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Shrinkage strain – Rates study of dental composites based on (BisGMA/TEGDMA) monomers



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Abstract The viscosity of the initial monomer mixture and the chemical structure of the monomers are both important variables in the kinetic behavior of resin composites. This paper aims to determine the effect of opaque mineral fillers and monomer ratios on the shrinkage strain-rate and time at maximum shrinkage strain (S_{max}) rate, of experimental composites based on (BisGMA/TEGDMA) monomers. Polymerization shrinkage and the degree of conversion (DC) of resin composites are closely related manifestations of the same process. The proportionality of these two properties was also investigated by studying the variation of the ratio: (total shrinkage strain/degree of conversion): (S_{max}/DC), as a function of mineral filler contents and monomer ratios.

Resin composites were prepared by mixing different monomer ratios of (BisGMA/TEGDMA) with camphoroquinone and dimethyl aminoethyl methacrylate (DMAEMA) as photo-initiator system. Five different radiopacifying filler agents: La_2O_3 , BaO, $BaSO_4$, SrO and ZrO_2 at various volume fractions ranging from 0 to 80 wt.% were added. The samples were cured at ca. 550 mW/cm². The shrinkage strain-rate, was calculated from the derivative of shrinkage strain using numerical differentiation. The shrinkage strain was measured by the bonded-disk technique at room temperature. Degree of conversion was calculated using FTIR/ATR spectroscopy.

The results revealed that the fraction of opaque filler had no significant effect on the shrinkage strain-rate and on the time at maximum shrinkage strain-rate but these two parameters are closely related to the monomer ratios and viscosity of the organic matrix. The results have confirmed the proportionality of the shrinkage strain and DC and showed that the filler contents and monomer ratios would not affect this proportionality.

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1. Introduction

The viscous aromatic dimethacrylate monomer: 2,2-Bis[4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl] propane, Bis-GMA, is the main part of the organic matrix of dental resin composites due to its low contraction rate when compared to

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other similar monomers (Lovell et al., 1999; Asmussen and Peutzfeldt, 1998). The matrix when used unfilled for the restoration of teeth shows a poor wear resistance (Sideridou et al., 2002). This can be improved by the incorporation of mineral fillers. The high viscosity of BisGMA indicates that there is less degree of freedom in the BisGMA molecule, which kinetically leads to a low degree of conversion, and results in a low shrinkage. Due to this high viscosity, it requires dilution with a low viscosity dimethacrylate such as TEGDMA (triethylene glycol dimethacrylate) (Lovell et al., 1999; Peutzfeldt, 1997). BisGMA has a greater viscosity than TEGDMA and a chemical structure with stiff central core and hydroxyl groups which can reduce the mobility of the BisGMA chains and hence the final conversion. The relative concentration of each monomer can have an important effect on the mobility of molecules and the kinetics of the reaction. Since these monomers form cross-linked networks, the mobility of the reaction system decreases as the reaction progresses. Therefore, the conversion of the network is also a significant parameter in the mobility of polymer chains. As a consequence, the initial monomer ratio plays an important role in the kinetics of the Bis-GMA/TEGDMA system (Lovell et al., 1999; Atai and Watts, 2006; Atai, 2005). As the network forms, the movements of the macro-radicals are restricted and the termination step, becomes diffusion limited (Kloosterboer, 1988; Soh and Sundberg, 1982). A decrease in the termination rate leads to an increase in the polymerization rate which is known as the gel effect or auto-acceleration that commonly occurs in dimethacrylate systems. During the phase of gelation, as the polymerization progresses, the system becomes more cross-linked and the environment becomes more restricted, so the propagation step becomes diffusion-controlled (Gayosso et al., 2004; Hay and Shortall, 1988). This decline in rate is called the auto-deceleration effect. A balance between diffusion-controlled propagation which decreases the rate of polymerization, and diffusion-controlled termination, which increases it, results in a maximum in the rate of polymerization (Lovell et al., 1999; Cook, 1992). This complex behavior is due to the fact that the mobility of the reacting system decreases as the polymerization proceeds. The unreacted double bonds may either be present in free monomer or as pendant groups on the network (Lovell et al., 1999). It has been shown (Sideridou et al., 2002; Braga, 2005) that physical and mechanical properties of dental resin composites are influenced by the level of conversion attained during polymerization (Sideridou et al., 2002; Gayosso et al., 2004; Stansbury and Dickens, 2001). At low levels of conversion, when the resin is transformed from a liquid to a solid three-dimensional network, dramatic property changes are expected. Because of limitations imposed by vitrification of the polymer network, typical levels of DC in photo-cured composite restorative materials are of the order of 55–75% (Baroudi et al., 2007; Silikas et al., 2000; Ferracane and Greener, 1984). The purpose of this work was to study the effect of the nature, volume and concentration of five radiopacifying fillers: La₂O₃, BaO, BaSO₄, SrO and ZrO₂ on the shrinkage strain-rate and time at maximum shrinkage strain-rate of experimental composites based on the mixture (BisGMA/TEGDMA) at different ratios: (50/50), (25/75) and (75/25). The importance of resin matrix viscosity on the network forming kinetics has also been deduced. This work was also focused on the effect of opaque mineral fillers and monomer ratios on the proportionality of the shrinkage strain and the DC of experimental resin composites.

