. In order to avoid premature phase transformation it is necessary to use a seal that only opens in the autosorbtion machine. This way the sample can be kept under an inert atmosphere or vacuum until measurement starts and again after the sample is removed from the machine. The zirconia sample is evacuated to the relative pressure, P = 0.01 x P0; where P0 is the ambient pressure. The sample is then titrated with water in gaseous form by the procedure of finding a relative pressure and then noting the amount of water necessary to get this pressure. At a given end-point (a given p/p0) the sample was re-evacuated and taken to a glove box. The zirconia was matrix dispersed as described above and subjected directly to the XRD measurement for phase analysis.

Results

Triazine tests

The effect of addition of different potential activators on light initiated phase transformation is listed in Tab. 1. It is observed that besides from some of the alcohols and octane thiol only acetamide is able to activate the zirconia. Out of the tested activators 1,5-pentanediol results in the highest monoclinic volume fraction in the samples. For the reference sample without any activator added, very little phase transformation was detected even after 2 h of light exposure.

Tab. 1 effect of addition of 1 mmol of potential activators to the resin on the monoclinic volume fraction of zirconia caused by initiation of phase transformation by 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine exposed to blue light

Tested activators	v_m
Tert-Butylamine	0
Diethylamine	0
Triethylamine	0
Ethylenediamine	0
Methanol	0.53
Iso-propanol	0.55
Iso-octanol	0.46
Ethylene glycol	0
1,3-propanediol	0
1,4-butanediol	0
1,5-pentanediol	0.63
Glycerol	0
Octane thiol	0.50
N,N-Dimethylformamide	0
Chloroform	0
Acetamide	0.24
Cyanamide	0
Unmodified zirconia	0

Effect of activators

The XRD patterns of the water stored matrix dispersed zirconia are illustrated in Fig. 1. The methanol treated zirconia has a $v_m = 0.67$ after water storage for 2 days and already after 8 h the sample has a $v_m = 0.57$. The untreated samples, however, need more than 21 days to reach $v_m = 0.47$. From Fig. 1 it is observed that the reference sample only contains traces of the monoclinic phase prior to water storage and the tetragonal 101 reflection of zirconia at $30.2^\circ = 2\vartheta$ is dominating. Broad peaks in the XRD patterns are a result of small crystal sizes. The powder is very moisture sensitive and the diffusion of water to the crystallite surface induces the martensitic tetragonal to monoclinic (t→m) phase transformation [9]. During water storage the two monoclinic reflections (-111 and 111) grows in intensity and the (101) reflection decreases, indicating a t→m transformation.

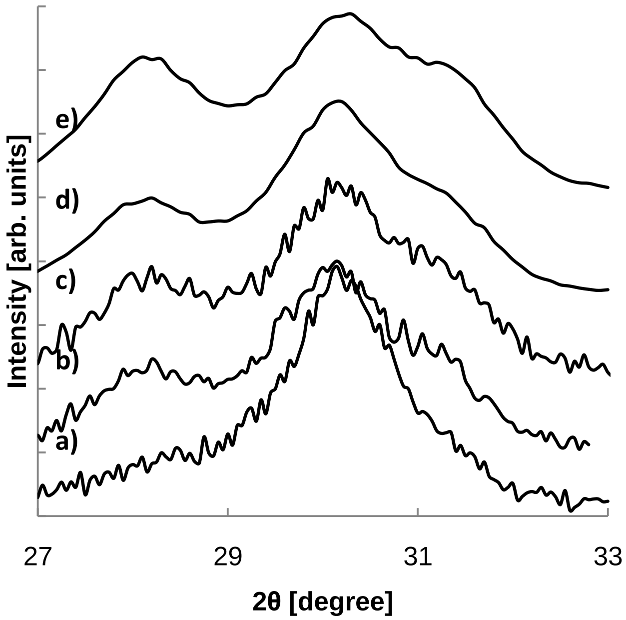

Fig. 1 XRD patterns of matrix dispersed unmodified zirconia after (a) 0 hour, (b) 3 days and (c) 21 days water storage at 40˚C and of a methanol modified matrix dispersed zirconia after water storage at 40˚C in (d) 8 hours and (e) 3 days.

IR studies

The results from the analysis of unmodified and methanol treated zirconia samples are plotted in Fig. 2 The observed carbonate species on the synthesized zirconia are: ionic carbonate CO_3^{2-}: 1444 cm^{-1}, bidentate bicarbonate HCO_3^-: 1598 cm^{-1}, bidentate covalent surface carbonate "CO_3": 1558 and 1325 cm^{-1} and finally ionic carboxylate CO_2^-: 1423 cm^{-1}. The intensities of the ionic carbonate and carboxylate are the same, creating a double peak in the IR spectrum. The bidentate covalent surface carbonate is just shoulders to the double peak and the bicarbonate is a small peak and only a shoulder to the bidentate covalent surface carbonate peak. After exposure to methanol three peaks at 1614, 1471 and 1359 cm^{-1} respectively appears.

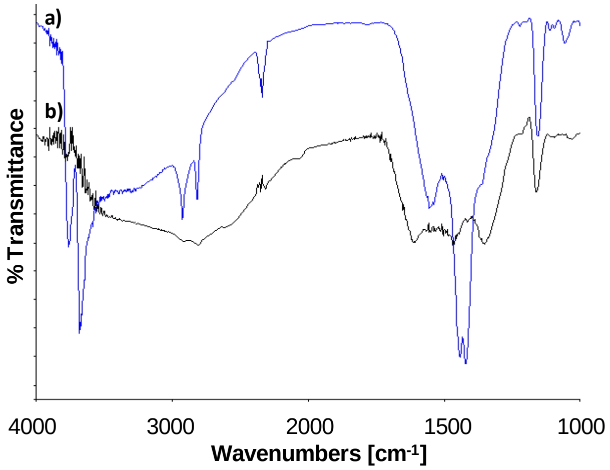

Fig. 2 IR Spectra of a) zirconia and b) methanol treated zirconia

Autosorbtion

In the autosorbtion study different zirconia samples were analyzed. In Fig. 3 the result from the analysis of the untreated zirconia and the methanol treated zirconia are plotted. In both samples a discontinuity is observed at relative pressure of ~0.1 and for the unmodified zirconia this increase is 6 times larger than for the methanol treated zirconia sample.

From Tab. 1 it is observed that ethylene glycol does not work as an activator, for this reason ethylene glycol modified zirconia were subjected to an autosorbtion analysis and the results are also plotted in Fig. 3. In this sample the slope steepens at a relative pressure of ~0.16. Comparing with the methanol treated sample, 7 times as much water can be added without any significant increase of the relative pressure.

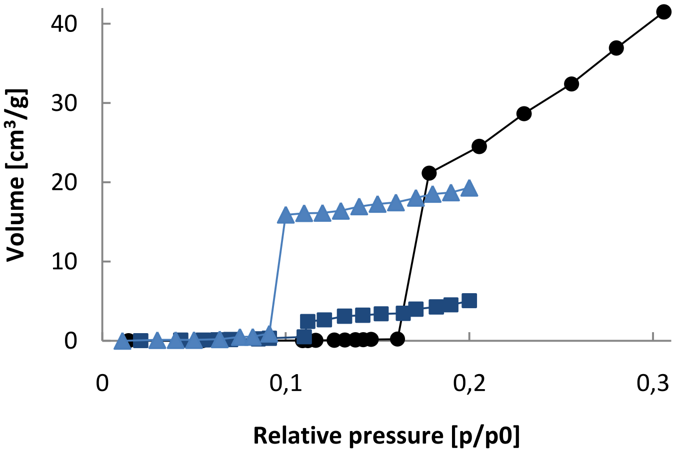

Fig. 3 Autosorbtion curves of ■) methanol treated zirconia, ▲) untreated zirconia and ●) ethylene glycol treated zirconia.

The methanol treated zirconia was analyzed further and the analyses were stopped at different relative pressures. The zirconia samples were handled to prevent further phase transition. The XRD patterns obtained from these samples are illustrated in Fig. 4. It is observed that some of the zirconia is phase transformed at a relative pressure of 0.05 and the level of phase transformation increases with increasing relative pressure. Again the reference sample only contains traces of the monoclinic phase prior to water storage and the tetragonal 101 reflection of zirconia at 30.2˚ = 2ϑ is dominating. The growth in intensity of the two monoclinic reflections (-111 and 111) indicates a t→m transformation.

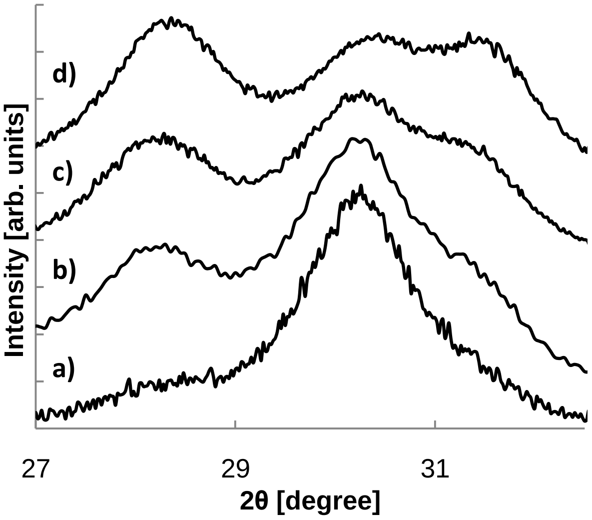

Fig. 4 XRD patterns of methanol treated zirconia (a) before and (b) after autosorbtion stopped at p/p0 = 0.05, (c) p/p0 = 0.1, (d) p/p0 = 0.9

Discussion

Evaluation of phase transformation activators

In an effort to inactivate the carbonates towards reaction initiator molecules, various molecules were used to modify the zirconia surface. Very little phase transformation was detected in the reference sample without any activator added. Apparently, the initiator species derived from the triazine was almost completely "consumed" by the carbonates present at the surface of the zirconia particles.

When the zirconia surface is covered with carbonates higher amounts of initiator molecules are needed to initiate the phase transformation - as carbonates are reactive towards water and that reaction will lower the number of water molecules reacting with the surface. This is crucial for the speed of phase transformation in resin, as the activity of water is low. This is observed from the water storage experiments, where the matrix dispersed methanol treated zirconia phase transforms much faster than the unmodified matrix dispersed samples. Already after 8 h the methanol treated samples have a higher monoclinic volume fraction than the untreated samples have after 21 days.

From the results of the test of potential activators it is concluded that alcohols, thiols and primary amides are able to activate the zirconia surface. An exception from alcohols is short chained di- and tri-alcohols with less than five carbon molecules separating the OH-groups e.g. ethylene glycol, glycol and 1,4 butanediol. These molecules inhibit the phase transformation. It has been experimentally shown that molecules able to make a bidentate bond to the zirconia surface have a stabilizing effect, e.g., the ethylene glycol treated sample did not phase transform at all as a result of exposure to ambient atmosphere (not shown). The untreated zirconia is previously proven to have a monoclinic volume fraction of 0.68 after exposure to ambient atmosphere [12]. Ethylene glycol is a bidentate molecule, which can potentially stabilize the tetragonal zirconia in the same manner as trimethoxy silanes and phosphates by binding two OH-groups across a Zr-O-Zr bridge because of a chelate effect. Probably an increased strain in the crystal lattice results [13].

In order to avoid bridge bonding the activator should be monodentate (only able to bind with one group) or the functional groups should be far away from each other. The distance between the functional groups can be determined by intervals of C-bonds in the dialcohol. Ethylene glycol, 1,3 propanediol and 1,4 butanediol block the phase transformation, whereas 1,5 butanediol does not. The distance between the bonding groups should be more than 4 carbon bonds in order to avoid stabilizing the tetragonal phase. Actually 1,5 butanediol results in a higher v_m than methanol. Possibly 1 mmol activator not is enough to inactivate all the carbonates on the surface and since 1,5 butanediol can react with two carbonates it can potentially deactivate a larger fraction of the carbonates. Methanol is smaller than 1,5 butanediol and is for this reason chosen. Addition of the smallest possible amount of solvent is preferable for the mechanical properties of the dental composites.

IR spectroscopy

During the calcination of the zirconia powder, remaining solvent from the drying process will burn and result in formation of CO_2. This is known to react with zirconia surfaces under formation of carbonates. The adsorption of CO_2 on zirconia has been widely studied [14]. The kind of species formed on the surface of zirconia is very dependent on the process condition such as temperature, amount of CO_2 and the surface of the zirconia. All the observed carbonates can react with methanol and form methyl carbonates. Methyl carbonates give rise to IR spectra with three significant peaks at: 1600, 1474 and 1370 cm^{-1} [15]. Methanol treatment of the zirconia particles give rise to peaks at 1614, 1471 and 1359 cm^{-1}. The formation of a substituted carbonate can therefore be observed in IR as a change of the carbonate peaks into the substituted species peaks. The above mentioned peaks are all assigned to the C-O (or C=O) vibrations as these are the modes with the highest extinction and are by far the easiest way to recognizing a change in carbonates on the surface of zirconia.

Autosorbtion

Looking at the autosorbtion curves of water on different zirconia surfaces several observations can be made. It is observed that the unmodified zirconia has a very steep adsorption curve at a partial pressure of ~0.1. This sharp adsorption increase can also be found in other autosorbtion studies of zirconia with surface modification. The increase varies in size and a little in position (in relative pressure). The unmodified and methanol modified zirconia differ significantly in the amount of water adsorbed on zirconia. The origin of the increase cannot be associated with phase transformation of zirconia since some phase transformation is observed already at p/p0 = 0.05 (Fig. 4). The increase is more likely to be associated with adsorption/absorption of water on the surface of zirconia.

The results show that with a more hydrophobic surface the discontinuous part of the curve appears at a higher relative pressure. We cannot explain the reason for the differences in the magnitude of this increase. It could, however, be a result of the reaction between water and the surface carbonates. The discontinuity has the same magnitude for the untreated and the ethylene glycol treated sample. We speculate that the ethylene glycol prefers to bind the zirconia surface due to the possibility of bidentate binding, rather than reacting with the surface carbonates, this can explain the differences. In the methanol treated samples the methoxylated carbonates are unable to react with water and can for this reason not absorb as much water as the unmodified and ethylene glycol treated samples. This leads to an increase in the relative pressure comparing with the two other samples.

Conclusion

Carbonates on the zirconia surface reduce the transformation rate in the composite due to competing reactions with the initiator molecule water. The competing reaction can be inhibited by modification with alcohols, thiols and molecules with other functional groups, which react with the carbonates. The carbonates are prevented from reacting with water – and thus the molecules works as activators making the phase transformation faster. Through methanol treatment of the zirconia prior to dispersion in a polymer matrix, the monoclinic volume fraction can be increased from 0.47 within 21 days of water storage to 0.67 after 48 h water storage, with most of the phase transition occurring within the first 8 h. Dialcohols and polyalcohols, however, such as ethylene glycol, which have the possibility for bidentate coordination, hinder phase transformation.

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III

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(71) **Applicant** *(for all designated States except US)*: **DENTOFIT A/S** [DK/DK]; c/o Forskningscenter Risø, Frederiksborgvej 399, DK-4000 Roskilde (DK).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **VAN LELIEVELD, Alexander** [DK/DK]; Engelstedsgade 32, 2., DK-2100 Copenhagen Ø (DK). **NIELSEN, Mette Skovgaard** [DK/DK]; Parkvej 19 D, DK-2630 Taastrup (DK).

(74) **Agents**: **THORSEN, Jesper** et al.; P.O. Box 45, Kogle Allé 2, DK-2970 Hørsholm (DK).

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(54) **Title**: DENTAL FILLING MATERIALS WITH SURFACE MODIFIED ZIRCONIA PARTICLES

(57) **Abstract**: The present application discloses a dental filling material comprising fillers and a polymerizable resin base, the fillers comprising metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase, and having surface functionalities of the formula: $-Zr-O-Zr-O-C(=O)-X-C(R^1)(R^2)(R^3)$, wherein X = -O-, -NH-, -S-; R^1 / R^2 = hydrogen, opt.subst. C_{1-30}-alkyl, a (meth)acrylate moiety moiety, a (meth)acrylate-C_{1-12}-alkyl moiety, opt.subst. C_{2-30}-alkenyl, opt.subst. C_{5-30}-alkadienyl, opt.subst. C_{8-30}-alkatrienyl, or when X = -NH-, R^1 / R^2 = =O; R^3 = hydrogen, C_{1-6}-alkyl, hydroxy, halogen. A method of controlling the volumetric shrinkage of a dental filling material upon curing, and the dental filling material for use in medicine, in particular in dentistry, are also disclosed.

WO 2010/049522 A2

DENTAL FILLING MATERIALS WITH SURFACE MODIFIED ZIRCONIA PARTICLES

FIELD OF THE INVENTION

The present invention relates to the field of dental materials, in particular dental materials in which shrinkage of the resin base upon polymerization is countered by volumetric expansion of zirconia particles.

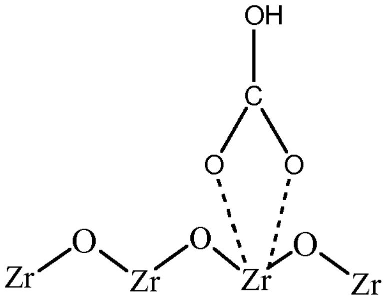
BACKGROUND OF THE INVENTION

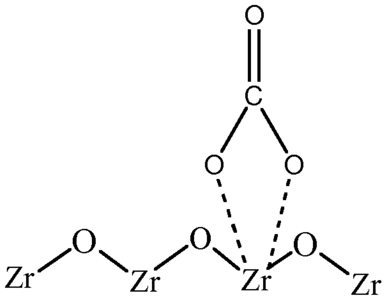
The applicant's earlier PCT application No. WO 2005/099652 A1 discloses a composite material exhibiting a low or even negligible volumetric shrinkage upon curing, or even a small expansion (*e.g.* up to 0.5 %), in particular composite materials in the form of dental filling materials, as well as a method of controlling volumetric shrinkage of a composite material upon curing. According to WO 2005/099652 A1, a volume stable composite material for dental use can, *e.g.*, be obtained by the use of metastable zirconia particles.

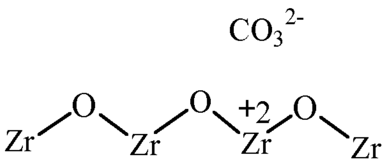
The phase transformation of such metastable zirconia can be induced by trigger molecules such as H_2O, HF, HCl, HBr and NH_3 (see in particular WO 2007/104312). The mechanism behind the initiation of phase transformation of zirconia is believed to be cleavage of Zr-O-Zr bridges with the use of trigger molecules. In the case where the amount of trigger molecules is limited, the generated amount of trigger molecules becomes the rate determining step of phase transformation. In other words the generation of trigger molecules limits the phase transformation in effect limiting the possible degree of phase transformation within a given period of time. This is the case where zirconia is encapsulated in a solid material where the diffusion is slow. Such a case can be illustrated by dental filling materials, where the filler is metastable zirconia and the resin material has been cured. The diffusion is very slow in a polymeric material (like dental filling materials) below its glass transition temperature. When such a material is subject to trigger molecules, *e.g.* water present in the mouth, triggering molecules (water) will be limited by diffusion, and phase transformation will be relatively slow. Another example is the system, where the triggering molecules is provided by photo-active molecules (*e.g.* a triazine), which upon light exposure liberates Cl radicals. The Cl radicals will then be used in the polymerization reaction with the monomers in the resin or will abstract a hydrogen atom and provide HCl to the surface of zirconia. When the resin cures, the diffusion will again be reduced in the dental filling material and the radicals will be subject to the "cage effect". Both the reaction with other monomers and the caging effect limits the amount of HCl available for the initiation of phase transformation on the surface of the metastable zirconia particles.

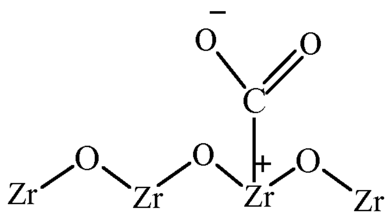
It is therefore very important to find ways of minimizing the amount of trigger molecules necessary to initiate a phase transformation.

Since the initiation of metastable zirconia is initiated on the surface of zirconia, a key element of making metastable zirconia is a high surface area. To ensure that the zirconia will not sinter (to much) in the calcination process, the surface should be covered with an organic surfactant (*e.g.* ethanol). The surfactants will be burned off during the calcination step and provide CO_2 to the zirconia surface. Some of species that are formed include bicarbonate, covalent bound carbonates, ionic carbonates and carboxylates illustrated below (commonly referred to as "carbonyl species" and broadly described as carbonates).









Such species react with trigger molecules like water and HCl and will thereby "consume" at least some of the trigger molecules intended for initiation of the phase transformation.

In some embodiments, it is a great advantage to minimize the effects of carbonyl species.

In other embodiments, it may be an advantage that at least some of the trigger molecules are "consumed" by the carbonyl species so that the rate of phase transformation is reduced.

In view of the above, it is one object of the invention to provide dental filling materials wherein the degree of phase transformation and the rate at which the phase transformation takes place can be refined.

BRIEF DESCRIPTION OF THE INVENTION

In view of the objective mentioned above, the present invention provides a dental filling material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase, said zirconia particles having surface functionalities of the formula:

$-Zr-O-Zr-O-C(=O)-X-C(R^1)(R^2)(R^3)$

wherein X is selected from -O-, -NH- and -S-; R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, a (meth)acrylate moiety, a (meth)acrylate-C_{1-12}-alkyl moiety, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, <u>or</u> when X is –NH-, R^1 and R^2 may together designate =O; and R^3 is selected from hydrogen, C_{1-6}-alkyl, hydroxy and halogen.

The invention further provides, a dental filling material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase, said zirconia particles being prepared by a process comprising the sequential steps of:

a) preparation of an amorphous powder of zirconia;

b) calcination of the amorphous powder of zirconia at a temperature in the range of 400-600 °C so as to obtain metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase;

c) treatment of the metastable zirconia particles with a compound of the formula H-X-C(R^1)(R^2)(R^3),

wherein X is selected from -O-, -NH- and -S-; R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, a (meth)acrylate moiety, a (meth)acrylate-C_{1-12}-alkyl moiety, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, <u>or</u> when X is –NH-, R^1 and R^2 may together designate =O; and R^3 is selected from hydrogen, C_{1-6}-alkyl, hydroxy and halogen.

Moreover, the present invention provides a method of controlling the volumetric shrinkage of a dental filling material upon curing, comprising the step of:

(a) providing a dental filling comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase, said zirconia particles having surface functionalities of the formula:

-Zr-O-Zr-O-C(=O)-X-C(R^1)(R^2)(R^3)

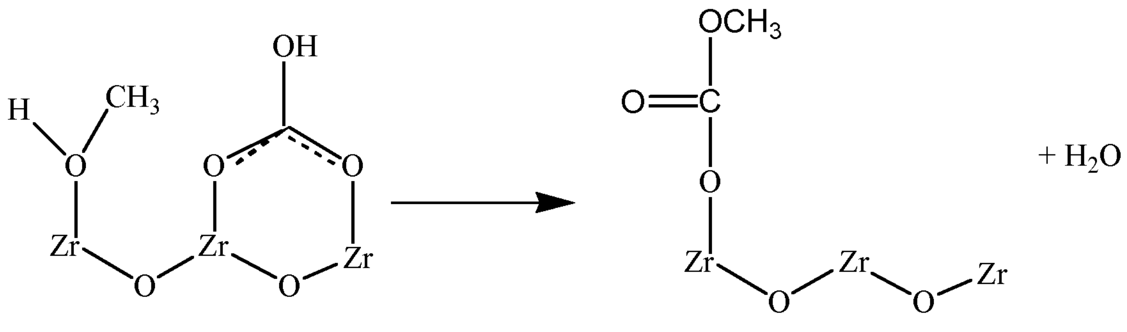
wherein X is selected from -O-, -NH- and -S-; R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, a (meth)acrylate moiety, a (meth)acrylate-C_{1-12}-alkyl moiety, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, <u>or</u> when X is –NH-, R^1 and R^2 may together designate =O; and R^3 is selected from hydrogen, C_{1-6}-alkyl, hydroxy and halogen;

(b) allowing the resin base to polymerize and cure, and allowing the metastable zirconia particles to undergo a martensitic transformation from a first metastable phase to a second stable phase.

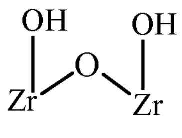
Still further, the present invention provides a dental filling material as defined herein for use in medicine, in particular in dentistry.

DETAILED DESCRIPTION OF THE INVENTION

It is known (see *e.g.* Bell et al, J. Catal., 204, 330 (2001) that absorbed carbonates can react with methanol and form methyl carbonate. In this way the carbonate is less prone to react with the triggering molecules as described above.



This reaction is not limited to methanol alone, in fact other substances capable of making an addition to the carbonates without providing chemical groups that can react with the trigger molecules are believed to be suitable. Two important groups include alcohols and thiols. A criterion for these appears to be that the alcohol and thiol groups are available for reaction, thus not engaged in intramolecular bonding. A further criterion for these substances appears to be that they are not blocking the reactive sites for initiating the phase transformation on zirconia. These sites are believed to be Zr-O-Zr bonds with vicinal hydroxyl groups on the zirconium atom (see figure below).



Based on the observations made by the present inventors, it has been found that the rate of phase transformation of dental filling materials comprising metastable zirconia intended for phase transformation can be more accurately controlled, and, in particular, the "consumption" of trigger molecules can be suppressed, by modification of the "carbonates" present at the surface of the zirconia particles.

Hence, one aspect of the present invention relates to a dental filling material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase, said zirconia particles having surface functionalities of the formula:

$-Zr-O-Zr-O-C(=O)-X-C(R^1)(R^2)(R^3)$

wherein X is selected from -O-, -NH- and -S-; R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, a (meth)acrylate moiety, a (meth)acrylate-C_{1-12}-alkyl moiety, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, or when X is –NH-, R^1 and R^2 may together designate =O; and R^3 is selected from hydrogen, C_{1-6}-alkyl, hydroxy and halogen.

Another aspect of the present invention relates to a dental filling material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase (preferably less than 25 % (v/v), such as less than 20 % (v/v), in particular less than 15 % (v/v), such as less than 10 % (v/v), more preferable virtually none, are in the monoclinic phase), said zirconia particles being prepared by a process comprising the sequential steps of:

a) preparation of an amorphous powder of zirconia;

b) calcination of the amorphous powder of zirconia at a temperature in the range of 400-600 °C so as to obtain metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase;

c) treatment of the metastable zirconia particles with a compound of the formula $H-X-C(R^1)(R^2)(R^3)$,

wherein X is selected from -O-, -NH- and -S-; R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, a (meth)acrylate moiety, a (meth)acrylate-C_{1-12}-alkyl moiety, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, or when X is –NH-, R^1 and R^2 may together designate =O; and R^3 is selected from hydrogen, C_{1-6}-alkyl, hydroxy and halogen.

These and other characteristics of the invention will be explained in the following.

Dental filling material

The present invention relates to dental filling material comprising one or more fillers including metastable zirconia and a polymerizable resin base.

It is well known that many resin bases used in dentistry exhibit volumetric shrinkage upon curing thereof. Thus, a particular feature of the present invention is the presence of zirconia particles that will reduce or eliminate the volumetric shrinkage caused by the polymerizable resin base, or even counteract this volumetric shrinkage to such an extent that the dental filling material exhibits a net volumetric expansion upon curing of the polymeric resin base.

Thus, in a preferred embodiment of the dental filling material, the resin base, upon polymerization and in the absence of any compensating effect from the one or more zirconia particles, causes a volumetric shrinkage (ΔV_{resin}) of the dental filling material of at least 0.50 %, and wherein said dental filling material, upon polymerization of said resin base and upon phase transformation of said zirconia particles, exhibits a total volumetric shrinkage (ΔV_{total}) of at least 0.25 %-point less than the uncompensated volumetric shrinkage (ΔV_{resin}) caused by the resin base. More particularly, the volumetric shrinkage (ΔV_{resin}) is at least 1.00 %, such as at least 1.50 %, and the total volumetric shrinkage (ΔV_{total}) is at least 0.50 %-point less, such as at least 1.00 %-point less than the uncompensated volumetric shrinkage.

The dental filling material typically comprises 5-95 %, or 10-90 %, by weight of the one or more fillers (including zirconia particles) and 5-95 %, or 10-90 %, by weight of the polymerizable resin base, in particular 30-95 %, or 30-90 %, by weight of the one or more fillers and 5-70 %, or 10-70 %, by weight of the polymerizable resin base.

Filler/Filler ingredient

In view of the above, it is apparent that the one or more fillers, and in particular the surface-modified metastable zirconia particles, are important constituents of the dental filling material.

Fillers are frequently used in connection with polymeric materials in order to provide desirable mechanical properties of such materials, *e.g.* abrasion resistance, opacity, colour, radiopacity, hardness, compressive strength, compressive modulus, flexural strength, flexural modulus, etc.

Such fillers may be selected from one or more of a wide variety of materials, *e.g.* those that are suitable for the use in dental and/or orthodontic dental filling materials.

Fillers can be inorganic materials or cross-linked organic materials that are insoluble in the resin component of the composition. Cross-linked organic materials may as such be filled with an inorganic filler. The filler should – in particular for dental uses - be nontoxic and suitable for use in the mouth. The filler can be radiopaque or radiolucent. The filler typically is substantially insoluble in water.

The term "filler" is to be understood in the normal sense, and fillers conventionally used in dental filling materials in combination with polymer are also useful in the present context. The polymerizable resin base (see further below) can be said to constitute the "continuous" phase wherein the filler is dispersed.

Some examples of suitable inorganic fillers are naturally occurring or synthetic materials including, but not limited to: quartz; nitrides (*e.g.* silicon nitride); glasses derived from, for example, Zr, Sr, Ce, Sb, Sn, Ba, Zn, and Al; feldspar; borosilicate glass; kaolin; talc; titania; low Mohs hardness fillers such as those described in U.S. Pat. No. 4,695,251 (Randklev); and silica particles (*e.g.* submicron pyrogenic silicas such as those available under the trade designations AEROSIL, including "OX 50," "130," "150" and "200" silicas from Degussa AG, Hanau, Germany and CAB-O-SIL M5 silica from Cabot Corp., Tuscola, Ill.). Examples of suitable organic filler particles include filled or unfilled pulverized polycarbonates, polyepoxides, and the like.

Other illustrative examples of fillers are barium sulfate ($BaSO_4$), calcium carbonate ($CaCO_3$), magnesium hydroxide ($Mg(OH)_2$), quartz (SiO_2), titanium dioxide (TiO_2), zirconia (ZrO_2), alumina (Al_2O_3), lantania (La_2O_3), amorphous silica, silica-zirconia, silica-titania, barium oxide (BaO), barium magnesium aluminosilicate glass, barium aluminoborosilicate glass (BAG), barium-, strontium- or zirconium-containing glass, milled glass, fine YF_3 or YbF_5 particles, glass fibres, metal alloys, etc. Metal oxides, *e.g.* titanium dioxide (TiO_2) and zirconia (ZrO_2), alumina (Al_2O_3), lantania (La_2O_3), constitute a particularly useful group of fillers for use in the dental filling materials of the present invention.

In one interesting embodiment, at least 5 %, *e.g.* at least 10 %, or even at least 20 %, by weight of the one or more fillers are glass particles. It is believed that inclusion of glass particles may further improve the optical (and thereby aesthetic) properties of the dental filling material by making it more transparent.

The weight content of the one or more filler materials in the dental filling material is typically in the range of 5-95 %, or 10-90 %, such as 30-95 %, such as 40-95 %, *e.g.* 60-95 %. It should be understood that a combination of two or more fillers may be desirable, just as the particle size distribution of the filler(s) may be fairly broad in order to allow a dense packing of the filler and thereby facilitate incorporation of a high amount of fillers in the dental filling material. Typically, dental filling materials have a distribution of one or more sizes of fine particles plus nanofillers (5-15 %). This distribution permits more efficient packing, whereby the smaller particles fill the spaces between the large particles. This allows for filler content, *e.g.*, as high as 77-87 % by weight. An example of a one size distribution filler would be 0.4 µm structural micro-filler, with the distribution as follows: 10 % by weight of the filler particles have a mean particle size of less than 0.28 µm; 50 % by weight of the filler particles have a mean particle size of less than 0.44 µm; 90 % by weight of the filler particles have a mean particle size of less than 0.66 µm.

Typically, the particle size of the filler(s) is in the range of 0.01-50 µm, such as in the range of 0.02-25 µm.

In some embodiments, the particle size of the filler(s) is/are in the range of 0.2-20 µm with some very fine particles of about 0.04 µm. As an example, fairly large filler particles may be used in combination with amorphous silica in order to allow for a dense packing of the fillers.

The term "particle size" is intended to mean the shortest dimension of the particulate material in question. In the event of spherical particles, the diameter is the "particle size", whereas the width is the "particle size" for a fiber- or needle-shaped particulate material. It should of course be understood that an important feature of such particles is the actual crystal size in that the crystal size (and not the particle size) will be determinative for the preferred crystal phase under given conditions (see also further below).

For aesthetic reasons, it is preferred to include a certain amount of nanofillers in the dental filling material. As used herein the term "nanofiller" refers to filler particles having a size of at the most 100 nm (nanometers). As used herein for a spherical particle, "size" refers to the diameter of the particle. As used herein for a non-spherical particle, "size" refers to the longest dimension of the particle.

This being said, the weight ratio between (i) the nanofillers and (ii) fraction of the one or more fillers not being said nanofillers appears to play a certain role, and is typically in the range of 10:90 to 100:0, preferably 10:90 to 40:60, in particular 10:90 to 30:70.

In some embodiments, particularly useful fillers are zirconia, amorphous silica, milled barium-, strontium- or zirconium-containing glass, milled acid-etchable glass, fine YF_3 or YbF_5 particles, glass fibres, etc.

The zirconia particles typically constitute(s) 20-100 % of the total weight of the one or more fillers, *e.g.* 30-100 %, such as 40-100 % or 50-100 %.

When calculated on the basis of the total weight of the dental filling material, the zirconia particles typically constitute(s) 15-95 % of the total weight of the dental filling material, *e.g.* 25-95 %, such as 30-95 %, more specifically 60-95 %.

In the present context, the term "metastable first phase" means that the zirconia particles existing in such as phase has a free energy that is higher than the free energy of the second phase, and that an activation barrier (F*) must be overcome before transformation from the first phase (high energy state) to the second phase (low energy state) can proceed. Thus, the phase transformation does not proceed spontaneously. It should be understood that the "system" in which the zirconia particles is metastable is the dental filling material including all its constituents, *i.e.* the dental filling material before curing.

The phase transformation is martensitic, which by definition means that the crystal structure of the zirconia particles needs no extra atoms to undergo the transformation. Thus, the transformation can be very fast, almost instantaneous.

The expression "free energy" refers to the sum of free energies from the particle bulk, the particle surface and strain contributions. For most practical purposes, only the free energies from the particle bulk and the particle surface need to be considered.

Thus, when considering potential zirconia particles, it is relevant to take into consideration the two main requirements:

A first requirement for the zirconia particles is that the second crystalline phase thereof, within the selected particle size range, is "stable" under "standard" conditions, *i.e.* standard pressure (101.3 kPa) and at least one temperature in the range of 10-50°C, *i.e.* corresponding to the conditions under which the product is used.

A second requirement for the zirconia particles is that a metastable first crystalline phase of the zirconia particles can exist under the same "standard" conditions.

The expression "stable" refers to a phase which does not transform spontaneously under the conditions required for transforming the zirconia particles from the first metastable phase. Thus, the "stable" phase need not always be the phase with the "globally" lowest free energy, but it often will be.

Zirconia can exist in three major crystalline phases: the tetragonal phase, the cubic phase and the monoclinic phase. The specific volume (density^{-1}) of the three phases is 0.16, 0.16 and 0.17 cm^3/g, respectively. Thus, the monoclinic (the second phase) and one of the former two phases (the first phase) have a volume ratio of 1.045 and 1.046, respectively. The tetragonal and the cubic phases have higher bulk energy than the monoclinic phase at the standard conditions.

The surface energy of the tetragonal phase of zirconia is lower than the one of the monoclinic phase at standard temperature and pressure, which results in stable tetragonal (pure) zirconia crystals at room temperature. The crystals must be small (typically with an average crystal size of 5-12 nm) for the difference of surface energy to compete with difference of in bulk energy of the tetragonal and monoclinic phase.

In the present context, the metastable zirconia particles are present in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase, *i.e.* of the bulk of material (the particles) less than 30 % (v/v) represent monoclinic phase crystals which are not capable of exhibiting a volumetric expansion. Preferably, less than 25 % (v/v), such as less than 20 % (v/v), in particular less than 15 % (v/v), such as less than 10 % (v/v), preferably virtually none, are in the monoclinic phase.

For zirconia in the metastable tetragonal or cubic crystalline phase, the particle size is preferably in the range of 5-2000 nm, though it is believed that the presence of particles of a mean particle size in the range of 20-120 nm and in a range of 500-1000 nm (*i.e.* a bimodal particle size distribution), provides the best balance between optical and structural properties.

It is further possible to include dopants, although not currently preferred. The rationale and consideration behind the use of dopants are, *e.g.*, discussed in WO 2007/104312.

In its native form, the metastable zirconia particles comprise zirconia in the tetragonal and cubic crystalline phases, possibly with a small amount of the material in the monoclinic phase (*i.e.* in the phase corresponding to already phase-transformed material). The highest degree of phase transformation in a dental material (*e.g.* provoked by water (gas) diffusing into the dental material) corresponds to the degree of phase transformation possible in a moist environment (*i.e.* at 100 % humidity (100 % water (gas)). With reference to the examples given herein, it appears that this "highest degree of phase transformation" by the action of water (gas) is approx. 60 %. In order to obtain an even higher degree of phase transformation, the sample may be placed in water (liquid), whereby the degree of phase transformation typically will be close to 100 %. The difference in the degree of phase transformation between the use of water (gas) and water (liquid) as the trigger molecule is believed to be caused by the difference in "activity".

Polymerizable resin base

Another important constituent of the dental filling material is the polymerizable resin base.

The term "polymerizable resin base" is intended to mean a composition of a constituent or a mixture of constituents such as monomer, dimers, oligomers, prepolymers, etc. that can undergo polymerization so as to form a polymer or polymer network. By polymer is typically meant an organic polymer. The resin base is typically classified according to the major monomer constituents.

The weight content of the polymerizable resin base in the dental filling material is typically in the range of 5-95 %, or 5-90 %, *e.g.* 5-70 %, such as 5-60 %, *e.g.* 5-40 %.

Virtually any polymerizable resin base can be used within the present context. Polymerizable resin bases of particular interest are, of course, such that upon curing will cause a volumetric shrinkage of the dental filling material when used without a compensating filler ingredient.

The term "curing" is intended to mean the polymerisation and hardening of the resin base.

One class of preferred hardenable resins are materials having free radically active functional groups and include monomers, oligomers, and polymers having one or more ethylenically unsaturated groups. Alternatively, the hardenable resin can be a material from the class of resins that include cationically active functional groups. In another alternative, a mixture of hardenable resins that include both cationically curable and free radically curable resins may be used for the dental materials of the invention. In a still further alternative, the hardenable resin is a condensation-curing resin base, *i.e.* one where the polymer is formed by condensation polymerisation.

In the class of hardenable resins having free radically active functional groups, suitable materials for use in the invention contain at least one ethylenically unsaturated bond, and are capable of undergoing addition polymerization. Such free radically polymerizable materials include mono-, di- or poly- acrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-hexyl acrylate, stearyl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate, the diglycidyl methacrylate of bis-phenol A ("Bis-GMA"), bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyldimethylmethane, 2,2-bis(4-(2-Methacryloxyethoxy)phenylpropane (Bis-EMA), and trishydroxyethyl-isocyanurate trimethacrylate; the bis-acrylates and bis-methacrylates of polyethylene glycols of molecular weight 200-500, copolymerizable mixtures of acrylated monomers such as those in U.S. Pat. No. 4,652,274, and acrylated oligomers such as those of U.S. Pat. No. 4,642,126; and vinyl compounds such as styrene, diallyl phthalate, divinyl succinate, divinyladipate and divinylphthalate. Mixtures of two or more of these free radically polymerizable materials can be used if desired.

An alternative class of hardenable resins useful in the dental materials of the invention may include cationically active functional groups. Materials having cationically active functional groups include cationically polymerizable epoxy resins, vinyl ethers, oxetanes, spiro-orthocarbonates, spiro-orthoesters, and the like.

Preferred materials having cationically active functional groups are epoxy resins. Such materials are organic compounds having an oxirane ring which is polymerizable by ring opening. These materials include monomeric epoxy compounds and epoxides of the polymeric type and can be aliphatic, cycloaliphatic, aromatic or heterocyclic. These materials generally have, on the average, at least 1 polymerizable epoxy group per molecule, preferably at least about 1.5 and more preferably at least about 2 polymerizable epoxy groups per molecule. The polymeric epoxides include linear polymers having terminal epoxy groups (*e.g.* a diglycidyl ether of a polyoxyalkylene glycol), polymers having skeletal oxirane units (*e.g.* polybutadiene polyepoxide), and polymers having pendent epoxy groups (*e.g.* a glycidyl methacrylate polymer or copolymer). The epoxides may be pure compounds or may be mixtures of compounds containing one, two, or more epoxy groups per molecule. The "average" number of epoxy groups per molecule is determined by dividing the total number of epoxy groups in the epoxy-containing material by the total number of epoxy-containing molecules present.

These epoxy-containing materials may vary from low molecular weight monomeric materials to high molecular weight polymers and may vary greatly in the nature of their backbone and substituent groups. Illustrative of permissible substituent groups include halogens, ester groups, ethers, sulfonate groups, siloxane groups, nitro groups, phosphate groups, and the like. The molecular weight of the epoxy-containing materials may vary from about 58 to about 100,000 or more.