2. Materials and methods

2,2-Bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl] propane (BisGMA) and triethylene glycol dimethacrylate (TEGDMA), were obtained from Aldrich (France). Camphoroquinone (CQ) and N,N'-dimethyl aminoethyl methacrylate (DMAEMA) were purchased from Fluka (Germany). Five different radiopacifying agents were used: lanthanum oxide (La₂O₃), Barium oxide (BaO), Barium sulfonate (BaSO₄), Zirconium oxide (ZrO₂), and strontium oxide (SrO). They were obtained from Aldrich (France).

Experimental composites were prepared by mixing (BisGMA/TEGDMA) at different ratios by weight: (50/50), (75/25) and (25/75) as matrix phase 0.5 wt.% CQ and 0.5 wt.% DMAEMA, as photo-initiator system. The radiopacifying filler powders were then added, in various proportions, into the mixture to provide loadings ranging from 0 to 80 wt.%. Each experimental composite was well blended to obtain a homogenous mixture.

The shrinkage strain was measured at room temperature using the Watt's bonded-disk technique (Watts and Cash, 1991a,b). The specimen was light-cured for 40 s, using a visible light source (LA 500 Blue light curing light, 500 mW/cm², 450–490 nm, Aposa Enterprise). The shrinkage strain was measured continuously and total shrinkage strain data of each sample were recorded during 1 h. Three repetitive tests (*n* = 3) were carried out per sample. The shrinkage strain-rate of samples, was calculated from the derivative of shrinkage strain data using numerical differentiation.

The degree of conversion (DC%) was measured using FTIR spectroscopy (Nicolet 360 Avatar 360 FTIR spectrometer) with an attenuated total reflectance (ATR) sampling accessory (type Pike miracle ATR, Diamond/ZnSeW/Pike technology).

Each sample was light polymerized for 40 s using a visible light source (LA 500 Blue light curing light, 500 mW/cm², 450–490 nm, Aposa Enterprise). The spectrum of each sample before end after curing was than obtained.

The DC of each specimen was determined from the ratio of absorbance intensities of aliphatic (C=C) peak at 1638 cm⁻¹ and aromatic (C=C) peak at 1608 cm⁻¹ considered as internal standard. It was calculated using the following expression:

$$DC(\%) = [1 - \{(C_{\text{aliphatic}}/C_{\text{aromatic}})/(U_{\text{aliphatic}}/U_{\text{aromatic}})\}] \times 100$$

where $C_{\text{aliphatic}}$ is the absorption peak at 1638 cm⁻¹ of the cured specimen, C_{aromatic} is the absorption peak at 1608 cm⁻¹ of the cured specimen, $U_{\text{aliphatic}}$ is the absorption peak at 1638 cm⁻¹ of the uncured specimen and A_{aromatic} is the absorption peak at 1608 cm⁻¹ of the uncured specimen.

3. Results and discussion

The maximum shrinkage rate (%/s) and time at the maximum shrinkage strain-rate (s) with standard deviations (SD) of experimental composites based on (BisGMA/TEGDMA): (50/50), (75/25), (25/75), containing photo-initiator system and mixed with five different radiopacifying agents: La₂O₃, BaO, BaSO₄, SrO, ZrO₂ at different weight fractions, ranging from: 0 to 80 wt.% are summarized in Tables 1 and 2. Figs. 1 and 2 illustrate, respectively, typical shrinkage strain-rate

Table 1 Maximum shrinkage strain-rate (%/s) (standard deviation in parentheses) of samples based on (Bis-GMA/TEGDMA) blended with five radiopacifying agents (salts): BaO, BaSO₄, La₂O₃, ZrO₂, and SrO ranging from 0 to 80 wt. %.

Opaque fillers (BisGMA/ TEGDMA) salt, wt. %	La ₂ O ₃			BaO			BaSO ₄			SrO			ZrO ₂		
	(25/75)	(50/50)	(75/25)	(25/75)	(50/50)	(75/25)	(25/75)	(50/50)	(75/25)	(25/75)	(50/50)	(75/25)	(25/75)	(50/50)	(75/25)
0	0.017 (0.001)	0.021 (0.008)	0.023 (0.003)	0.017 (0.001)	0.021 (0.008)	0.023 (0.003)	0.017 (0.001)	0.021 (0.008)	0.023 (0.003)	0.017 (0.001)	0.021 (0.008)	0.023 (0.003)	0.017 (0.001)	0.021 (0.008)	0.023 (0.003)
10	0.022 (0.002)	0.025 (0.004)	0.020 (0.006)	0.014 (0.006)	0.033 (0.007)	0.026 (0.001)	0.019 (0.001)	0.038 (0.002)	0.029 (0.014)	0.019 (0.001)	0.029 (0.003)	0.023 (0.003)	0.015 (0.002)	0.025 (0.084)	0.021 (0.002)
20	0.021 (0.005)	0.021 (0.01)	0.020 (0.014)	0.013 (0.002)	0.028 (0.008)	0.023 (0.013)	0.018 (0.005)	0.033 (0.013)	0.024 (0.006)	0.017 (0.071)	0.030 (0.013)	0.026 (0.005)	0.017 (0.007)	0.026 (0.005)	0.022 (0.005)
40	0.016 (0.002)	0.017 (0.009)	0.021 (0.033)	0.014 (0.005)	0.018 (0.016)	0.023 (0.016)	0.005 (0.016)	0.026 (0.036)	0.022 (0.041)	0.016 (0.003)	0.026 (0.004)	0.018 (0.048)	0.016 (0.007)	0.027 (0.018)	0.018 (0.001)
0.0179(0.002)	0.008 (0.017)	0.027 (0.006)	0.025 (0.008)	0.021 (0.005)	0.036 (0.008)	0.022 (0.041)	0.021 (0.003)	0.026 (0.026)	0.021 (0.009)	0.016 (0.007)	0.027 (0.018)	0.019 (0.006)	0.014 (0.033)	0.021 (0.009)	0.018 (0.001)
60	0.014 (0.003)	0.018 (0.002)	0.015 (0.07)	0.014 (0.011)	0.025 (0.013)	0.018 (0.019)	0.021 (0.009)	0.026 (0.066)	0.021 (0.009)	0.016 (0.007)	0.027 (0.017)	0.021 (0.019)	0.014 (0.007)	0.021 (0.022)	0.018 (0.016)
80	0.017 (0.003)	0.017 (0.001)	0.016 (0.005)	0.019 (0.03)	0.014 (0.002)	0.019 (0.008)	0.007 (0.007)	0.017 (0.003)	0.019 (0.04)	0.016 (0.025)	0.023 (0.040)	0.007 (0.027)	0.007 (0.008)	0.022 (0.021)	0.016 (0.024)