Useful epoxy-containing materials include those which contain cyclohexane oxide groups such as epoxycyclohexanecarboxylates, typified by 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate,3,4-epoxy-2-meth ylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate, and bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate. For a more detailed list of useful epoxides of this nature, reference is made to the U.S. Pat. No. 3,117,099, which is hereby incorporated herein by reference.

Particularly interesting resin bases that are useful for dental applications are those based on compounds selected from the group consisting of methacrylic acid (MA), methylmethacrylate (MMA), 2-hydroxyethyl-methacrylate (HEMA), triethyleneglycol dimethacrylate (TEGDMA), bisphenol-A-glycidyl dimethacrylate (BisGMA), bisphenol-A-ethyl dimethacrylate (BisEMA), bisphenol-A-propyl dimethacrylate (BisPMA), urethane-dimethacrylate (UDMA), and HEMA condensed with butanetetracarboxylic acid (TCB), as well as those based on combinations of the above-mentioned compounds. Such resin bases are, *e.g.*, disclosed and discussed in US 6,572,693. A particularly useful combination of compounds is TEGDMA and BisGMA, see, *e.g.*, US 3,066,112.

Other constituents of the dental filling material

The dental filling material may comprise other constituents which provide beneficial rheological, cosmetic, etc. properties. Examples of such other constituents are dyes, flavorants polymerisation initiators and co-initiators, stabilizers, fluoride releasing materials, sizing agents, antimicrobial ingredients.

Thus, the resin base may include initiators and co-initiators, and illustrative examples of such compounds, particularly for use in dental applications, are benzoylperoxide (BPO), camphorquinone (CPQ), phenylpropanedione (PPD) and N,N-di(2-hydroxyethyl)-p-toluidine (DEPT), N,N-dimethyl-p-aminobenzoic acid ethyl ester (DABE).

Shading can be achieved by using a number of color pigments. These include metal oxides, which provide the wide variety of colors of the dental filling material; for example, oxides of iron can act as a yellow, red to brown pigment, copper as a green pigment, titanium as a yellowish-brown pigment, and cobalt imparts a blue color.

Fluorescence is more subtle optical properties that further enhance the natural-looking, life-like appearance or "vitality" of the tooth. Fluorescence is defined as the emission of electromagnetic radiation that is caused by the flow of some form of energy into the emitting body, which ceases abruptly when the excitation ceases. In natural teeth, components of the enamel, including hydroxyapatite, fluorescence under long wavelength ultraviolet light, emitting a white visible light. This phenomenon is subtle in natural daylight but still adds further to the vitality of the tooth. In contrast, under certain lighting conditions, the lack of fluorescence in a restorative material may become alarming. Under "black light" conditions, such as that often used in discotheque-type night clubs, if a restoration does not fluoresce, the contrast between the tooth and restoration may be so great that the tooth may actually appear to be missing. Fluorescence can, *e.g.*, be achieved by adding an anthracene-like molecule.

The weight content of other constituents in the dental filling material is typically in the range of 0-10 %, such as 0-5 %, *e.g.* 0-4 % or 1-5 %.

The dental filling material may further comprise one or more water- or acid-releasing agent which typically constitute 0.01-5 % by weight, *e.g.* 0.1-1 % by weight, of the dental filling material. Examples of such constituents are disclosed in the applicant's earlier WO 2007/104312.

Preferably, the dental filling material is substantially solvent free and water free. By the term “substantially solvent free and water free” is meant that the dental filling material comprises less than 1 %, such as less than 0.5 % or less than 150 ppm, by weight of solvents and/or water.

In order to avoid premature curing of the polymerizable resin base, it may be advantageous to prepare and store the dental filling material as a two-component material intended for mixing immediately prior to use.

Definitions

In the present context, the term "C_{1-30}-alkyl" is intended to mean a linear, cyclic or branched hydrocarbon group having 1 to 30 carbon atoms, such as methyl, ethyl, propyl, *iso*-propyl, pentyl, cyclopentyl, hexyl, cyclohexyl, decyl, dodecyl, etc. The term "C_{1-6}-alkyl" is intended to mean a linear, cyclic or branched hydrocarbon group having 1 to 6 carbon atoms, such as methyl, ethyl, propyl, *iso*-propyl, pentyl, cyclopentyl, hexyl, cyclohexyl.

Similarly, the term "C_{2-30}-alkenyl" is intended to cover linear, cyclic or branched hydrocarbon groups having 2 to 30 carbon atoms and comprising one unsaturated bond. Examples of alkenyl groups are vinyl, allyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, heptadecaenyl, etc. In line herewith, the terms "C_{5-30}-alkadienyl" and "C_{8-30}-alkatrienyl" are intended to cover linear, cyclic or branched hydrocarbon groups having 5 to 30 carbon atoms, or 8-30 carbon atoms, respectively, and comprising two unsaturated bonds, or three unsaturated bonds, respectively.

In the present context, *i.e.* in connection with the terms "alkyl", "alkenyl", "alkadienyl", "alkatrienyl" and the like, the term "optionally substituted" is intended to mean that the group in question may be substituted one or several times, preferably 1-3 times, with group(s) selected from hydroxy (which when bound to an unsaturated carbon atom may be present in the tautomeric keto form), C_{1-6}-alkoxy (*i.e.* C_{1-6}-alkyl-oxy), C_{2-6}-alkenyloxy, oxo (forming a keto or aldehyde functionality), amino, mono- and di(C_{1-6}-alkyl)amino, carbamoyl, mono- and di(C_{1-6}-alkyl)aminocarbonyl, cyano, where any alkyl, alkoxy, and the like, representing substituents may be substituted with hydroxy, C_{1-6}-alkoxy, amino, mono- and di(C_{1-6}-alkyl)amino, C_{1-6}-alkylcarbonylamino, or C_{1-6}-alkylaminocarbonyl.

Typically, the substituents are selected from hydroxy, C_{1-6}-alkoxy (*i.e.* C_{1-6}-alkyl-oxy), C_{2-6}-alkenyloxy, and oxo.

The term "a (meth)acrylate moiety" and the like is intended to mean a group derived from an acrylate- or methacrylate-containing compound by abstraction of a hydrogen atom. In the present context, the (meth)acrylate moiety is preferably intended to be involved in a polymerization process upon polymerization of the resin base. Hence, the (meth)acrylate moiety may be derived from the types of (meth)acrylates which suitably are used as constituents of the resin base, *e.g.* mono-, di- or poly- acrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-hexyl acrylate, stearyl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate, the diglycidyl methacrylate of bis-phenol A ("Bis-GMA"), bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyldimethylmethane, and trishydroxyethyl-isocyanurate trimethacrylate; and the bis-acrylates and bis-methacrylates of polyethylene glycols of molecular weight 200-500.

As illustrative examples, the (meth)acrylate moiety may be of any one of the formulae:

CH_2=CH-C(=O)-O∼,
CH_2=C(CH_3)-C(=O)-O∼,
CH_2=C(∼)-C(=O)-O-(C_{1-6}-alkyl),
∼CH=CH-C(=O)-O-(C_{1-6}-alkyl),
∼CH=C(CH_3)-C(=O)-O-(C_{1-6}-alkyl),
CH_2=CH-C(=O)-O-(C_{1-6}-alkylene)∼,
CH_2=C(CH_3)-C(=O)-O-(C_{1-6}-alkylene)∼,
CH_2=C(CH_2(∼))-C(=O)-O-(C_{1-6}-alkyl),
etc. (where "∼" designates the bond to which the moiety is attached)

The term "alkylene" means the biradical corresponding to "alkyl".

The terms "halogen" and "halo" include fluoro, chloro, bromo, and iodo.

Moreover, it should be understood that the compounds may be present as enantiomers or diastereomers. The present invention encompasses each and every of such possible enantiomers and diastereomers as well as racemates and mixtures enriched with respect to one or the possible enantiomers or diastereomers.

Embodiments

In order to obtain zirconia particles that could undergo a fast phase transformation, a large surface area, *e.g.* 10-250 m^2/g or even better 50-200 m^2/g, of the particles is preferred.

As mentioned above, the average crystal size of the zirconia is preferably in the range of 5-12 nm, such as 6-10 nm, in particular 6-9 nm or 6-8 nm. "Crystals" refers to crystal domains with a homogeneous crystal lattice.

In a currently interesting embodiment, the zirconia particles have an average crystal size in the range of 5-12 nm and a BET surface area of in the range of 10-250 m^2/g.

As also mentioned above, the average particle size is typically in the range of 50-2000 nm, such as in the range of 50-1000 nm, in particular 100-600 nm.

Furthermore, it is believed that the zirconia particles advantageously may have a certain porosity in order to allow for a rapid transformation (as described herein). Thus, the average pore size of the particles is preferably in the range of 1-50 nm.

With respect to the porosity, it is believed that zirconia particles having a porosity in the range of 0.1-20 %, such as 0.2-10 %, are particularly interesting.

The dental filling material according to any one of the preceding claims, wherein the improvement, "T", (in fact a reduction) in the required amount of water (trigger molecule) is at least 30 %, such as at least 50 %, preferably at least 70 %, and in particular at least 90 %, when compared to a native sample metastable zirconia, and determined according to the method described herein ("Determination of water adsorption") with reference to the formula:

$T=(100\ \%*((tu-tm)/tu))$.

In one interesting embodiment, the dental filling material described herein, consists of:

40-85 % by weight of the one or more fillers including the metastable zirconia;
15-60 % by weight of the a polymerizable resin base;
0-25 % by weight, such as 0-5 % by weight of additives; and
0-4 % by weight of solvents and/or water.

With respect to the type of surface functionalities of the formula -Zr-O-Zr-O-C(=O)-X-CH(R^1R^2) and the corresponding compounds used to introduce the surface functionalities, it is in one embodiment preferred that X is selected from -O-, -NH- and -S-; and R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, <u>or</u> when X is –NH-, R^1 and R^2 may together designate =O.

In one variant hereof, X is -O-; and R^1 and R^2 are independently selected from hydrogen and optionally substituted C_{1-12}-alkyl and optionally substituted C_{1-12}-alkenyl. More particular, the surface functionality is derived from a molecule H-X-CH(R^1R^2), which is selected from methanol (H-O-CH_3) and 2-propanol (CH_3-CHOH-CH_3).

In another interesting variant hereof, X is -NH-; and R^1 and R^2 are independently selected from hydrogen and optionally substituted C_{1-12}-alkyl and optionally substituted C_{1-12}-alkenyl, or R^1 and R^2 together designate =O. More particular, the surface functionality is derived from a molecule H-NH-CH(R^1R^2), which is formamide ($NH_2C(=O)$).

In another embodiment, the surface functionality is selected from methanol, ethanol, iso-propanol, n-propanol, n-butanol, iso-butanol, iso-octanol, 1,5-pentanediol, octane thiol, and acetamide.

Within the various embodiments described herein, the intra-molecular distance between the X-group in the surface functionality and any heteroatoms included in R^1 and/or R^2 should preferably be at least 3 carbon atoms, in particular at least 4 carbon atoms.

In the currently most preferred embodiments, R^1 and R^2 do not include any heteroatoms.

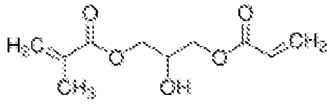
In some variant of the before-mentioned embodiments, R^3 is selected from hydrogen and C_{1-6}-alkyl.

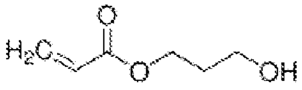
The before-mentioned surface functionalities are particularly interesting with respect to blocking the carbonyl species on the surface of the zirconia particles.

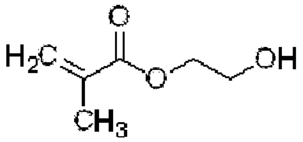
In another highly interesting embodiment, which of course may be combined with the foregoing, the surface functionalities are blocking the carbonyl species, but are on the other hand capable of being involved in the polymerization process upon polymerization of the resin base.

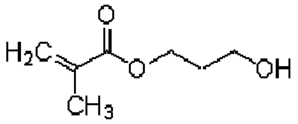
Hence, in this embodiment, and with respect to the type of surface functionalities of the formula -Zr-O-Zr-O-C(=O)-X-CH(R^1R^2) and the corresponding compounds used to introduce the surface functionalities, X is selected from -O- and -S-; and R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, a (meth)acrylate moiety, a (meth)acrylate-C_{1-12}-alkyl moiety, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, with the proviso that at least one of R^1 and R^2 are selected from a (meth)acrylate moiety and a (meth)acrylate-C_{1-12}-alkyl moiety. In one variant hereof, X is -O-; and R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-12}-alkyl, a (meth)acrylate moiety, a (meth)acrylate-C_{1-12}-alkyl moiety, optionally substituted C_{2-12}-alkenyl, and optionally substituted C_{5-12}-alkadienyl, with the proviso that at least one of R^1 and R^2 are selected from a (meth)acrylate moiety and a (meth)acrylate-C_{1-12}-alkyl moiety. In some interesting variants hereof, R^3 is selected from hydrogen and C_{1-6}-alkyl.

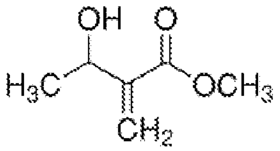
Examples of acrylate molecules which may be used to prepare corresponding surface functionalities of the type including (meth)acrylate moieties and (meth)acrylate-C_{1-12}-alkyl moieties are the following:











In a further interesting embodiment, which of course may be combined with the foregoing embodiments, the surface functionalities are blocking the carbonyl species, but are at the same time capable of releasing -OH, halogen ions or radicals, or other trigger molecules or species. A detailed description of the concept of trigger molecules is disclosed in WO 2007/104312. Such hydroxyl, halogen ions and radicals may either react with hydrogens in the monomer matrix of the resin base under formation of trigger molecules, or may as such act as trigger molecules. It is envisaged that such compounds (*e.g.* those specifically disclosed in WO 2007/104312) which are capable of releasing trigger molecules can be incorporated as corresponding surface functionalities on the zirconia particles, *i.e.* as described above.

Hence, in one variant hereof, R^3 is selected from hydroxy and halogen. In other variants, R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, of which at least one is substituted with hydroxy and/or halogen.

In another embodiment, the surface functionality may be a photo-active moiety (*e.g.* a triazine moiety), which upon light exposure liberates hydroxyl or halogen radicals. The radicals will then be involved in the polymerization reaction with the monomers of the resin base or will abstract a hydrogen atom and provide trigger molecules to the surface of zirconia.

Use of the dental filling materials

The present invention further provides the dental filling material as defined herein for use in medicine, in particular in dentistry.

The dental filling materials may be used and are cured essentially as conventional dental filling materials of the same type, except for the fact that the martensitic transformation should be controlled along with the curing of the resin base, *i.e.* at least in part by the chemical trigger(s), or afterwards by the diffusion of water into the dental filling material.

Generally, it is believed that the martensitic transformation can be activated either by physical means (*e.g.* application of mechanical pressure, tension, ultrasound, Roentgen irradiation, microwaves, longitudinal waves, electromagnetic irradiation such as light, near infrared irradiation, heating, etc.) or by chemical means (*e.g.* modification of the surface free energy by contacting the surface of the zirconia particles with a chemical, *e.g.* a constituent of the dental filling material or an additive such as water). Hence, it should be understood that the martensitic transformation may be further triggered by physical means, although it is believed that the chemical means (*i.e.* a trigger molecule) will contribute significantly, or even completely, to the triggering of the martensitic transformation of the zirconia particles.

It should be understood that the martensitic transformation of the zirconia particles preferably shall take place with the curing (polymerization and hardening) of the resin base. However, since the crystals are small, the expansion due to phase transformation will not cause deterioration of the mechanical properties of the cured compound. Therefore, transformation triggered by slow mechanisms, *e.g.*, diffusion of water into the cured compound upon curing and subsequent to curing is the currently preferred mechanism of triggering the phase transformation. Triggering the transformation before the curing is undesired since the volume compensating effect will be less or lost depending on how much is transformed before curing is initiated.

Method of the invention

In view of the above, the present invention also provides a method of controlling the volumetric shrinkage of a dental filling material upon curing, comprising the step of:

(a) providing a dental filling comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase, said zirconia particles having surface functionalities of the formula:

$-Zr-O-Zr-O-C(=O)-X-C(R^1)(R^2)(R^3)$

wherein X is selected from -O-, -NH- and -S-; R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, a (meth)acrylate moiety, a (meth)acrylate-C_{1-12}-alkyl moiety, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, or when X is –NH-, R^1 and R^2 may together designate =O; and R^3 is selected from hydrogen, C_{1-6}-alkyl, hydroxy and halogen;

(b) allowing the resin base to polymerize and cure, and allowing the metastable zirconia particles to undergo a martensitic transformation from a first metastable phase to a second stable phase.

Various embodiments of the meanings of the substituents X, R^1, R^2 and R^3 are as described further above.

Preferably, the zirconia particles should be triggered to undergo the martensitic transformation either simultaneous with the curing or subsequent to the curing in order to fully benefit from the volumetric expansion of the zirconia particles.

In one currently preferred embodiment, the triggering of the metastable zirconia particles in order to facilitate the martensitic transformation takes place simultaneous and subsequent to the curing by means of water diffusion into the dental filling material.

In another embodiment, the martensitic transformation of the zirconia particles is initiated by exposure of the surface of the zirconia particles to a chemical trigger. In this instance, the martensitic transformation is preferably triggered simultaneously with or after the curing is initiated, but before the curing is completed.

More specifically, the present invention further provides a method of reconstructing a tooth, comprising the step of

(a) preparing a cavity in the tooth;

(b) filing said cavity with a dental filling material as defined above; and

(c) allowing the resin base of the dental filling material to polymerize and cure, and allowing the zirconia particles of the dental filling material to undergo a martensitic transformation from a first metastable phase to a second stable phase.

The above-defined method for the reconstruction of a tooth may generally comprise further steps obvious to the person skilled in the art of dentistry.

EXPERIMENTALS

General procedure

Metastable zirconia is prepared according to the following general procedure:

1. Precipitation of amorphous zirconia

Reaction: $ZrOCl_2 + 2\ NH_3 \rightarrow ZrO(OH)_2 + 2\ NH_4Cl$

A solution of 0.5 M $ZrOCl_2$ and an aqueous solution of 5 M NH_3 is prepared. The two solutions are added together at a rate of approx. 2.8 times as much by volume 5 M NH_3 as 0.5 M $ZrOCl_2$ in this way the pH is kept at a constant level of 10 at room temperature and with stirring. A precipitate is thereby formed.

2. Washing

The precipitate is filtered and washed with water at room temperature in a basket centrifuge in order to exclude chlorine and ammonium ions. Completion of the washing procedure is detected with lack of any AgCl precipitate (white) after treatment of the washing water with a 0.5 M $AgNO_3$.

3. Conditioning

The washed precipitate is suspended in water and refluxed for 10 hours.

4. Washing

The precipitate is then filtered and washed with water again as in step 2.

5. Alcohol Treatment

The precipitate is treated with a suitable alcohol (*e.g.* ethanol or iso-propanol) using an azeotropic distillation principle to remove water from the amorphous zirconia to a content of less than 1 % of the distillate. (The distillate was checked with a zirconium(IV) butoxide, 80 wt% solution in 1-butanol. A white precipitate in this test indicated that the water content was lower than 0.7 % in the distillate.)

6. Drying

The powder is dried at 60°C for 2 days.

7. Calcination

The amorphous powder is calcinated at 450°C for approx. 1½ hour under a dry air flow.

8. Surface modification

Under an inert atmosphere, the tetragonal zirconia is treated 8 h with dry methanol (or another compound as specified herein) and filtered off and left drying overnight under an inert atmosphere.

Analysis

Determination of types of carbonyl species

IR: The adsorption of CO_2 on zirconia has been widely studied (especially by Teichner et al: D. Bianchi, T. Chafik, M. Khalfallah and S. J. Teichner; Appl. Catal., 105 (1993) 223). The kind of species formed on the surface of zirconia is very dependent on the process condition like, temperature, amount of CO_2 and the surface of zirconia. However by following the synthesis steps above the most common species are: ionic carbonate CO_3^{2-}: 1444 cm^{-1}, bidented bicarbonate HCO_3^-: 1598 cm^{-1}, bidented covalent surface carbonate "CO_3": 1558 and 1325 cm^{-1} and ionic carboxylate CO_2^-: 1423 cm^{-1}. The intensities of the ionic carbonate and carboxylate are the same, creating a double peak in the IR spectrum. The bidentate covalent surface carbonates are shoulders to the double peak and the bicarbonate is a small peak and only a shoulder to the bidentate covalent surface carbonate peak.

All of these carbonates can react with methanol and form methyl carbonates. Methyl carbonates give rise to an IR spectrum with three significant peaks at: 1600, 1474 and 1370 cm^{-1}. The formation of a substituted carbonate can therefore be observed in IR as a change of the carbonate peaks into the substituted species peaks. The above standing peaks are all designated to the C-O (or C=O) vibration as these are the most intensity strong peak and are by far the easiest way of recognising a change in carbonates on the surface of zirconia.

Determination of water adsorption

The amount of water adsorped on the zirconia surface at a given partial pressure can be determined using an "autosorbtion" machine, *e.g.* a Quantachrome XT autosorb 1 analyser. The degree of water adsorption can be used to determine the amount of trigger molecules (water) necessary to phase transform zirconia. In fact, an autosorbtion study can be used to study the amount needed to phase transform zirconia.

A sample of zirconia is kept at 0°C (ice bath) during the experiment. In order to avoid premature phase transformation it is necessary to use a seal that only opens in the autosorbtion machine. This way the sample can be kept under an inert atmosphere or vacuum until the measurement starts and again after the sample is removed from the machine.

1) The zirconia (metastable) sample is evacuated to the relative pressure, P, being of 0.01 x P_0; P_0 being the ambient pressure, *i.e.* 1 atm.

2) The sample is then titrated with water in gaseous form by the procedure of finding a relative pressure and then noting the amount of water necessary to get this pressure.

3) at a given end-point (a given P/P_0) the sample re-evacuated and taken to a glove-box.

4) The sample is then mixed in a dental resin (see Example 1) which is cured by blue light, *e.g.* Bluephase.

5) The degree of phase transformation is determined by the use of X-ray diffraction (XRD).

6) The point where the zirconia does not phase transform more upon added water moisture can be found. This point is found by comparing the degree of phase transformation for a series of samples as a function of water moisture added. This point can be used to compare unmodified zirconia and modified zirconia, and thereby the effect of the compound used for the surface modification.

The water adsorption for a sample of surface-modified zirconia can be compared with a sample of unmodified zirconia so as to determine the improvement (*i.e.* reduction) in the amount of water (trigger molecule) needed in order to provoke the same phase transformation as would be obtainable when the sample was place in a chamber with 100 % humidity at room temperature (25 °C).

Improvement of amount of trigger molecules to phase transform the modified zirconia relative to the unmodified zirconia, (T), is calculated as:

$T=(100\ \%*((tu-tm)/tu))$

wherein tu= mL/g adsorbed water moisture needed to trigger the phase transformation of unmodified zirconia, and wherein tm=mL/g adsorbed water moisture needed to trigger the phase transformation of modified zirconia.

In this way the minimum of amount of trigger molecules needed to induce a phase transformation corresponding to that obtainable at 100 % humidity can be determined. The effect of surface modifying the zirconia surface is lowering the amount of trigger molecules needed to phase transform the zirconia. This can be described in mL gaseous water per gram zirconia. The effect can also be described as relative to the amount needed to phase transform the unmodified zirconia at a given partial pressure.

To find the extent to which an uncharacterised sample of zirconia is surface modified, several analysis methods can be used of which two are outlined below.

1) The zirconia particles (suspected of being surface modified metastable zirconia) in an uncured dental material can be isolated by dissolving the resin with a suitable solvent *e.g.* acetone. The surface modification for a sample can be removed by vacuum and heating. To remove any surface modification, the sample can be heated to 450°C under a flow of dry air. The autosorption analysis can show if the trigger amount (water adsorption) is more for the sample than for the native sample (*i.e.* the isolated sample before the heating and vacuum treatment). This method only reveals if there were a surface modification and whether it is

removed. If there are different kinds of filler particles it can not be determined on which particles the surface modification is present. However the autosorption study can be complemented with IR and surface sensitive analysis method like XPS.

2) The particles from the dental material can be isolated by dissolving the resin in a suitable solvent *e.g.* acetone. A sample of the particles can then be modified with methanol by suspending them in the solvent for 8 hours and dried overnight. The autosorption analysis can then be used to determine the trigger amount necessary to phase transform the particles before and after modification to determine if the modification had an effect. If not this indicates that the particles were surface modified before they were exposed to methanol. Further determination can be complemented with IR and surface sensitive analysis method like XPS to see whether the zirconia were initially modified.

Determination of the degree of phase transformation

The metastable zirconia particles prepared represent tetragonal and/or cubic crystalline phase zirconia. After complete martensitic phase transformation, the zirconia particles are present in the monoclinic crystalline phase. It is important to understand that "metastability" of zirconia particles is not just a result of the particles being in the tetragonal and/or cubic crystalline phase. Hence, a number of other factors also play an important role, *e.g.* the crystal size, the surface structure, the surface functionalities (*i.e.* amount of reactive sites), etc.

Within the present context, the metastable zirconia particles representing tetragonal and/or cubic crystalline phase zirconia with not representation of monoclinic crystalline phase zirconia are defined as being 0 % phase transformed. Correspondingly, stable zirconia particles representing monoclinic crystalline phase zirconia with no representation of tetragonal and/or cubic crystalline phase zirconia are defined as being 100 % phase transformed.

The degree of phase transformation is expressed as the volume ratio of zirconia in the monoclinic phase and is determined by means of X-ray diffraction (XRD).

The phase transformation is measured by means of powder XRD of a sample of the resin+zirconia material. The volume fraction of monoclinic zirconia (V_m) can be determined from the following relationships:

$$X_m=(I_m(111) + I_m(11\text{-}1))/(I_m(111) + I_m(11\text{-}1) + I_t(111))$$

$V_m=1.311\ X_m/(1+0.311X_m)$

where $I_m(111)$ and $I_m(11\text{-}1)$ are the line intensities of the (111) and (11-1) peaks for monoclinic phase zirconia and $I_t(111)$ is the sum of the intensities of the (111) peaks for tetragonal phase zirconia and cubic phase zirconia.

Determination of the average crystal size

The average crystal size (x) can be found using Scherrers expression:

$x=K\cdot\lambda/(B\cdot\cos\theta)$,

where K is a equipment dependent constant typically between 0.89 and 1, λ is the wavelength of x-rays, θ is the center angle of the peak and B is the width of the peak at half peak height.

Example 1

A solution of 0.5 M $ZrOCl_2$ was prepared from $ZrOCl_2\cdot 8H_2O$ and water. The amorphous zirconia $ZrO_x(OH)_{4-2x}$ was precipitated with a 5 M NH_3 aqueous solution at a constant pH of 10. To keep the pH constant at 10 the two solutions were added together at a rate of 2.8 times as much 5 M NH_3 as 0.5 M $ZrOCl_2\cdot 8H_2O$. 92 mL 0.5 M $ZrOCl_2$ and 258 mL 5 M NH_3 solution were used. The suspension was then filtered and washed on a basket centrifuge until a negative chlorine test was obtained (with 960 mL water). The filter cake was then suspended in 300 mL water and refluxed for 10 h. The suspension was allowed to cool and was then filtered. The filter cake was washed with 200 mL water and suspended in 300 mL dry iso-propanol and was dried using a azeotropic distillation principle. The drying was done with a rotorvapor and 1200 mL iso-propanol. The distillate was checked with a zirconium(IV) butoxide, 80 wt% solution in 1-butanol. A white precipitate in this test indicated that the water content was lower than 0.7 % in the distillate. The amorphous was then dried in an oven at 60°C for 2 days. The powder was then calcined in a tube oven at 450°C with a dry air flow of 20 mL/min; the dew-point was -43.2°C. The following handling and preparation of analysis was done in a glove-box in inert atmosphere.

The average crystal size was about 8 nm and the BET area of the particles was 150 m^2/g.

The "native" particles represented metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 5 % (v/v) in the monoclinic phase.

An IR spectrum of the calcined and dried sample was obtained by pressing a pellet with the diameter of 30 mg zirconia and placing it between two CaF_2 windows in an airtight holder.

The IR showed ionic Carbonate CO_3^{2-}: 1444 cm^{-1}, bidented covalent surface carbonate "CO_3": 1558 and 1325 cm^{-1} and ionic carboxylate CO_2^-: 1423 cm^{-1}.

A sample of 0.123 g zirconia was run on Quantachrome XT autosorb 1 analyser. The analysis showed that at a relative pressure of 0.15 P/P_0, 17 mL/g water was adsorbed. The sample was then re-evacuated and mixed with 0.2 g of a dental resin (containing: 35.5 % (w/w) BisGMA, 44 % (w/w) UDMA, 19.5 % (w/w) TEGDMA. 0.5 % (w/w) camphorquinone (CQ), 0.5 % (w/w) N,N-dimethyl-*p*-aminobenzoic acid ethylester (DABE)).

The curing was initiated by light from a curing device at max intensity 1100 mW/cm^2 (Bluephase from Ivoclar Vivadent). The material was cured for a period of 2 min. The cured sample was then analysed with XRD. The degree of phase transformation was 60 %.

A sample of 1 g zirconia (calcined and dried; see above) was suspended in dry methanol for 8 h. The suspension was filtered and left to dry in the filter overnight under an inert atmosphere. An IR spectrum was obtained by pressing a pellet with the diameter of 30 mg modified zirconia and placing it between two CaF_2 windows in an airtight holder, all done in a glove-box with inert atmosphere. The IR showed three significant peaks at: 1600, 1474 and 1370 cm^{-1}. The formation of methyl carbonate could therefore be observed in IR.

A sample of 0.118 g zirconia was run on Quantachrome XT autosorb 1 analyser. The analysis showed that at a relative pressure of 0.15 P/P_0, 3.6 mL/g water was adsorbed. The sample was then re-evacuated and mixed with 0.2 g of a dental resin (containing: 35.5 % (w/w) BisGMA, 44 % (w/w) UDMA, 19.5 % (w/w) TEGDMA. 0.5 % (w/w) camphorquinone (CQ), 0.5 % (w/w) N,N-dimethyl-*p*-aminobenzoic acid ethylester (DABE)).

The material was cured for a period of 2 min as above. The cured sample was then analysed with XRD. The degree of phase transformation was 60 %.

This shows that the modified zirconia only needed

$(100\ \% - 100\ \% * (17\ mL/g - 3.6\ mL/g)/17\ mL/g) = 20\ \%$

of the amount of trigger molecules to obtain the same partial pressure, indicating that far less trigger molecules are needed to phase transform the modified zirconia.

Example 2

Modified and unmodified zirconia were prepared as in Example 1. Sample of modified and unmodified zirconia, respectively, were each mixed with 0.2 g of a dental resin (35.5 % (w/w) BisGMA, 44 % (w/w) UDMA, 19.5 % (w/w) TEGDMA. 0.5 % (w/w) camphorquinone (CQ), 0.5 % (w/w) N,N-dimethyl-*p*-aminobenzoic acid ethylester (DABE)), and the resin was cured.

The two samples were put in water at 37°C and taken out for measurements with XRD to observe the phase transformation as a function of time.

After two days, the sample with the modified zirconia was phase transformed to an extent of 57 %, no further phase transformation was observed after prolonged storage. The unmodified zirconia was phase transformed to an extent of 25 % after 3 days and to 40 % after 21 days. No further study of this sample was conducted.

Example 3

A test dental filling material was prepared by mixing 200 mg of the methanol modified zirconia particles (prepared as in Example 1) and 500 mg of a polymer resin system (36 % (w/w) BisGMA, 43 % (w/w) UDMA, 19.35 % (w/w) TEGDMA. 0.5 % (w/w) camphorquinone (CQ), 0.5 % (w/w) N,N-dimethyl-*p*-aminobenzoic acid ethylester (DABE), 0.05 % (w/w)) with 100 mg of the trigger molecule 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine.

The phase transformation was initiated by light from a curing device at max intensity 1100 mW/cm^2 (Bluephase from Ivoclar Vivadent), simultaneously with the curing of resin. After 2 min, 15 % of the zirconia particles were phase transformed. After 30 min, 53 % of the zirconia particles were phase transformed.

Example 4

A test dental filling material was prepared by mixing 200 mg of the non-modified zirconia particles (prepared as in Example 1, but without methanol treatment) and 500 mg of a polymer resin system (36 % (w/w) BisGMA, 43 % (w/w) UDMA, 19.35 % (w/w) TEGDMA. 0.5

% (w/w) camphorquinone (CQ), 0.5 % (w/w) N,N-dimethyl-*p*-aminobenzoic acid ethylester (DABE), 0.05 % (w/w)) with 100 mg of the trigger molecule 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine.

The phase transformation was initiated by light from a curing device at max intensity 1100 mW/cm^2 (Bluephase from Ivoclar Vivadent), simultaneously with the curing of resin.

After 2 h of light exposure very little phase transformation was detected. Apparently, the trigger species derived from the triazine was almost completely "consumed" by the "carbonates" present at the surface of the zirconia particles.

Example 5

A test dental filling material was prepared by mixing 200 mg of the zirconia particles (prepared as in Example 1) and 500 mg of a polymer resin system (36 % (w/w) BisGMA, 43 % (w/w) UDMA, 19.35 % (w/w) TEGDMA. 0.5 % (w/w) camphorquinone (CQ), 0.5 % (w/w) N,N-dimethyl-*p*-aminobenzoic acid ethylester (DABE)) with 100 mg of the trigger molecule 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine.

Beforehand, the resin system was mixed with 1 mmol of dry methanol. The phase transformation was initiated by light from a curing device at max intensity 1100 mW/cm^2 (Bluephase from Ivoclar Vivadent), simultaneously with the curing of resin. After 30 min, 45 % of the zirconia particles were phase transformed.

Example 6

Samples were prepared and tested using the same methods as described in Example 5, but substituting methanol with different other chemical substances (1 mmol) as described in the table below.

Substance	Molecular weight (added amount in mg)	Phase transformation in %
tert-Butylamine	73.14	0
Diethylamine	73.14	0
Triethylamine	101.19	0
Ethylenediamine	60.10	0
Methanol	32.04	45
Iso-propanol	60.10	48
Iso-octanol	130.23	39
Ethylene glycol	62.07	0
1,3-Propanediol	76.09	0
1,4-Butanediol	90.12	0
1,5-Pentanediol	104.15	56
Glycerol	92.09	0
Octane thiol	146.29	43
N,N-Dimethylformamide	73.09	0
Chloroform	119.38	0
Acetamide	59.07	19
Cyanamide	42.04	0
Unmodified zirconia	-	0

It has been shown (experimentally) that the substances used for the addition reaction on the carbonates are blocking the reactive groups if the substance is able to make a bond to hydroxylic groups by making a bidentate bond as a bridge over the hydroxylic groups. It is believed that the Zr-O-Zr bond is protected by the bridge. In order to avoid bridge bonding the substances can be monodentate (only able to bind with one group) or the bonding groups should be far away far each other. The distance between the binding groups can be determined by intervals of C-bonds in the substance. Ethylene glycol and 1,3 propanediol are blocking the phase transformation, whereas 1,4 butanediol is blocking the phase transformation to some extend and 1,5 butanediol is not. The distance between the bonding groups should be more than 3 carbon bonds and even better more than 4 carbon bonds.

Example 7

20 g zirconia, 16 g commercial methacrylate monomer for dental use, 1 g 3-(acryloyloxy)-2-hydroxy-propyl methacrylate 60 ml anhydrous acetonitrile were dispersed with a high speed dissolver for 20 min. 20 ml acetonitrile was added, due to evaporation and the mixture was dispersed of 5 min longer. The mixture was transferred to an airtight chamber and ultrasonicated 45 min with a 1000 w transducer at 100 % amplitude. The acetonitrile was evaporated under vacuum and camphorquinone and N,N-dimethyl-*p*-aminobenzoic acid ethylester (DABE) and the resin was cured. The sample was stored in water at 37 °C. After three days, the sample was phase transformed to an extent of 61 % (determined with XRD).

CLAIMS

1. A dental filling material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase, said zirconia particles having surface functionalities of the formula:

$-Zr-O-Zr-O-C(=O)-X-C(R^1)(R^2)(R^3)$

wherein X is selected from -O-, -NH- and -S-; R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, a (meth)acrylate moiety, a (meth)acrylate-C_{1-12}-alkyl moiety, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, <u>or</u> when X is –NH-, R^1 and R^2 may together designate =O; and R^3 is selected from hydrogen, C_{1-6}-alkyl, hydroxy and halogen.

2. The dental filling material according to claim 1, wherein said zirconia particles having surface functionalities of the formula:

$-Zr-O-Zr-O-C(=O)-X-CH(R^1R^2)$

wherein X is selected from -O-, -NH- and -S-; and R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, <u>or</u> when X is –NH-, R^1 and R^2 may together designate =O.

3. A dental filling material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase, said zirconia particles being prepared by a process comprising the sequential steps of:

a) preparation of an amorphous powder of zirconia;

b) calcination of the amorphous powder of zirconia at a temperature in the range of 400-600 °C so as to obtain metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase;

c) treatment of the metastable zirconia particles with a compound of the formula

H-X-C(R^1)(R^2)(R^3),wherein X is selected from -O-, -NH- and -S-; R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, a (meth)acrylate moiety, a (meth)acrylate-C_{1-12}-alkyl moiety, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, <u>or</u> when X is –NH-, R^1 and R^2 may together designate =O; and R^3 is selected from hydrogen, C_{1-6}-alkyl, hydroxy and halogen.

4. The dental filling material according to any of the preceding claims, wherein the average crystal size is in the range of 5-12 nm, such as 6-10 nm, in particular 6-9 nm or 6-8 nm.

5. The dental filling material according to any one of the preceding claims, wherein the zirconia particles have a BET surface area of 10-250 m^2/g.

6. The dental filling material according to any one of the preceding claims, wherein the zirconia particles have an average crystal size in the range of 5-12 nm and a BET surface area of in the range of 10-250 m^2/g.

7. The dental filling material according to any one of the preceding claims, wherein the improvement, "T", in the required amount of water (trigger molecule) is at least 30 %, when compared to a native sample metastable zirconia, and determined according to the method described herein ("Determination of water adsorption") with reference to the formula: T=(100 %*((tu-tm)/tu)).

8. The dental filling material according to any one of the preceding claims, consisting of:

40-85 % by weight of the one or more fillers including the metastable zirconia;
15-60 % by weight of the a polymerizable resin base;
0-25 % by weight of additives; and
0-4 % by weight of solvents and/or water.

9. The dental filling material according to any one of the preceding claims, wherein X is -O-; and R^1 and R^2 are independently selected from hydrogen and optionally substituted C_{1-12}-alkyl and optionally substituted C_{1-12}-alkenyl.

10. The dental filling material according to claim 9, wherein the surface functionality is derived from H-X-CH(R^1R^2), which is selected from methanol and 2-propanol.

11. The dental filling material according to any one of the claims 1-8, wherein X is selected from -O- and -S-; and R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, a (meth)acrylate moiety, a (meth)acrylate-C_{1-12}-alkyl moiety, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, with the proviso that at least one of R^1 and R^2 are selected from a (meth)acrylate moiety and a (meth)acrylate-C_{1-12}-alkyl moiety.

12. A method of controlling the volumetric shrinkage of a dental filling material upon curing, comprising the step of:

(a) providing a dental filling comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise metastable zirconia particles in the tetragonal and/or cubic crystalline phase with less than 30 % (v/v) in the monoclinic phase, said zirconia particles having surface functionalities of the formula:

$-Zr-O-Zr-O-C(=O)-X-C(R^1)(R^2)(R^3)$

wherein X is selected from -O-, -NH- and -S-; R^1 and R^2 are independently selected from hydrogen, optionally substituted C_{1-30}-alkyl, a (meth)acrylate moiety, a (meth)acrylate-C_{1-12}-alkyl moiety, optionally substituted C_{2-30}-alkenyl, optionally substituted C_{5-30}-alkadienyl, and optionally substituted C_{8-30}-alkatrienyl, or when X is –NH-, R^1 and R^2 may together designate =O; and R^3 is selected from hydrogen, C_{1-6}-alkyl, hydroxy and halogen;

(b) allowing the resin base to polymerize and cure, and allowing the metastable zirconia particles to undergo a martensitic transformation from a first metastable phase to a second stable phase.

13. The method according to claim 12, wherein the triggering of the metastable zirconia particles in order to facilitate the martensitic transformation takes place simultaneous and subsequent to the curing by means of water diffusion into the dental filling material.

14. A dental filling material as defined in any one of the claims 1-11 for use in medicine, in particular in dentistry.

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Effect of microscale shear stresses on the martensitic phase transformation of nanocrystalline tetragonal zirconia powders

Mette Skovgaard[a,c], Anwar Ahniyaz[b,*], Bent F. Sørensen[c], Kristoffer Almdal[d], Alexander van Lelieveld[e]

[a] *DentoFit A/S, Frederiksborgvej 399, DK-4000 Roskilde, Denmark*
[b] *YKI, Institute for Surface Chemistry, 11486 Stockholm, Sweden*
[c] *Materials Research Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, DK-4000 Roskilde, Denmark*
[d] *Department of Micro- and Nanotechnology, Technical University of Denmark, DK-4000 Roskilde, Denmark*
[e] *Aneedle, Engelstedsgade 322, DK-2100 Copenhagen East, Denmark*

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Abstract

For the first time, the effect of microscale shear stress induced by both mechanical compression and ball-milling on the phase stability of nanocrystalline tetragonal zirconia (t-ZrO_2) powders was studied in water free, inert atmosphere. It was found that nanocrystalline t-ZrO_2 powders are extremely sensitive to both macroscopic uniaxial compressive strain and ball-milling induced shear stress and easily transform martensitically into the monoclinic phase. A linear relationship between applied compressive stress and the degree of tetragonal to monoclinic (t → m) phase transformation was observed. Ball-milling induced microscale stress has a similar effect on the t → m phase transformation. Furthermore, it was found that even very mild milling condition, such as 120 rpm, 1 h (0.5 mm balls) was enough to induce phase transformation. Surfactant assisted ball-milling was found to be very effective in de-agglomeration of our nanocrystalline porous ZrO_2 particles into discrete nanocrystals. However, the t → m phase transformation could not be avoided totally even at very mild milling condition. This suggests that the metastable t-ZrO_2 is extreme sensitive to microscale shear stress induced by both mechanical compression and ball-milling. The findings presented in this work are very important in further understanding the stress-induced phase transformation of nanocrystalline t-ZrO_2 powders in a water free atmosphere and their further stabilization in industrially relevant solvents.

Keywords: ZrO_2; Phase transformation; Milling; Biomedical application; Composites

1. Introduction

Zirconia (ZrO_2) ceramics have found broad applications in energy,[1] catalysis,[2,3] catalysis support,[4] composites[5,6] coatings,[7–9] dental and body implants,[10–14] and solid electrolytes,[15] because of their unusual combination of strength, fracture toughness, ionic and thermal conductivity. These attractive characteristics are largely associated with the stabilization of the tetragonal and cubic phases through alloying with aliovalent ions.

At room temperature (RT) and atmospheric pressure, the thermodynamic stable phase of pure zirconia is the monoclinic and it goes through the following crystal phase as the temperature is raised:

monoclinic → tetragonal → cubic → melt

By suitable control of the processing parameters, however, it is possible to create ZrO_2 in a metastable tetragonal phase at room temperature.[16] The metastable tetragonal phase easily transforms to the monoclinic phase. As a result of the t → m phase transformation, the density of the zirconia crystals is decreased since the crystals expand 3–5 vol%. This volume increase, caused by the martensitic phase transformation, is an important property of t-ZrO_2 (tetragonal zirconia) as it is the basis for transformation toughening, which is used in various applications, e.g. dental inlays, dental crowns and dental bridges where high tensile strength is important.[17]

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* Corresponding author. Tel.: +46 10 516 6059.
E-mail address: anwar.ahniyaz@yki.se (A. Ahniyaz).

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In the last few decades, numerous efforts have been made to understand the phase transformation behaviour of doped zirconia. Effect of particle size, water, and oxygen vacancies on phase transformation of YSZ has been reported.[18,19]

Effect of uniaxial stress on tetragonal to monoclinic (t-m) phase transformation has been reported.[20]

There are only a few reports on the effect of external mechanical stress on the phase transformation behaviour of undoped ZrO_2.

The most often described phase transformation is from monoclinic to tetragonal[21–23] as well as the direct transformation from monoclinic to cubic is seen,[24] but also the reverse reaction (tetragonal to monoclinic) is reported.[25] These varying and contradicting results can be expected to be an effect of different milling conditions (e.g. wet or dry milling) and the history of the zirconia. Regarding the stabilizing effect of ball-milling on the tetragonal and the cubic phase at room temperature several theories have been proposed: lattice imperfections caused by quenching on high-energy impact,[24] incorporations of impurities due to wearing of the milling media,[21,22] and small crystallite size have been suggested.[26]

Unfortunately, however, in most cases, ball-milling experiments were done in uncontrolled atmosphere, like open air, where phase transformation may occur also under the influence of water vapor, for example. Therefore, it is very difficult to evaluate the effect of milling and stress on the phase stability of zirconia crystals and this leads to different conclusions. Moreover, all these previous studies were limited on doped-zirconia, such as yttria-stabilized zirconia (YSZ) and ceria-stabilized zirconia (CSZ).[27–29]

To our knowledge, effect of microscale shear stress on the martensitic phase transformation of nanocrystalline t-ZrO_2 has never been reported.

It is well known that yttria-stabilized zirconia (YSZ) particles embedded in a ceramic matrix can display autocatalysis. That is, the t → m phase transition of one particle induces a strain field in the surrounding matrix that triggers the phase transition in neighbour particles.[30]

The behaviour of YSZ powder alone is anticipated to be very different from that of YSZ particles in a ceramic matrix. In the latter case, the ceramic matrix encloses the YSZ particles and acts as an elastic medium that transfers stresses between YSZ particles that are not in direct contact. In contrast, for YSZ powder, stress transfer can only occur by direct particle-to-particle contact. This implies that the microscale stress state differs from the macroscale stress state. As an example, consider powder subjected to macroscopic compression in a rigid die (Fig. 1). At the macroscale, the YSZ powder is subjected to uniaxial strain. However, at the microscale, individual particles touch each other and transfer stresses via the contact points. Then, at the microscale, the particles are subjected to a complicated stress state involving compressive, shear and possibly also tensile stresses. The presence of shear stresses at the microscale can induce the t → m phase transition in some crystal in some of the YSZ particles. The transforming crystals may bring on autocatalytic phase transition in the crystals they are bonded to. The similar autocatalytic behaviour can be expected for undoped t-ZrO_2. The hypothesis is that a macroscopic compression stress may cause a t → m phase transition in t-ZrO_2 powders due to microscale shear stresses. If true, this hypothesis has the important implications on the ways that pure t-ZrO_2 powder should be handled, since any mechanical treatment of t-ZrO_2 powder will generate microscale stresses that can induce the t → m phase transition.

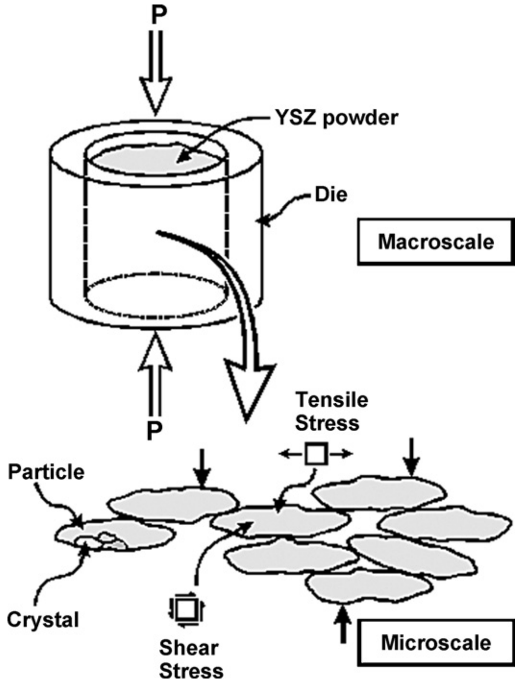

Fig. 1. A schematic illustration showing how particle-to-particle contact can generate microscale shear stresses and tensile stresses although the macroscopic applied stress in compression.

In the present work, the effect of microscale shear stress originating at particle scale during uniaxial strain test and low speed ball-milling on the crystal phase of zirconia are investigated in carefully controlled atmosphere with XRD, transmission electron microscopy (TEM) and photo correlation spectroscopy. Special attention was paid to avoid any possible water contact with the zirconia samples to evaluate the effect of shear stress on the stability of t-ZrO_2.

2. Experimental methods

All chemicals were supplied by Aldrich and they were all used as received. Highly porous nanocrystalline tetragonal zirconia powders were synthesized by controlled hydrolysis of $ZrOCl_2$ followed by careful calcination.[31] The t-ZrO_2 powders are extremely porous and have specific surface area of $\sim 150\,m^2/g$. The powder is very sensitive to water vapor and a few seconds air exposure is enough to cause martensitic phase transformation from tetragonal to monoclinic phase. Therefore synthesized t-ZrO_2 powders were kept in water free environment for further treatment.

2.1. Uniaxial strain testing

In inert atmosphere in a glove box, 200 mg zirconia was placed in pressing tools with a diameter of 13 mm. The press was sealed from atmosphere with nitrile rubber to prevent phase transformation due to reaction of zirconia with water vapor in the air.[32] The samples were exposed to macroscopic compression to pressures of 60, 120 or 188 MPa. The pressure was applied with a speed of 2 kN/min until the maximum value reached and thereafter the pressure was decreased linearly with time back to zero. Data for time, piston position and load was collected at a PC at a data acquisition rate of 10 Hz.

After releasing the pressure, the samples were carefully transferred back to the glove box and mixed with a methacrylic monomer mixture consisting of Bisphenol-A diglycidyl ether dimethacrylate (Bis-GMA), urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA) in the ratio (36/44/20 wt%) in combination with a polymerization system composed of champhorquinone and ethyl 4-dimethylamino benzoate both in contents of 0.5 wt% of resin. A sample of this was placed between two glass plates and cured for 2 min using blue light (1100 mW) from a Bluephase® light source (Ivoclar Vivadent, Lichtenstein). This treatment was done as the polymer matrix prevents the tetragonal crystals to undergo phase transformation. The cured samples were then subjected directly to the XRD measurement for the phase analysis.

2.2. Ball-milling

A 250 ml Si_3N_4 coated stainless steel grinding bowl was filled with 60 g of aggregated t-zirconia nanocrystals in anhydrous isopropanol (35 wt%), ~12 g of either polyethylene hexamine or a 1:1 mixture of urethane dimethacrylate:triethylene glycol dimethacrylate and ~150 g of 0.5 mm $ZrSiO_4$ in Ar atmosphere in the glove box and after sealed carefully with tape. The 0.5 mm zircon balls ($ZrSiO_4$) used in our milling experiment were kindly provided by Comballs Corp., Graphtech Materials Co. Ltd., Qing Dao, China. The zirconia powder was milled with Fritsch P6 planetary monomill at 120, 250 or 500 rpm. Samples of the milled dispersion were collected after 1, 3 and 18 h. After milling, the zirconia dispersions were moved into pre-dried anhydrous isopropanol. It was transferred into the glass bottles; the $ZrSiO_4$ balls remained in the grinding bowl. The milled zirconia samples were dried under vacuum and mixed, in the glove box, with a methacrylic monomer mixture consisting of Bisphenol-A diglycidyl ether dimethacrylate (Bis-GMA), urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA) in the ratio (36/44/20 wt%) in combination with a polymerization system composed of champhorquinone and ethyl 4-dimethylamino benzoate both in contents of 0.5 wt% of resin. A sample of this was placed between two glass plates and cured for 2 min using blue light (1100 mW) from a Bluephase® (Ivoclar Vivadent, Lichtenstein). The samples were subjected directly to the XRD measurement for the phase analysis.

2.3. Characterization

2.3.1. X-ray diffraction (XRD)

XRD patterns were scanned in 0.1 steps (2θ), in the 2θ range from 26.5° to 33°, with a fixed counting time (40 s). The XRD patterns were analyzed using WinX^{POW} software (STOE & Cie GmbH, Darmstadt, Germany). The obtained values of the t-ZrO_2 and m-ZrO_2 volume fractions (v_t and v_m) were compared with the values obtained from the integral intensities of the monoclinic diffraction lines (−1 1 1) and (1 1 1) and the tetragonal diffraction line (1 0 1), following a procedure proposed by Toraya et al.[33]

2.3.2. Transmission electron microscopy (TEM)

Low- and high-resolution TEM images and Selected Area Electron Diffraction (SAED) patterns were obtained using a JEOL JEM-3010 microscope operating at 300 kV (Cs = 0.6 mm, point resolution 0.17 nm). Images were recorded with a CCD camera (MultiScan model 794, Gatan, 1024 μm × 1024 μm) at a magnification of 4000–400,000 times. TEM samples were prepared by applying a drop of zirconia–isopropanol dispersion onto a carbon coated Cu grid and the solvent was allowed to slowly evaporate at room temperature.

2.3.3. Photon correlation spectroscopy

Particle size distribution was analyzed using a Zetasizer (Nano ZS, 2003, Malvern Instruments, UK). Refractive indices for isopropanol and zirconia were set at 1.39 and 2.2, respectively. Viscosity of the solvent at 25 °C was set to 2.32×10^{-3} Pa s. The standard general-purpose algorithm was the default for the analysis.

All mixing was done by shaking and measurement was carried out immediately after mixing. The sample bottle was thoroughly shaken by hand for 10 s before diluting it with isopropanol and the diluted sample was analyzed by size measurement. This procedure was chosen to be able to measure the overall size distribution of the samples.

3. Results

3.1. Uniaxial strain test

Recorded XRD patterns of the casted ZrO_2 samples from the uniaxial strain test are shown in Fig. 2. For the sample exposed to 60 MPa the (1 0 1) reflection at 30.2° (2θ) is dominating, but as the applied pressure increases, the reflection from the tetragonal zirconia diminishes and the two reflections at 28.2° and 31.4° (−1 1 1 and 1 1 1) from monoclinic zirconia grow in intensity. It can be seen in Fig. 2 that an increased applied compressive stress increases the monoclinic volume fraction in the sample.

In Fig. 3, the volume fraction of phase-transformed crystals are plotted against the maximum applied pressure. The figure shows that the volume fraction increases approximately linearly with the maximum pressure.

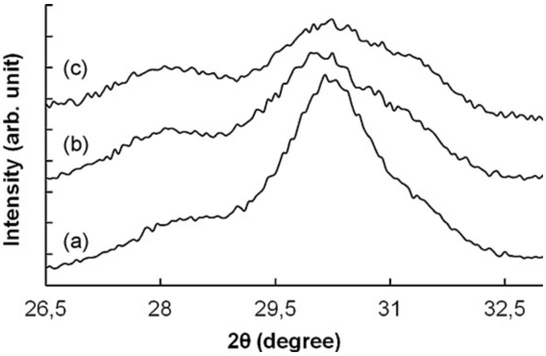

Fig. 2. XRD of zirconia after one axial strain test at different applied pressures, (a) 60 MPa, (b) 120 MPa and (c) 188 MPa.

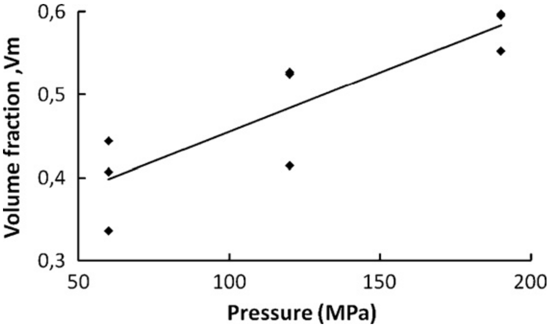

Fig. 3. Volume fraction of formed monoclinic zirconia as a function of applied pressure.

3.2. Ball-milling

The XRD patterns recorded from the milled and in casted samples at different milling speed after 1 and 18 h are illustrated in Figs. 4 and 5. For both experiments, the reflection (1 0 1) of tetragonal zirconia at $30.2^\circ = 2\theta$ dominates after 1 h milling. The two reflections (−1 1 1 and 1 1 1) from monoclinic zirconia grow during milling and the (1 0 1) reflection decreased, indicating a tetragonal to monoclinic transformation.[33] It is also seen that when milling speed is increased to 500 rpm, transformation rate is also significantly higher than 250 rpm.

Phase transformation of the zirconia crystals caused by milling is shown in Fig. 6. It can be seen that the monoclinic volume fraction (v_m) increases with elongated milling time and that the results from the 120 and 250 rpm experiments have approximately the same curve progression. As indicated in Fig. 6 the effect of milling speeds at low speed, such as 120 and 250 rpm is not very significant in respect to transformation rate.

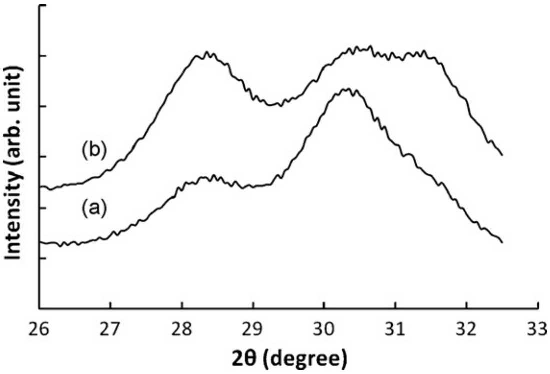

Fig. 5. XRD of zirconia milled (a) 1 h and (b) 18 h at 250 rpm.

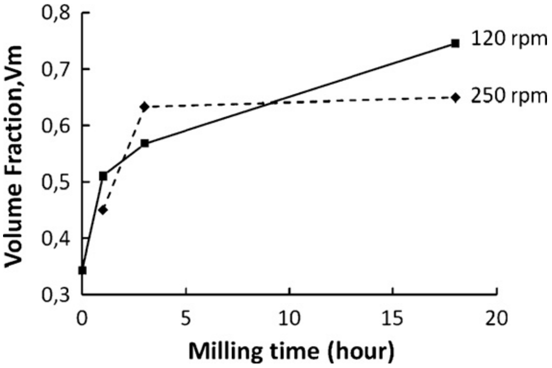

Fig. 6. Volume fraction of formed monoclinic zirconia function a milling time at 120 and 250 rpm.

Fig. 7 shows the XRD patterns before and after milling. Before milling, the sample mainly consists of tetragonal ZrO_2 giving broad peaks in the XRD patterns as a result of small crystal sizes. The amount of tetragonal phase diminishes as a result of milling but the crystal size remains at 8 nm, calculated by the Scherrer equation:

$$\tau = \frac{K\lambda}{\beta \cos\theta},$$

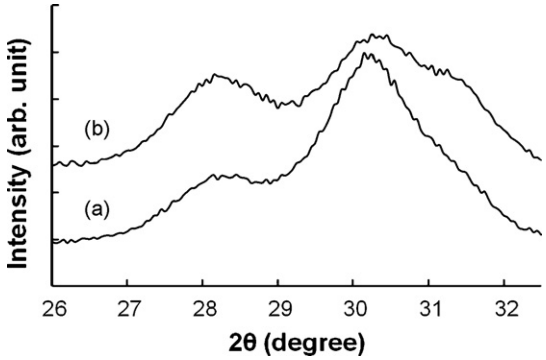

Fig. 4. XRD patterns showing the evolution of m-phase produced by ball-milling of tetragonal zirconia nanoparticles at 120 rpm, (a) 1 h and (b) 18 h.

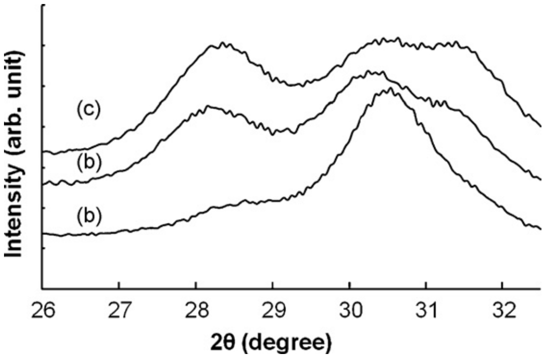

Fig. 7. XRD patterns of zirconia powders before and after milling, (a) before milling, (b) milling at 120 rpm, 18 h and (c) 250 rpm, 18 h.

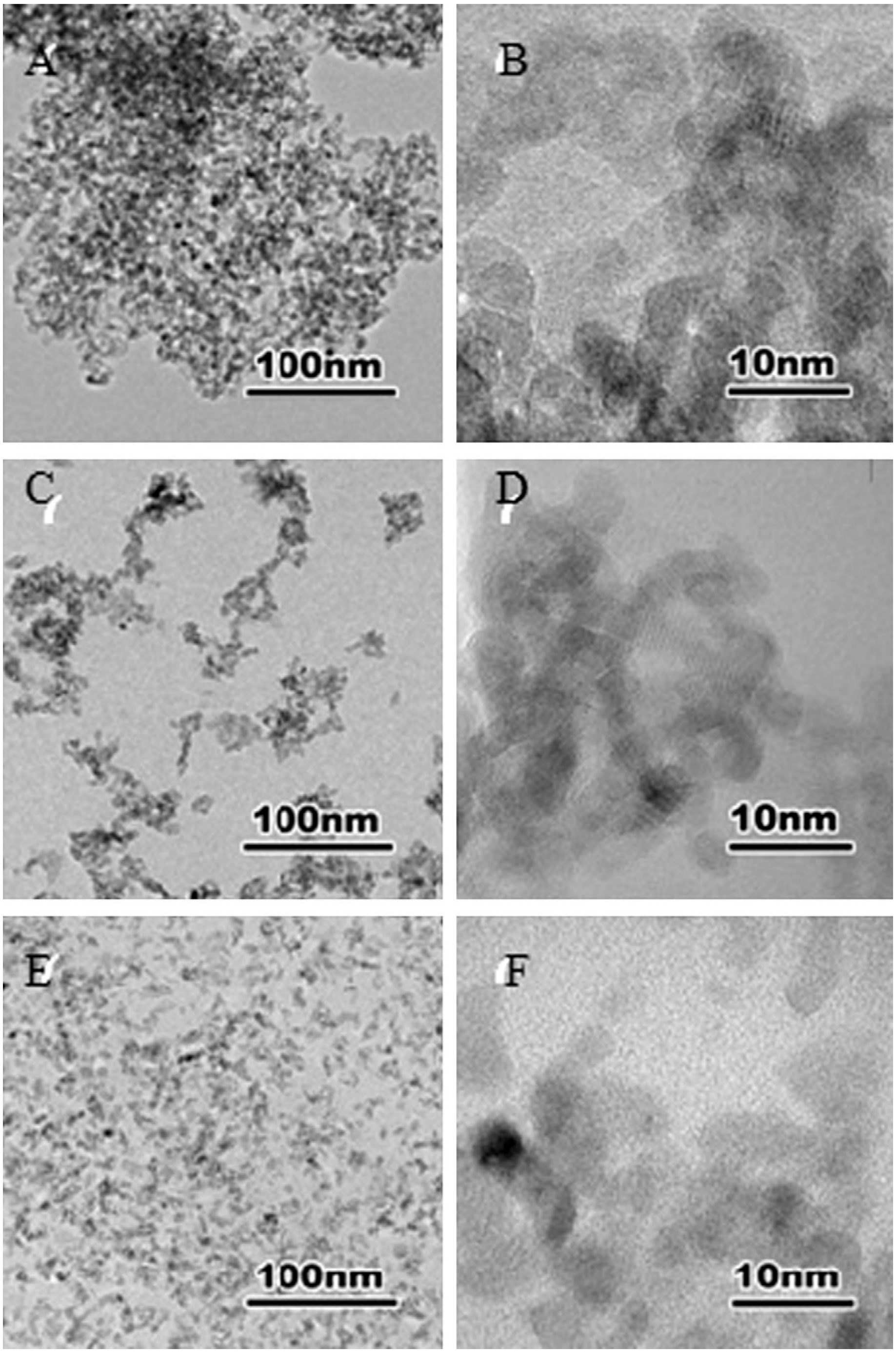

Fig. 8. TEM images of the zirconia particles milled with 0.5 mm $ZrSiO_4$ balls: (A and B) prior to milling; (C and D) milled at 500 rpm, 4 h (E and F) 500 rpm, 18 h.

where τ is the mean crystallite dimension, K is the shape factor, λ is the X-ray wavelength (1.54 Å for Cu K_α), β is the full widths at half maximum intensity (FWHM) in radians, and θ is the Bragg angle. The dimensionless shape factor varies with the shape of the crystallite, but has typically a value about 0.9.[34]

It was confirmed by the transmission electron microscope analysis (Fig. 8a and b) that as prepared samples indeed composed of very small, about 8–10 nm size nanocrystals which are interconnected and makes three dimensional porous networks with an average particle size of about 2.0 μm.

The average size of the milled ZrO_2 particles was determined using photo correlation spectroscopy. The results from the milling experiment performed at a speed of 120 rpm are shown in Fig. 9. The size distribution of milled ZrO_2 that was obtained from DSL analysis agrees well with the result obtained by TEM analysis. For both milling speeds, the particle size reaches a minimum at which point further milling only will give more phase transformation and not lead to further de-agglomeration. Although it is not possible to reduce the average size of milled ZrO_2 particles to less than approximately 300 nm with speed

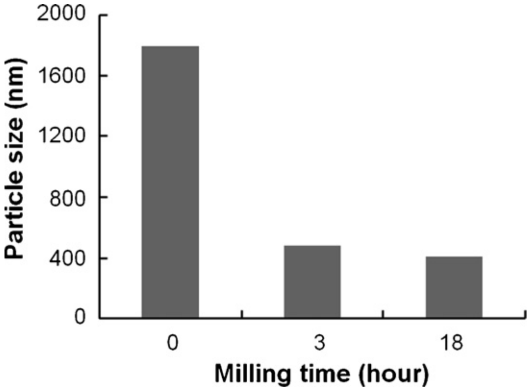

Fig. 9. Size distribution of zirconia particles milled at 120 rpm that is dispersed in isopropanol obtained by dynamic light scattering analysis.

milling such as 120 rpm or 250 rpm, it is interesting, however, to observe the possibility of reducing the particle size to less than 100 nm by prolonged milling of the powders together with suitable surfactants at 500 rpm (Fig. 8). TEM result (Fig. 8e and f) showed that by high energetic ball-milling it is possible to break down the porous network of the zirconia particles and de-aggregate them almost to their primary crystals.

4. Discussion

During the experimental work with the high surface area zirconia powder it became clear that the nanocrystalline t-ZrO_2 is very sensitive towards shear stress. In the compression tests we found phase transformation; this may result from the multi-axial stress field at micro/nanoscale. Likewise, milling test also generates a complicated microscale stress field that induces zirconia undergo a martensitic phase transformation. The increase in the monoclinic volume fraction with increasing applied maximum pressure could be due to an increase in the microscale shear stresses causing enhanced transformation. It is remarkable to observe the similar phase transformation can occur even with our undoped t-ZrO_2.

Furthermore, in the uniaxial strain tests, we have observed a correlation between t → m phase transformation rate and specific surface area. Higher the surface area, faster the transformations is. This observation makes us believe that t → m phase transformation must be caused by the structural rearrangement of atoms to compensate the accumulated stress at the outermost surface of the t-ZrO_2 nanocrystals, which is further enhanced by the additional shear stress that is provided to the system with extra energy to overcome the activation energy for phase transformation. The porous t-ZrO_2 powders are formed from interconnected nanocrystals. Transforming nanocrystals at the surface may bring autocatalytic phase transformation in the neighbour nanocrystals that they bound to. Although it is impossible for us to determine the defect concentration of the nanocrystalline ZrO_2 powder, it is most likely that the high surface area of our zirconia powders can be correlated to an increased defect concentration on the surface compared with the surface defect concentration of low surface area t-ZrO_2 powders and we assume that the tested zirconia powder, with a high surface area will have more defects per gram, than the low surface area t-ZrO_2. Therefore, we have a reason to believe that t → m phase transformation must follow the similar reaction pathway that was reported for doped zirconia.[20,32]

The observed phase transformation in the milling experiments, probably also caused by the complicated stress field, which will cause some shear stresses and shear strains resulting in the phase transformation, just as in the uniaxial strain tests. It is also seen from the XRD patterns that this transformation is little more pronounced in the sample milled at 250 rpm (Figs. 5 and 6). This makes sense as the produced shear stresses depend on the energy supplied to the system. Higher speed will probably cause higher stresses causing an increasing transformation rate. That the difference between the two transformation rates is not more pronounced could be due to the fact that at these relatively low rpm's the balls are still circling at the bottom of the grinding bowl. As shown in Fig. 6 the transformation rate (t → m) increases with the increasing milling time, but seems to approach a maximum value. This indicates that milling alone will not cause 100% phase transformation, at least not at these low milling speeds.

In comparison with t-zirconia powders which have relatively low surface area, the nanocrystalline zirconia powder that was obtained with our method[31] possesses very high surface area (150 m^2/g). But even though the zirconia powder is very porous (Fig. 8a and b) and milling makes the zirconia change from tetragonal to monoclinic phase. Indeed, mild milling condition, such as 250 rpm, is not strong enough to separate other than loosely agglomerated particles. However, it is possible to break up these interconnected nanocrystals under more energetic milling conditions, such as 500 rpm or higher. This must be due the fact that the zirconia crystals are sintered during the calcinations and apparently milling at low speed does not give enough force to break the sintered crystals from each other.

5. Conclusion

Low milling speed can induce the martensitic phase transformation from tetragonal to monoclinic crystal phase of nanocrystalline zirconia powders. Likewise, macroscopic compression was found to generate the t → m phase transition of zirconia powders. At the microscale, both tests induce shear stress in the nanocrystalline zirconia particles. It is proposed that the phase transition caused by milling and compression of zirconia powders induces microscale shear stresses that are responsible for phase transformation.

The present study provides an improved understanding to the phase transformation behaviour of undoped t-ZrO_2 powders under shear stress that was induced by uniaxial compression and ball-milling.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jeurceramsoc.2010.05.025.

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Supplimentary Information

Effect of Microscale Shear Stresses on the Martensitic Phase Transformation of the Nanocrystalline Tetragonal Zirconia Powders

Mette Skovgaard[1,3], Anwar Ahniyaz[2]*, Bent F. Sørensen[3], Kristoffer Almdal[4] Alexander van Lelieveld[5]

[1] DentoFit A/S, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

[2]YKI, Institute for Surface Chemistry, 11486 Stockholm, Sweden

[3]Materials Research Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, DK-4000 Roskilde, Denmark

[4]Department of Micro- and Nanotechnology, Technical University of Denmark, DK-4000 Roskilde, Denmark

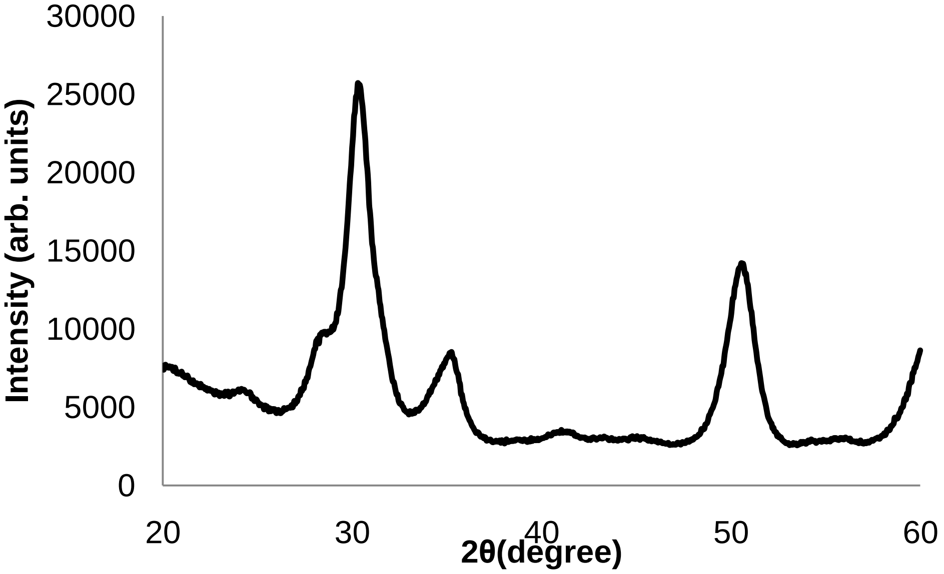
[5]Aneedle, Engelstedsgade 322, DK-2100 Copenhagen East, Denmark

To whom correspondence should be addressed: anwar.ahniyaz@yki.se

Surface Area Measurement

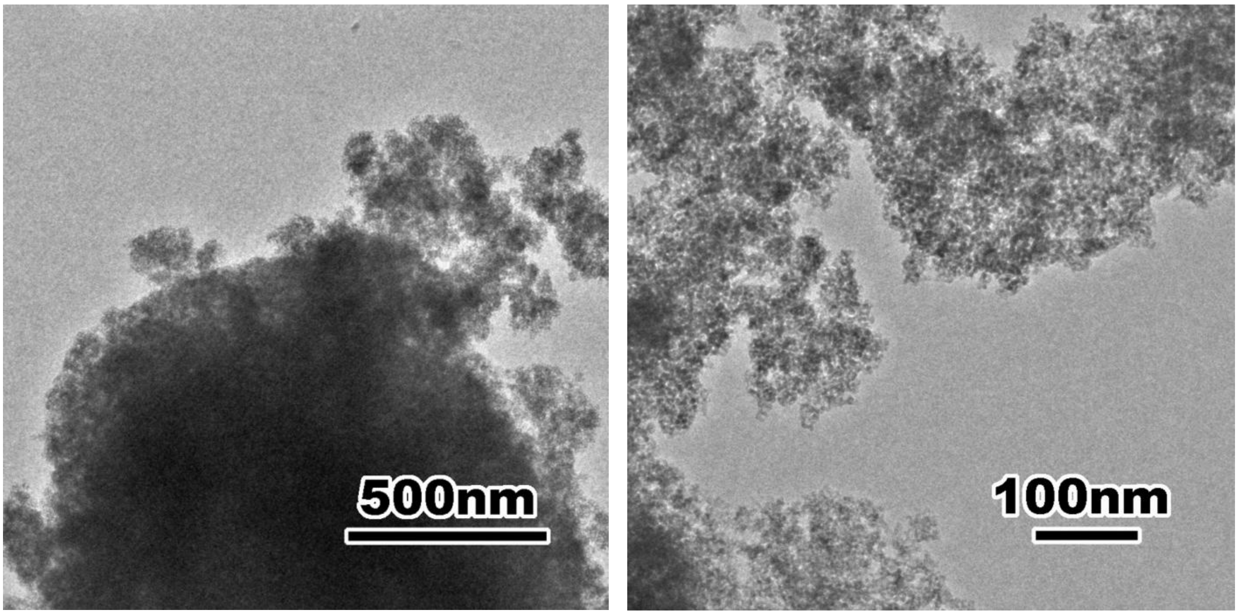
The specific surface area of the zirconia powder was done with N_2 adsorption for BET determination (Autosorb-AS6, Quantachrome, Boynton Beach, FL). A number of samples were analyzed the specific surface area was determent to ≈150 m^2/g.

Figure S1. XRD pattern of highly porous nanocrystalline t- ZrO2 powders



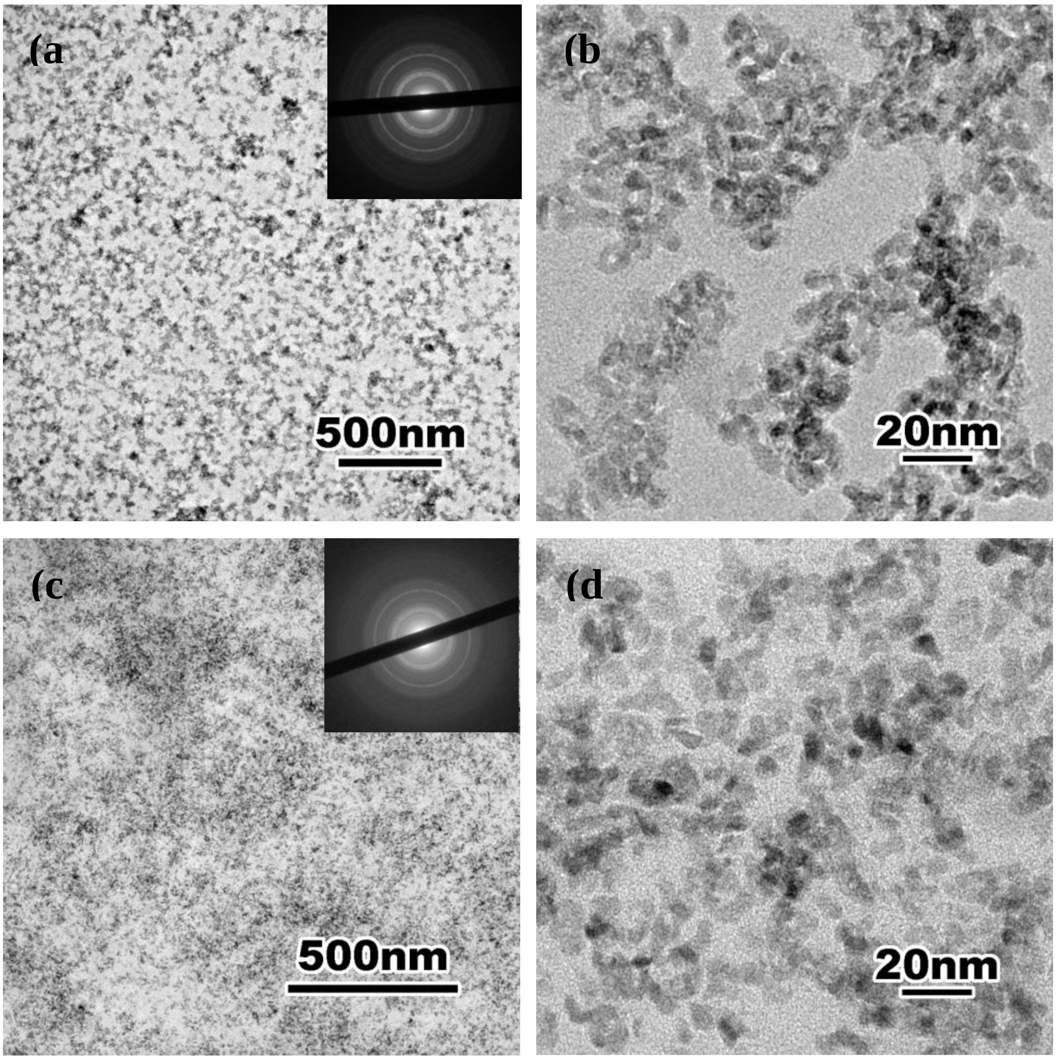
It is clear from the high angle powder diffraction pattern that synthesized zirconia powders are tetragonal with only a small fraction of the monoclinic phase and broad peaks indicates the nanocrystalline nature of the powders.

Figure S2. Low resolution transmission electron micrographs of highly porous nanocrystalline t- ZrO2 powders at different magnification



It is clear from TEM image that as synthesized t-ZrO2 powders are micron sized aggregates of three-dimensionally interconnected nanocrystallites. Highly porous nature of the powders is evident.

Figure S3. Low resolution transmission electron micrographs of milled ZrO2 powders with 0,5 mm $ZiSiO_4$ balls at different conditions (a), (b) 500 rpm, 4 hrs; (c), (d) 500 rpm, 18hrs



It is clear from these selected area diffraction patterns that longer milling time enhanced the t-m phase transformation. TEM images showed that particle size is gradually decreased with increasing milling time.

V

Light activated phase transformation of metastable tetragonal nanocrystalline zirconia

M. Skovgaard

DentoFit A/S, Frederiksborgvej 399, 4000 Roskilde, Denmark

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Department of Micro- and Nanotechnology, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark

Direct: +45 46 77 42 84, fax: +45 46 77 47 91, ms@dentofit.com

K. Almdal

Department of Micro- and Nanotechnology, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark

kral@nanotech.dtu.dk

A. van Lelieveld

DentoFit A/S, Frederiksborgvej 399, 4000 Roskilde, Denmark

avl@aneedle.net

Abstract

In order to identify candidate initiator molecules for light activated phase transformation of metastable tetragonal zirconia nanocrystallites, different molecules were tested for their ability to initiate phase transformation. The zirconia powder was exposed to the molecules in alcohol suspensions, and the samples were analyzed with x-ray diffraction (XRD). Changes in the monoclinic volume fraction were calculated. It was found that water, HCl, HF and NH_3 all initiate phase transformation of tetragonal zirconia at room temperature, whereas NBu_4Cl and NBu_4OH does not. Furthermore the relation between the initiator/zirconia concentration and the measured phase transformation was investigated. From these results photoacid generators were chosen and their ability to mediate photo induced phase transformation in metastable tetragonal zirconia crystals were tested in methanol. Four different photoacid generators were able to initiate phase transformation. 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine) was most efficient (monoclinic volume fraction reached 0.57). The triazine was also tested for its ability to phase transform zirconia crystals dispersed in a dimethacrylate matrix. After 2 min exposure to light a monoclinic volume fraction of 0.19 was observed. This increased to 0.6 after 30 minutes.

Keywords: metastable tetragonal zirconia, photoacid generators, phase transformation, powder, low temperature degradation

Introduction

Shrinkage during polymerization of dental resin composites is unavoidable and the leading problem in the usage of composite resin restorations. Stresses are induced on the filling/tooth interface, the filling can loosen from the tooth leading to the formation of a crack between tooth and the composite material or micro-cracks in the composite material itself. This can lead to discoloration or, worse, to secondary caries and infection of the dental pulp due to bacteria and colorants from e.g. coffee and red wine entering the crack [1]. During the last few decades substantial efforts have addressed the shrinkage in dental resin composites by an approach based on modification of the monomer system to achieve less polymerization shrinkage. The typical dimethacrylate monomers have e.g. been replaced with ring-opening systems [2-4]. The overall curing shrinkage has an effect on the clinical properties of the composite and a low shrinkage composite will reduce the preparation time because of the possibility to make bulk fillings instead of have to use the more time consuming technique, where the filling is build up of layers [5].

We have investigated an alternative approach to minimizing the polymerization shrinkage. Instead of trying to reduce the polymerization shrinkage of the monomer system, the shrinkage problem is addressed by counteracting the polymerization shrinkage with an expanding inorganic filler. We have developed an expandable metastable tetragonal zirconia filler, which upon reaction with water, is able to counteract the polymerization shrinkage of the monomer system [6]. The tetragonal to monoclinic (t→m) phase transformation is accompanied by a decrease in density, where the crystals expand ~4 vol%. This expansion is for instance used in transformation toughening of ceramic materials [7]. The tetragonal to monoclinic phase transformation is known to be initiated by the following: Chemical reaction with e.g. water [8], annealing [9] and mechanical stress [10].