curves indicating the maximum shrinkage strain-rate at a corresponding time, and the maximum shrinkage strain-rate as a function of mole number of BisGMA in the experimental composite organic matrix without fillers. The rising and falling of shrinkage strain-rate, Fig. 1, confirm that the shrinkage strain-rate of di-functional monomers follows the same pattern as the polymerization reaction rate of these monomers. As it has been shown in Fig. 2, the maximum shrinkage strain-rate increased gradually with the increasing of BisGMA content in the (BisGMA/TEGDMA) mixture. This result confirms that the viscosity of reaction medium plays an important role in the kinetic polymerization reaction. It has been reported (Lovell et al., 1999) that a few seconds after irradiation, the auto-accelerative gel effect started. The segmental movement of radicals is restricted and termination becomes diffusion-controlled, leading to an increase in the polymerization rate. The increasing of shrinkage strain-rate with the increasing of the BisGMA concentration, as it is shown in Fig. 2, could be attributed to the high molecular weight of BisGMA. The hydroxyl groups and a rigid aromatic group cause much barriers to free rotation around the bond. The hydroxyl groups of BisGMA, capable to form intermolecular hydrogen bonding, restrict sliding of polymer chains and thus, increase gradually the viscosity of the system with increasing of BisGMA content in the composite. This restriction of monomer mobility affects the propagation of free radicals and leads to a significantly lower termination rate. The addition of a less viscous dimethacrylate co-monomer such as TEGDMA allows the movement of macro-radicals thus delaying the auto-deceleration step and the onset of diffusion-controlled propagation as well. Fig. 3 shows the time at maximum shrinkage strain-rate of experimental composite without fillers as a function of BisGMA mole number in the organic matrix. This figure illustrates that the time decreased with the increasing of BisGMA content. The high viscosity of BisGMA disadvantages the mobility of the growing macro-radicals and thus causes the termination of diffusion-controlled mechanism at early stages of polymerization, which explains the high maximum of shrinkage strain-rate being reached in a short time.

Fig. 4 illustrates the typical shrinkage strain-rate curves for the experimental composites (BisGMA/TEGDMA): (50/50) containing SrO opaque filler at different weight percents. We notice, there is no significant difference among the maximum shrinkage strain-rate values of the composites with the increasing of SrO weight percent. Similar results have been observed with all the investigated composites containing different opaque filler salts and monomer ratios: (50/50), (25/75) and (75/25).

Figs. 5 and 6 show the maximum shrinkage strain-rate and the time at maximum shrinkage strain-rate as a function of ZrO₂ weight content for the composite (BisGMA/TEGDMA) at different monomer ratios. The variation of these two parameters is insignificant with the increasing of ZrO₂ weight content. Similar results have been observed with all the different opaque filler salts studied. These two figures show also that for given filler weight content, the maximum shrinkage strain-rate increases with the increasing of BisGMA concentration in the composite, while the time at maximum shrinkage strain-rate decreases. These results confirmed the importance of the viscosity system on the kinetic behavior of the filled resin composites studied. It can be concluded that the opaque filler loadings had no significant effect on the shrinkage strain-rate and time at maximum shrinkage strain-rate of resin composites.

Table 2 Time at maximum shrinkage strain-rate (s) (standard deviation in parentheses) of samples based on (BisGMA/TEGDMA) blended with five radiopacifying agents (salts): BaO, BaSO₄, La₂O₃, ZrO₂, and SrO ranging from 0 to 80 wt. %.

Opaque fillers (BisGMA/ TEGDMA) salt, wt. %	La ₂ O ₃			BaO			BaSO ₄			SrO			ZrO ₂		
	(25/75)	(50/50)	(75/25)	(25/75)	(50/50)	(75/25)	(25/75)	(50/50)	(75/25)	(25/75)	(50/50)	(75/25)	(25/75)	(50/50)	(75/25)
0	32 (0)	27 (0)	25 (0)	32 (0)	27 (0)	25 (0)	32 (0)	27 (0)	25 (0)	32 (0)	27 (0)	250	32 (0)	27 (0)	25 (0)
10	32 (0)	26 (0)	26 (1)	31 (1)	26 (1)	25 (1)	29 (2)	26 (1)	25 (0)	30 (1)	26 (1)	26 (1)	31 (0)	29 (1)	26 (0)
20	32 (1)	26 (1)	25 (0)	33 (2)	26 (1)	25 (0)	35 (1)	26 (1)	26 (0)	27 (3)	27 (1)	24 (1)	33 (2)	26 (0)	25 (0)
40	31 (1)	27 (0)	26 (0)	33 (0)	27 (0)	24 (2)	30 (2)	27 (1)	25 (0)	31 (0)	26 (0)	25 (0)	33 (1)	26 (0)	26 (1)
60	36 (2)	26 (0)	27 (1)	33 (1)	26 (0)	26 (2)	32 (0)	26 (0)	26 (1)	27 (2)	27 (0)	24 (0)	33 (1)	28 (1)	27 (2)
80	30 (1)	27 (0)	26 (1)	32 (0)	27 (0)	25 (0)	33 (1)	27 (0)	25 (0)	32 (0)	27 (0)	27 (1)	33 (2)	28 (1)	26 (0)