When developing a dental resin composite restorative a lot of different material properties have to be taken into consideration such as mechanical properties, solubility and water sorption, color stability, polymerization shrinkage, depth of cure, radiopacity and biocompatibility [1]. All these issues have to be addressed also for expandable filler approach. In this paper we concentrate on the ability to induce the t→m phase transition at will. Until now we have tested the potential of the filler to counteract the polymerization shrinkage by initiating the phase transformation by water diffusing into the polymer matrix [11]. We found that the overall shrinkage of a composite containing 42 wt-% zirconia was reduced with 44 % comparing with an equivalent sample stored in air, when the composite was stored in water at 40˚C for 7 days. This is, however, to slow to give a good dental composite; where the shrinkage reduction optimally should happen within the time it takes to prepare the filling. The most desirable scenario is to make the zirconia phase transform during curing, while the resin is in the gel state, because then the expansion will have the largest effect with the possibility of causing stresses in the matrix. As annealing and mechanical stress, for obvious reasons, not are possible ways to initiate the phase transformation. We have decided to focus on light initiated release of initiator molecules, where it should be possible to control the initiation of the phase transformation. This study investigates the degrading effect of possible phase transformation initiators in order to find possible initiator molecules for light activated phase transformation.

Experimental

Materials

All chemicals were supplied by Sigma-Aldrich (St. Louis, MO, USA) and used as received. Highly porous (specific surface area of ~150 m^2 /g) nanocrystalline tetragonal zirconia powders were synthesized as previously described [12] by controlled hydrolysis of $ZrOCl_2$ followed by careful calcination. The synthesized t-ZrO_2 powders were kept in water-free environment for further treatment to prevent the t→m phase transformation [13, 14] which is induced by exposure to water vapor.

Testing of potential phase transformation initiators

Solutions of potential phase transformation initiators in anhydrous methanol or isopropanol were prepared. In a glove box (< 10 ppm water) zirconia was added to the solution and allowed to react. The reaction mixture was filtered and the zirconia was dried at RT in the glove box. To prevent further phase transformation and make it possible to handle the zirconia samples in ambient atmosphere the sample was mixed with a dimethacrylate monomer mixture (bisphenol-A diglycidyl ether dimethacrylate, urethane dimethacrylate, and triethylene glycol dimethacrylate - Bis-GMA/UDMA/TEGDMA, 36/44/20 wt%) and a photo polymerization system (camphorquinone and ethyl 4-dimethylamino benzoate - CQ/DABE both 0.5 wt%). A sample was placed between two glass plates and cured for 2 min using blue light (1,100 mW) from a Bluephase® light probe (Ivoclar Vivadent, Liechtenstein). The polymer matrix prevents the tetragonal crystals from undergoing phase transformation. Such samples are termed matrix dispersed zirconia. The cured samples were then subjected directly to the X-ray diffraction (XRD) measurement for phase analysis.

Test of potential photoacid generators (PAG's) in solvent

In a glove-box (< 10 ppm water) 200 mg of the zirconia particles and 150 mg photoacid generator (PAG) were weighted into a glass flask (100 mg LiOH was added to the samples with photo acid generators, which only releases a protons. OH^- from the LiOH will react with the proton under formation of water). Then 21 g methanol was added. The suspension was exposed to 22 hours of UV (BlueWave™ 50, Dymax Corp., CT, USA) while stirred with a magnetic stirring bar. The suspension was filtered and dried in vacuum. The samples were matrix dispersed as described above.

Test of 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine in resin

In a glove box 200 mg zirconia particles was mixed with 100 mg 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (CAS number: 42573-57-9) in 5 ml anhydrous methanol and the methanol was evaporated. The dried zirconia powder was dispersed in the dimethacrylate matrix as described above, with prolonged curing, and subjected to XRD measurements.

HCl yield

1 g 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine) was dissolved in 50 ml methanol and the solution was irradiated with the light from a Bluephase® light probe (Ivoclar Vivadent, Liechtenstein) for 20 min. 0.5 M $AgNO_3$ was added in order to precipitate the formed HCl. The precipitate was filtered and dried.

Characterization

XRD patterns were scanned in 0.1 steps (2θ), in the 2θ range from 27° to 34°. The XRD patterns were analyzed using WinX^{POW} software. The tetragonal and monoclinic volume fractions (v_t and v_m) were calculated from the integral intensities of the monoclinic diffraction lines (-1 1 1) and (1 1 1) and the tetragonal diffraction line (1 0 1), following the procedure proposed by Toraya et al [18].

Results

Testing of potential phase transformation initiators

The matrix dispersed zirconia samples were analyzed using XRD and the results are shown in Table 1. It is observed that water, HCl and HF initiates the tetragonal to monoclinic (t→m) phase transformation. NH_3 also has some effect on the stability of the tetragonal phase.

Table 1 degrading effect of different solutions on metastable tetragonal zirconia

Potential initiator	***PT***	***Potential initiator***	***PT***
H_2O	Yes	Bu_4NOH	No
HCl	Yes	LiCl	No
HF	Yes	Bu_4NCl	No
NH_3[a]	Some	Organic acid[b]	No[c]
LiOH	No	Organic solvents	No

[a] Tested in dioxane. [b] Tested acids are: CF_3CO_2H, $CHCl_2CO_2H$, CCl_3CO_2H, CH_3CO_2H and CF_3SO_3H. [c] Some phase transformation was observed due to a condensation reaction of the acids with OH-groups on the surface under formation of measurable amounts of water (Karl Fischer analysis), which initiates phase transformation.

The XRD patterns from the testing of potential phase transformation initiators are illustrated in Fig. 1. It is observed that the reference sample only contains traces of the monoclinic phase prior to exposure to potential phase transformation initiators and the tetragonal (101) reflection of zirconia at $2\theta = 30.2°$ is dominating. The broad peaks in the XRD patterns are a result of small crystal sizes. After exposure to a phase transformation initiator the two monoclinic reflections (-111 and 111) grow in intensity and the (101) reflection decreases, indicating a t→m transformation. It is also observed that water and HCl initiate phase transformation the most. HF and NH_3 initiate less phase transformation. HBr was also tested and showed a tendency to initiate the transformation.

Fig. 1 XRD patterns of zirconia (a) reference and zirconia exposed to (b) NH3, (c) HF, (d) H2O and (e) HCl

In a 1.5 M HCl aqueous solution the degree of phase transformation of the zirconia particles reaches 92 %, indicating a synergistic effect of water and HCl as phase transformation initiators (Fig. 2). When the zirconia was exposed to 1.5 M HCl in isopropanol 60% of the tetragonal zirconia was phase transformed to the monoclinic phase.

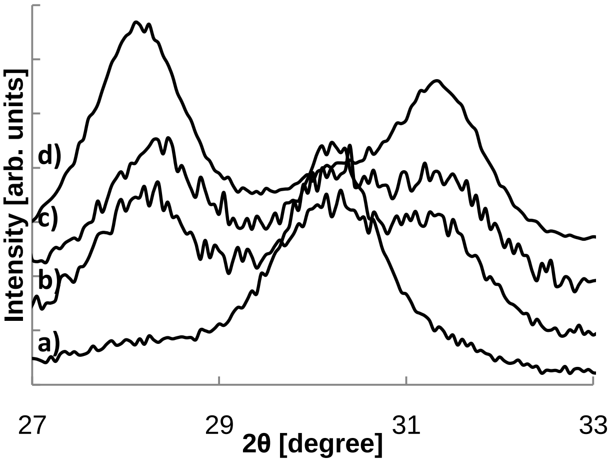

Fig. 2 XRD patterns of zirconia (a) reference, (b) exposed to 1.5 M HCl in MeOH, (c) exposed to 1.5 M water in MeOH and (d) exposed to 1.5 M HCl in water.

The amount of phase transformation initiator relative to zirconia was investigated. Fig. 3 shows the monoclinic volume fraction of zirconia as a function of phase transformation initiator concentration (HCl or H_2O). The amount of phase transformation initiator is given relative to the amount of zirconia (n%). The increase of phase transformation with increasing amount of phase transformation initiator is the same for the two compounds and $v_m \sim 0.7$ at an amount of 83 n% of water.

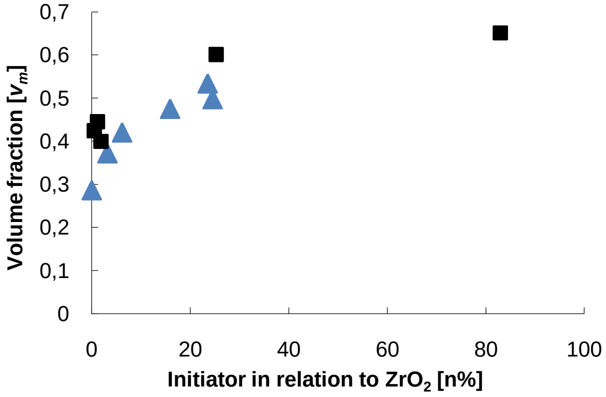

Fig. 3 Phase transformation as a function of mole percent of the initiator in relation to zirconia for HCl (▲) and for water (■)

The ability of PAG's to phase transform zirconia

The results from the screening of the ability of the different photo acid generators to induce phase transformation of metastable tetragonal zirconia in anhydrous methanol are shown in *Table*. Out of the tested PAG's 2-(4-ethoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine results in the highest monoclinic volume fraction (v_m) in the samples.

Table 2 monoclinic volume fraction (v_m) in samples phase transformed by different PAG's

PAG	v_m
Diphenyl idonium chloride	0.47
2-(4-Methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine	0.57
Triphenyl sulfonium triflate + LiOH	0.48
Triarylsulfonium hexafluoro phosphate + LiOH	0.46
Ortho nitro benzylalcohol	0

The XRD patterns from the test of 2-(4-Methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine in resin are illustrated in Fig. 4. In the matrix dispersed zirconia samples containing triazine a monoclinic volume fraction (v_m) of 0.19 was observed after two minutes of curing with the Bluephase® light probe. v_m= 0.60 was reached after 30 min of exposure.

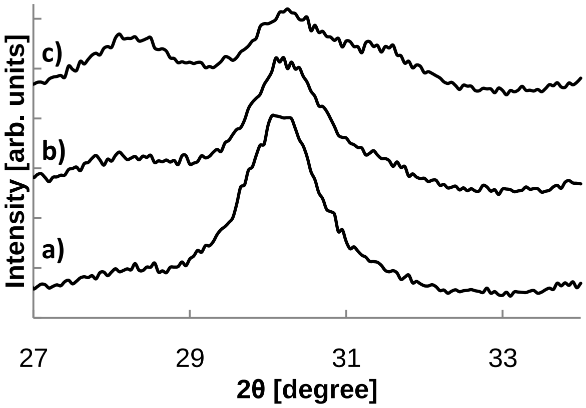

Fig. 4 Phase transformation initiated by PAG (triazine) after (a) 0 min - reference without triazine, (b) 2 min and (c) 30 min.

The yield of HCl from the light initiated reaction was measured by precipitation with $AgNO_3$. The yield of HCl from 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine was found to be 2.8% after 20 min of irradiation at maximum intensity.

Discussion

Qualitative assessment of phase transformation initiators

A number of molecules are found to initiate the t→m phase transformation: H_2O, HCl, HF and NH_3 (*Table* and Fig. 1). The most effective of those are water and HCl, with a tendency that water induces more phase transformation than HCl and that an aqueous solution of HCl results in highest v_m (Fig. 2). Sato and Shimada [15] also found that an aqueous solution of HCl had a little higher degradable effect on tetragonal zirconia comparing with pure water.

The phase transformation is not, to our knowledge, initiated by any organic solvent, not even after boiling for 48h (*Table*). This is in contrast to the results published by Sato and Shimada [15], who found that solvents with a lone pair all have a degrading effect on tetragonal zirconia. However, in the study by Sato and Shimada the water content in the tested solvents were as high as 15,000 ppm, whereas we in this study has used anhydrous solvents with a water content of <0.005 ppm. Also a number of bases and acids were tested and no phase transformation was found. Apparently the initiator molecules need to be both a proton donor and provide a small nucleophile to initiate the phase transformation. LiCl or LiOH do for instance not initiate the phase transformation and the same is the case for carboxylic and sulfonic acids. Phase transformation to a small extend is, however, observed as a result of exposure to organic acids. This is a result of formation of measurable amounts of water (Karl Fischer titrator, Metrohm Ltd., Herisau, Switzerland) due to condensation reactions with the OH-groups on the zirconia surface. We have also, previously, shown that the zirconia does not transform as a result of exposure to phosphoric acid or sulfuric acid. These acids actually stabilize the metastable tetragonal phase towards water initiated phase transformation [16]. These results show that the initiator has to be a proton donor and also provide a small nucleophile in order to induce the m→t phase transformation. For both water and HCl there are a strong correlation between the concentration of initiator molecules and the monoclinic volume fraction in the sample (Fig. 3). Based on several experiments in various solvents it is observed that the degree of phase transformation appears more dependent on the initiator-zirconia ratio than on the initiator concentration in the solvent (data not shown). It is found that the phase transformation is dependent upon the activity of the initiator molecule. Thus the zirconia particles phase transform to a higher degree when exposed to humidity in the atmosphere or water in solvents such as methanol than in the more hydrophobic dimethacrylate matrix [11, 14, 17].

Light activated phase transformation

Molecules, which generate acid upon exposure to radiation, are called photoacid generators (PAG). A large number of photoacid generators are known because of their wide applications, especially in the field of photolithography[18, 19]. Photoacid generators split into two radicals, which form a strong acid after chemical reaction with each other or the medium. They can, *e.g.,* be used to initiate the phase transformation, if one of the formed radicals is either hydroxide or halogen radicals. These radicals will abstract hydrogen from either the monomer or another PAG molecule during the curing resulting in formation of initiator molecules (HX)[20]. PAG’s were selected for their ability to form either water or HCl, because of the conclusion that these two molecules induce most phase transformation. From the screening of potential PAG´s it was found that 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine caused most phase transformation. Consequently the ability of triazine to phase transform matrix dispersed tetragonal zirconia was tested. It was found that a phase transformation in the tetragonal zirconia powder can be induced and that a v_m of 0.6 was observed after 30 min of exposure to the blue light.

The yield of HCl from the triazine is low, only 2.8 % of expected yield after 20 min. The polymerization is fast and when the polymer reaches the glass transition is the mobility of the initiator molecule decreased. It is here necessary to point out, that we have not used the most optimal triazine for the system, but used the commercially available 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (Fig. 5), which has a $_{max}$ of 379 nm. This is not the optimal value as the light probe (Bluephase® Ivoclar Vivadent) used for these experiments has a wave length range of 430-490 nm.

We expect that the system could be optimized by finding (or developing) a small photo acid generator with $_{max}$ ~460 nm, which releases an initiator molecule. It may furthermore be important to decrease the diffusion distance to diminish the necessary PAG amount by placing the PAG as close as possible to the zirconia surface. This is the rationale for dissolving the triazine in methanol and subsequently evaporating the methanol in an effort to precipitate the triazine on the surface of zirconia. This will presumably generate the HCl as close to the zirconia surface as possible.

Triazines are large yellow molecules, which is the reason for the sensitivity towards blue light. This leads to discoloration of the cured resin due to the need for large amounts of triazine to initiate the phase transformation of the zirconia. The phase transformation preferable has to be done before the resin reaches the glassy state, since at this stage the expanding filler will have the most effect on the overall shrinkage. The high triazine concentration is needed to ensure that a sufficient amount of initiator molecules reach the zirconia surface.

As a result of the photo activation the composite turns brown. For optimization of this system there is a need for a photo bleaching PAG. This could for instance be a merocyanine dye linked bis(trichloromethyl)-1,3,5-triazine[21]. These molecules are photo bleaching and have $_{max}$ in the region 400-500 nm. This will result in a higher quantum yield but the high molecular weight of this compound is a drawback due to need for large amounts to initiate the phase transformation.

Besides from the low HCl yield from the triazine, another reason for the slow phase transformation may be due to the fact that the diffusion rate of HCl in the curing dimethacrylate matrix is low. This will increase the time for the formed HCl molecules to reach the zirconia surface. The mobility of radicals is highly affected by the viscosity of the system. Dental composites are highly viscous systems, where both high filler content and monomers contribute to the viscosity. When the resin is cured, viscosity is significantly increased. This leads to substantial increases of life time of the generated radicals. The half-life of radicals at a degree of polymerization of 40% is 4 sec which increases to 30 sec at 60%. Polymerization of commercial resin composite restoratives normally stops at 60-80% conversion at room temperature. At this conversion are the half-lives of radicals 53 hrs [22]. The experiments in this study were conducted at RT due practical limitations in the glove box. By increasing the temperature to 37 °C, the radicals are able to diffuse at higher rates. This will most likely lead to a higher degree of phase transformation of the tetragonal zirconia. Furthermore will a dental filling absorbs water from saliva, which over time is expected to lead to further phase transformation because of diffusion of water through the composite.

Conclusion

During the investigations it was found that out of the tested molecules, water and HCl induces most m→t transformation and that HF and NH_3 induces some transformation. It was furthermore concluded that the phase transformation initiators need to be a proton donor and provide a small nucleophile in order to be able to induce transformation. Initial experiments with PAG´s were performed and of the tested PAG's, triazines were the most promising. The tested PAG´s were; a triazine, diphenyl idonium chloride, ortho nitro benzylalcohol and two sulfonium salts. It was found possible to phase transform zirconia in resin by exposure to blue light by adding 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine to the composite. A monoclinic volume fraction of 0.6 was reached after 30 min exposure. However, the phase transformation is too slow to be of commercial interest and further investigations have to be conducted.

Acknowledgement

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(12) **Patent Application Publication**

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(43) **Pub. Date: Jan. 21, 2010**

(54) **COMPOSITE MATERIAL COMPRISING A WATER-OR ACID-RELEASING AGENT**

(76) Inventors: **Alexander Van Lelieveld**, Frederiksberg (DK); **Mette Skovgaard Nielsen**, Taastrup (DK); **Kristoffer Almdal**, Roskilde (DK); **Søren Linderoth**, Roskilde (DK)

Correspondence Address:
HARNESS, DICKEY & PIERCE, P.L.C.
P.O. BOX 8910
RESTON, VA 20195 (US)

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A61K 6/08 (2006.01)

(52) **U.S. Cl.** **523/116**

(57) **ABSTRACT**

The present invention discloses a composite material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise at least one filler ingredient, said filler ingredient(s) being present in a metastable first phase and being able to undergo a martensitic transformation to a stable second phase, the volume ratio between said stable second phase and said metastable first phase of said filler ingredient(s) being at least 1.005, and wherein said material further comprises one or more water- or acid- releasing agents; as well as a corresponding method of controlling the volumetric shrinkage of a composite material upon curing.

COMPOSITE MATERIAL COMPRISING A WATER-OR ACID-RELEASING AGENT

FIELD OF THE INVENTION

[0001] The present invention relates to composite materials comprising a water- or acid-releasing agent.

BACKGROUND OF THE INVENTION

[0002] The applicant's earlier PCT application No. WO 2005/099652 A1 discloses a composite material exhibiting a low or even negligible volumetric shrinkage upon curing, or even a small expansion (e.g. up to 0.5%), in particular composite materials in the form of dental filling materials, as well as a method of controlling volumetric shrinkage of a composite material upon curing. According to WO 2005/099652 A1, a volume stable composite material for dental use can, e.g., be obtained by the use of metastable zirconia particles. Since a volume stable composite can minimize crack formation, such a technology is of great commercial importance. It was suggested that the martensitic transformation of such composite materials could be activated either by physical means or by chemical means (e.g. modification of the surface free energy by contacting the surface of the filler ingredient particles with a chemical, e.g. a constituent of the composite material or an additive such as water).

[0003] However, in order to obtain the best possible properties, it is desirable to more accurately control the transformation process, e.g. by means of more refined chemical means.

BRIEF DESCRIPTION OF THE INVENTION

[0004] One aspect of the present invention relates to a composite material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise at least one filler ingredient, said filler ingredient(s) being present in a metastable first phase and being able to undergo a martensitic transformation to a stable second phase, the volume ratio between said stable second phase and said metastable first phase of said filler ingredient(s) being at least 1.005, and wherein said material further comprises one or more water- and/or acid-releasing agents.

[0005] Another aspect of the present invention relates to a composite material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise at least one filler ingredient, said filler ingredient(s) including metastable zirconia in the tetragonal or cubic crystalline phase, wherein said resin base, upon polymerization and in the absence of any compensating effect from the one or more filler ingredients, causes a volumetric shrinkage (ΔV_{resin}) of the composite material of at least 0.50%, and wherein said composite material, upon polymerization of said resin base and upon phase transformation of said filler ingredient(s), exhibits a total volumetric shrinkage (ΔV_{total}) of at least 0.25%-point less than the uncompensated volumetric shrinkage (ΔV_{resin}) caused by the resin base, and wherein said material further comprises one or more water- or acid-releasing agents.

[0006] The invention further relates to a method of controlling the volumetric shrinkage of a composite material upon curing, comprising the step of:

[0007] (a) providing a composite material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise at least one filler ingredient, said filler ingredient(s) being present in a metastable first phase and being able to undergo a martensitic transformation to a stable second phase, the volume ratio between said stable second phase and said metastable first phase of said filler ingredient(s) being at least 1.005, and wherein said material further comprises one or more water- or acid-releasing agents;

[0008] (b) allowing the resin base to polymerize and cure, and allowing the filler ingredient(s) to undergo a martensitic transformation from said first metastable phase to said second stable phase.

[0009] Moreover, the present invention provides the composite materials defined herein for use in medicine, in particular in dentistry.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The present invention, i.a., provides a composite material with improved control of the volumetric shrinkage upon curing of the material.

[0011] More particularly, the present invention provides composite material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise at least one filler ingredient, said filler ingredient(s) being present in a metastable first phase and being able to undergo a martensitic transformation to a stable second phase, the volume ratio between said stable second phase and said metastable first phase of said filler ingredient(s) being at least 1.005, and wherein said material further comprises one or more water- or acid-releasing agents.

[0012] A particular feature of the present invention is the presence of one or more water- or acid-releasing agents. The one or more water- or acid-releasing agents represent a well-controlled chemical trigger mechanism with the purpose of contributing to the martensitic transformation of the filler ingredient(s) (see further below).

[0013] It is well known that many polymeric resin bases (see also below) exhibit volumetric shrinkage upon curing thereof. Thus, a particular feature of the present invention is the presence of a filler ingredient that will reduce or eliminate the volumetric shrinkage caused by the polymerizable resin base, or even counteract this volumetric shrinkage to such an extent that the composite material exhibits a net volumetric expansion upon curing of the polymeric resin base.

[0014] Thus, in a preferred embodiment of the composite material, the resin base, upon polymerization and in the absence of any compensating effect from the one or more filler ingredients, causes a volumetric shrinkage (ΔV_{resin}) of the composite material of at least 0.50%, and wherein said composite material, upon polymerization of said resin base and upon phase transformation of said filler ingredient(s), exhibits a total volumetric shrinkage (ΔVt_{total}) of at least 0.25%-point less than the uncompensated volumetric shrinkage (ΔV_{resin}) caused by the resin base. More particularly, the volumetric shrinkage (ΔV_{resin}) is at least 1.00%, such as at least 1.50%, and the total volumetric shrinkage (ΔV_{total}) is at least 0.50%-point less, such as 1.00%-point less than the uncompensated volumetric shrinkage, and wherein said material further comprises one or more water- or acid-releasing agents.

[0015] Alternatively, the present invention provides a composite material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise at least one filler ingredient, said filler ingredient(s) including metastable zirconia in the tetragonal or cubic crystalline phase, wherein said resin base, upon polymerization and in the absence of any compensating effect from the one or more filler ingredients, causes a volumetric shrinkage (ΔV_{resin}) of the composite material of at least 0.50%, and wherein said composite material, upon polymerization of said resin base and upon phase transformation of said filler ingredient(s), exhibits a total volumetric shrinkage (ΔV_{total}) of at least 0.25%-point less than the uncompensated volumetric shrinkage (ΔV_{resin}) caused by the resin base, and wherein said material further comprises one or more water- or acid-releasing agents.

[0016] The composite material typically comprises 5-95%, or 10-90%, by weight of the one or more fillers (including nanofillers and filler ingredient(s)) and 5-95%, or 10-90%, by weight of the polymerizable resin base, in particular 30-95%, or 30-90%, by weight of the one or more fillers and 5-70%, or 10-70%, by weight of the polymerizable resin base.

[0017] The one or more water- or acid-releasing agent typically constitute 0.01-5% by weight, e.g. 0.1-1% by weight, of the composite material.

[0018] Preferably, the composite material is substantially solvent free and water free. By the term "substantially solvent free and water free" is meant that the composite material comprises less than 1%, such as less than 0.5% or less than 150 ppm, by weight of solvents and/or water.

[0019] Water- or Acid-Releasing Agents (Chemical Triggers)

[0020] The one or more water- and/or acid-releasing agents play a role as chemical trigger(s) in the composite materials, i.e. the water-releasing agent will—upon release of water or acid—contribute to or even be solely responsible for the triggering of the martensitic transformation of the filler ingredient(s).

[0021] The acids of relevance as chemical triggers are proton-releasing molecules, preferably small molecules like HCl, HF and HBr.

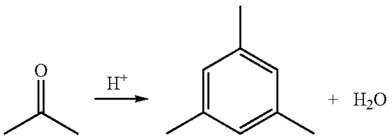
[0022] In a particularly interesting embodiment, the chemical triggering is effected by a combination of water and an acid, i.e. the composite material comprises a combination at least one water-releasing agent and at least one acid-releasing agent.

[0023] Examples of water- or acid-releasing agents are those which, e.g., under the influence of light or heat, decompose or condense by the simultaneous liberation of water or an acid.

[0024] A particular preferred application is a light induced release of water or a strong acid or a combination of both, since the curing of dental composites most commonly is done by light (blue).

[0025] Advantageously, the phase transformation takes place along with the curing of the composite material, in particular dental material. It is believed that this can be achieved by a number of water- or acid-releasing agents, e.g. agents releasing water or acid as a result of

[0026] A. Aldol/Clalsen Condensations



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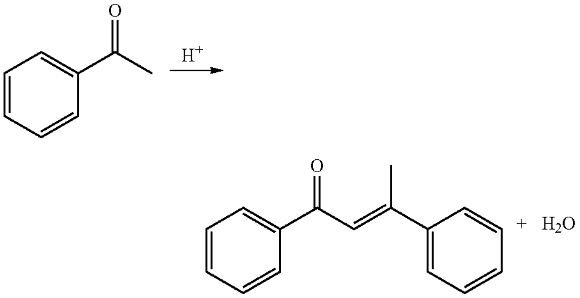
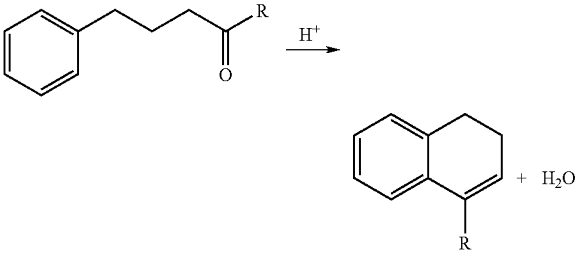
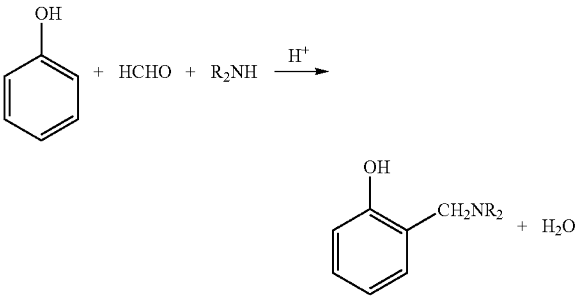


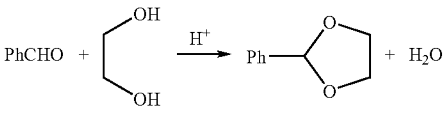
[0027] B. Cyclodehydration



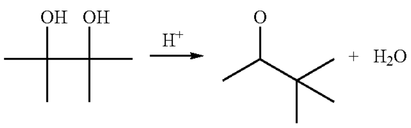
[0028] C. Amino-alkylation (the Mannich-Reaction)



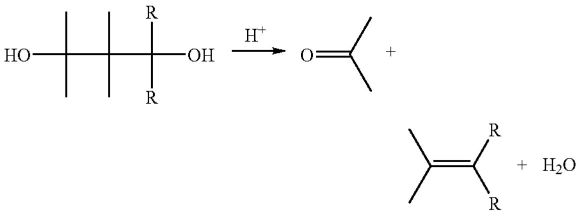
[0029] D. Formation of Acetals



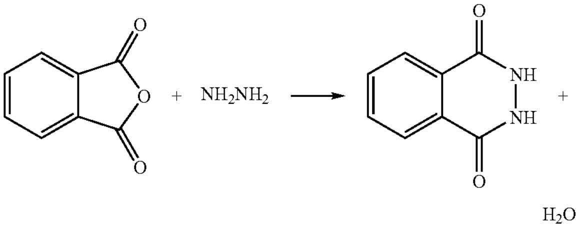
[0030] E. Pinacol-Rearrangement



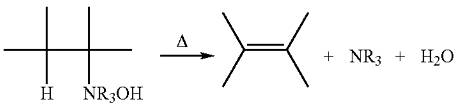
[0031] F. Hydroxyalkyl-hydroxy-Elimination



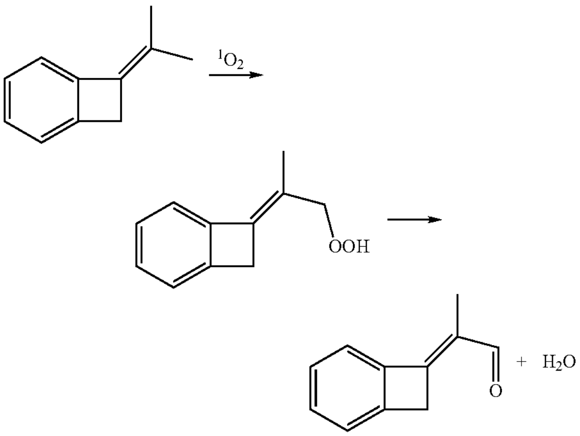
[0032] G. Hydrazines in Condensation Reactions



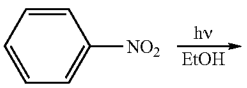
[0033] H. Cleavage of Quaternary Ammonium Hydroxides



[0034] I. Hydro-Peroxides



[0035] J. Condensation of Nitro-Functionalized Molecules



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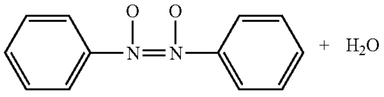
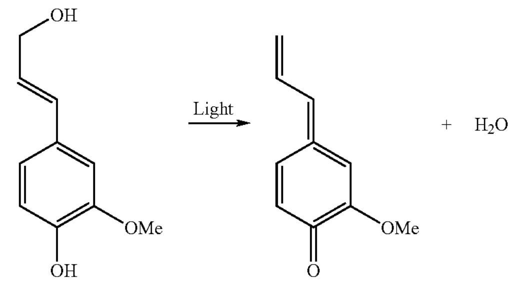
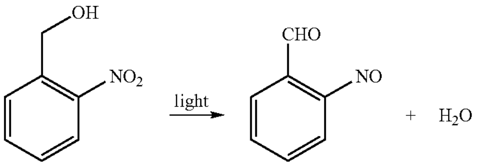


[0036] K. A Number of Molecules can Undergo an Elimination to form Water and a Double Bond upon Exposure to Light, some Examples are given below:

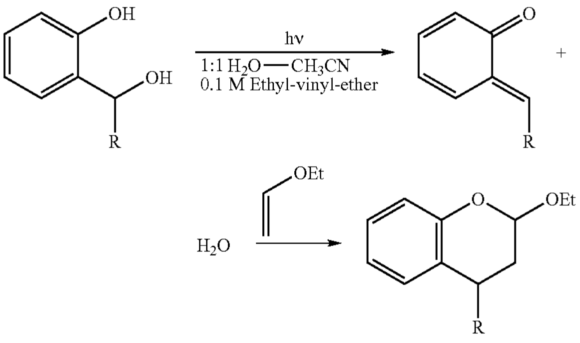
Coniferyl alcohol



Para-nitrobenzyl alcohol



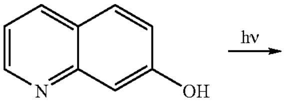
o-Hydroxy-benzyl alcohols



R = H, Ph

[0037] Examples hereof are given, e.g., in *J. Am. Chem. Soc.* 117 (1995) 5369, *J. Org. Chem.* 68 (2003) 9643, *J. Am. Chem. Soc.* 123 (2001) 8089, and *J. Org. Chem.* 66 (2001) 41.

[0038] L. Acidity of Photo-Excited Hydroxyarenes



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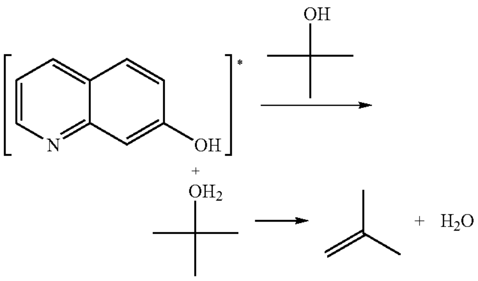


[0039] M. Acid-Releasing Photoacids

[0040] Ref.: *Acc. Chem. Res.* 35 (1999) 19 and *J. Am. Chem. Soc.* 116 (1994) 10593: 5-cyano-1-naphthol; 5,8-dicyano-1-naphthol; 5-, 6-, 7-, and 8-cyano-2-naphthols; 5,8-dicyano-2-naphthol and 5-(methanesulfonyl)-1-naphthol.

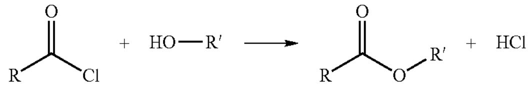
[0041] Ref.: *Luminescence* 20 (2005) 358: 7-hydroxy-1-naphthalenesulphonic acid.

[0042] Ref.: *Tetrahedron Lett.* 46 (2005) 5563: Anthracene-9-methanol derived esters.

[0043] N. Acid-Forming Agents

[0044] Metastable zirconia particles can be phase transformed by HCl soluted in iso-propanol. A hydrohalogen compound could be used to release hydrohalogen upon light radiation. This could be done in a resin base with the metastable zirconia filler particles.

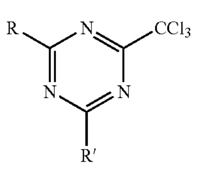
[0045] O. Acid-Releasing Esterification



[0046] P. Halogen Containing Photo-Acids

[0047] In principle it is possible to use halogen-containing radiation-sensitive compounds which form hydrohalogenic acid from any organic halogen compound. The following illustrative halogen-containing organic compounds can be found useful as triggers: carbon tetrabromide, tetra(bromomethyl)-methane: tetrabromoethylene; 1,2,3,4-tetrabromobutane; trichloroethoxyethanol; p-iodophenol; p-bromophenol; p-iodo-biphenyl; 2,6-dibromophenol; 1-bromo-2-naphthol; p-bromoaniline; hexachloro-p-xylene; trichloriacetanilide; p-bromodimethylaniline; tetrachloritetrahydronaphthalene; α,α'-dibromozylene, α,α,α',α'-tetrabromoxylene; hexabromoethane; 1-chloroanthraquinone; ω,ω,ω-tribromoquinaldine; hexabromocyclohexane; 9-bromofluorene; bis(pentachloro)cyclopentadienyl. It appears probable that halogen radicals are produced from the halogen containing triggers upon adequate radiation. The radicals then react with hydrogen atoms available from a hydrogen donor component to form hydrogen halide which then serves as trigger molecule upon reaction with the zirconia particles.

[0048] A currently highly preferred subgroup of the halogen containing compounds are compounds containing a triazine group, in particular triazine compounds comprising one or two trihalomethyl groups represented by the following general formula (I):

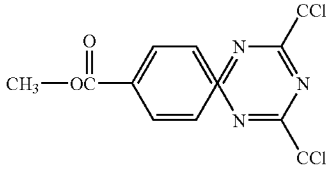


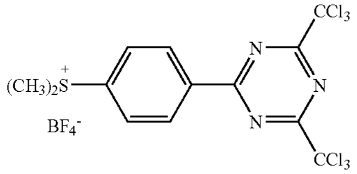
(I)

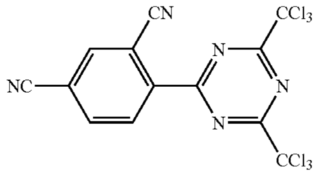
wherein CCl_3 may be replaced by a CF_3 group; R represents the attachment point for an organic moiety; and R' is selected from the group consisting of a hydrogen atom, a trihalomethyl group (e.g. trichloromethyl group or a trifluoroalkyl group), a substituted C_{1-6}-alkyl group, an unsubstituted C_{1-6}-alkyl group, a substituted aryl group, an unsubstituted aryl group, and a substituted C_{2-6}-alkenyl group.

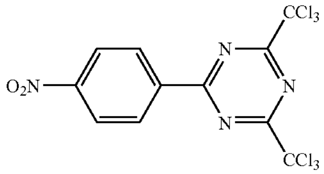
[0049] Preferred examples of the substituent R' are trichloromethyl and trifluoromethyl groups Examples of the organic moiety R include 4-styrylphenyl and 4-(substituted)-styrylphenyl groups, these molecules typically absorb UV-light.

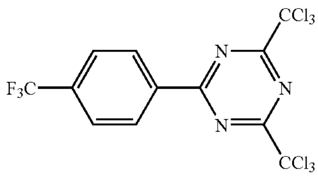
[0050] Illustrative examples of useful mono- or di-trihalomethyl-triazine compounds are those disclosed EP 0 563 925 A1:











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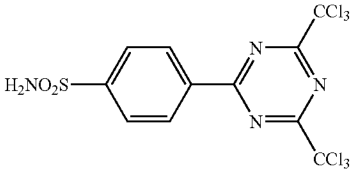
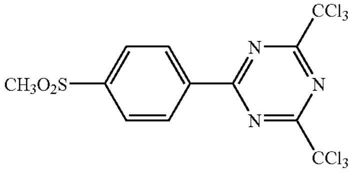
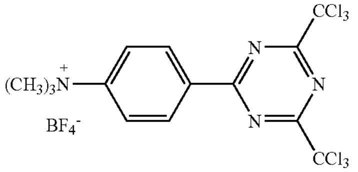
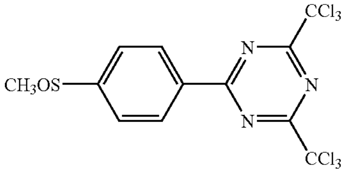
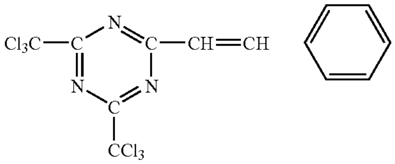


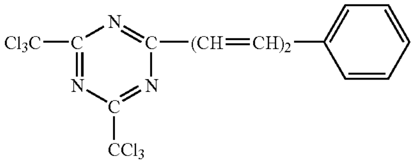


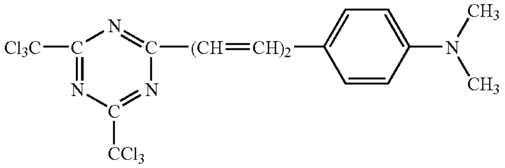


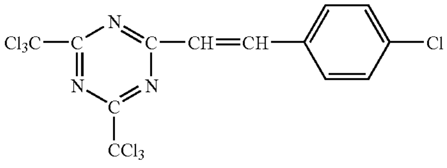


[0051] Other useful examples of the organic moiety are styryl and substituted styryl groups, cf. U.S. Pat. No. 3,987,037 and *J. Am. Chem. Soc.* 121 (1999) 6167, because of the C_{2-6}-alkenyl group these molecules absorb UV-light and sometimes blue light making them more preferable in dental applications;









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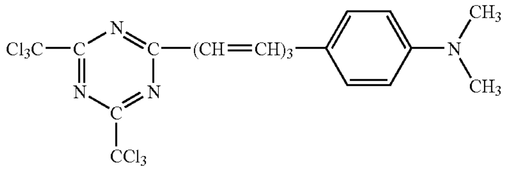

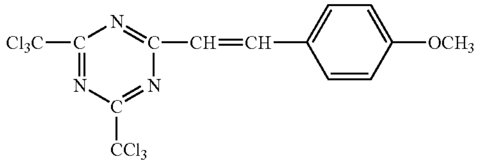

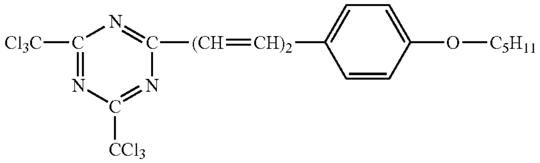

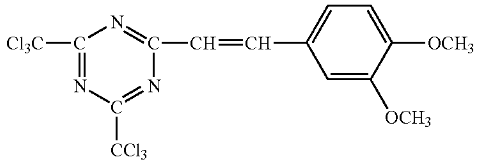

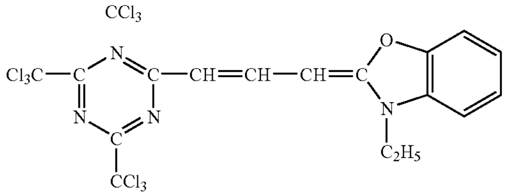

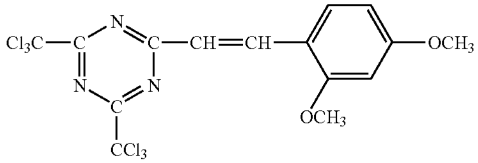

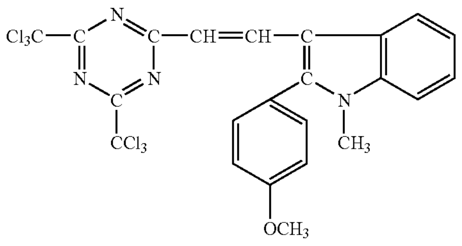

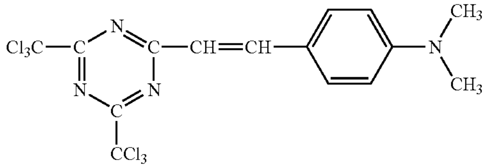

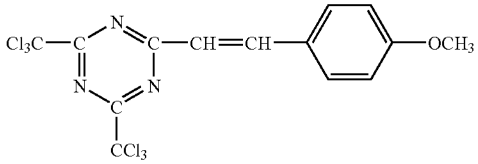

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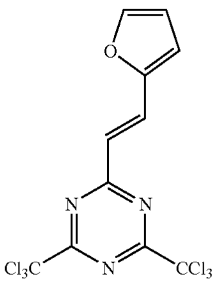
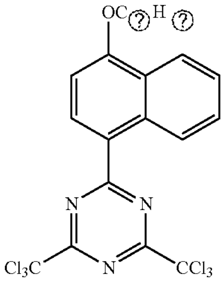
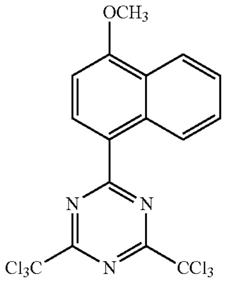


[0052] Moreover, other currently preferred examples of organic moieties are residues of polynuclear aromatic compounds such as naphthyl group and residues of heteroaromatic compounds such as thiofuran, *J. Am. Chem. Soc.* 121 (1999) 6167.





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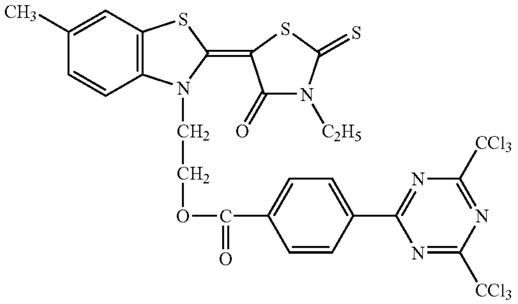
[0053] Examples of functional groups required for forming a coupling with the light absorbing moiety S include those listed above in connection with the compounds shown below cf. the compounds disclosed in U.S. Pat. No. 5,262,276. By designing the moiety S the trigger molecules can be "tuned" to the wavelength that is usually used in dental applications (blue light). Furthermore these molecules are reported to bleach upon exposure to light this making them ideal to dental applications were the color of the composite is very important.



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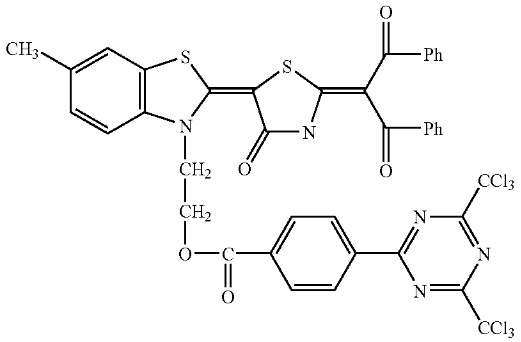

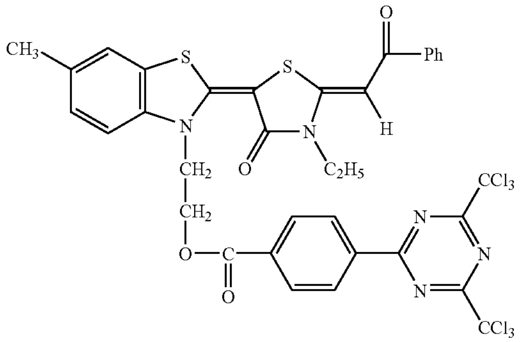

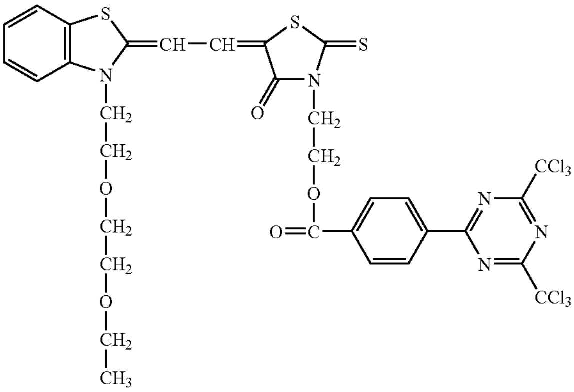

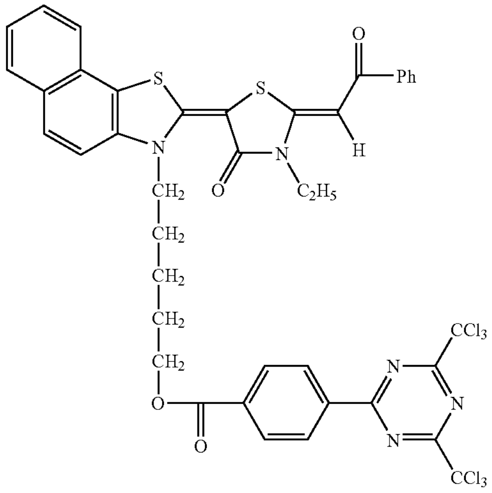

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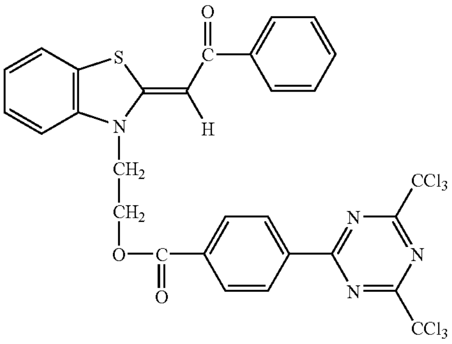

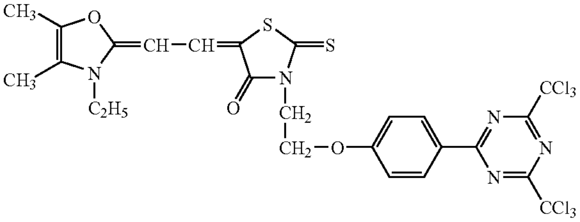

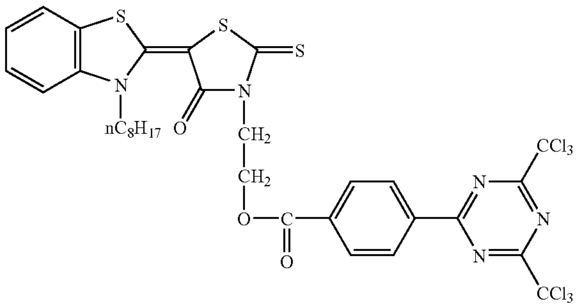

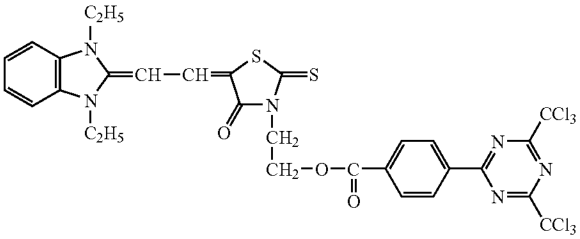

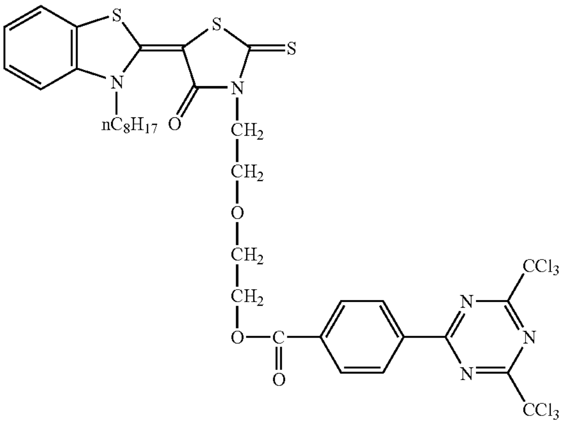

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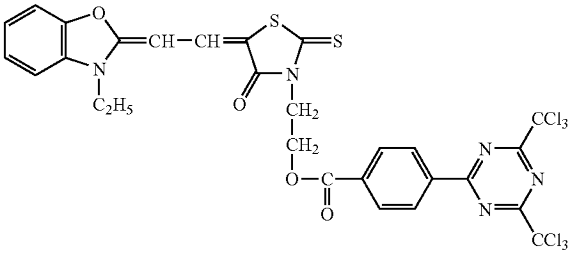
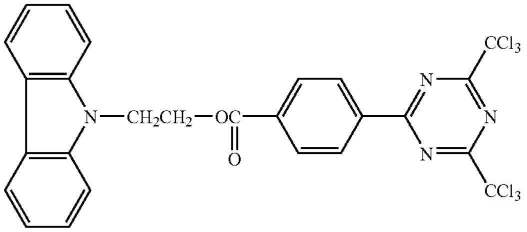
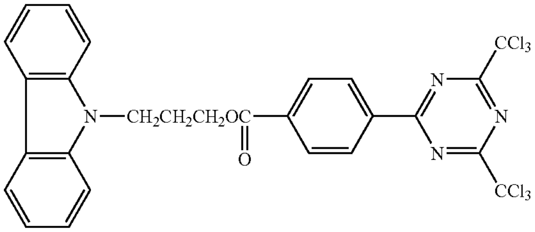
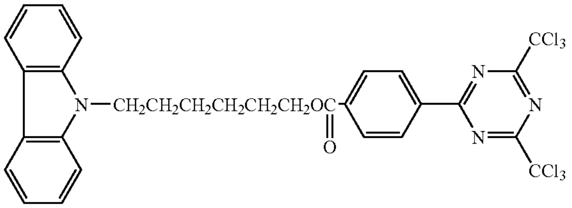
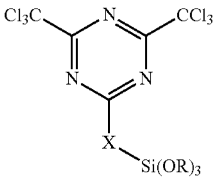






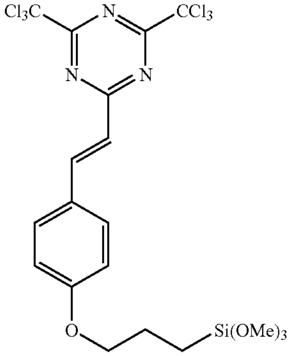


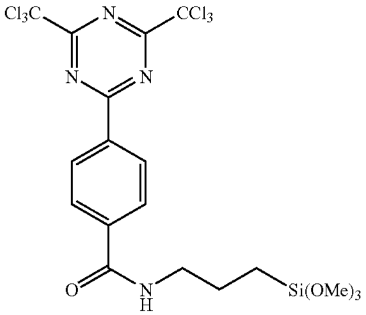
[0054] It is envisaged that a further improved application of the above-mentioned triggers would be to chemically anchor the triggers to the surface of the metastable zirconia particles. This would ensure that the triggering molecules were close to the reactive sites of zirconia thereby inducing a fast phase-transformation and reducing the risk of other chemical reactions e.g. with the monomer resin. The chemical anchoring could be done with the use of a silane-, phosphate-, carboxylic acid, hydroxamic acid or a carbamate- group and done with surface treatment of the zirconia particles. E.g.:



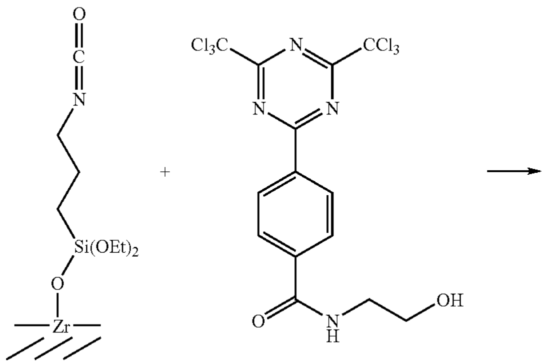
[0055] In the formula, X represents an organic moiety as described and illustrated above. In some embodiments, X independently is selected from a substituted C_{1-6}-alkyl group, an unsubstituted C_{1-6}-alkyl group, a substituted aryl group, an unsubstituted aryl group, and a substituted C_{2-6}-alkenyl group, provided that X must have at least one functional group which absorbs light. R in $Si(OR)_3$ is a substituted or unsubstituted C_{1-6}-alkyl group, typically methyl.

[0056] Examples of silane containing novel light-free radical generator compounds which may be used in the present invention are as follows but the present invention is not restricted to these specific examples:





[0057] Another way to chemically anchor the triggers to the surface of the metastable zirconia particles are to treat the zirconia surface with e.g. a silane and then react the triazine with a functional group on the silane. E.g.:



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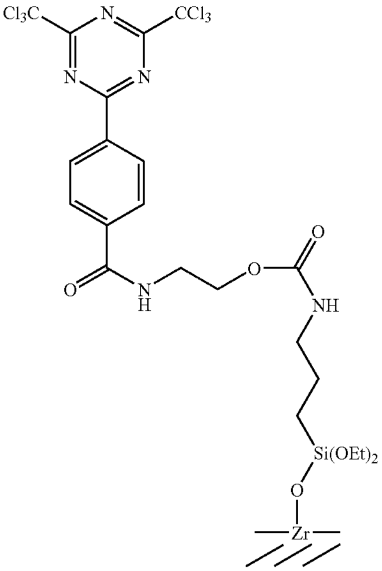

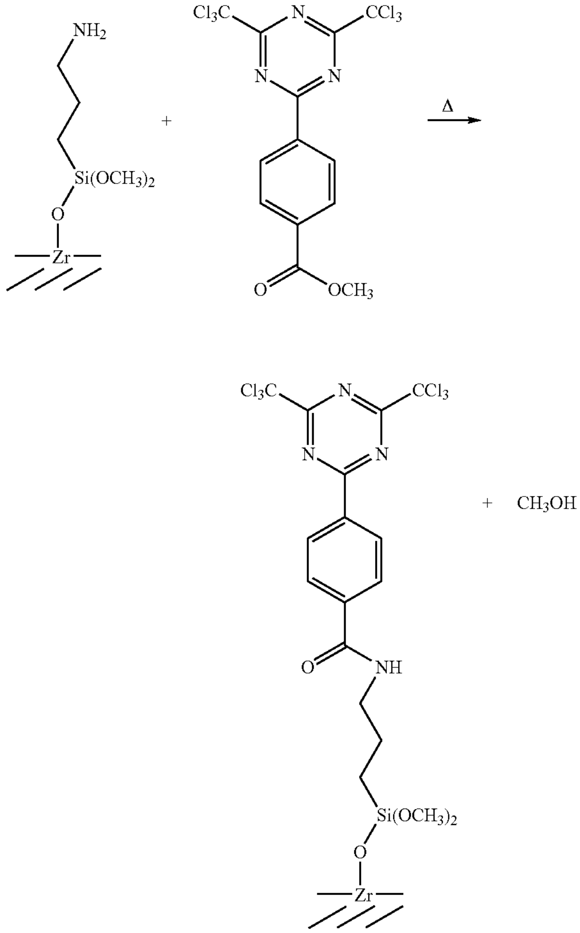

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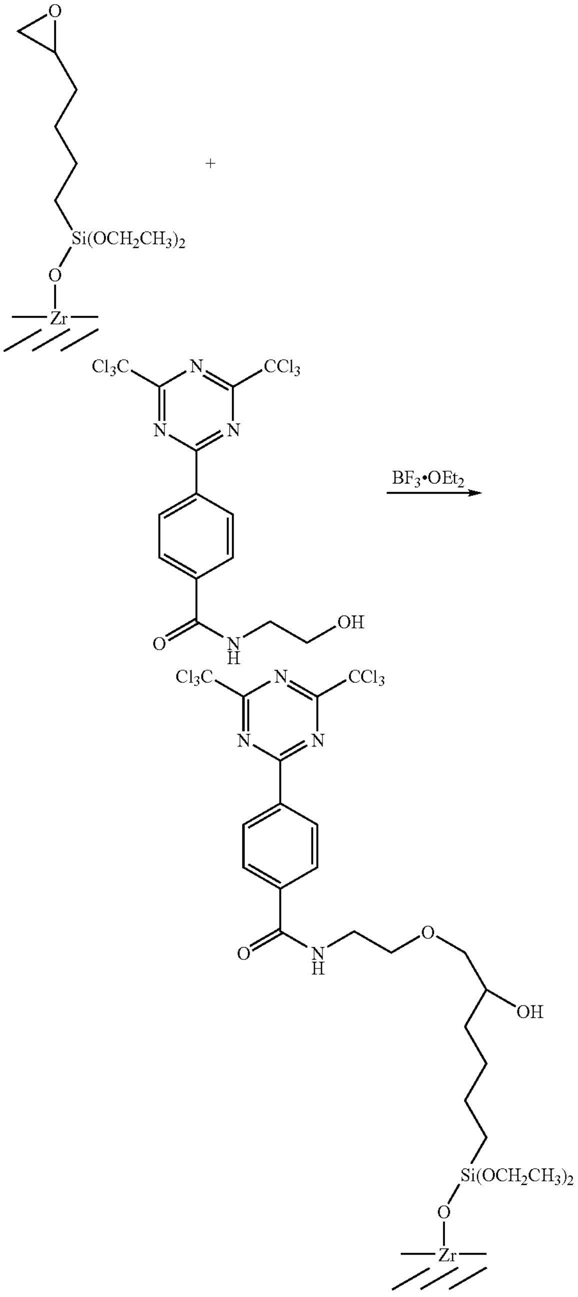


[0058] Q. Light Induced Acid Onium Salts

[0059] A large number of known compounds and mixtures are suitable for use as radiation-sensitive components which on irradiation form or eliminate preferentially strong acids, such as diazonium, phosphonium, sulfonium and iodonium salts, o-quinonediazide sulfochlorides combinations. It appears probable that acid (even superacids) are produced from these radiation-sensitive components, the reaction can be described by the following.

$$Ar_2I^+X^- \rightarrow ArI^+X^- + Ar^{\cdot}$$

$$ArI^+X^- + RH \rightarrow ArI + R + HX$$

[0060] Where X can be number of different anions:

[0061] 1) X═F, Cl^-, Br^-, where the product upon light irradiation will be HF, HCl or HBr, a trigger molecule for the phase conversion of zirconia.

[0062] 2) The corresponding base of a strong acid (not X═F^-, Cl^-, Br^-) such as AsF_6^-, SbF_6^-, PF_6^-, BF_4^- or $CF_3SO_3^-$. The trigger molecule can be produced by having the corresponding base (F^-, Cl^-, Br^- or OH^-) of the known trigger molecules in the resin or on the zirconia e.g.

$$HX + LiCl \rightarrow HCl + LiX \text{ or}$$

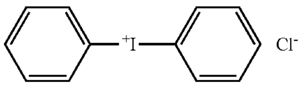
$$HX + LiOH \rightarrow H_2O + LiX$$

[0063] 3) The special case where X═OH^-, where the product upon light irradiation will be water H_2O, a trigger molecule for the phase conversion of zirconia.

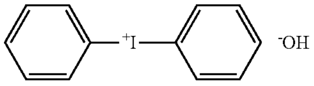
[0064] Photolysis of diaryliodonium salts may be photosensitized in the 400-500 nm region by acridine dyes whereas perylene and other polynuclear aromatic hydrocarbons are effective electron-transfer photosensitizers for the triggering of the acid cleavage of triarylsulfonium salts and dialkylphenacylsulfonium salts.

[0065] Below is given some examples of the radiation-sensitive components which on irradiation form or eliminate strong acids:

[0066] A special case of this is where HX (X═F^-, Cl^-, Br^-) releasing agents can be made by substituting the anion of the below standing compounds with a halogen anion. These molecules release trigger molecules (HF, HCl, HBr) upon exposure to UV-light e.g.: diphenyliodonium chloride



[0067] Another special case of this is where water (H_2O) releasing agents can be made by substituting the anion of the below standing compounds with a hydroxyl anion (OH^-). These molecules release trigger molecules (water) upon exposure to UV-light e.g.: diphenyliodonium hydroxide



[0068] Ref.: U.S. Pat. No. 5,736,296:

[0069] (i) Bissulfonyldiazomethanes such as bis(p-toluenesulfonyl)diazomethane, methylsulfonyl-p-toluenesulfonyldiazomethane, 1-cyclohexylsulfonyl-1-(1,1-dimethylethylsulfonyl)diazomethane, bis(1,1-dimethylethylsulfonyl)diazomethane, bis(1-methylethylsulfonyl) diazomethane, bis(cyclohexylsulfonyl)diazomethane, bis(2,4-dimethylphenylsulfonyl)diazomethane, bis-(4-ethylphenylsulfonyl)diazomethane, bis(3-methylphenylsulfonyl)diazomethane, bis(4-methoxyphenylsufonyl)diazomethane, bis(4-fluorophenylsulfonyl)diazomethane, bis(4-chlorophenylsulfonyl)diazomethane, and bis(4-tert-butylphenylsulfonyl)diazomethane;

[0070] (ii) sulfonylcarbonyl alkanes such as 2-methyl-2-(p-toluenesulfonyl)propiophenone, 2-(cyclo-hexyl-carbonyl)-2-(p-toluene sulfonyl)propane, 2-methanesulfonyl-2-methyl-(4-methylthio)proplophenone, and 2,4-dimethyl-2-(p-toluenesulfonyl)pentane -3-one;

[0071] (iii) sulfonyl carbonyldiazomethanes such as 1-p-toluenesulfonyl-1-cyclohexylcarbonyldiazomethane, 1-diazo-1-methylsulfonyl-4-phenyl-2-butanone, 1-cyclohexyl-sulfonyl-1-cyclohexylcarbonyldiazomethane, 1-diazo-1-cyclohexylsulfonyl -3,3-di-methyl-2-butanone, 1-diazo-1-(1,1-di-methylethyl sulfonyl)-3,3-di-methyl-2-butanone, 1-acetyl-1-(1-methylethyl sulfonyl)diazomethane, 1-diazo-1-(p-toluenesulfonyl)-3,3-dimethyl-2-butanone, 1-diazo-1-benzenesulfonyl-3,3-di-methyl-2-butanone, 1-diazo-1-(p-toluene sulfonyl)-3-methyl-2-butanone, 2-diazo-2-(p-toluenesulfonyl)cyclohexylacetate, 2-diazo-2-benzene sulfonyl tert-butyl acetate, 2-diazo-2-methanesulfonyl iso-propyl acetate, 2-diazo-2-benzenesulfonyl cyclohexyl acetate, and 2-diazo-2-(p-toluenesulfonyl)tert-butyl acetate;

[0072] (iv) nitrobenzyl derivatives such as 2-nitrobenzyl-p-toluenesulfonate, 2,6-dinitrobenzyl-p-toluenesulfonate, and 2,4-dinitrobenzyl-p-trifluoro-methylbenzenesulfonate; and

[0073] (v) esters of polyhydroxy compounds and aliphatic or aromatic sulfonic acids such as pyrogallic methane sulfonate ester (pyrogallol trimesylate), pyrogallic benzene sulfonate ester, pyrogallic p-toluene sulfonate ester, pyrogallic p-methoxy benzene sulfonate ester, pyrogallic mesitylene sulfonate ester, pyrogallic benzylsulfonate ester, alkyl gallic acid methane sulfonate ester, alkyl gallic acid benzene sulfonate ester, alkyl gallic acid p-toluene sulfonate ester, alkyl gallic acid p-methoxy benzene sulfonate ester, alkyl gallic acid mesitylene sulfonate ester, and alkyl gallic acid benzylsulfonate ester.

[0074] Preferred is the alkyl group in the afore-mentioned alkyl gallic acid where the alkyl group has from 1 to 15 carbon atoms, and especially octyl group or lauryl group. (vi) onium salt-based acid-generating agents to be in a general formula (II) and (III), and (vii) benzoin tosylate-based acid-generating agents to be in a general formula (IV) may be used. A general formula (II);

$$RI^{+}R'X^{-} \tag{II}$$

where R and R' are aryl groups or aryl groups having a substituent and may be respectively identical or different; X^- is any of AsF_6^-, SbF_6^-, PF_6^-, BF_4^-, or $CF_3\,SO_3^-$, F^-, Cl^-, Br^-, OH^-;

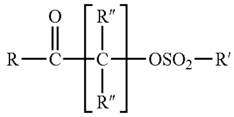
[0075] and a general formula (III);

$$R(R')S^{+}R''X^{-} \tag{III}$$

where R, R', and R" are aryl groups or aryl groups having a substituent and may be respectively identical or different; X^- is any of AsF_6^-, SbF_6^-, $PF_6^-BF_4^-$, or $CF_3\,SO_3^-$, F^-, Cl^-, Br^-, OH^-

[0076] A general formula (IV);

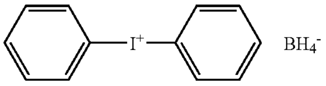
(IV)



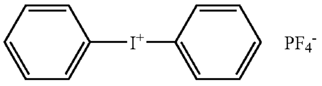
$$R-\overset{\displaystyle O}{\overset{\|}{C}}-\left[\begin{array}{c}R''\\|\\C\\|\\R''\end{array}\right]-OSO_2-R'$$

where R and R' are aryl groups or aryl groups having a substituent and may be identical or different; R" and R"' are hydrogen atoms, C_{1-6}-groups, hydroxyl groups, or aryl groups and may be identical or different. n is 0 or 1.

[0077] The following are offered as specific onium salts presented by general formulas (II) and (III).



dipheny (?)



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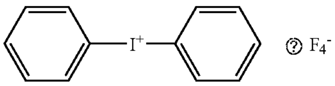

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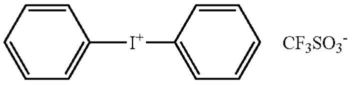

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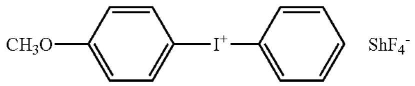

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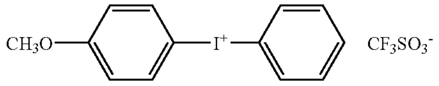

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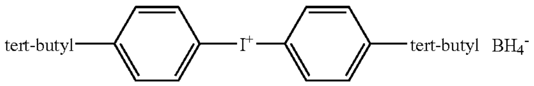

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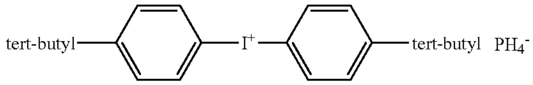

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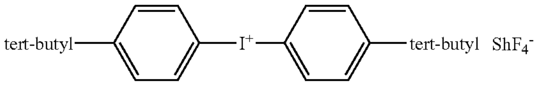

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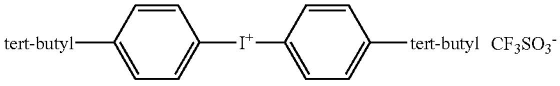

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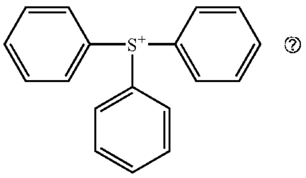

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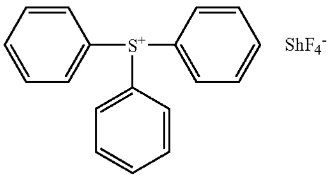

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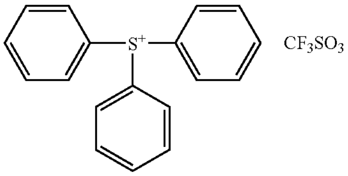

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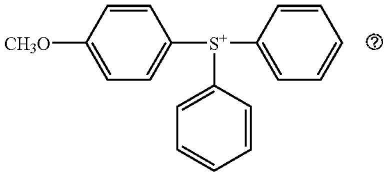

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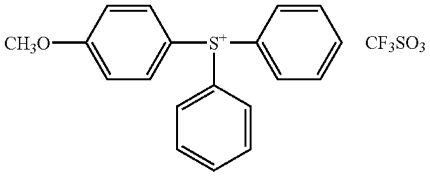

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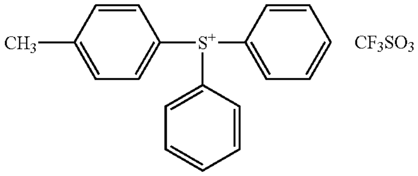

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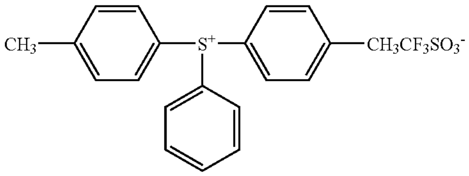

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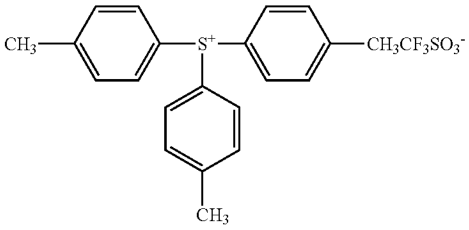

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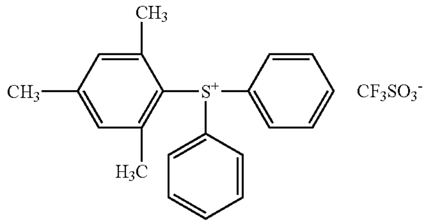

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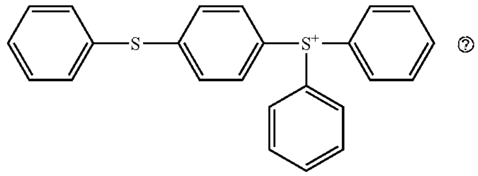

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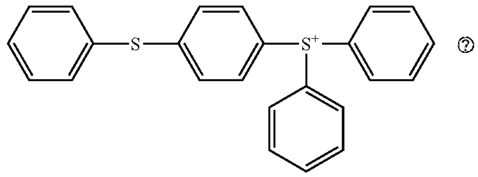

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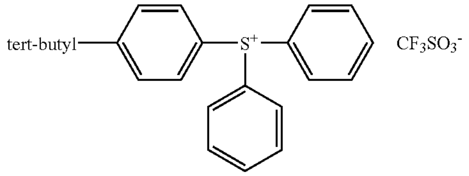

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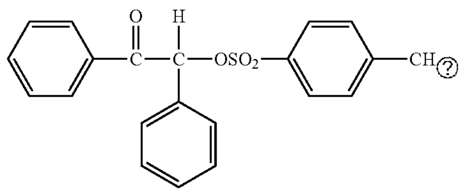
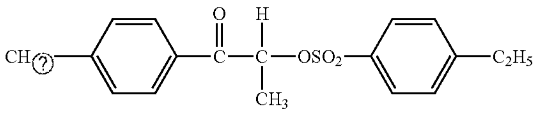
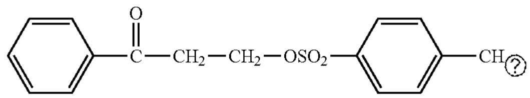
[0078] (vii) The following compounds are offered as specific benzoin tosylate-based acid-forming agents.







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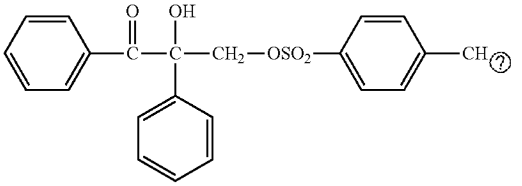

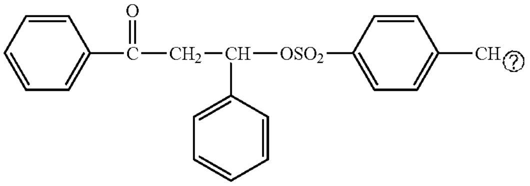

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[0079] One of these acid-forming agents may be used, or two or more may be used in combination. Particularly, the combination is preferred since the composition containing the mixture has high sensitivity.

[0080] As the acid-generating agents to be in the resists for light (blue), other acid-generating agents than the above-mentioned (i) and (iii) can be employed.

[0081] Ref.: U.S. Pat. No. 6,770,419 B2:

[0082] Onium salts such as triaryl sulfonium or diaryliodonium hexafluoroantimonate, hexafluoroarsenates, triflates, perfluoroalkane sulfonates (e.g., perfluoromethane sulfonate, perfluorobutane, perfluorohexane sulfonate, perfluorooctane sulfonate, etc.), perfluoroalkyl sulfonyl imide, perfluoroalkyl sulfonyl methide, perfluoroaryl sulfonyl imide, perfluoroaryl sulfonyl methide; substituted aryl sulfonates such as pyrogallols (e.g. trimesylate of pyrogallol or tris(sulfonate) of pyrogallol), sulfonate esters of hydroxyimides, N-sulfonyloxynaphthalimides (N-camphorsulfonyloxynaphthalimide, N-pentafluorobenzenesulfonyloxynaphthalimide), (α-α'bis-sulfonyl diazomethanes, naphthoquinone-4-diazides, alkyl disulfones and others. R: Water-Releasing Agent

[0083] A better application of the above mentioned water-releasing triggers would be to chemical anchor the triggers to the surface of the metastable zirconia particles. This would ensure that the triggering molecules were close to the reactive sites of zirconia thereby inducing a fast phase-transformation and reducing the risk of other chemical reactions e.g. with the monomer resin. The chemical anchoring could be done with the use of a silane-, phosphate-, carboxylic acid, hydroxamic acid or a carbamate- group and done with surface treatment of the zirconia particles.

[0084] Definitions

[0085] In the present context, the term "C_{1-6}-alkyl" is intended to mean a linear, cyclic or branched hydrocarbon group having 1 to 6 carbon atoms, such as methyl, ethyl, propyl, iso-propyl, pentyl, cyclopentyl, hexyl, cyclohexyl.

[0086] Similarly, the term "C_{2-6}-alkenyl" is intended to cover linear, cyclic or branched hydrocarbon groups having 2 to 6 carbon atoms and comprising one unsaturated bond. Examples of alkenyl groups are vinyl, allyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, heptadecaenyl. Preferred examples of alkenyl are vinyl, allyl, butenyl, especially allyl.

[0087] In the present context, i.e. in connection with the terms "alkyl", "alkenyl" and the like, the term "optionally substituted" is intended to mean that the group in question may be substituted one or several times, preferably 1-3 times, with group(s) selected from hydroxy (which when bound to an unsaturated carbon atom may be present in the tautomeric keto form), C_{1-6}-alkoxy (i.e. C_{1-6}-alkyl-oxy), C_{2-6}-alkenyloxy, carboxy, oxo (forming a keto or aldehyde functionality), C_{1-6}-alkoxycarbonyl, C_{1-6}-alkylcarbonyl, formyl, aryl, aryloxy, aryl-amino, arylcarbonyl, aryloxycarbonyl, arylcarbonyloxy, arylaminocarbonyl, arylcarbonyl-amino, heteroaryl, heteroaryloxy, heteroarylamino, heteroarylcarbonyl, heteroaryloxy-carbonyl, heteroarylcarbonyloxy, heteroarylaminocarbonyl, heteroarylcarbonylamino, heterocyclyl, heterocyclyloxy, heterocyclylamino, heterocyclylcarbonyl, heterocyclyloxy-carbonyl, heterocyclylcarbonyloxy, heterocyclylaminocarbonyl, heterocyclylcarbonylamino, amino, mono- and di(C_{1-6}-alkyl)amino, —N(C_{1-4}-alkyl)$_3^+$, carbamoyl, mono- and di(C_{1-6}-alkyl)-aminocarbonyl, C_{1-6}-alkylcarbonylamino, cyano, guanidino, carbamido, C_{1-6}-alkyl-sulphonyl-amino, aryl-sulphonyl-amino, heteroaryl-sulphonyl-amino, C_{1-6}-alkanoyloxy, C_{1-6}-alkyl-sulphonyl, C_{1-6}-alkyl-sulphinyl, C_{1-6}-alkylsulphonyloxy, nitro, C_{1-6}-alkylthio, and halogen, where any aryl, heteroaryl and heterocyclyl may be substituted as specifically described below for aryl, heteroaryl and heterocyclyl, and any alkyl, alkoxy, and the like, representing substituents may be substituted with hydroxy, C_{1-6}-alkoxy, amino, mono- and di(C_{1-6}-alkyl)amino, carboxy, C_{1-6}-alkylcarbonylamino, C_{1-6}-alkylaminocarbonyl, or halogen(s).

[0088] Typically, the substituents are selected from hydroxy (which when bound to an unsaturated carbon atom may be present in the tautomeric keto form), C_{1-6}-alkoxy (i.e. C_{1-6}-alkyl-oxy), C_{2-6}-alkenyloxy, carboxy, oxo (forming a keto or aldehyde functionality), C_{1-6}-alkylcarbonyl, formyl, aryl, aryloxy, arylamino, arylcarbonyl, heteroaryl, heteroaryloxy, heteroarylamino, heteroarylcarbonyl, heterocyclyl, heterocyclyloxy, heterocyclylamino, heterocyclylcarbonyl, amino, mono- and di(C_{1-6}-alkyl)amino; carbamoyl, mono- and di(C_{1-6}-alkyl)aminocarbonyl, amino-C_{1-6}-alkyl-aminocarbonyl, mono- and di(C_{1-6}-alkyl)amino-C_{1-6}-alkyl-aminocarbonyl, C_{1-6}-alkylcarbonylamino, guanidino, carbamido, C_{1-6}-alkyl-sulphonyl-amino, C_{1-6}-alkyl-sulphonyl, C_{1-6}-alkyl-sulphinyl, C_{1-6}-alkylthio, halogen, where any aryl, heteroaryl and heterocyclyl may be substituted as specifically described below for aryl, heteroaryl and heterocyclyl.

[0089] In some embodiments, substituents are selected from hydroxy, C_{1-6}-alkoxy, amino, mono- and di(C_{1-6}-alkyl) amino, carboxy, C_{1-6}-alkylcarbonylamino, C_{1-6}-alkylaminocarbonyl, or halogen.

[0090] The terms "halogen" and "halo" include fluoro, chloro, bromo, and iodo.

[0091] In the present context, the term "aryl" is intended to mean a fully or partially aromatic carbocyclic ring or ring system, such as phenyl, naphthyl, 1,2,3,4-tetrahydronaphthyl, anthracyl, phenanthracyl, pyrenyl, benzopyrenyl, fluorenyl and xanthenyl, among which phenyl is a preferred example.

[0092] The terms "heteroaryl" and "heteroaromatic" are intended to refer to a fully or partially aromatic carbocyclic ring or ring system where one or more of the carbon atoms have been replaced with heteroatoms, e.g. nitrogen (=N— or —NH—), sulphur, and/or oxygen atoms. Examples of such heteroaryl groups are oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, pyrrolyl, imidazolyl, pyrazolyl, pyridinyl, pyrimidinyl, pyrazinyl, pyridazinyl, triazinyl, coumaryl, furanyl, thienyl, quinolyl, benzothiazolyl, benzotriazolyl, benzodiazolyl, benzooxozolyl, phthalazinyl, phthalanyl, triazolyl, tetrazolyl, isoquinolyl, acridinyl, carbazolyl, dibenzazepinyl, indolyl, benzopyrazolyl, phenoxazonyl. Particularly interesting heteroaryl groups are benzimidazolyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, pyrrolyl, imidazolyl, pyrazolyl, pyridinyl, pyrimidinyl, pyrazinyl, pyridazinyl, furyl, thienyl, quinolyl, triazolyl, tetrazolyl, isoquinolyl, indolyl in particular benzimidazolyl, pyrrolyl, imidazolyl, pyridinyl, pyrimidinyl, furyl, thienyl, quinolyl, tetrazolyl, and isoquinolyl.

[0093] The term “heterocyclyl” is intended to mean a non-aromatic carbocyclic ring or ring system where one or more of the carbon atoms have been replaced with heteroatoms, e.g. nitrogen (═N— or —NH—), sulphur, and/or oxygen atoms. Examples of such heterocyclyl groups (named according to the rings) are imidazolidine, piperazine, hexahydropyridazine, hexahydro-pyrimidine, diazepane, diazocane, pyrrolidine, piperidine, azepane, azocane, aziridine, azirine, azetidine, pyroline, tropane, oxazinane (morpholine), azepine, dihydroazepine, tetrahydroazepine, and hexahydroazepine, oxazolane, oxazepane, oxazocane, thiazolane, thiazinane, thiazepane, thiazocane, oxazetane, diazetane, thiazetane, tetrahydrofuran, tetrahydropyran, oxepane, tetrahydrothiophene, tetrahydrothiopyrane, thiepane, dithiane, dithiepane, dioxane, dioxepane, oxathiane, oxathiepane. The most interesting examples are tetrahydrofuran, imidazolidine, piperazine, hexahydropyridazine, hexahydropyrimidine, diazepane, diazocane, pyrrolidine, piperidine, azepane, azocane, azetidine, tropane, oxazinane (morpholine), oxazolane, oxazepane, thiazolane, thiazinane, and thiazepane, in particular tetrahydrofuran, imidazolidine, piperazine, hexahydropyridazine, hexahydropyrimidine, diazepane, pyrrolidine, piperidine, azepane, oxazinane (morpholine), and thiazinane.