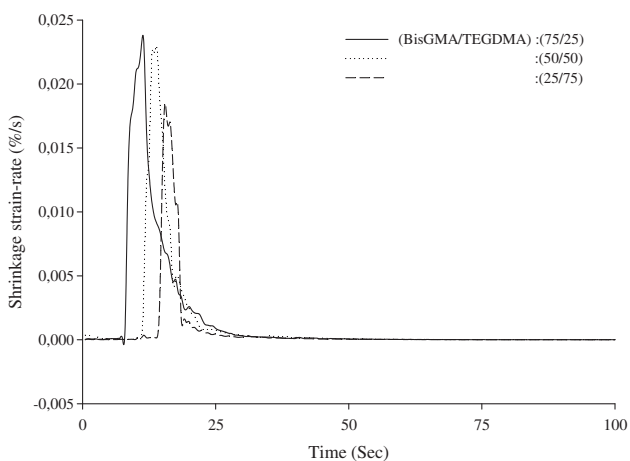


Figure 1 Shrinkage strain-rate vs. time of composite (BisGMA/TEGDMA), 0% opaque filler at different monomer ratios.

Figs. 7 and 8 represent, respectively, the variation of the maximum shrinkage strain-rate and the time at maximum shrinkage strain-rate as a function of filler weight content of composites (BisGMA/TEGDMA): (50/50) containing different opaque fillers. The results indicate that the nature and

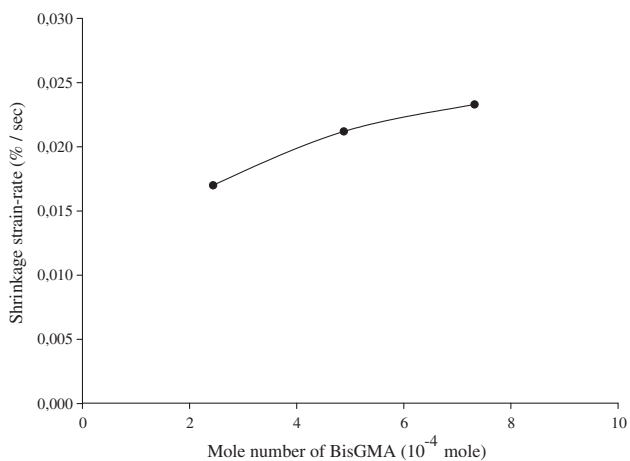


Figure 2 Shrinkage strain-rate vs. mole number of BisGMA in the composite (BisGMA/TEGDMA) containing 0% opaque filler.

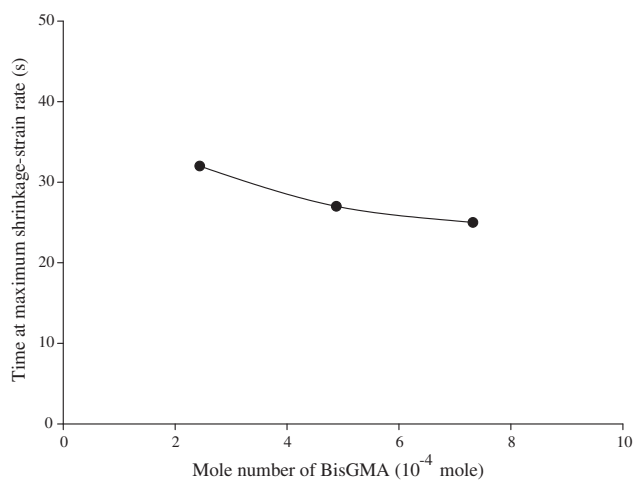


Figure 3 Time at maximum shrinkage strain-rate vs. mole number of BisGMA in the composite (BisGMA/TEGDMA) containing 0% opaque filler.

the volume of opaque fillers does not affect the kinetic behavior of resin composites studied since no significant variation of the maximum shrinkage strain-rate and time at max-