[0094] In the present context, i.e. in connection with the terms “aryl”, “heteroaryl”, “heterocyclyl” and the like (e.g. “aryloxy”, “heterarylcarbonyl”, etc.), the term “optionally substituted” is intended to mean that the group in question may be substituted one or several times, preferably 1-5 times, in particular 1-3 times, with group(s) selected from hydroxy (which when present in an enol system may be represented in the tautomeric keto form), C_{1-6}-alkyl, C_{1-6}-alkoxy, C_{2-6}-alkenyloxy, oxo (which may be represented in the tautomeric enol form), carboxy, C_{1-6}-alkoxycarbonyl, C_{1-6}-alkylcarbonyl, formyl, aryl, aryloxy, arylamino, aryloxy-carbonyl, arylcarbonyl, heteroaryl, heteroarylamino, amino, mono- and di(C_{1-6}-alkyl)amino; carbamoyl, mono- and di(C_{1-6}-alkyl) aminocarbonyl, amino-C_{1-6}-alkyl-aminocarbonyl, mono- and di(C_{1-6}-alkyl)amino-C_{1-6}-alkyl-aminocarbonyl, C_{1-6}-alkylcarbonylamino, cyano, guanidino, carbamido, C_{1-6}-alkanoyloxy, C_{1-6}-alkyl-sulphonyl-amino, aryl-sulphonyl-amino, heteroaryl-sulphonyl-amino, C_{1-6}-alkyl-suphonyl, C_{1-6}-alkyl-sulphinyl, C_{1-6}-alkylsulphonyloxy, nitro, sulphanyl, amino, amino-sulfonyl, mono- and di(C_{1-6}-alkyl)amino-sulfonyl, dihalogen-C_{1-4}-alkyl, trihalogen-C_{1-4}-alkyl, halogen, where aryl and heteroaryl representing substituents may be substituted 1-3 times with C_{1-4}-alkyl, C_{1-4}-alkoxy, nitro, cyano, amino or halogen, and any alkyl, alkoxy, and the like, representing substituents may be substituted with hydroxy, C_{1-6}-alkoxy, C_{2-6}-alkenyloxy, amino, mono- and di(C_{1-6}-alkyl)amino, carboxy, C_{1-6}-alkylcarbony-lamino, halogen, C_{1-6}-alkylthio, C_{1-6}-alkyl-sulphonyl-amino, or guanidino.

[0095] Typically, the substituents are selected from hydroxy, C_{1-6}-alkyl, C_{1-6}-alkoxy, oxo (which may be represented in the tautomeric enol form), carboxy, C_{1-6}-alkylcarbonyl, formyl, amino, mono- and di(C_{1-6}-alkyl)amino; carbamoyl, mono- and di(C_{1-6}-alkyl)aminocarbonyl, amino-C_{1-6}-alkyl-aminocarbonyl, C_{1-6}-alkylcarbonylamino, guanidino, carbamido, C_{1-6}-alkyl-sulphonyl-amino, aryl-sulphonyl-amino, heteroaryl-sulphonyl-amino, C_{1-6}-alkyl-suphonyl, C_{1-6}-alkyl-sulphinyl, C_{1-6}-alkylsulphonyloxy, sulphanyl, amino, amino-sulfonyl, mono- and di(C_{1-6}-alkyl) amino-sulfonyl or halogen, where any alkyl, alkoxy and the like, representing substituents may be substituted with hydroxy, C_{1-6}-alkoxy, C_{2-6}-alkenyloxy, amino, mono- and di(C_{1-6}-alkyl)amino, carboxy, C_{1-6}-alkylcarbonylamino, halogen, C_{1-6}-alkylthio, C_{1-6}-alkyl-sulphonyl-amino, or guanidino. In some embodiments, the substituents are selected from C_{1-6}-alkyl, C_{1-6}-alkoxy, amino, mono- and di(C_{1-6}-alkyl)amino, sulphanyl, carboxy or halogen, where any alkyl, alkoxy and the like, representing substituents may be substituted with hydroxy, C_{1-6}-alkoxy, C_{2-6}-alkenyloxy, amino, mono- and di(C_{1-6}-alkyl)amino, carboxy, C_{1-6}-alkylcarbonylamino, halogen, C_{1-6}-alkylthio, C_{1-6}-alkyl-sulphonyl-amino, or guanidino.

[0096] Moreover, it should be understood that the compounds may be present as enantiomers or diastereomers. The present invention encompasses each and every of such possible enantiomers and diastereomers as well as racemates and mixtures enriched with respect to one or the possible enantiomers or diastereomers.

[0097] Filler/Filler Ingredient

[0098] In view of the above, it is apparent that the one or more fillers, and in particular the one or more filler ingredients and the nanofillers, are important constituents of the composite material.

[0099] Fillers are frequently used in connection with polymeric materials in order to provide desirable mechanical properties of such materials, e.g. abrasion resistance, opacity, colour, radiopacity, hardness, compressive strength, compressive modulus, flexural strength, flexural modulus, etc.

[0100] Such fillers may be selected from one or more of a wide variety of materials, e.g. those that are suitable for the use in dental and/or orthodontic composite materials.

[0101] Fillers can be inorganic materials or cross-linked organic materials that are insoluble in the resin component of the composition. Cross-linked organic materials may as such be filled with an inorganic filler. The filler should—in particular for dental uses—be nontoxic and suitable for use in the mouth. The filler can be radiopaque or radiolucent. The filler typically is substantially insoluble in water.

[0102] The term “filler” is to be understood in the normal sense, and fillers conventionally used in composite materials in combination with polymer are also useful in the present context. The polymerizable resin base (see further below) can be said to constitute the “continuous” phase wherein the filler is dispersed.

[0103] Some examples of suitable inorganic fillers are naturally occurring or synthetic materials including, but not limited to: quartz; nitrides (e.g. silicon nitride); glasses derived from, for example, Zr, Sr, Ce, Sb, Sn, Ba, Zn, and Al; feldspar; borosilicate glass; kaolin; talc; titania; low Mohs hardness fillers such as those described in U.S. Pat. No. 4,695,251 (Randklev); and silica particles (e.g. submicron pyrogenic silicas such as those available under the trade designations AEROSIL, including “OX 50,” “130,” “150” and “200” silicas from Degussa AG, Hanau, Germany and CAB-O-SIL M5 silica from Cabot Corp., Tuscola, Ill.). Examples of suitable organic filler particles include filled or unfilled pulverized polycarbonates, polyepoxides, and the like.

[0104] Other illustrative examples of fillers are barium sulfate ($BaSO_4$), calcium carbonate ($CaCO_3$), magnesium hydroxide ($Mg(OH)_2$), quartz (SiO_2), titanium dioxide (TiO2), zirconia (ZrO_2), alumina (Al_2O_3), lantania (La_2O_3), amorphous silica, silica-zirconia, silica-titania, barium oxide (BaO), barium magnesium aluminosilicate glass, barium aluminoborosilicate glass (BAG), barium-, strontium- or zirconium-containing glass, milled glass, fine YF_3 or YbF_5 particles, glass fibres, metal alloys, etc. Metal oxides, e.g. titanium dioxide (TiO_2) and zirconia (ZrO_2), alumina (Al_2O_3), lantania (La_2O_3), constitute a particularly useful group of fillers for use in the composite materials of the present invention.

[0105] In one interesting embodiment, at least 5%, e.g. at least 10%, or even at least 20%, by weight of the one or more fillers are glass-particles. It is believed that inclusion of glass particles may further improve the optical (and thereby aesthetic) properties of the composite material by making it more transparent.

[0106] The weight content of the one or more filler materials in the composite material is typically in the range of 5-95%, or 10-90%, such as 30-95%, such as 40-95%, e.g. 60-95%. It should be understood that a combination of two or more fillers may be desirable, just as the particle size distribution of the filler(s) may be fairly broad in order to allow a dense packing of the filler and thereby facilitate incorporation of a high amount of fillers in the composite material. Typically, composite materials have a distribution of one or more sizes of fine particles plus microfine and/or nano-size filler (5-15%). This distribution permits more efficient packing, whereby the smaller particles fill the spaces between the large particles. This allows for filler content, e.g., as high as 77-87% by weight. An example of a one size distribution filler would be 0.4 μm structural micro-filler, with the distribution as follows: 10% by weight of the filler particles have a mean particle size of less than 0.28 μm; 50% by weight of the filler particles have a mean particle size of less than 0.44 μm; 90% by weight of the filler particles have a mean particle size of less than 0.66 μm.

[0107] Typically, the particle size of the filler(s) is in the range of 0.01-50 μm, such as in the range of 0.02-25 μm, and—as mentioned above—include nanofillers having a particle size of at the most 100 nm.

[0108] In some embodiments, the particle size of the filler (s) is/are in the range of 0.2-20 μm with some very fine particles of about 0.04 μm. As an example, fairly large filler particles may be used in combination with amorphous silica in order to allow for a dense packing of the fillers.

[0109] The term "particle size" is intended to mean the shortest dimension of the particulate material in question. In the event of spherical particles, the diameter is the "particle size", whereas the width is the "particle size" for a fiber- or needle-shaped particulate material. It should of course be understood that an important feature of such particles is the actual crystal size in that the crystal size (and not the particle size) will be determinative for the preferred crystal phase under given conditions (see also further below).

[0110] As used herein the term "nanofiller" is used synonymously with "nanosized particles" and "nanoparticles" and refers to filler particles having a size of at the most 100 nm (nanometers). As used herein for a spherical particle, "size" refers to the diameter of the particle. As used herein for a non-spherical particle, "size" refers to the longest dimension of the particle.

[0111] This being said, the weight ratio between (i) the nanofillers and (ii) fraction of the one or more fillers not being said nanofillers appears to play a certain role, and is typically in the range of 10:90 to 100:0, preferably 10:90 to 40:60, in particular 10:90 to 30:70.

[0112] In the embodiment where the composite material is for dental use, particularly useful fillers are zirconia, amorphous silica, milled barium-, strontium- or zirconium-containing glass, milled acid-etchable glass, fine YF_3 or YbF_5 particles, glass fibres, etc.

[0113] The one or more fillers comprise at least one filler ingredient. The term "filler ingredient" is intended to mean the filler or a fraction of the filler having particular physical properties, namely the inherent ability to compensate (by expansion) for volumetric shrinkage caused by polymerization and curing of the resin base. Thus, a certain filler, e.g. zirconia, may be included in the composite material, and a certain fraction of these filler particles may have particular physical properties, i.e. exist in a metastable crystalline phase (see the following), and thereby constitute the filler ingredient.

[0114] The particle size of the filler ingredient(s) is/are typically in the range of 0.01-50 μm. The filler ingredient(s) typically constitute(s) 20-100% of the total weight of the one or more fillers, e.g. 30-100%, such as 40-100% or 50-100%.

[0115] When calculated on the basis of the total weight of the composite material, the filler ingredient(s) typically constitute(s) 15-95% of the total weight of the composite material, e.g. 25-95%, such as 30-95%, more specifically 60-95%.

[0116] The one or more filler ingredients are present in a metastable first phase and are able to undergo a martensitic transformation to a stable second phase, where the volume ratio between said stable second phase and said metastable first phase of said filler ingredient(s) is at least 1.005, such as at least 1.01 or even at least 1.02 or at least 1.03.

[0117] In the present context, the term "metastable first phase" means that the filler ingredient existing in such as phase has a free energy that is higher than the free energy of the second phase, and that an activation barrier (F*) must be overcome before transformation from the first phase (high energy state) to the second phase (low energy state) can proceed. Thus, the phase transformation does not proceed spontaneously. It should be understood that the "system" in which the filler ingredient is metastable is the composite material including all its constituents, i.e. the composite material before curing.

[0118] The phase transformation is martensitic, which by definition means that the crystal structure of the filler ingredient needs no extra atoms to undergo the transformation. Thus, the transformation can be very fast, almost instantaneous.

[0119] The expression "free energy" refers to the sum of free energies from the particle bulk, the particle surface and strain contributions. For most practical purposes, only the free energies from the particle bulk and the particle surface need to be considered.

[0120] Thus, when considering various materials as potential filler ingredients, it is relevant to take into consideration the three main requirements:

[0121] 1. A first requirement for the filler ingredient is that the second crystalline phase thereof, within the selected particle size range, is “stable” under “standard” conditions, i.e. standard pressure (101.3 kPa) and at least one temperature in the range of 10-50° C., i.e. corresponding to the conditions under which the product is used.

[0122] 2. A second requirement for the filler ingredient is that a metastable first crystalline phase of the filler ingredient can exist under the same “standard” conditions.

[0123] 3. A third requirement for the filler ingredient is that the specific volume ratio between said stable second phase and said metastable first phase of said filler ingredient(s) is at least 1.005.

[0124] The expression “stable” refers to a phase which does not transform spontaneously under the conditions required for transforming the filler ingredient from the first metastable phase. Thus, the “stable” phase need not always be the phase with the “globally” lowest free energy, but it often will be.

[0125] The filler ingredients relevant in the present context comprise particular crystalline forms of some of the fillers mentioned above, in particular of the metal oxide fillers. A very useful example hereof is ZrO_2 (see in particular the section “Populations of zirconia particles” further below). Zirconia can exist in three major crystalline phases: the tetragonal phase, the cubic phase and the monoclinic phase. The specific volume (density^{-1}) of the three phases is 0.16, 0.16 and 0.17 cm^3/g, respectively. Thus, the monoclinic (the second phase) and one of the former two phases (the first phase) have a volume ratio higher than 1.005 (i.e. 1.045 and 1.046, respectively). The tetragonal and the cubic phases have higher bulk energy than the monoclinic phase at the standard conditions.

[0126] Illustrative examples of filler ingredients are:

[0127] Zirconia in the metastable tetragonal phase (specific volume=0.16 cm^3/g) which can transform into the monoclinic phase (specific volume=0.17 cm^3/g) (volume ratio=1.045);

[0128] Zirconia in the metastable cubic phase (specific volume=0.16 cm^3/g) which can transform into the monoclinic phase (specific volume=0.17 cm^3/g) (volume ratio=1.046);

[0129] Lanthanide sesquioxides (Ln_2O_3), where Ln=Sm to Dy. Transforms from monoclinic to cubic phase at 600-2200° C. with a volume expansion of 10%.

[0130] Nickel sulfide (NIS). Transforms from rhombohedral to hexagonal phase at 379° C. with a volume expansion of 4%. Density 5.34 g/mi.

[0131] Dicalcium silicate (belite) (Ca_2SiO_4). Transforms from monoclinic to orthorhombic phase at 490° C. with a volume expansion of 12%. Density 3.28 g/ml.

[0132] Lutetium borate ($LuBO_3$). Transforms from hexagonal to rhomhedral phase at 1310° C. with a volume expansion of 8%.

[0133] The surface energy of the tetragonal phase of zirconia is lower than the one of the monoclinic phase at standard temperature and pressure, which results in stable tetragonal (pure) zirconia crystals at room temperature. The crystals must be small (<10 nm) for the difference of surface energy to compete with difference of in bulk energy of the tetragonal and monoclinic phase.

[0134] For zirconia in the metastable tetragonal or cubic crystalline phase, the particle size is preferably in the range of 5-80,000 nm, such as 20-2000 nm, though it is believed that a mean particle size in the range of 50-1000 nm, such as 50-500 nm, provides the best balance between optical and structural properties.

[0135] In one embodiment, the filler ingredient(s) is/are able to undergo the martensitic transformation under the influence of ultrasound.

[0136] In view of the above, the filler ingredient(s) preferably include(s) zirconia (ZrO_2) in metastable tetragonal or cubic crystalline phase (see in particular the section “Populations of zirconia particles” further below).

[0137] In another embodiment, the filler ingredient(s) is/are able to undergo the martensitic transformation upon exposure to a chemical trigger.

[0138] In some instances, the activation barrier (F*) is not sufficiently large to prevent premature transformation from the first phase to the second phase. This may result in a spontaneous transformation upon storage of the composite material. Thus, in some embodiments, it is advantageous to stabilize the native filler ingredient in order to obtain a metastable phase that will not undergo more or less spontaneous, i.e. premature, transformation upon storage of the composite material. Stabilization of the metastable phase can, e.g., be achieved by doping, by surface modification of the filler particles, etc. as will be explained in the following.

[0139] In one variant, at least 50% of the nanofillers are zirconia particles.

[0140] Doping

[0141] Many crystal phases can be stabilized using doping materials. Generally, with increasing amounts of dopant, the more the phase is stabilised. In energy-terms, the activation barrier (F*) becomes higher the more dopant used. In order to trigger the phase transformation, the activation barrier must, however, be low enough for the trigger method to overcome the activation barrier, but high enough so that the transformation does not occur spontaneously.

[0142] Zirconia is typically stabilized using up to 20 mol-% of one or more dopants. Zirconla can be stabilized with stabilizer such as calcium, cerium, barium, yttrium, magnesium, aluminum, lanthanum, caesium, gadolinium and the like, as well as oxides and combinations thereof. More specifically, the recommended mol-% content for some useful dopants (if it is decided to include a dopant) is: Y_2O_3 (1-8%), MgO (1-10%), CaO (1-18%), CeO_2 (1-12%), and Sc_2O_2 (1-10%). A dopant level of, e.g., Y_2O_3 of 0-1% will typically not sufficiently stabilize the tetragonal phase and the cubic phase of zirconia, and such doped zirconia will, therefore, still undergo a phase transformation spontaneously to the monoclinic phase at room temperature. Adding too high a level of Y_2O_3, e.g. 8% or more, will stabilise the tetragonal phase and the cubic phase to such an extent that the activation barrier will become too high to overcome with most trigger process. At some point in between the activation barrier, the transformation can be triggered as described below. Adding more dopant will make the triggering more difficult and thus slower. Adding less dopant could make the zirconia unstable and not useful as a filler ingredient. [It should be noted that commercial grade zirconia contains a small fraction of hafnium. Such small amounts of hafnium are neglected in the discussion above, because hafnium is viewed as an integral part of zirconia.]

[0143] In a preferred embodiment, the metastable phase of the zirconia is stabilized by doping with an oxide selected from Y_2O_3, MgO, CaO, CeO_2, and Sc_2O_3.

[0144] Depending on the activation energy as explained--above, the levels of dopants for ZrO_2 could be Y_2O_3 (1-5%), MgO (1-5%), CaO (1-10%), and CeO_2 (1-6%), but for ideal zirconia crystal doping is not necessary so more specifically about 0-2%.

[0145] Surface Modification

[0146] Surface energy can be changed by surface modification. By modification of the surface by adsorption of a chemical constituent, it is possible to lower the surface energy of the first phase so that the sum of the surface energy and the bulk energy becomes lower than the surface energy and the bulk energy for the second phase, and thereby “reverse” the stability order of the first and second phase. In this way, the “metastability” of the first phase arises because the first phase is only “stable” as long as the chemical constituent is adsorbed thereto. Thus, the first phase is stabilised until the surface modification is altered or removed, e.g. by treatment with a chemical trigger.

[0147] Generally, the surface of the filler particles (nanofillers, filler ingredients, etc.) can also be treated with a coupling agent in order to enhance the bond between the filler and the resin. Suitable coupling agents include gamma-methacryloxypropyltrimethoxysilane, gamma-mercaptopropyltriethoxysilane, gamma-aminopropyltrimethoxysilane, and the like. Examples of useful silane coupling agents are those available from GE silicones, as SILQUEST A-174 and SILQUEST A-1230. For some embodiments of the composite material, the composite materials may include at least 1% by weight, more preferably at least 2% by weight, and most preferably at least 5% by weight other filler, based on the total weight of the composite material. For such embodiments, composite materials of the present invention preferably include at most 40% by weight, more preferably at most 20% by weight, and most preferably at most 15% by weight other filler, based on the total weight of the composite material.

[0148] Polymerizable Resin Base

[0149] Another important constituent of the composite material is the polymerizable resin base.

[0150] The term “polymerizable resin base” is intended to mean a composition of a constituent or a mixture of constituents such as monomer, dimers, oligomers, prepolymers, etc. that can undergo polymerization so as to form a polymer or polymer network. By polymer is typically meant an organic polymer. The resin base is typically classified according to the major monomer constituents.

[0151] The weight content of the polymerizable resin base in the composite material is typically in the range of 5-95%, or 5-90%, e.g. 5-70%, such as 5-60%, e.g. 5-40%.

[0152] Virtually any polymerizable resin base can be used within the present context. Polymerizable resin bases of particular interest are, of course, such that upon curing will cause a volumetric shrinkage of the composite material when used without a compensating filler ingredient.

[0153] The term “curing” is intended to mean the polymerisation and hardening of the resin base.

[0154] One class of preferred hardenable resins are materials having free radically active functional groups and include monomers, oligomers, and polymers having one or more ethylenically unsaturated groups. Alternatively, the hardenable resin can be a material from the class of resins that include cationically active functional groups. In another alternative, a mixture of hardenable resins that include both cationically curable and free radically curable resins may be used for the dental materials of the invention.

[0155] In the class of hardenable resins having free radically active functional groups, suitable materials for use in the invention contain at least one ethylenically unsaturated bond, and are capable of undergoing addition polymerization. Such free radically polymerizable materials include mono-, di- or poly- acrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-hexyl acrylate, stearyl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate, the diglycidyl methacrylate of bis-phenol A (“Bis-GMA”), bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyldimethylmethane, and trishydroxyethyl-isocyanurate trimethacrylate; the bis-acrylates and bis-methacrylates of polyethylene glycols of molecular weight 200-500, copolymerizable mixtures of acrylated monomers such as those in U.S. Pat. No. 4,652,274, and acrylated oligomers such as those of U.S. Pat. No. 4,642,126; and vinyl compounds such as styrene, diallyl phthalate, divinyl succinate, divinyladipate and divinylphthalate. Mixtures of two or more of these free radically polymerizable materials can be used if desired.

[0156] An alternative class of hardenable resins useful in the dental materials of the invention may include cationically active functional groups. Materials having cationically active functional groups include cationically polymerizable epoxy resins, vinyl ethers, oxetanes, spiro-orthocarbonates, spiro-orthoesters, and the like.

[0157] Preferred materials having cationically active functional groups are epoxy resins. Such materials are organic compounds having an oxirane ring which is polymerizable by ring opening. These materials include monomeric epoxy compounds and epoxides of the polymeric type and can be aliphatic, cycloaliphatic, aromatic or heterocyclic. These materials generally have, on the average, at least 1 polymerizable epoxy group per molecule, preferably at least about 1.5 and more preferably at least about 2 polymerizable epoxy groups per molecule. The polymeric epoxides include linear polymers having terminal epoxy groups (e.g. a diglycidyl ether of a polyoxyalkylene glycol), polymers having skeletal oxirane units (e.g. polybutadiene polyepoxide), and polymers having pendent epoxy groups (e.g. a glycidyl methacrylate polymer or copolymer). The epoxides may be pure compounds or may be mixtures of compounds containing one, two, or more epoxy groups per molecule. The “average” number of epoxy groups per molecule is determined by dividing the total number of epoxy groups in the epoxy-containing material by the total number of epoxy-containing molecules present.

[0158] These epoxy-containing materials may vary from low molecular weight monomeric materials to high molecular weight polymers and may vary greatly in the nature of their backbone and substituent groups. Illustrative of permissible substituent groups include halogens, ester groups, ethers, sulfonate groups, siloxane groups, nitro groups, phosphate groups, and the like. The molecular weight of the epoxy-containing materials may vary from about 58 to about 100,000 or more.

[0159] Useful epoxy-containing materials include those which contain cyclohexane oxide groups such as epoxycyclohexanecarboxylates, typified by 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, 3,4-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate, and bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate. For a more detailed list of useful epoxides of this nature, reference is made to the U.S. Pat. No. 3,117,099, which is incorporated herein by reference.

[0160] Particularly interesting resin bases that are useful for dental applications are those based on compounds selected from the group consisting of methacrylic acid (MA), methylmethacrylate (MMA), 2-hydroxyethyl-methacrylate (HEMA), triethyleneglycol dimethacrylate (TEGDMA), bisphenol-A-glycidyl dimethacrylate (BisGMA), bisphenol-A-propyl dimethacrylate (BisPMA), urethane-dimethacrylate (UDMA), and HEMA condensed with butanetetracarboxylic acid (TCB), as well as those based on combinations of the above-mentioned compounds. Such resin bases are, e.g., disclosed and discussed in U.S. Pat. No. 6,572,693. A particularly useful combination of compounds is TEGDMA and BisGMA, see, e.g., U.S. Pat. No. 3,066,112.

[0161] Other Constituents of the Composite Material

[0162] The composite material may comprise other constituents which provide beneficial Theological, cosmetic, etc. properties. Examples of such other constituents are dyes, flavorants polymerisation initiators and co-initiators, stabilizers, fluoride releasing materials, sizing agents, antimicrobial ingredients, fire retardants.

[0163] Thus, the resin base may include initiators and co-initiators, and illustrative examples of such compounds, particularly for use in dental applications, are benzoylperoxide (BPO), camphorquinone (CPQ), phenylpropanedione (PPD) and N,N-di(2-hydroxyethyl)-p-toluidine (DEPT), N,N-dimethyl-p-aminobenzoic acid ethyl ester (DAEM).

[0164] Shading can be achieved by using a number of color pigments. These include metal oxides, which provide the wide variety of colors of the composite; for example, oxides of iron can act as a yellow, red to brown pigment, copper as a green pigment, titanium as a yellowish-brown pigment, and cobalt imparts a blue color.

[0165] Fluorescence is more subtle optical properties that further enhance the natural-looking, life- like appearance or "vitality" of the tooth. Fluorescence is defined as the emission of electromagnetic radiation that is caused by the flow of some form of energy into the emitting body, which ceases abruptly when the excitation ceases. In natural teeth, components of the enamel, including hydroxyapatite, fluoresce under long wavelength ultraviolet light, emitting a white visible light. This phenomenon is subtle in natural daylight but still adds further to the vitality of the tooth. In contrast, under certain lighting conditions, the lack of fluorescence in a restorative material may become alarming. Under "black light" conditions, such as that often used in discotheque-type night clubs, if a restoration does not fluoresce, the contrast between the tooth and restoration may be so great that the tooth may actually appear to be missing. Fluorescence can, e.g., be achieved by adding an anthracene-like molecule.

[0166] The weight content of other constituents in the composite material is typically in the range of 0-10%, such as 0-5%, e.g. 0-4% or 1-5%.

[0167] Dental Filling Materials

[0168] In view of the above, the present invention also provides a dental filling material in the form of a composite material as defined above. In particular, the filler ingredient(s) of the composite material include(s) zirconia (ZrO_2) in metastable tetragonal or cubic crystalline phase.

[0169] In a particularly interesting embodiment, the dental filling material consists of:

[0170] 40-90% (e.g. 40-85%) by weight of the one or more fillers, wherein said one or more fillers comprise at least one filler ingredient, said filler ingredient(s) include(s) metastable zirconia in the tetragonal or cubic crystalline phase, and wherein said material further comprises one or more water- or acid-releasing agents;

[0171] 10-60% (e.g. 15-60%) by weight of the a polymerizable resin base, said resin base being based on one or more compound selected from the group consisting of methacrylic acid (MA), methylmethacrylate (MMA), 2-hydroxyethyl-methacrylate (HEMA), triethyleneglycol dimethacrylate (TEGDMA), bisphenol-A-glycidyl dimethacrylate (BisGMA), bisphenol-A-propyl dimethacrylate (BisPMA), urethane-dimethacrylate (UDMA), and HEMA condensed with butanetetracarboxylic acid (TCB);

[0172] 0-5% by weight of additives; and

[0173] 0-4% by weight of solvents and/or water.

[0174] In order to avoid premature curing of the polymerizable resin base, it may be advantageous to prepare and store the composite material as a two-component material intended for mixing immediately prior to use.

[0175] Use of the Composite Materials

[0176] The composite materials may be used and are cured essentially as conventional composite materials of the same type, except for the fact that the martensitic transformation should be controlled along with the curing of the resin base, i.e. at least in part by the chemical trigger(s) resulting from the water- and/or acid-releasing agents.

[0177] Generally, it is believed that the martensitic transformation can be activated either by physical means (e.g. application of mechanical pressure, tension, ultrasound, Roentgen irradiation, microwaves, longitudinal waves, electromagnetic irradiation such as light, near infrared irradiation, heating, etc.) or by chemical means (e.g. modification of the surface free energy by contacting the surface of the filler ingredient particles with a chemical, e.g. a constituent of the composite material or an additive such as water). Hence, it should be understood that the martensitic transformation may be further triggered by such means, although it is believed that the water- and/or acid-releasing agents will contribute significantly, or even completely, to the triggering of the martensitic transformation of the filler ingredient(s).

[0178] It should be understood that the martensitic transformation of the filler ingredient preferably shall take place with the curing (polymerization and hardening) of the resin base. However, since the crystals are small, the expansion due to phase transformation will not cause deterioration of the mechanical properties of the cured compound. Therefore, transformation triggered by slow mechanisms, e.g., diffusion of water into the cured compound or inner tensile stress build up by shrinkage from curing, will happen after the curing. Triggering the transformation before the curing is undesired since the volume compensating effect will be less or lost depending on how much is transformed before curing is initiated.

[0179] In order to make a phase transformation of a system where the first phase is metastable, but where the activation barrier is high because of a low surface energy of the first phase, the activation barrier can be lowered by surface modification. The activation of the phase transformation can be initiated by surface modification. The activation barrier will be the energy needed to make a surface modification that makes the surface energy of the phase higher (or make it more similar to the surface of the second phase).

[0180] Method of the Invention

[0181] In view of the above, the present invention also provides a method of controlling the volumetric shrinkage of a composite material upon curing, comprising the step of:

[0182] (a) providing a composite material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise at least one filler ingredient, said filler ingredient(s) being present in a metastable first phase and being able to undergo a martensitic transformation to a stable second phase, the volume ratio between said stable second phase and said metastable first phase of said filler ingredient(s) being at least 1.005, and wherein said material further comprises one or more water- or acid-releasing agents;

[0183] (b) allowing the resin base to polymerize and cure, and allowing the filler ingredient(s) to undergo a martensitic transformation from said first metastable phase to said second stable phase.

[0184] Preferably, the filler ingredient(s) should be triggered to undergo the martensitic transformation either simultaneous with the curing or subsequent to the curing in order to fully benefit from the volumetric expansion of the filler ingredient(s).

[0185] In another embodiment, the martensitic transformation of the filler ingredient(s) is initiated by exposure of the surface of the filler ingredient(s) to a chemical trigger. In this instance, the martensitic transformation is preferably triggered simultaneously with or after the curing is initiated, but before the curing is completed.

[0186] More specifically, the present invention further provides a method of reconstructing a tooth, comprising the step of

[0187] (a) preparing a cavity in the tooth;

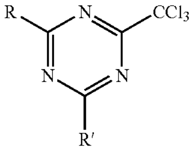
[0188] (b) filing said cavity with a dental filling material as defined above; and

[0189] (c) allowing the resin base of the dental filling material to polymerize and cure, and allowing the filler ingredient (s) of the dental filling material to undergo a martensitic transformation from a first metastable phase to a second stable phase.

[0190] The above-defined method for the reconstruction of a tooth may generally comprise further steps obvious to the person skilled in the art of dentistry.

[0191] In one embodiment, the martensitic transformation of the filler ingredient(s) is initiated by application of ultrasound (10-1000 kHz). In another embodiment, the martensitic transformation of the filler ingredient(s) is initiated by exposure of the surface of the filler ingredient(s) to a chemical trigger.

[0192] In a currently highly preferred embodiment of the above described methods, the water- or acid-releasing agent (s) comprise(s) at least one triazine compound, said triazine compound comprising one or two trihalomethyl groups represented by the following general formula (I):



(I)

wherein CCl_3 may be replaced by a CF_3 group; R represents the attachment point for an organic moiety; and R' is selected from the group consisting of a hydrogen atom, a further trihalomethyl group, a substituted C_{1-6}-alkyl group, an unsubstituted C_{1-6}-alkyl group, a substituted aryl group, an unsubstituted aryl group, and a substituted C_{2-6}-alkenyl group.

[0193] More generally, the present invention also relates to a composite material as defined herein for use in medicine, in particular in dentistry.

[0194] The present invention also relates to the use of a filler ingredient for the preparation of a composite material for reconstructing a tooth in a mammal, said filler ingredient having a metastable first phase and being able to undergo a martensitic transformation to a stable second phase, the volume ratio between said stable second phase and said metastable first phase of said filler ingredient being at least 1.005, and wherein said material further comprises one or more water- or acid-releasing agents. The nanofillers, filler ingredient(s) and the composite material are preferably as defined herein.

[0195] A Population of Zirconia Particles

[0196] It has been found that metastable zirconia may be used as a particularly suitable filler in composite materials. In particular, it has been found that zirconia which is capable of allowing a martensitic transformation to a stable second phase is particularly useful in order to counter the shrinkage normally occurring in composite materials.

[0197] Thus, a further aspect of the present invention relates to a population of zirconia particles having an average particle size in the range of 50-2000 nm, said particles being present in a metastable first phase and being able to undergo a martensitic transformation to a stable second phase, said transformation being effected to an extent of at least 80% within 300 sec when tested in the "Zirconia Particle Transformation Test" defined herein.

[0198] Furthermore, the present invention also relates to method for preparing such populations of zirconia particles.

[0199] The zirconia particles of the above-defined populations are present in a metastable first phase and are able to undergo a martensitic transformation to a stable second phase. Preferably, the volume ratio between said stable second phase and said metastable first phase of said zirconia particles is at least 1.005, such as at least 1.01 or even at least 1.02 or at least 1.03.

[0200] As mentioned above, the particles of the population of the first aspect of the invention are present in a metastable first phase and being able to undergo a martensitic transformation to a stable second phase, said transformation being effected to an extent of at least 80% within 300 sec when tested in the "Zirconia Particle Transformation Test" defined herein. Preferably, the transformation is effected to an extent of at 80% within 10-100 sec, such as within 20-60 sec.

[0201] Thus, when considering various crystal forms and particle sizes of the zirconia particles, it is relevant to take into consideration the two main requirements:

[0202] 1. A first requirement for the zirconia particles is that the second crystalline phase thereof, within the selected particle size range, is "stable" under "standard" conditions, i.e. standard pressure (101.3 kPa) and at least one temperature in the range of 10-50° C., i.e. corresponding to the conditions under which the product (typically a composite material) is used.

[0203] 2. A second requirement for the zirconia particles is that a metastable first crystalline phase of the zirconia particles can exist the under the same "standard" conditions.

[0204] For zirconia in the metastable tetragonal or cubic crystalline phase, the particle size is preferably in the range of 50-2000 nm, though it is believed that a mean particle size in the range of 50-1000 nm provides the best balance between optical and structural properties.

[0205] The zirconia particles are able to undergo the martensitic transformation under the influence of ultrasound. The zirconia particles may also undergo the martensitic transformation upon exposure to a chemical trigger.

[0206] In view of the above, the filler ingredient(s) preferably include(s) zirconia (ZrO_2) in metastable tetragonal or cubic crystalline phase.

[0207] Stabilization of the metastable phase can, e.g., be achieved by doping, by surface modification of the zirconia, etc. as it is explained hereinabove.

Embodiments

[0208] In order to obtain zirconia particles that could undergo a fast phase transformation, a large surface area, e.g. 10-250 m^2/g or even better 50-200 m^2/g, of the particles is preferred and also obtainable by the means described herein.

[0209] Thus, a further aspect of the present invention relates to a population of zirconia particles having an average particle size in the range of 50-2000 nm and a BET surface area of in the range of 10-250 m^2/g, said particles being present in a metastable first phase and being able to undergo a martensitic transformation to a stable second phase.

[0210] Preferably, this population of zirconia particles allows for a martensitic transformation to be effected to an extent of at least 80% within 300 sec when tested in the "Zirconia Particle Transformation Test" defined herein.

[0211] As mentioned above, the average particle size is typically in the range of 50-2000 nm, such as in the range of 50-1000 nm, in particular 100-600 nm.

[0212] Although the particles size of the zirconia particles generally is in the range of 50-2000 nm, it is believed that the particles may comprise smaller crystal domains with a homogeneous crystal lattice. Accordingly, it is preferred that the particles have crystal domain sizes in the range of 1-100 nm, such as in the range of 4-50 nm, such as 5-9 nm.

[0213] Furthermore, it is believed that the zirconia particles advantageously may have a certain porosity in order to allow for a rapid transformation (as described herein). Thus, the average pore size of the particles is preferably in the range of 10-50 nm.

[0214] With respect to the porosity, it is believed that zirconia particles having a porosity in the range of 0.1-20%, such as 0.2-10%, are particularly interesting.

[0215] Particularly interesting populations are those where the zirconia particles have

[0216] a. an average particle size in the range of 50-2000 nm and a BET surface area of in the range of 10-250 m^2/g, or

[0217] b. an average particle size in the range of 50-1000 nm and a BET surface area of in the range of 10-250 m^2/g, or

[0218] c. an average particle size in the range of 100-600 nm and a BET surface area of in the range of 10-250 m^2/g, or

[0219] d. an average particle size in the range of 50-2000 nm and a BET surface area of in the range of 50-200 m^2/g, or

[0220] e. an average particle size in the range of 50-1000 nm and a BET surface area of In the range of 50-200 m^2/g, or

[0221] f. an average particle size in the range of 100-600 nm and a BET surface area of in the range of 50-200 m^2/g, or

[0222] g. an average particle size in the range of 50-2000 nm and a BET surface area of in the range of 50-80 m^2/g, or

[0223] h. an average particle size in the range of 50-1000 nm and a BET surface area of in the range of 50-80 m^2/g, or

[0224] i. an average particle size in the range of 100-600 nm and a BET surface area of In the range of 50-80 m^2/g, or

[0225] j. an average particle size in the range of 50-2000 nm and a BET surface area of in the range of 75-150 m^2/g, or

[0226] k. an average particle size in the range of 50-1000 nm and a BET surface area of in the range of 75-150 m^2/g, or

[0227] l. an average particle size in the range of 100-600 nm and a BET surface area of in the range of 75-150 m^2/g, or

[0228] m. an average particle size in the range of 50-2000 nm and a BET surface area of in the range of 125-200 m^2/g, or

[0229] n. an average particle size in the range of 50-1000 nm and a BET surface area of in the range of 125-200 m^2/g, or

[0230] o. an average particle size in the range of 100-600 nm and a BET surface area of in the range of 125-200 m^2/g, or

[0231] p. an average particle size in the range of 100-350 nm and a BET surface area of in the range of 50-80 m^2/g, or

[0232] q. an average particle size in the range of 250-500 nm and a BET surface area of in the range of 50-80 m^2/g, or

[0233] r. an average particle size in the range of 400-600 nm and a BET surface area of in the range of 50-80 m^2/g, or

[0234] s. an average particle size in the range of 100-350 nm and a BET surface area of in the range of 75-150 m^2/g, or

[0235] t. an average particle size in the range of 250-500 nm and a BET surface area of in the range of 75-150 m^2/g, or

[0236] u. an average particle size in the range of 400-600 nm and a BET surface area of in the range of 75-150 m^2/g, or

[0237] v. an average particle size in the range of 100-350 nm and a BET surface area of in the range of 125-200 m^2/g, or

[0238] w. an average particle size in the range of 250-500 nm and a BET surface area of in the range of 125-200 m^2/g, or

[0239] x. an average particle size in the range of 400-600 nm and a BET surface area of In the range of 125-200 m^2/g.

[0240] Preparation of a Population of Zirconia Particles

[0241] The populations of particles defined above may be prepared by one of the methods described in the following.

[0242] Method A

[0243] One method for the preparation of a population of the above-defined zirconia particles involves heating of amorphous zirconia within a narrow temperature range. Thus, the present invention provides a method for the preparation of a population of zirconia particles as defined hereinabove, said method comprising the step of heating a sample of amorphous zirconia to a temperature within the crystal formation temperature and not higher than the transition temperature of the zirconia from tetragonal to monoclinic both can determined by DSC or XRD. Heating a sample to a temperature that is below the crystal formation temperature will lead to a sample with few or none crystals with no possibility of phase transformation. Heating a sample to a temperature that is much higher (e.g. 200° C. higher) than the crystal formation will gradually turn the sample from the tetragonal phase to a monoclinic phase. However this may be preferably to have heated to a temperature somewhat (say 20° C.) higher than the crystal formation temperature. This ensures that the zirconia is transformed from the amorphous state into the tetragonal phase.

[0244] The heating process can be done in normal air standard pressure, but preferably in dry air because humidity (water) promotes the monoclinic phase of zirconia. A dry air flow is therefore preferably, other dry inert atmospheres such as nitrogen, argon or helium could also be used. Since a controlled heating is necessary in order not to create overshoot depending on the oven a heating ramp of 5° C. is useful. Once reached-the set-point temperature the sample should be kept at that temperature long (say 30-120 min) enough to enable the crystallisation process to occur, but not to long (say 24 hours) since sintering of the crystals could create too much of the monoclinic phase.

[0245] Preferably, the amorphous zirconia particles have a BET surface area of in the range of 250-550 m^2/g, or 250-500 m^2/g, such as in the range of 350-500 m^2/g.

[0246] Such amorphous zirconia may be synthesized from a zirconate, e.g. $ZrOCl_2.8H_2O$, by precipitation with a basic solution, e.g. a NH_3 solution. After precipitation and filtration, the zirconia is preferably digested at 100° C. in deionised water for a suitably period of time, e.g. in the range of ½-48 hours, such as in the range of 6-12 hours. Alternatively, the amorphous zirconia is synthesized from a zirconate, e.g. $ZrOCl_2.8H_2O$, by precipitation with a basic solution at pH 10, e.g. a conc. NH_3 solution. After precipitation, the zirconia is preferably digested under reflux (at 100° C.) in the mother liquid for a suitably period of time, e.g. In the range of 6-24 hours, such as in the range of 8-20 hours.

[0247] Method B

[0248] Another method for the preparation of a population of the above-defined zirconia particles involves the step forming a suspension of a powder of small tetragonal crystals of zirconia in a strong aqueous base e.g. alkali base such as KOH or NaOH under reflux for 24 h. The crystals are then grown in a strong base suspension (1-5 M) to a size, where the bulk energy of the crystals becomes comparable to the surface energy stabilising the tetragonal phase, thus, lowering the activation barrier. The crystals are grown under hydrothermal conditions e.g. high temperatures in the range of 150-200° C. using a closed reactor (an autoclave, pressure reactor) only with use of waters vapour pressure (because of the heating) creating pressures up to 20 bars. Under these conditions a resolvation and reprecipitation takes place. To achieve large enough crystals the zirconia particles must remain in the pressure reactor for 24 h.

[0249] Preferably, the suspension is heated for a period of not less than 2 hours.

[0250] Composite Materials

[0251] Generally, the populations of particles defined above are believed to be particularly useful as filler ingredients-in composite materials. In particular, the zirconia particles of the present invention are useful for applications where volumetric shrinkage upon curing of the composite material would otherwise be undesirable or even prohibitive.

[0252] More particularly, the present invention provides a composite material comprising one or more fillers (including the zirconia particles defined herein) and a polymerizable resin base.

[0253] A particular feature of the present invention is that the martensitic transformation of the zirconia particles can be provoked by a trigger mechanism.

[0254] Thus, in a preferred embodiment of the composite material, the resin base, upon polymerization and in the absence of any compensating effect from the zirconia particles, causes a volumetric shrinkage (ΔV_{resin}) of the composite material of at least 0.50%, and wherein said composite material, upon polymerization of said resin base and upon phase transformation of said zirconia particles, exhibits a total volumetric shrinkage (ΔV_{total}) of at least 0.25%-point less than the uncompensated volumetric shrinkage (ΔV_{resin}) caused by the resin base. More particularly, the volumetric shrinkage (ΔV_{resin}) is at least 1.00%, such as at least 1.50%, and the total volumetric shrinkage (ΔV_{total}) is at least 0.50%-point less, such as 1.00%-point less than the uncompensated volumetric shrinkage.

[0255] The composite material typically comprises 5-95%, or 10-90%, by weight of the one or more fillers (including the zirconia particles) and 5-95%, or 10-90%, by weight of the polymerizable resin base, in particular 30-95%, or 30-90%, by weight of the one or more fillers and 5-70%, or 10-70%, by weight of the polymerizable resin base.

[0256] Calculated by volume, the composite material typically comprises 20-80% by volume of the one or more fillers (including zirconia particles) and 20-80% by volume of the polymerizable resin base, such as 25-80%, or 25-75%, by volume of the one or more fillers and 25-75% by volume of the polymerizable resin base.

[0257] Preferably, the composite material is substantially solvent free and water free. By the term "substantially solvent free and water free" is meant that the composite material comprises less than 1%, such as less than 0.5% or less than 150 ppm, by weight of solvents and/or water.

[0258] Alternatively, the present invention provides a composite material comprising one or more fillers (including zirconia particles) and a polymerizable resin base, wherein said one or more fillers comprises metastable zirconia in the tetragonal or cubic crystalline phase, wherein said resin base, upon polymerization and in the absence of any compensating effect from the zirconia particles, causes a volumetric shrinkage (ΔV_{resin}) of the composite material of at least 0.50%, and wherein said composite material, upon polymerization of said resin base and upon phase transformation of said filler ingredient(s), exhibits a total volumetric shrinkage (ΔV_{total}) of at least 0.25%-point less than the uncompensated volumetric shrinkage (ΔV_{resin}) caused by the resin base, and wherein said material further comprises one or more water- or acid-releasing agents.

[0259] It is apparent that the one or more fillers, and in particular the zirconia particles, are important constituents of the composite material. Fillers are generally described above under "Fillers/Filler ingredients".

[0260] The one or more fillers comprise at least one filler ingredient which (for the purpose of this section) at least include the zirconia particles. The term "filler ingredient" is intended to mean the filler or a fraction of the filler having particular physical properties, namely the inherent ability to compensate (by expansion) for volumetric shrinkage caused by polymerization and curing of the resin base.

[0261] The zirconia particles typically constitute(s) 20-100% of the total weight of the one or more fillers, e.g. 30-100%, such as 40-100% or 50-100%.

[0262] When calculated on the basis of the total weight of the composite material, the zirconia particles typically constitute(s) 15-90% of the total weight of the composite material, e.g. 25-90%, such as 30-90%, more specifically 60-85%.

[0263] Another important constituent of the composite material is the polymerizable resin base which is described in detail under "Polymerizable resin base".

[0264] The composite material may comprise other constituents as disclosed under "Other constituents of the composite material".

[0265] The population of zirconia particles is particularly useful in connection with dental filling material, see, e.g., under "Dental filling materials". The general use of the population of zirconia particles in composite materials is described above under "Use of the composite materials".

[0266] The initiation of martensitic transformation of the population of zirconia particles by means of application of ultrasound can advantageously be combined with the curing of the resin base by means of ultrasound, see, e.g., under "Combined initiation of martensitic transformation and curing of resin base by means of ultrasound".

Examples

[0267] The phase transformation is measured with the use of powder XRD. The volume fraction of monoclinic zirconia V_m can be determined from the following relationships:

$$X_m=(I_m(111)+I_m(11-1)/(I_m(111)+I_m(11-1)+I_t(111))$$

$$V_m=1.311\,X_m/(1+0.311X_m)$$

[0268] Where $I_m(111)$ and $I_m(11-1)$ are the line intensities of the (111) and (11−1) peaks for monoclinic zirconia and $I_t(111)$ is the intensity of the (111) peak for tetragonal zirconia.

Example 1

[0269] Metastable tetragonal zirconia particles were subjected to normal air and phase transformed by the water content in less than 1 minute. With the use of XRD it was determined that the 70% of the tetragonal zirconia were phase transformed to the monoclinic phase.

Example 2

[0270] Metastable tetragonal zirconia particles were subjected to a 1.5 M HCl solution in iso-propanol and phase transformed by the HCl content. With the use of XRD it was determined that the 60% of the tetragonal zirconia were phase transformed to the monoclinic phase.

Example 3

[0271] Metastable tetragonal zirconia particles were subjected to a 1.5 M HCl solution in water and phase transformed by the water and HCl content. With the use of XRD it was determined that the 90% of the tetragonal zirconia were phase transformed to the monoclinic phase.

Example 4

[0272] A test composite material is prepared by mixing 65 vol % of the zirconia particles to be tested and 35 vol % of a polymer resin system (36% (w/w) BisGMA, 43% (w/w) UDMA, 19.35% (w/w) TEGDMA. 0.3% (w/w) camphorquinone (CQ), 0.3% (w/w) N,N-dimethyl-p-amino-benzoic acid ethylester (DABE), 0.05% (w/w) 2,6-di-tert-butyl-4-methylphenol (BHT) and 1% (w/w) o-hydroxybenzyl ethanol. The phase transformation is initiated by UV-radiation, simultaneously with the curing of resin with light (blue).

Example 5

[0273] A test composite material is prepared by mixing 65 vol % of the zirconia particles to be tested and 35 vol % of a polymer resin system (36% (w/w) BisGMA, 43% (w/w) UDMA, 19.350% (w/w) TEGDMA. 0.3% (w/w) camphorquinone (CQ), 0.3% (w/w) N,N-dimethyl-p-amino-benzoic acid ethylester (DABE), 0.05% (w/w) 2,6-di-tert-butyl-4-methylphenol (BHT) and 1% (w/w) 1-chloroanthraquinone). The phase transformation is initiated by UV-radiation, simultaneously with the curing of resin with light (blue).

Example 6

[0274] A test composite material is prepared by mixing 65 vol % of the zirconia particles to be tested and 35 vol % of a polymer resin system (36% (w/w) BisGMA, 43% (w/w) UDMA, 19.35% (w/w) TEGDMA. 0.3% (w/w) camphorquinone (CQ), 0.3% (w/w) N,N-dimethyl-p-amlno-benzoic acid ethylester (DABE), 0.05% (w/w) 2,6-di-tert-butyl-4-methylphenol (BHT), 0.8% (w/w) diphenyliodonium hexafluorophosphate and 0.2% acridine dye). The phase transformation is initiated by light, simultaneously with the curing of resin.

Example 7

[0275] A test composite material was prepared by mixing 200 mg of the zirconia particles to be tested and 500 mg of a polymer resin system (36% (w/w) BisGMA, 43% (w/w) UDMA, 19.35% (w/w) TEGDMA. 0.5% (w/w) camphorquinone (CQ), 0.5% (w/w) N,N-dimethyl-p-aminobenzoic acid ethylester (DABE), 0.05% (wlw)) with 50 mg of the trigger molecule (2-(4-Methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine). The phase transformation was initiated by light from a curing device at max. intensity 1100 mW/cm^2 (Bluephase from Ivoclar Vivadent), simultaneously with the curing of resin. After 2 minutes 15% of the zirconia particles were phase transformed. After 30 min. 53% of the zirconia particles were phase transformed.

Example 8

[0276] In a glove-box with a water content of <10 ppm water 210 mg of the zirconia particles and 150 mg Ph_2ICl were weighted into a glass flask. Then 21 g. MeOH was added with a magnetic stirring bar. The suspension was exposed to 22 hours of UV (9 W). The suspension was then filtered on a paper filter and dried in vacuum. The powder was cured in a dental resin (36% (w/w) BisGMA, 43% (w/w) UDMA, 19.35% (w/w) TEGDMA. 0.5% (w/w) camphorquinone (CQ), 0.5% (w/w) N,N-dimethyl-p-aminobenzoic acid ethylester (DABE), 0.05% (w/w)). The phase transformation was measured to 40%.

1. A composite material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise at least one filler ingredient, said filler ingredient(s) being present in a metastable first phase and being able to undergo a martensitic transformation to a stable second phase, the volume ratio between said stable second phase and said metastable first phase of said filler ingredient(s) being at least 1.005, and wherein said material further comprises one or more water- or acid-releasing agents.

2. A composite material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise at least one filler ingredient, said filler ingredient(s) including metastable zirconia in the tetragonal or cubic crystalline phase, wherein said resin base, upon polymerization and in the absence of any compensating effect from the one or more filler ingredients, causes a volumetric shrinkage (ΔV_{resin}) of the composite material of at least 0.50%, and wherein said composite material, upon polymerization of said resin base and upon phase transformation of said filler ingredient(s), exhibits a total volumetric shrinkage (ΔV_{total}) of at least 0.25%-point less than the uncompensated volumetric shrinkage (ΔV_{resin}) caused by the resin base, and wherein said material further comprises one or more water- or acid-releasing agents.

3. The composite material according to claim **1**, which is a dental filling material.

4. The dental filling material according to claim **3**, wherein the filler ingredient(s) of the composite material include(s) zirconia (ZrO_2) in metastable tetragonal or cubic crystalline phase.

5. The dental filling material according to claim **4**, consisting of:

40-85% by weight of the one or more fillers, wherein said one or more fillers comprise at least one filler ingredient, said filler ingredient(s) include(s) metastable zirconia in the tetragonal or cubic crystalline phase;

15-60% by weight of the a polymerizable resin base, said resin base being based on one or more compound selected from the group consisting of methacrylic acid (MA), methylmethacrylate (MMA), 2-hydroxyethylmethacrylate (HEMA), triethyleneglycol dimethacrylate (TEGDMA), bisphenol-A-glycidyl dimethacrylate (BisGMA), bisphenol-A-propyl dimethacrylate (BisPMA), urethane-dimethacrylate (UDMA), and HEMA condensed with butanetetracarboxylic acid (TCB);

0.01-5% by weight of water-releasing agents;

0-5% by weight of additives; and

0-4% by weight of solvents and/or water.

6. The composite material according to claim **1**, wherein the one or more water- or acid-releasing agents comprises at least one water-releasing agent.

7. The composite material according to claim **1**, wherein the one or more water- or acid-releasing agents comprises at least one acid-releasing agent.

8. The composite material according to claim **1**, wherein the one or more water- or acid-releasing agents is a combination at least one water-releasing agent and at least one acid-releasing agent.

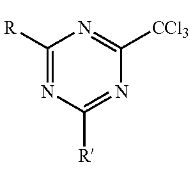
9. A method of controlling the volumetric shrinkage of a composite material upon curing, comprising the step of:

(a) providing a composite material comprising one or more fillers and a polymerizable resin base, wherein said one or more fillers comprise at least one filler ingredient, said filler ingredient(s) being present in a metastable first phase and being able to undergo a martensitic transformation to a stable second phase, the volume ratio between said stable second phase and said metastable first phase of said filler ingredient(s) being at least 1.005, and wherein said material further comprises one or more water- or acid-releasing agents;

(b) allowing the resin base to polymerize and cure, and allowing the filler ingredient(s) to undergo a martensitic transformation from said first metastable phase to said second stable phase.

10. The method according to claim **9**, wherein the composite material is as defined in claim **4**.

11. The composite material according to claim **1**, wherein the water- or acid-releasing agent(s) comprise(s) at least one triazine compound, said triazine compound comprising one or two trihalomethyl groups represented by the following general formula (I):



(I)

wherein CCl_3 may be replaced by a CF_3 group; R represents the attachment point for an organic moiety; and R is selected from the group consisting of a hydrogen atom, a further trihalomethyl group, a substituted C_{1-6}-alkyl group, an unsubstituted C_{1-6}-alkyl group, a substituted aryl group, an unsubstituted aryl group, and a substituted C_{2-6}-alkenyl group.

12. A composite material as defined in claim **1** for use in medicine.

13. The composite material according to claim **2**, which is a dental filling material.

14. The dental filling material according to claim **13**, wherein the filler ingredient(s) of the composite material include(s) zirconia (ZrO_2) in metastable tetragonal or cubic crystalline phase.

15. The dental filling material according to claim **14**, consisting of:

40-85% by weight of the one or more fillers, wherein said one or more fillers comprise at least one filler ingredient, said filler ingredient(s) include(s) metastable zirconia in the tetragonal or cubic crystalline phase;

15-60% by weight of the a polymerizable resin base, said resin base being based on one or more compound selected from the group consisting of methacrylic acid (MA), methylmethacrylate (MMA), 2-hydroxyethyl-methacrylate (HEMA), triethyleneglycol dimethacrylate (TEGDMA), bisphenol-A-glycidyl dimethacrylate (BisGMA), bisphenol-A-propyl dimethacrylate (BisPMA), urethane-dimethacrylate (UDMA), and HEMA condensed with butanetetracarboxylic acid (TCB);

0.01-5% by weight of water-releasing agents;

0-5% by weight of additives; and

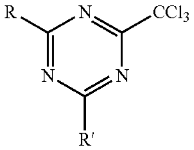
0-4% by weight of solvents and/or water.

16. The composite material according to claim **2**, wherein the one or more water- or acid-releasing agents comprises at least one water-releasing agent.

17. The composite material according to claim **2**, wherein the one or more water- or acid-releasing agents comprises at least one acid-releasing agent.

18. The composite material according to claim **2**, wherein the one or more water- or acid-releasing agents is a combination at least one water-releasing agent and at least one acid-releasing agent.

19. The composite material according to claim **2**, wherein the water- or acid-releasing agent(s) comprise(s) at least one triazine compound, said triazine compound comprising one or two trihalomethyl groups represented by the following general formula (I):



(I)

wherein CCl_3 may be replaced by a CF_3 group; R represents the attachment point for an organic moiety; and R is selected from the group consisting of a hydrogen atom, a further trihalomethyl group, a substituted C_{1-6}-alkyl group, an unsubstituted C_{1-6}-alkyl group, a substituted aryl group, an unsubstituted aryl group, and a substituted C_{2-6}-alkenyl group.

* * * * *

VII

Shrinkage reduction of dental composites by addition of expandable zirconia filler

M. Skovgaard[1,2*], K. Almdal[2], B. F. Sørensen[3], S. Linderoth[3], A. van Lelieveld[4]

[1] *DentoFit A/S, Frederiksborgvej 399, 4000 Roskilde, Denmark,*

[2] *Department of Micro- and Nanotechnology, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark*

[3]*Risø National Laboratory for Sustainable Energy, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark*

[4]*Aneedle, Engelstedsgade 32 2., 2100 Copenhagen East, Denmark*

**Phone: +45 46774284, Fax: +45 46774791, e-mail address: ms@dentofit.com*

Abstract

A problem with dental resin composites is the polymerization shrinkage, which makes the filling loosen from the tooth or induces crack formation. We have developed an expandable metastable tetragonal zirconia filler, which upon reaction with water, is able to counter the polymer shrinkage. The shrinkage of the composite was calculated from density measurements using Archimedes method. The rate of the phase transformation in resin was measured by determining the volume fraction of monoclinic zirconia (v_m). The composite had a v_m of 0.5 after 8 h of water storage. The overall shrinkage of the composites was reduced from 3.2% (initially) to 1.7%.

Keywords: dental composite material, polymerization shrinkage, zirconia, phase transformation

Introduction

When a dental resin composite cures, polymerization shrinkage of the material will occur. For most commercial composites the free polymerization shrinkage is 2-3.5 % and can result in high stresses as at the interface between composite and tooth structure. These stresses can lead to the formation of a crack along the interface between the composite and the tooth. The formation of a crack can give raise to discoloration due to colorants from *e.g.* coffee and red wine entering the crack or - worse - to secondary caries and infections of the dental pulp due to bacteria[1].

During the last few decades substantial efforts have addressed the shrinkage in dental resin composites by an approach based on modification of the monomer system to reduce the polymerization shrinkage. The typical dimethacrylate monomers has been replaced with ring-opening systems such as photocurable oxirane/polyols[2, 3], alicyclic spiroortocarbonates/epoxy comonomers[4] and recently a new composite material (Filtek Silorane) based on silorane monomers has been introduced[5-7]. Another approach is the use of cyclopolymerizable monomers, which gives both a higher degree of conversion (90%) and a 40% reduction of polymerization shrinkage in comparison with the commonly used triethylene glycol dimethacrylate[8]. Furthermore, the use of liquid crystal monomers[9] and branched[10], hyperbranched[11] and dendritic monomers[12] has been proposed as modifications of the resin system which can lead to reduction of the curing contraction in dental resin composites.

Zirconia particles currently find use, in combination with glass particles, as fillers in dental resin composites in order to improve the cured resin mechanical properties or to make the material radiopaque (attenuation of electromagnetic radiation). Radiopacity can be useful in resin composites as distinguishing between composite and tooth becomes feasible with x-ray imaging.

For aesthetic reasons a low visual opacity (the degree to which light is attenuated) is desired to give the cured composite a life-like luster. The refractive index of zirconia is substantially higher than that of the cured methacrylate matrix and zirconia particles have depending on the particles size, a large potential for light scattering and thereby a potential for increasing the opacity. Thus small particles are desirable since small sizes promote both low opacity, good depth of cure, and also low abrasion. The maximum particle size should be substantially below the wave length of visible light to prevent scattering and particle size below 60 nm are considered optimal[13]. Addition of zirconia to resin composites is known from the commercial products such as Filtek™ supreme plus and Filtek™ Z250 (3M ESPE, St. Paul, MN, USA).

At room temperature (RT) and atmospheric pressure, the thermodynamic stable phase of pure zirconia is the monoclinic phase which goes through the following phases as the temperature is raised:

$$\text{monoclinic} \rightarrow \text{tetragonal} \rightarrow \text{cubic} \rightarrow \text{melt}$$

The manufacture of metastable tetragonal phase ZrO_2 at RT is feasible through suitable control of the crystal size and processing parameters. The metastable tetragonal phase easily transforms to the monoclinic phase. The tetragonal to monoclinic (t→m) phase transformation is accompanied by a decrease in density. The crystals expand 3-5 vol%. This expansion is for instance used in transformation toughening of ceramic materials[14]. The known triggers for this transformation are: chemical reaction with e.g. water[15], annealing[16] or mechanical stress[17]. The stability of the tetragonal phase at RT has been widely studied and a number of degradation mechanisms have been proposed; some based on hydrolysis of the surface[18] others on reactions with point defects and oxygen vacancies in the crystal structure[19].

We have developed a metastable tetragonal zirconia filler that transforms to the monoclinic phase upon exposure to water. In the present work we analyze the ability of this filler to counteract the polymerization shrinkage in a polymer matrix and reduce the overall curing shrinkage of the composite upon exposure to water.

Experimental

Materials

All chemicals were supplied by Sigma-Aldrich (St. Louis, MO, USA) and used as received. Highly porous (specific surface area of ~150 m^2 /g) nanocrystalline tetragonal zirconia powders were synthesized as previously described[17] by controlled hydrolysis of $ZrOCl_2$ followed by careful calcination. The synthesized t-ZrO_2 powders were kept in water-free environment for further treatment to prevent the t→m phase transformation[20] which is induced by exposure to water vapor.

Compounding of zirconia powder

Three composites were prepared by compounding zirconia powder and silanized glass particles into a standard methacrylic dental resin containing a camphorquinone/ ethyl 4-dimethylamino benzoate photoinitiator system. 1) 42 wt-% tetragonal zirconia, 21 wt-% silanized glass and 37 wt-% resin. 2) 32 wt-% tetragonal zirconia, 33 wt-% silanized glass and 35 wt-% resin. Monoclinic zirconia was obtained by exposing the metastable zirconia to humidity in the air over night followed by drying under vacuum for two days at 120˚C and used for compound 3) 32 wt-% phase transformed zirconia, 33 wt-% silanized glass and 35 wt-% resin. After compounding, the samples were exposed to vacuum in order to remove air bubbles from the composites.

Curing

Discs (15 mm in diameter and 1.3 mm in thickness) of composite were prepared between to glass plates and cured by exposing the samples to the light of a Bluephase® light probe (Ivoclar Vivadent, Liechtenstein) for 2 minutes on each side.

Water testing

The cured samples were stored in water at 40˚C for 0, 8, 24, 48, 72, 120 and 168 hours. After storage the samples were subjected directly to the XRD measurements for the phase analysis.

Density measurement

The change in density between a sample stored at 40˚C in water and in air at 40˚C was determined for all three materials by the use of Archimedes method. The volume change compared with the uncured composite was calculated.

Characterization

The composite samples were analyzed by x-ray diffraction: XRD patterns were scanned in 0.1 steps (2θ), in the 2θ range from 20˚ to 65˚, with a fixed counting time (30 sec.). The XRD patterns were analyzed using WinX^{POW} software. The t-ZrO_2 and m-ZrO_2 volume fractions (v_t and v_m) were calculated from the integral intensities of the monoclinic diffraction lines (-111) and (111) and the tetragonal diffraction line (101), following a procedure proposed by Toraya et al[21].

Results

The XRD patterns recorded from the water stored discs of composite 1 after 0 h and 168 h are illustrated in Figure 1. It is observed that the reflection (101) of tetragonal zirconia at 30.3˚ = 2θ is the dominating in the 0 h sample. The sample consists mainly of tetragonal ZrO_2 that gives broad peaks in the XRD patterns as a result of small crystal sizes. The two reflections ((-111) and (111) at 2θ = 28.2° and 31.5° respectively) from monoclinic zirconia increases in intensity with increasing water storage time and the (101) reflection decreases, indicating a tetragonal to monoclinic transformation.

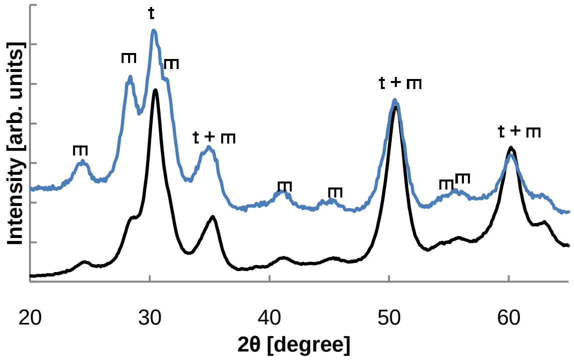


Figure 1. XRD patterns of composite 1 after 0 hour (black) and 168 hours (blue) water storage at 40˚C t=tetragonal reflection, m=monoclinic reflection.

The calculated volume fractions of the monoclinic crystals (v_m) in the samples are plotted against the storage time (Figure 2). The plot shows that after 48 hours is the volume fraction of the monoclinic phase stabilized at ~0.6 and that most of the phase transformation happens within the first 8 hours.

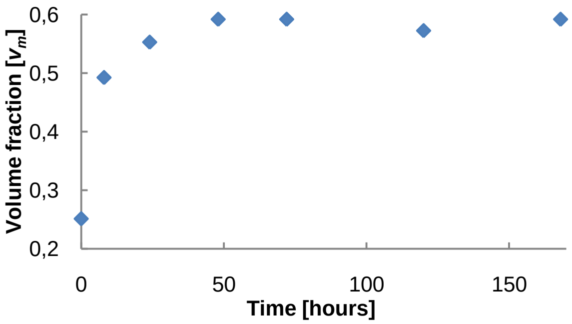


Figure 2. Volume fraction of the monoclinic phase in composite 1 plotted against storage time in water at 40˚C.

The volume change over time for composite 1 and 2 stored in water and in air at 40˚C is illustrated in Figure 3. Increased polymerization shrinkage is observed during the first 24 h for all four samples, but is followed by subsequent decreases in the volume change for the two samples stored in water. The volume change in the two samples stored in air is fairly constant after the first 24 h. Composite 1 was subjected to prolonged measurements and the volume change stabilized at ~ -1.5 % after 21 days (results not shown).

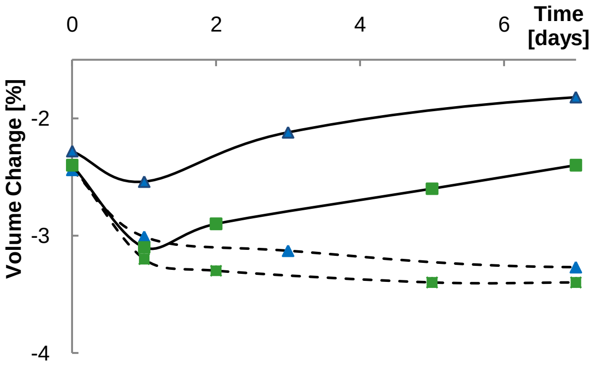


Figure 3. Volume change compared with the uncured composite for composite 1 (▲) and 2 (■) during water storage at 40˚C (solid line) and storage in air at 40˚C (dotted line). The lines are just added as a guideline for the eye.

For composite 3, which contains phase transformed zirconia, only a small difference in the volume change between the sample stored in water and the sample stored in air is observed (Figure 4). Similarly to the air stored samples of composite 1 and 2 (Figure 3), the composite shrinks the first 24 h and then stabilizes.

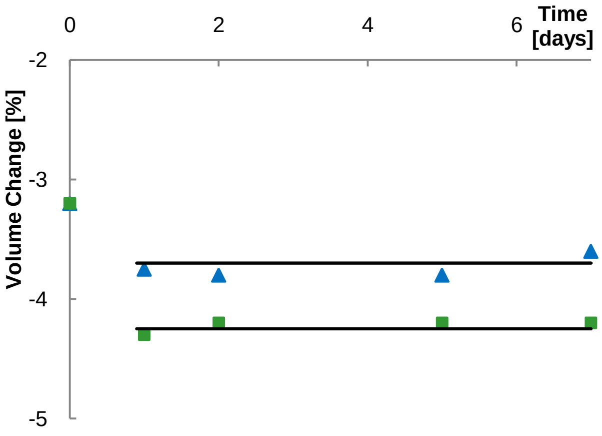


Figure 4. Volume change compared with the uncured composite for composite 3 during water storage at 40˚C (▲) and storage in air at 40˚C (■).

Discussion

Based on the recorded XRD patterns it is observed that phase transformation of the metastable tetragonal zirconia filler into the monoclinic phase occurs by exposure to water. The water diffuses into the composite and reacts with the surface of the zirconia crystals. Most of the phase transformation happened within the first 8 h where a volume fraction of the monoclinic phase of ~0.5 was reached. The monoclinic volume fraction continues to increase further and the level of phase transformation stabilized at 0.6 after two days. This stabilization of the monoclinic volume fraction during aging has previous been documented[22]. The phase transformation can be increased even further by using a more hydrophilic monomer system (data not included). The increased number of water molecules that reaches the zirconia surface will increase both the transformation rate and the final transformation level. However, the higher water uptake in the polymer matrix achieved with a more hydrophilic monomer system will compromise the mechanical properties of the composite.

The water induced phase transformation of metastable tetragonal zirconia into the monoclinic phase has an effect on the overall shrinkage of the composite. The density measurements show that the observed polymerization shrinkage during the first 24 h is followed a counteracting expansion due to the expansion of the zirconia filler which leads to stabilization of the cured composite volume after 3 weeks at a lower level of contraction.

Figure 3 shows that addition of 42 wt-% zirconia to a composite gives rise to a 44% reduction of the shrinkage in comparison with the equivalent sample stored in air. The corresponding volume reduction for the test composite containing 32 wt-% zirconia is 29%. This difference is expected since composite 1 has a higher volume fraction of the expandable filler; this leads to a higher reduction of the overall composite shrinkage. In order to test whether the shrinkage reduction was caused by differences in water uptake rather than differences in filler expansion, the third composite containing volume stable zirconia (composite 3) was prepare. As shown in Figure 4, the time dependence of volume change for this sample is qualitatively different (no minimum) from samples of composite 1 and 2. Furthermore, the overall shrinkage is only reduced with 11% compared with samples stored in air. Thus iy can be concluded that at least 62% of the overall shrinkage reduction in composite 2 is caused by expansion of the zirconia filler and of cause this figure will be even higher for composite 1.

The expected volume change after a week of water storage was calculated for composite 2. The calculation was based on a change in v_m of 0.35, a transformation expansion of 4.4 vol.-% for zirconia and that the water uptake is independent of the phase state of the zirconia particles such that the aging of composite 3 (0.55 vol.-%) is taken as a measure of the water uptake. The expected volume change was calculated to -2.7 %. The calculated volume change can be compared with the actual volume change of -2.4 % for composite 2. The measured shrinkage is thus less than expected. We ascribe the difference to higher initial water content of composite 3 than composite 2 since the particles used for composite 3 were exposed to ambient atmosphere prior to compounding. The phase transformed zirconia in composite 3 was dried at 120 °C for 48 h before compounding, but there is no guarantee that this procedure will remove water from the surface of the zirconia particles to the same extend as the calcination process used for the fabrication of the particles used for composite 2. Higher initial water content in the composite will reduce the amount of water absorbed before equilibrium is reached. This would lead to a lower reduction of the shrinkage of composite 3. Prior to compounding the water content in two composite samples was analyzed with Karl Fisher titration and the water content were determined to 0.017% and 0.19%, respectively, for composite 2 and 3. If this difference in water content is added to the shrinkage reduction in composite 2, the expected volume change will be -2.5 %. This is close to the observed volume change of -2.4%.

Possibilities for further reduction of the overall shrinkage include addition of increased amounts of zirconia filler, and combination of the expandable zirconia filler with a low shrinkage monomer or a low shrinkage composite system. A composite with an overall shrinkage below 1% seems attainable. This will increase the durability of dental restorations and allow the dentist to make bulk fillings using polymer based composites and hence reduce chair time. Another interesting idea is to the use the expandable zirconia filler in a two-component composite containing a condensating monomer system. It is expected that the stabilization time in such a system will be shorter, possible hours rather than days, since the phase transformation will be induced due to the formation of water in the condensation polymerization. The presented results are based on initial tests of the zirconia material and they show a potential for further reduction of the overall composite shrinkage. Additional work has been initiated to improve the system further to reach an end target of a composite system with an overall shrinkage below 1 %.

Conclusion

The results of the present study show that polymerization shrinkage of resin composites can be decreased by addition of metastable tetragonal zirconia filler particles, which expand upon exposure to water molecules. The phase transformation happens in composite stored in water over 2 days after curing – most within the first 8 h. The overall shrinkage of the composite (42 wt-% zirconia) sample stored in water at 40˚C was reduced with 44 % within the first 7 days compared with an equivalent sample stored in air. For the composite containing 32 wt-% metastable zirconia the shrinkage was reduced with 29%. It was shown that the reduced shrinkage of the composite was not a result of water uptake, as the composite containing the stable monoclinic zirconia filler showed a much smaller reduction in shrinkage (11% reduction).

Acknowledgement

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VIII

Stabilization of metastable tetragonal zirconia nanocrystallites by surface modification

M. Skovgaard

DentoFit A/S, Frederiksborgvej 399, 4000 Roskilde, Denmark

&

Department of Micro- and Nanotechnology, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark

ms@dentofit.com, direct: +45 46 77 42 84, fax: +45 46 77 47 91

K. Almdal

Department of Micro- and Nanotechnology, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark

kral@nanotech.dtu.dk

A. van Lelieveld

DentoFit A/S, Frederiksborgvej 399, 4000 Roskilde, Denmark

avl@aneedle.net

Abstract

Metastable tetragonal zirconia nanocrystallites were studied in humid air and in water at room temperature. A stabilizing effect of different surfactants on the tetragonal phase was observed. Furthermore, the phase stability of silanized metastable tetragonal zirconia nanocrystallites was tested by prolonged boiling in water. The samples were analyzed with X-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD). Changes in the monoclinic volume fraction in the samples were calculated. A number of surfactants were screened for their ability to stabilize the tetragonal phase upon exposure to humidity. Only silanes and phosphate esters of these were able to stabilize the tetragonal phase in water. Even as small amounts of silanes as 0.25 silane molecule per nm^2 are able to stabilize the tetragonal phase in water at room temperature. Aminopropyl trimethoxy silane and γ-methacryloxypropyl trimethoxy silane were even capable of preventing phase transformation during boiling for 48 hours in water.

Keywords: Metastable tetragonal zirconia, phase stabilization, powder, low temperature degradation.

Introduction

Zirconia, especially the tetragonal crystal phase, has gained increasing interest, primarily because of it high strength and resistance to fracture, and its ability to catalyze organic reactions, such as isomerization of n-butane [1], synthesis of derivatives of 1,5-benzodiazepine and diaryl sulfoxides [2], and benzylation of toluene [3]. Below 1175°C, the stable phase of zirconia is the monoclinic phase. Thus the tetragonal phase can only exist at a room temperature (RT) through stabilization. This is normally achieved by adding a dopant such as Y_2O_3 or by modifying the surface with sulfuric or phosphoric acid. It is, however, possible to obtain metastable tetragonal ZrO_2 at RT, by suitable control of the processing parameters and thereby crystal grain size. Zirconia nanocrystals can below a certain critical crystal size adopt the metastable tetragonal phase [4].

In resin composites for dental restoration zirconia particles can be added in combination with glass particles in order to render the material radiopaque (dense materials that prevent the passage of electromagnetic radiation) or to improve the mechanical properties and resistance to abrasion. Radiopacity can be useful in resin composites since it enables the distinction between composite and tooth with x-rays. Since stabilizing the tetragonal phase with yttria, which is less radiopaque than zirconia, lowers the overall radiopacity, limitation of the dopant amount is preferable [5]. Thus dopant free stabilization of tetragonal zirconia is desirable.

During the last couple of decades the tetragonal→monoclinic (t→m) martensitic phase transformation in zirconia has been studied and the exact mechanism is still under discussion. Different mechanisms have been proposed. Most of these deal with zirconia containing stabilizing oxides such as Y_2O_3 and CeO_2, and many of the proposed degradation mechanisms involve reactions with the stabilizing agent. Only limited work has been done to study the phase transformation of pure tetragonal zirconia at RT. However, some of the mechanisms based on stabilized zirconia studies are do not involve reactions with the stabilizing oxide. Sato and Shimada [6-8] based a model on reaction between water and Zr-O-Zr bonds on the surface resulting in formation of OH-groups which in turn cause the release of the strain, which acts to stabilize the tetragonal phase. Murase and Kato [9, 10] proposed that water adsorbed on the tetragonal zirconia surface reduces the surface energy difference between the tetragonal and the monoclinic phases. This reduces the critical size of the tetragonal crystals and lead to phase transformation. However, today it is commonly accepted that the existence of metastable tetragonal zirconia at RT is due to the stabilizing effect of oxygen vacancies in the crystal lattice. Yoshimuru et al [11, 12] proposed that phase transformation is a result of adsorption of water on the surface leading to formation of Zr-OH and/or Y-OH which creates stressed sites on the surface. This mechanism is based on the formation of strain in the surface and lattice, caused by occupation of oxygen vacancies by OH^- ions, nucleating monoclinic phase in the tetragonal crystallites. Kim et al [13] proposed a mechanism based on OH^- ions diffusing through oxygen vacancies and reacting with these under formation of Zr-OH bonds. This reaction leads to a build-up of tensile strain, which will induce the phase transformation. Guo [14-16] proposed a mechanism consisting of the following steps: 1) water is absorbed on the surface, 2) OH^- is formed by reaction of water with O^{2-} on the zirconia surface, 3) diffusion of OH^-, 4) formation of proton defects by filling of oxygen vacancies with hydroxyl, and 5) t→m phase transformation when the concentration of oxygen vacancies is reduced to the extent that the tetragonal phase is no longer stabilized.

Different types of surface modifying agents such as trimethoxy silanes and phosphate esters are used to secure a strong bond between the filler surface and the polymer matrix in dentistry. The present study investigates the effect of surface modification with different surface modifying agents, especially silanes, on the phase stability of metastable tetragonal zirconia crystals in humid atmosphere and in water. Furthermore the stability of the surface modified tetragonal crystals in boiling water is also investigated.

Experimental

All chemicals were supplied by Sigma-Aldrich (St. Louis, MO, USA) and they were all used as received. Highly porous nanocrystalline tetragonal zirconia powders were synthesized as previously described [17] by controlled hydrolysis of $ZrOCl_2$ followed by careful calcination. The tetragonal zirconia powder is extremely porous and has specific surface area of ~150 m^2/g. The synthesized tetragonal zirconia powders were kept in water free environment for further treatment.

Surface modification of zirconia powder

In inert atmosphere in a glovebox, 7 g zirconia powder was stirred with 40 ml anhydrous methanol and 7 ml of surfactant overnight. The surface modified particles were filtered and washed three times with anhydrous methanol. The samples were exposed to air and analyzed with x-ray diffraction (XRD). For each sample, parts of the modified zirconia was mixed in the glovebox with a di-methacrylic monomer mixture consisting of bisphenol-A diglycidyl ether dimethacrylate (Bis-GMA), urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA) in the ratio (36/ 44/ 20 wt%) in combination with a photo-polymerization system composed of camphorquinone and ethyl 4-dimethylamino benzoate both in a content of 0.5 wt-%. A sample was placed between two glass plates and cured on each side for 2 min using blue light (1100mW/cm^2) from a Bluephase® light probe (Ivoclar Vivadent). Such samples are termed matrix dispersed zirconia. After curing, the resulting composites were stored at 37˚C in water for 2-30 days and subsequently subjected to XRD analysis.

Stability test in air

1 g zirconia powder was stirred with 10 ml anhydrous methanol and γ-methacryloxypropyl trimethoxy silane (MPTMS) in amounts ranging from 0 – 1000 µL in dry air in a glove box. After 2 hours the mixtures were filtered and washed twice with anhydrous methanol to remove unreacted silane and dried inside the glove box. The stability was tested by exposing the samples for XRD to ambient atmosphere prior to the analysis. A reference samples for each sample were prepare by mixing the modified samples with resin and cure as described above. The matrix dispersed zirconia samples were after curing analyzed with XRD.

Stability test in water

For the stability test 1 g zirconia powder was stirred with 10 ml anhydrous methanol and aminopropyl trimethoxy silane (APTMS) in amounts ranging from 0 – 2000 µL in dry air in a glove box. After 2 hours the mixtures were filtered and washed twice with anhydrous methanol to remove unreacted silane and dried inside the glove box. The stability was tested by adding a few drops of water to the samples for XRD analysis. A reference sample for each sample was prepared by mixing the modified sample with resin and cure as described above. The matrix dispersed zirconia samples were analyzed with XRD after curing.

Stability in boiling water

15 g zirconia powder was stirred with 100 ml anhydrous methanol and 10 ml of either APTMS or MPTMS for 2 hours in inert atmosphere in a glovebox. The mixture was filtered and the zirconia was washed twice with anhydrous methanol, 150 ml in total. The silanized zirconia samples were dried at RT in the glovebox. The silanized samples were then boiled in 400 ml water and samples were collected, filtered and dried at RT. After drying, the samples were subjected to XRD analysis. Samples were collected after 1, 2, 4, 8, 24 and 48 hours of boiling. 100 ml water was added after the first 8 h to prevent mixture from drying or burn.

Characterization

X-Ray Diffraction (XRD) evaluation

XRD patterns were scanned in 0.1 steps (2θ), in the 2θ range from 20° to 65°, with a fixed counting time (30 sec.). The XRD patterns were analyzed using WinX^{POW} software. The tetragonal and monoclinic volume fractions (v_t and v_m) were calculated from the integral intensities of the monoclinic diffraction lines (-1 1 1) and (1 1 1) and the tetragonal diffraction line (1 0 1), following a procedure proposed by Toraya et al [18].

X-ray photoelectron spectroscopy (XPS) evaluation

Surface analyses were performed with a K-alpha monochromated, XPS spectrometer from Thermo Fisher Scientific Inc., Waltham, MA United States.

Surface Area Measurement

The specific surface area of the zirconia powder analysis was done with N_2 adsorption for BET (Brunauer-Emmett-Teller) determination (Autosorb-AS6, Quantachrome, Boynton Beach, FL). A number of pure zirconia samples were analyzed the specific surface area was determent to ≈150 m^2/g.

Results

Surface modification and phase transformation

None of the analyzed samples phase transformed as a result of exposure to humidity in the air. A number of different surfactant classes were tested but only silanes and phosphates stabilize the tetragonal phase when exposed to water. All the tested surfactants were able to stabilize the tetragonal phase when exposed to humidity in the air (Table 1).