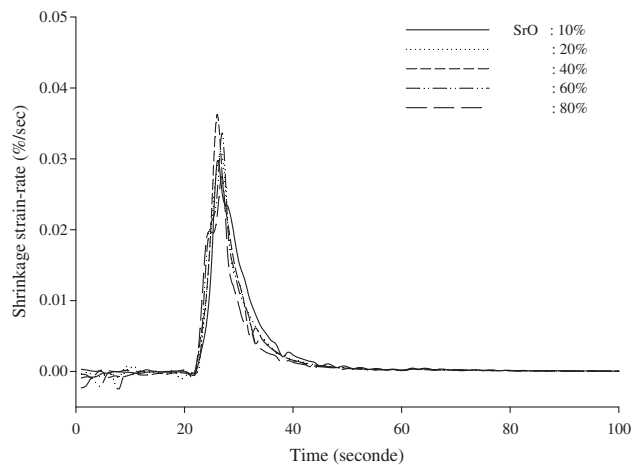


Figure 4 Shrinkage strain-rate vs. time of composite (BisGMA/TEGDMA): (50/50) with varying SrO filler content (wt. %).

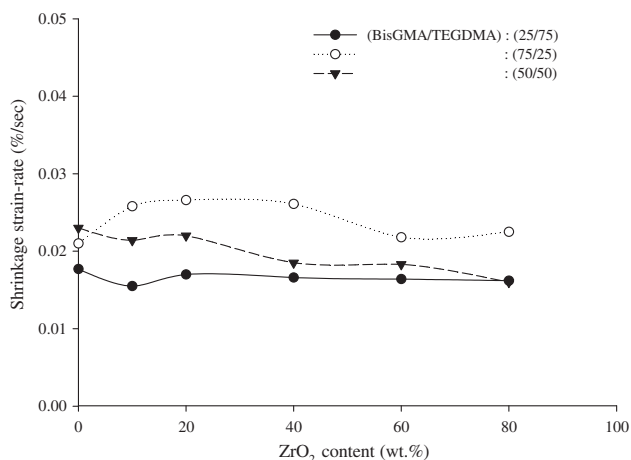


Figure 5 Shrinkage strain-rate vs. ZrO_2 content of the composite (BisGMA/TEGDMA) at different monomer ratios.

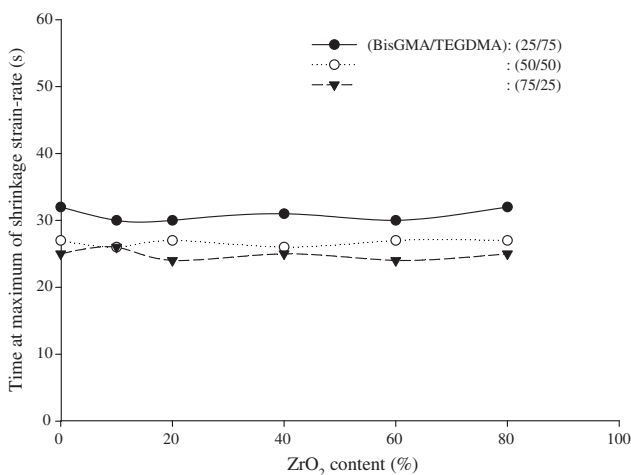


Figure 6 Time at maximum shrinkage strain-rate vs. ZrO_2 content of the composite (BisGMA/TEGDMA) at different monomer ratios.

imum shrinkage strain-rate has been observed. Similar results have been noticed with monomer ratios of (25/75) and (75/25).

The correlation between the final shrinkage strain and degree of conversion of the experimental composite containing (BisGMA/TEGDMA): (25/75), (50/50), (75/25), mixed with the five opaque fillers: La_2O_3 , BaO, $BaSO_4$, SrO and ZrO_2 at various loadings ranging from 0 to 80 wt.% has been investigated and confirmed in a submitted paper (Amirouche-Korichi et al., 2009).

In this work, we were intended to study the proportionality of these two properties by considering the variation of the ratio: (total shrinkage strain/degree of conversion): (S_{max}/DC), as a function of opaque filler contents and monomer ratios.