Table 1 Zirconia surface modified with different groups of surfactants tested for its ability to phase transform (PT) in air and in water (matrix dispersed zirconia)

Group of surfactants	**Name**	**PT in air**	**PT in water (matrix dispersed)**
Carboxylic acids	Hexylic acid	no	yes
	2-[2-(2-Methoxyethoxy)ethoxy]acetic acid	NA	yes
Sulfonic acid	4-Dodecylbenzenesulfonic acid	no	yes
Phosphate ester	Ethylene glycol methacrylate phosphate	no	no
Silanes	γ-Methacryloxypropyl trimethoxy silane (MPTMS)	no	no
	Aminopropyl trimethoxy silane (APTMS)	no	no
	Methyl trimethoxy silane	no	no
PEG	O-(2-aminopropyl)-o´-(2-methoxyethyl) polypropylenglycole 500	NA	yes
Amines	Tetrabutyl ammonium bromide	NA	yes

NA: not analyzed

Fig. 1 shows the XRD patterns of a silanized and an unmodified zirconia samples, respectively, exposed to humidity in air. The silanized zirconia exhibit a trace characteristic of the tetragonal phase (curve a) whereas the unmodified zirconia trace is dominated by monoclinic reflections (curve b). Thus, unmodified zirconia goes through the t→m transition after brief exposure to ambient atmosphere, whereas the tetragonal phase in silanized zirconia is stable in humid air. No phase transformation is observed even after a week of exposure. The same stability is seen with silanized tetragonal zirconia when cured in resin and stored in water at 37 ˚C for 30 days. Under these conditions the untreated zirconia phase transforms in less than 2 days (not shown).

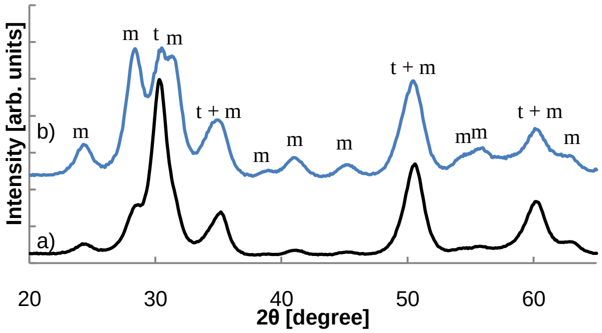

Fig. 1 XRD patterns for zirconia silanized with MPTMS exposed to air (a) and unmodified zirconia exposed to air (b) t=tetragonal reflection, m=monoclinic reflection.

Stability in air and water

In order to test how small amounts of silane are sufficient to hinder phase transformation of zirconia particles exposed to ambient atmosphere a set of zirconia particles with decreasing amount of silanization was prepared through treatment of particles with increasingly diluted solution of silanization agent. The lowest silane coverages were not detectable in XPS. It is chosen to use the theoretical number of silane molecules per nm^2 (assuming 100% conversion) and not the actual number when comparing data. This means the actual number is potentially lower as unreacted silanization agent in the reaction mixture is washed out during the silanization. The results are plotted in Fig. 2. It can be seen that even very small amounts of MPTMS are sufficient to achieve stabilization of the tetragonal phase. When the theoretical number of silane molecules per nm^2 gets down to 0.35 the volume fraction of monoclinic zirconia starts to increase and at coverage degree of ~0.017 the phase transformation reaches a v_m of ~0.6. This is close to, but not equal to the level of unmodified zirconia, which reaches a v_m of ~0.7 upon exposure to the ambient atmosphere.

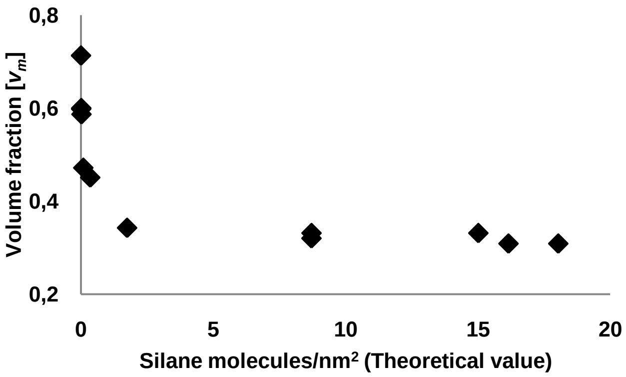

Fig. 2 Volume fraction of monoclinic zirconia in MPTMS modified samples in ambient atmosphere as a function of the theoretical number of silane molecules per nm^2

The same trend is observed for zirconia silanized with APTMS (Fig. 3) and exposed to water at RT. Below a surface coverage of 0.25 silane molecule per nm^2 the volume fraction of monoclinic zirconia starts to increase and at the coverage of 0.008 silane molecules per nm^2 the volume fraction reaches 0.63. Even this minute surfactant coverage prevent phase transformation to the same extend as the unmodified reference sample, which becomes almost entirely monoclinic after exposure to water [19]. The curve asymptotically approaches a monoclinic volume fraction of ~0.3. This level is as supported by XRD analysis of the reference samples due to phase transformation coursed by the silanization. Similar to the MPTMS experiments, the theoretical number of silane molecules per nm^2 is used as variable due to limitations in XPS.

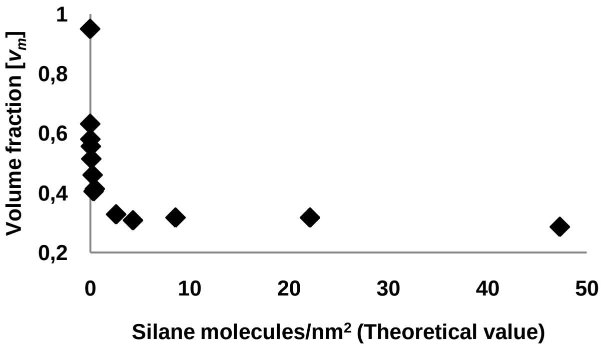

Fig. 3Volume fraction of monoclinic zirconia in APTMS modified samples exposed to water as a function of the theoretical number of silane molecules per nm^2

The XRD patterns (illustrated in Fig. 4 and Fig. 5) of the boiled samples show the stability of the tetragonal phase in the silanized samples. 48 h of boiling in water is insufficient to induce change in the monoclinic volume fraction in both of the samples. A small increase in the monoclinic phase occurs within the first hour. In XPS the atom-% of silicon were measured to 2-2.5% for both samples prior to the boiling test. No silane was found on unmodified zirconia samples.

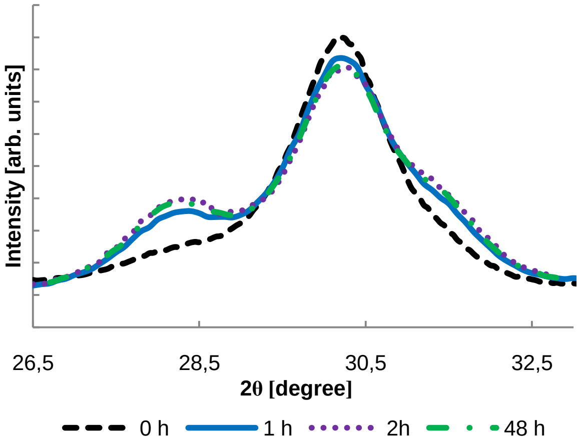

Fig. 4 XRD patterns of APTMS modified zirconia boiled for 0 (dashed black), 1 (solid blue), 2 (dotted purple) and 48 hours (green dash dot)

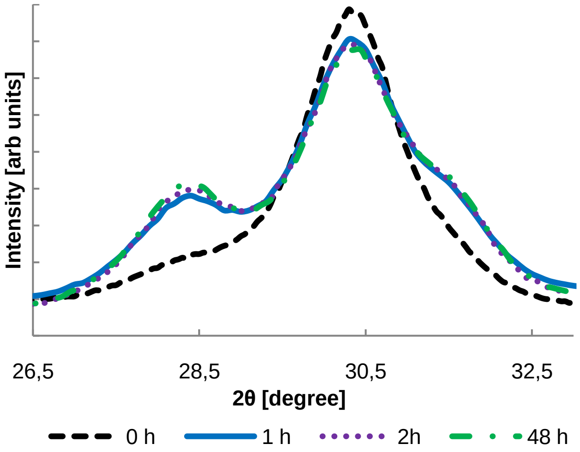

Fig. 5 XRD patterns of MPTMS modified zirconia boiled of 0 (dashed black), 1 (solid blue), 2 (dotted purple) and 48 hours (green dash dot)

Discussion

The results from the study of the ability of different surfactants to stabilize zirconia are summarized in table 1. It is observed that all the tested surfactants are able to stabilize the tetragonal phase on exposure to humidity in the air. But only silanes and phosphates were able to stabilize the tetragonal phase enough to withstand exposure to water, when aged in a di-methacrylate matrix. This is in accordance with the fact that silanes are the only tested surfactant forming covalent bonds to the surface and phosphate esters are known to bind zirconia strongly [20]. This means that the bonds between the zirconia surface and either the silane and the phosphate are strong enough to withstand hydrolysis. The necessity of testing the water stability of the zirconia crystal phase in a polymer matrix is due to the fact that the surface modified powder is hydrophobic to the extent that mixing with water is difficult thus hindering the access of water to the zirconia surface, whereas in the polymer matrix the water is forced to the surface as the polymer absorbs water. The polymer almost works as a surfactant facilitating wetting of the zirconia surface.

The powder is very sensitive to water vapor and few seconds of air exposure is sufficient to induce the martensitic t→m phase transformation [21]. This can be observed in Fig. 1, which shows x-ray patterns of pure tetragonal zirconia that is exposed to humid air and undergoes martensitic phase transformation resulting in monoclinic crystals. The silanization prevents the transformation probably due to the produced hydrophobic surface that hinders the access of water molecules to the surface. Furthermore surface treated zirconia floats on water where untreated zirconia disperses. Alternatively the stabilization of the tetragonal phase can also be a result of a change in the surface energy which increases the activation energy of the phase transformation. The initial amount of monoclinic zirconia in the sample is most likely due to small amounts of water in the methanol used for the silanization or other contamination with water.

Samples silanized with APTMS show a lower reactivity than MPTMS silanized samples during stability tests in air and water in spite of the fact that the APTMS modified samples are tested in water and as such are expected to have a higher monoclinic volume fraction. The differences in sensitivity of samples with the two different silane modifications are probably caused by a higher reactivity of APTMS due to the autocatalytic catalytically effect of the primary amine in the silanization reaction [22]. This will give a higher actual coverage of the APTMS modified zirconia powder than for the MPTMS modified zirconia powder leading to a lower sensitivity towards humidity.

The results of the boiling experiment show that the Si-O-Zr bonds are sufficiently stable that the surface bound silanes prevent the t→m zirconia phase transformation even after 48 hours in boiling water. The small initial phase transformation, observed in both Fig. 4 and Fig. 5, can be due to either a small number of unmodified zirconia crystals or crystals with very low silane densities. Such crystals will upon water contact rapidly transform into the monoclinic phase. The monoclinic volume fraction is stabilized at 0.5 after 2 hours for the APTMS modified sample and somewhat slower for the MPTMS modified sample. The silanized zirconia is very hydrophobic preventing wetting with water. However, boiling the silanized zirconia in water for a short time overcomes this resistance and the mixing with water ensues. This takes it little longer for the MPTMS modified samples. As expected the MPTMS modified zirconia is powder more hydrophobic than the APTMS modified. This difference in hydrophilicity is probably the reason for the lower transformation rate in the MPTMS modified samples.

The generally accepted models for the stability of metastability of tetragonal zirconia and the induction of phase transformation to monoclinic zirconia all involve interaction of absorbed water on the surface with oxygen vacancies to form proton defects in the crystal structure. In the models, the water absorption is followed by formation of OH^- that either stays in the surface or diffuses into the crystal. Thus from a surface point of view, it is the absorption of water that is the critical step. The observed stability of tetragonal zirconia surface modified with either silanes or phosphate esters cannot be reconciled with these models. The amount of *e.g.* silanization required to obtain stabilization is far from enough to hinder absorption of water since at a silane density of 0.25 molecules per nm^2 only 10 % of the possible sites are covered (determined as –OH group by titration with $LiAlH_4$). We hypothesize that the surface modification blocks the access of water to certain active sites – of presently unknown nature – which are crucial in the phase transformation mechanism. It remains a possibility, however, that the silanization reduces the surface energy more for the tetragonal phase than for the monoclinic phase and thereby shifts the critical crystal size upwards. Our data do not permit distinguishing between these two models.

Conclusion

Within the group of the screened surfactants surface modification with phosphates and silanes stabilize tetragonal zirconia in water. Even as small amounts of silane as 0.25 silane molecules per nm^2 are enough to stabilize the tetragonal phase in water at room temperature and the stabilizing properties of silanes are even sufficient to withstand boiling in water for 48 hours.

Acknowledgement

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IX

Experimental characterization of edges effects in simple adhesion tests

M. Skovgaard[1,2], K. B. Stibius[3], B. F. Sørensen[4] K. Almdal[1] and M.Della Negra[5]

[1] Department of Micro- and Nanotechnology, Technical University of Denmark, Frederiksborgvej 399,
4000 Roskilde, Denmark, kral@nanotech.dtu.dk

[2] DentoFit A/S, Frederiksborgvej 399, 4000 Roskilde, Denmark

[3] Aquaporin A/S, Ole Maaløes Vej 3, 2200 Copenhagen N, Denmark, ksj@aquaporin.dk

[4]Materials Research Division, Risø National Laboratory for Sustainable Energy, Technical University
of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark, bsqr@risoe.dtu.dk

[5]Fuel Cells and Solid State Chemistry Division, Risø National Laboratory for Sustainable Energy,
Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark, midn@risoe.dtu.dk

Corresponding author: M Skovgaard, e-mail: ms@dentofit.com, direct: +45 46774284, fax: +45 46774791

Abstract

The aim of this study was to uncover the effect of different chemical modifications of zirconia surfaces on the bond strength of zirconia/ resin interfaces, with limited mechanical adhesion. Zirconia thin films on silicon wafers were surface modified with hexamethyl disiloxane (HMDS), γ-methacryloxypropyl trimethoxysilane (MPTMS), Silquest® A-1230 or ethylene glycol methacrylate phosphate (EGMP) and a 100 μm methacrylate film was cured on top of the surfactant layer. Different fracture mechanics test methods were used (tape-peel adhesive test and cross-cut adhesion test). In order to avoid effects of physical adhesion between zirconia and polymer smooth wafers were used. The samples were tested under three conditions: dry, after water storage for 1 week at 37 ˚C and after water storage and drying at room temperature for 4 months.

Significant differences in interlaminar fracture energy were found in the samples. MPTMS gave the highest bond strength regardless of storage conditions. A detailed investigation of the cross-cut adhesion test method gave results dominated by edge effects rather than adhesive fracture revealing that the cross-cut adhesion test under certain condition is unsuitable as an adhesion testing method.

These results indicates that di-methacrylate resin binds more strongly to MPTMS modified zirconia than to EGMP modified surfaces and that the silane promote enhanced resistance to degradation from water storage for 1 week at 37 ˚C.

Keyword: primers and coupling agents, interfaces, peel, adhesion by chemical bonding

Introduction

Zirconia is commonly used in dental ceramics like crowns and veneers, and several studies have been conducted to understand and improve the resin to zirconia bond [1,2]. The resin is normally bonded to the zirconia surface with a difunctional coupling agent capable of creating a strong bond between the filler surface and the polymer matrix by copolymerization [3]. This coupling agent also has the function to increase the water resistance of the polymer/zirconia interface, since the surface modification reduces the accessibility of water to the interface and thereby decreases the hydrolytic degradation of the interface [4]. Several types of coupling agents are commonly used in dentistry. The most commonly used coupling agent in glass containing dental resin composites is γ-methacryloxypropyl trimethoxy silane (MPTMS), which not only increases the strength properties of the composite material but also increases the water resistance of the interface [3]. However, MPTMS is not considered being a good a choice of surfactant for zirconia surfaces since the Zr-O-Si bond is not as stable towards hydrolysis as the silane counterpart, siloxanes and it is not even always able to bind to zirconia [2]. A number of studies have showed that methacrylate-decyl dihydrogenphosphate (MDP) is a better coupling agent for zirconia systems than MPTMS [1,2,5].

Methods for proper mechanical characterization of polymer/ zirconia interfaces in dental materials are not well established. Several test methods have been used to evaluate the bond strength of resin to zirconia mainly tensile [5,6], microtensile [7,8] and shear [9-12] tests. There is no significant difference between the measured values of bond strength of microtensile- and the shear test methods when evaluating bond strength between resin and zirconia, but the shear bond strength test gave exclusively adhesive failure i.e. failure along resin/zirconia interface, and the mixed failure mode was dominating in the microtensile bond strength test [13].

From shear tests, it is however known that the shear bond strength not only is affected by the chemical bond between resin and ceramic surface, but also by ceramic-resin bond originating from mechanical adhesion. A surface with higher roughness will have a larger surface area able to bind the resin and will furthermore enhance the possibility for mechanical retention. Derand and coworkers [2] showed that a rough zirconia surface gives higher bond strength between zirconia and a polymer. It was shown that independent of surface modification the rougher hot-pressed zirconia surface gave a higher strength than the smoother glazed zirconia surface.

The effect of surface roughness on the tensile bond strength of resin composite to sandblasted and non sandblasted surfaces has been studied previously for alumina ceramics [14]. It was found that silanes and phosphates on a non-sandblasted surface did not give a stable long-term bond, and the samples debonded spontaneously after 150 days of water storage. The bond strength decreased only slightly for the sandblasted samples. It was proposed that the reason for this was the roughness of the surface causing micro retention and that the surfactant increased the wettability allowing the resin to flow deeper into the undercuts and porosities.

It is well-known that different elastic properties can cause stress concentrations or singular stress fields at bi-material corners [15]. The stress concentration of stress singularity of a bimaterial corner depend on γ, the corner angle and the four elastic constants, E_1, ν_1, E_2, ν_2, (where E_j and ν_j are the Young's modulus and Poisson's ratio, respectively of material number j)[15] (see Figure 1). Following Dundurs [16], the stress field of the corner depends on only two non-dimensional elastic properties. For plane strain they can be written as

$$D_\alpha = \frac{\bar{E}_1 - \bar{E}_2}{\bar{E}_1 + \bar{E}_2} \qquad D_\beta = \frac{\mu_1(1-2\nu_2) - \mu_2(1-2\nu_1)}{2\mu_1(1-\nu_2) + 2\mu_2(1-\nu_1)}, \qquad (1)$$

where $\bar{E}_j = E_j(1-\nu_i^2)$ is the plane strain modulus, and μ_j is the shear modulus ($\mu_j = E_j/2(1+\nu_j)$) of material number j.

For instance, for identical elastic properties ($D_\alpha = D_\beta = 0$), for $\gamma = 90°$, the corner stress field has a singularity of the form [15]

$$\sigma_{ij} \propto r^{p_1 - 1} \qquad (2)$$

where σ_{ij} represents the stress components, r is the distance from the tip of the corner and the non-dimensional parameter $p_1 \approx 0.545$. For $D_\alpha \approx 1$ and $D_\beta \approx 1$, p_1 takes complex values, generating a logarithmic singularity. For $\gamma = 0°$ (corresponding to an interface crack), the logarithmic singularity is given by $p_1 = 0.5 \pm \varepsilon$, where ε is the bimaterial constant, that only depends on the second Dundur's parameter, D_β [15]:

$$\varepsilon = \frac{1}{2\pi} \ln \frac{1 - D_\beta}{1 + D_\beta} \qquad (3)$$

It follows that simple tensile and shear tests, that are easy to perform, possess complicated stress fields and do not enable easy interpretation. Calculations of average stresses, ignoring the complicated (sometimes singular) stress fields at biomaterial corners have little merits. Instead, it is relevant to study strength, accounting for the complicated stress field at biomaterial corners.

Mohammad and Liechti [17] studied the effect of the corner angle γ on the crack initiation (Figure 1). Experimentally, they found that the load at crack initiation increased dramatically with increasing corner angle. For γ = 90°, the crack initiation load was twice that of a corner with γ = 0°, and a corner having γ = 120° had crack initiation load five times that of a corner with γ = 0°. Thus, details like the shape of a corner can have a strong effect on the measured microscopic strength.

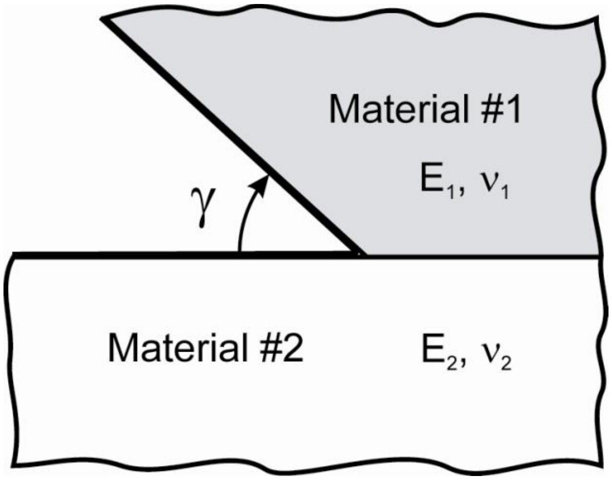

Figure 1 The stress field at a bimaterial corner depend on the four elastic constants, E_1, ν_1, E_2, ν_2, *(where* E_j *and* ν_j *are the Young's modulus and Poisson's ratio, respectively of material number j)and the corner angle,* γ.

One way to account for the singular stress field at biomaterial fracture is fracture mechanics testing, where the bond strength is characterized in terms of the fracture energy of the interface [18].

A simple method for qualitative assesment of bimaterial interfaces is the so-called peel test. The peel test is well suited for fracture mechanic charaterization of thin layers. Furthermore the failure mode of peel tests is generally adhesive i.e., cracking along the film/substrate interface [19]. The fracture energy is calculated according to the equation [20]:

$$G = \frac{P}{B}(1 - \cos(\theta)) \qquad (4)$$

where G is the fracture energy per area, P is the value of the peel force during separation, θ is the peel angle and B is the width of the flexible adherent. This equation applies if the adherent is flexible in bending, but inextensible [20].

Obviously, a simple qualitative test for the interface strength would be beneficial. Inspired by a recent publication [21], the method of cross-cut samples of cured resin on flat zirconia surfaces treated with the interface bonding agents of interest was used in the present study. In the process, a method for the coating of silicon wafers with zirconia without appreciable increase in roughness was developed. The availability of a very flat surface is important in order to separate intrinsic interfacial bonding properties from mechanical interactions originating from roughness or incomplete wetting of a rough surface.

The aim of this study was to analyze the effect of different chemical modifications of zirconia surfaces on the bond strength between zirconia and resin in the absence of physical adhesion between zirconia and polymer. Smooth surfaces were used in order to minimize the effect of roughness. Two different test methods (tape-peel adhesive test and cross-cut adhesive test) were tested. Therefore, the results were expected to be unaffected of physical adhesion and where it was possible to test the bond strength and water resistance of the coupling agent. These methods are only affected by the strength of the bonds between resin and ceramic and the water resistance of the interface. This study is also relevant for the understanding of zirconia filled resin composites strength properties, since zirconia particles sometimes are added to make the material radio-opaque or to improve the mechanical properties [22].

Material and Methods

All chemicals were supplied by Aldrich except for Silquest® A-1230 delivered by TriboTec AB and they were all used as received.

Preparation of thin zirconia film

Zirconia thin films were prepared by using a polymer precursor spin-coating process. The polymer precursor was prepared by refluxing 25 ml methylcellusolve and 4.9 g zirconium (IV) isopropoxide isopropanol complex for one hour. 2.6 ml ethanolamine was added and the mixture was refluxed for another hour. The mixture first turned orange and then colorless again. The mixture was filtered through a 45 μm filter and diluted 5 times with methylcellusolve and spin coated on a p-type Si-wafer (orientation <100>) at 1000 rpm for 1 min in ambient atmosphere. The as-coated film was dried at 150°C for 1 hour, and then calcined at 600°C for 1 hour in air. After calcination the wafers were cut into appropriate sizes.

Surface modification of zirconia films

The zirconia films were surface treated with hexamethyl disiloxane (HMDS) in a YES 6112 oven (Yield Engineering Systems, San Jose, US) at 150°C. Modification of the surfaces with γ-methacryloxypropyl trimethoxy silane (MPTMS), Silquest® A-1230 and ethylene glycol methacrylate phosphate (EGMP) were obtained by covering the specimens with a mixture of 10:1 dry methanol : surfactant for 2 hours. Subsequently the samples were washed three times with methanol and dried under an air flow. Reference samples were prepared with clean zirconia surfaces.

Preparation of methacrylate film

The dimethacrylate monomer system was composed of Bisphenol-A diglycidyl ether dimethacrylate (BisGMA), urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA) in the ratio (36/ 44/ 20 wt%) in combination with a polymerization system composed of camphorquinone and ethyl 4-dimethylamino benzoate both in a contents of 0.5 wt%. The specimens of surface treated zirconia were coated with the resin using a 100 μm spacer. The thin polymer film was cured for 2 min using blue light (1100 mW/cm^2) from a Bluephase® light source (Ivoclar Vivadent).

Structuring methacrylate surfaces by cross-cutting

20 mm x 20 mm films were cross-cut with a scalpel into approximately 2 mm × 2 mm squares and the adhesion of the polymer to the zirconia surfaces were assessed by tape peeling with a kapton tape. The procedure was done according to ASTM-standard: D3359-09. The patterned samples were tested by gluing a piece of adhesive tape to the specimen and peeling it off by hand. Afterwards, the number of squares removed from the surface was registered.

Structuring methacrylate surfaces by RIE

O_2 reactive ion etching on a Plasmatherm (Unaxis, St Petersburg, FL) 740 reactive ion etcher (RIE) was used to structure the surface of the methacrylate films. 1000 Å gold was deposited in a metal evaporator (Temescal FC1800 Technical Engineering Services Inc., Santa Cruz, CA, US) on to the methacrylate surface through a plate with hexagonally placed holes of radius 1.5 mm and spacing 1 mm. The methacrylate surface with gold spots were placed in the RIE and given sufficient O_2 plasma to etch through the uncoated methacrylate layer. The gold coated patches were protected from etching thus leaving a patterned surface (see figure 2).

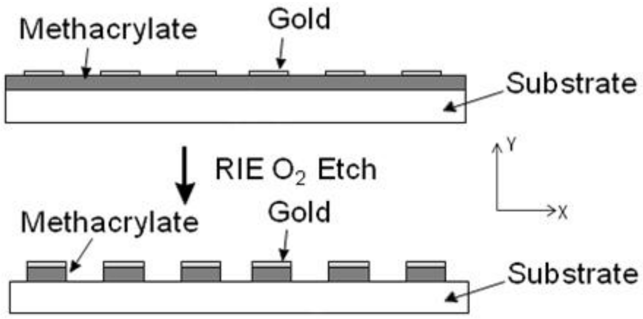

Figure 2 Structuring of films by RIE

Preparation of specimens for Tape-Peel Adhesive Tests

Tape-peel-adhesive samples were 20 mm in width and 60 mm in length. After curing of the methacrylate film, 1/3 of the specimens were cover with a kapton tape and edges of the film covering the substrate edges were removed with a scalpel to prevent adhesion to the backside of wafer. The rest of the samples (2/3) were water aged at 37°C for 7 days; they are henceforth denoted “wet” samples. After aging, the samples were covered with kapton tape and the edges were cut off with a scalpel to ensure no adhesion of the film to the substrate edges. The samples were prepared initially with the polymer going all the way to the back of the sample thus covering the otherwise exposed interface. For samples not prepared this way the films all loosen during water aging. The samples named “wet” were tested no later than 6 hours after ending water aging. Half of the water aged samples were dried for 4 months at room temperature (RT) – named “redried”.

Characterization

Scanning electron microscopy (SEM) evaluation

The structured surfaces were analyzed using an Inspect ‘S’ scanning electron microscope (FEI, Oregon, USA), secondary electrons (SE2) with an acceleration current of 5.00kV. No coating of the surface with gold were needed.

Atomic force microscopy (AFM) evaluation

The surface roughnesses of the calcinated zirconia thin films were analyzed with a PSIA XE-150, (Park Systems Corp. Suwon, Korea). The images were taken in air and using tapping mode. Fields of view at 10 µm x 10 µm were scanned.

X-ray photoelectron spectroscopy (XPS) evaluation

Analyses were performed with a K-alpha Monochromated, XPS spectrometer from Thermo Fisher Scientific Inc., Waltham, MA United States. In order to evaluate the quality of the surface modification.

Peel tests

The peel test were performed at a cross-headspeed of 1 mm/min. The testing machine was from Instron Material, model TT-CM no. A-0050 with a 2 kN load cell and 10 Hz data acquisition. The sample, glued on a 2 mm steel plate, was mounted at a rolling bearing that allowed horizontal translation so that the peel angle remained close to 90 degree.

The mean values of each group were statistically analyzed using two-way analysis of variance (ANOVA), ($\alpha = 0.05$). After testing, the samples were analyzed using a light microscope (Axioskop, Zeizz, Germany) at 50x magnification.

Results

AFM analysis

The AFM analysis of calcinated ZrO_2 films showed a very low roughness with average roughness values (R_a) of ~0.65 nm in an 10 x 10 µm area. This roughness is suspected to be low enough to prevent mechanical adhesion of the polymer film to the zirconia surface.

XPS analysis

The result of the surface modifications were examined with XPS and the existence of 1-2 atom% silicon and phosphorus on the silanized and phosphorylated samples respectively were detected. As the surfaces have been washed three times with methanol and are exposed to ultra high vacuum in the XPS chamber, it is assumed that the detected surfactants are chemically bound to the surface. Neither silicon nor phosphorus were detected on the reference samples.

Peel Tests of cross-cut samples

The number of squares released depends on the peel direction relative to the cut direction and also on the identity of the person doing the cutting. Anywhere from half to all squares could loosen from otherwise identical samples.

Peel testing at constant peel rate

The tape was peeled at steady speed until a maximum load was reached and the load curve flattens out (see Figure 3). Detachment of the film began at the point where the curve started to flatten. HMDS gave so weak adhesion that it was not possible to prepare the test specimens – the methacrylate films loosened prior to testing. The fracture energy for the other 2 silane coupling agents and the phosphate coupling agent was calculated using equation 4 and the results are given in Table 1.

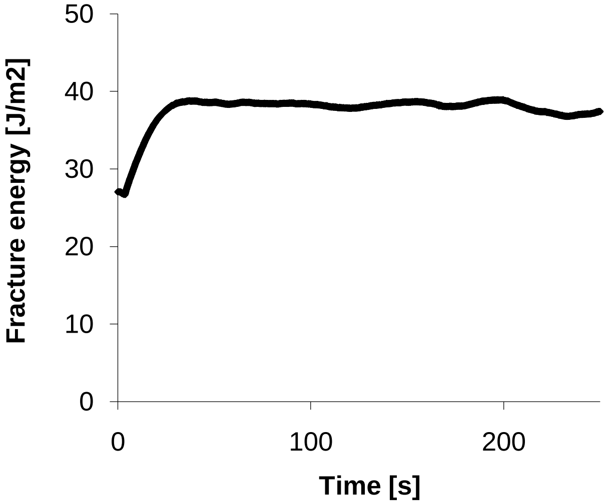

Figure 3. Measured force over time for a MPTMS treated sample (dry). Resin film peeled at 1 mm/min.

Table 1Mean (standard deviation) of fracture energy (J/m^2) recorded using peel-test. Mean with same subscript letters are not statistically different ($p > 0.05$)

Surface treatment	*Dry*	*Wet*	*Redried*
EGMP	35.2^a (4.3)	4.1 (0.1)	27.7^a (3.2)
MPTMS	30.0^{a,b} (13.4)	14.2 (0.5)	50.5 (6.4)
Silquest A-1230	17.6^b (10.8)	1.6 (0.05)	30.0^a (11.4)
Reference	9.2 (0.8)	3.0 (0.1)	12.3 (0.2)

Discussion

Qualitative assessment of interface strength through peel testing

In the case of the flat surface forced wetting is feasible and thus interfacial strength is characterized here independent of wetting.

It turned out that the qualitative peeling from cross-cut specimens gave somewhat irreproducible results. Thus peeling in the same or in the opposite direction of the cutting had significant influence on the result. Furthermore, the reproducibility between different experimenters was also unsatisfactory. Several reasons for this behavior can be envisioned including differences in the force and rate with which the cutting is performed. The knife (scalpel) will introduce a shear stress in the film which can lead to partial or total delamination (see Figure 4). This particular effect will render the test very sensitive to film thickness. It appears that the qualitative cross-cut technique is heavily influenced by edge effects. A new method to eliminate the edge effects and the irreproducibility of the cutting was developed in order to prove the hypothesis that edges effects were dominating.

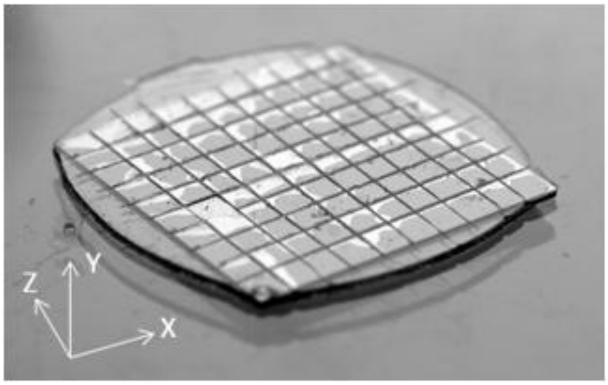

Figure 4 HMDS treated sample structured by cross-cutting. The light parts of the squares are areas where the film is delaminated.

The requirements to the new process were that it should eliminate the handicraft component and the stresses involved in cutting. Laser ablation and reactive ion etching was investigated before the described method was settled upon (see Figure 2).

The results from these experiments are very clear indeed. When there are no edge defects in the attachment of the 2×2 mm^2 squares as evidence by Figure 4 it is not possible to remove any of them through the peel test. Even in the case when the surface was deliberately modified to give poor adhesion (through HMDS treatment) the results was the same. In fact the squares were very difficult to remove from all surfaces including the HMDS treated surface even by pushing with a scalpel.

It is obvious that the results regarding the cross-cutting can be sensitive to crack initiation. Although the test method is intended to be a rough method for estimating the fracture energy, the measurement can be misleading if the load at crack initiation is significantly higher than the load corresponding to subsequent crack propagation. As discussed in the Introduction, the corner angle has an influence on crack initiation. As indicted in Figure 5, the strength of a 90° corner may depend on geometry details. For instance, if the corner is actually rounded outwards so that γ is large, a higher crack initiation strength is expected. Then, the problem may be initiation-controlled. In contrast, if the cut induces a small interface crack (γ = 0°), the corner singularity is stronger and the corner initiation strength becomes lower, comparable to that related to crack propagation. Only in the latter case the fracture energy determination is valid. The samples and especially the edges were studied with SEM and it was observed that the edges indeed in many places had angles larger than 90° (Figure 6). This can explain the high fracture resistance of the round dots and supports that the crack initiation is dominated by edges effects. We are not able to explain the existence of the thin film on the zirconia surface between the methacrylate dots, but as it does not bind to the dots, it is cannot affect the crack initiation or the bond strength of the dots.

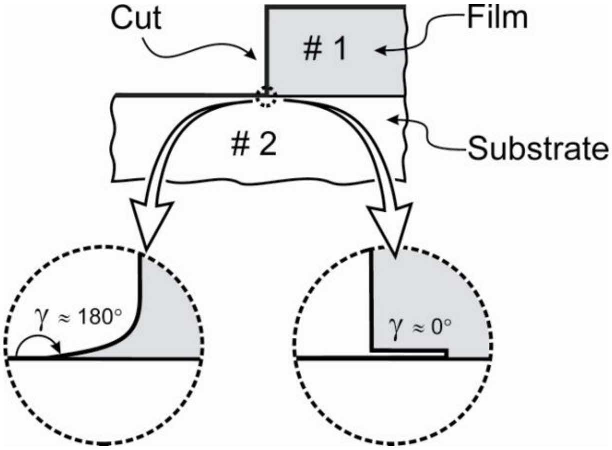

Figure 5 the Proposed hypothesis regarding the strength of the pattern test: Details of the corner geometry will have a strong effect on the stress field at the corner: A round corner (γ ≈ 180˚) will give a weaker stress singularity than a crack-type corner (α ≈ 0˚)

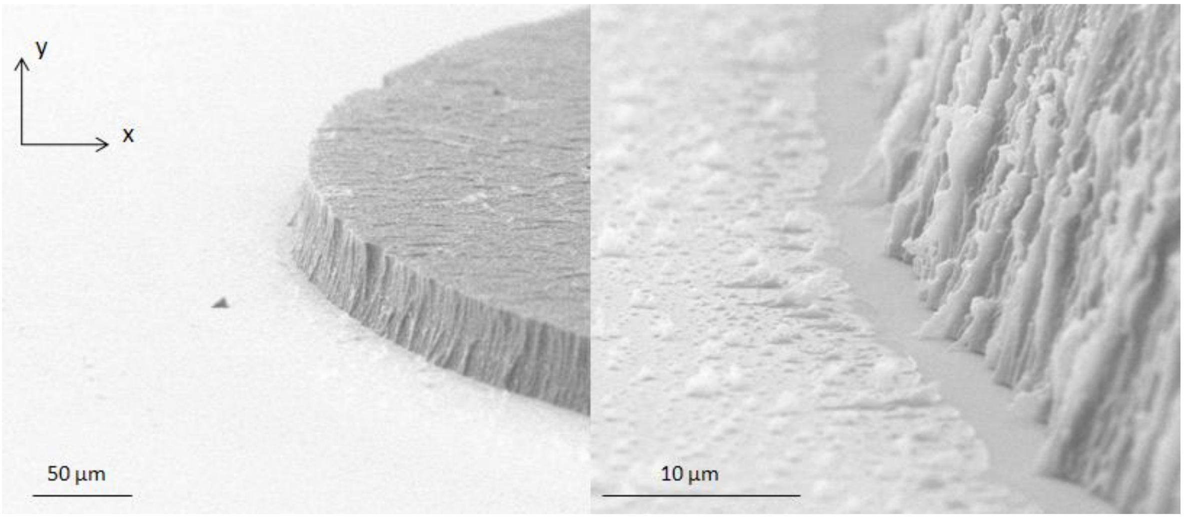

Figure 6 A scanning electron microscope view of structure on HMDS treated surface. Magnification of 1,000 and 10,000X

Different methods for creating the cut are likely to create different corner geometry and thus affecting the measurement. In case the cut is made manually, it is likely that different persons create different corner geometries.

It is, thus, demonstrated, that the qualitative testing of interface strength through peeling of film structured into small fields (here squares) are completely dominated by edge effects. Consequently these methods are unsuitable for the characterization of the interface strength [23].

Effect of water

The quantitative numbers obtained through peel testing at constant rate give determinations of the interfacial fracture energy between matrix and surface with reasonable certainty (see Figure 3). The fracture energy decreases significant after water aging although the MPTMS treated samples was less affected than the other. It is noted that samples prepared without the matrix covering the zirconia/matrix interface on the sides of the sample delaminated during the water treatment. This supports the notion that it is the effect of water on the zirconia/resin bond that weakens the interface in the wet state. The hypothesis is that the absorption of water into the interface leads to hydrolysis of the interface silanes and cause debonding. The debonded interface is the fastest path for entering of water molecules into the interior of the samples [24]. By covering the sides of the samples this debonding is hindered during the water aging.

Surprisingly, the interfaces regain their strength on drying and in fact in several cases are significantly stronger that the original interface. The reason for this behavior is not known at the present.

Coupling Agent Quality

The results of the peel tests show that MPTMS treated samples are less affected by water exposure. It is most likely due to the ability of MPTMS to bond covalently to both filler and polymer. The importance of covalent bonding of filler surface to the polymer matrix was also shown on zirconia in another study [25]. In this study the hydrolytic degradation was found to decrease when a methacryloxy- or a acryloxy trimethoxy silane was used for surface modification.

The increase of interface fracture energy of the MPTMS treated samples is probably due to cross linking of the silanes caused by the hydrolysis of the surplus methoxy groups. When the water is evaporated, cross linking is favored. This has previously been described [26] as an effect of less steric hindrance of the shorter hydroxyl group in comparison with the original methoxy group. The same effect is seen for the Silquest® A-1230 treated samples. The EGMP modified samples regained the original strength after drying and no increase in strength was observed. When the water disappeared from the interface the phosphate group coordinated to the zirconia surface again. According to the microscopy inspection after the peel testing (pictures not shown), the failure mode of all the samples was purely adhesive i.e. cracking along the methacrylate film/zirconia interface, independently of surface modification and aging conditions.

At all three test conditions, the MPTMS modified samples were stronger than the phosphorylated ones. In another study where the used coupling agent was 10-methacryloxo decyl dihydrogenphosphate, it was found that phosphates are the best coupling agent for zirconia surfaces [5,14]. This finding is surprising.

In the present study, EGMP was chosen as an example of a phosphate coupling agent in order to keep the spacer between surface binding functionality and polymerizable functional group unaltered compared to TMSMAP. Since EGMP has a substantially shorter spacer than the decyl phosphate, EGMP offers less screening of the interface against water. It is speculated that differences in hydrophilicity is an equally viable explanation for the observed differences in interface fracture energy as differences in interface bonding functional groups. In the present study, the different surface binding functionalities are compared at equal hydrophobicity. Thus, the present study indicates that trimethoxy silane groups bind zirconia stronger than phosphates do. The effect of the surfactant chain length has been investigated [3,27], and the more hydrophobic 10-methacryloxydecyl trimethoxysilane (MDTMS) was found to give higher flexural strength and better water resistance in composites than the shorter and less hydrophobic MPTMS. Furthermore, it was shown that surface modification with MDTMS enables higher filler loadings in resin composites, which indicates better compatibility with the resin leading to better wetting of the filler surface. It is probably the same effect we observe in this study; because of the shorter chain length of the phosphate, the silane is stronger. Based on this, it is speculated that MDTMS will be a candidate to enhance bonding of resin to e.g. zirconia crowns or a good coupling agent in zirconia based composites. This however has to be tested. This is beyond the scope of the present study.

Conclusion

Different tests methods for easy determination of interface fracture energy were tested and the best was peel test at constant peel rate. The qualitative interfacial test, which consists of counting the number of small delaminated fields of a cross-cut film that is removed in a simple tape peel test is dominated by edge effects; therefore this method cannot be trusted. Within the group of analyzed surfactants, MPTMS gave the highest adhesion, even higher than EGMP.

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