Fig. 9 illustrates the variation of (S_{max}/DC) vs. SrO content at different monomer ratios. These results indicate that DC and the shrinkage strain vary with the same proportion, since whatever the SrO content in the experimental composites is, the ratio (S_{max}/DC) value is approximately the same. Similar results have been obtained with all investigated experimental composites containing different opaque filler salts. Moreover,

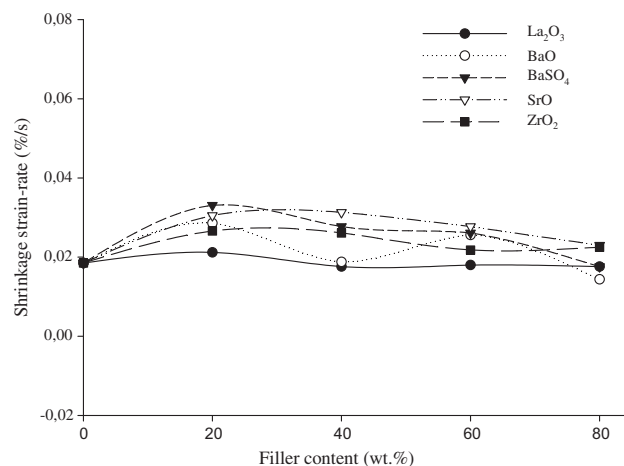


Figure 7 Shrinkage strain-rate vs. filler content of composite (BisGMA/TEGDMA): (50/50), containing different opaque fillers.

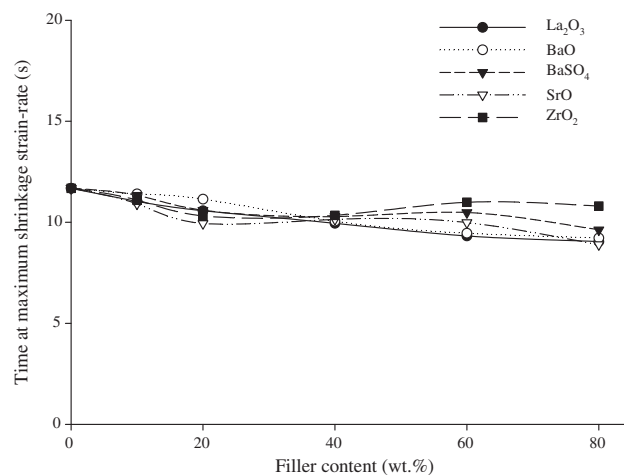


Figure 8 Time at maximum shrinkage strain-rate vs. filler content of composite (BisGMA/TEGDMA): (50/50), containing different opaque fillers.

for a given SrO weight content Fig. 9, the ratio (S_{max}/DC) increases with the increasing of the TEGDMA concentration in the organic matrix. It generally has been observed (Atai and Watts, 2006; Atai, 2005) that higher the DC in resin composites is, the higher the shrinkage strain was obtained. It has been suggested that the increasing of this ratio can be due to the more affected shrinkage strain of resin composites, by the dilution than the DC was. Otherwise the rising of S_{max} with the increasing of the TEGDMA concentration is more important than to the variation of the DC. Similar results have been obtained with all different opaque filler salts studied.

The effect of the nature and the volume of the opaque fillers on the proportionality of the shrinkage strain and the degree of conversion is shown in Fig. 10. It illustrates the variation of the ratio (S_{max}/DC) as a function of filler weight content at different opaque fillers of the composite (BisGMA/TEGDMA): (50/50), for given filler content, the ratio (S_{max}/DC) values are slightly the same, whatever the nature of the opaque filler is. The effect of the nature and the volume of heavy metals on the proportionality of the shrinkage strain and the degree of

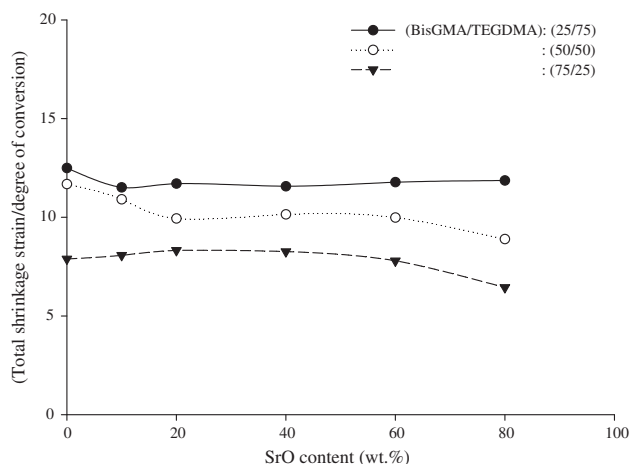


Figure 9 (Total shrinkage strain/degree of conversion) vs. SrO content of the composite (BisGMA/TEGDMA) at different monomer ratios.

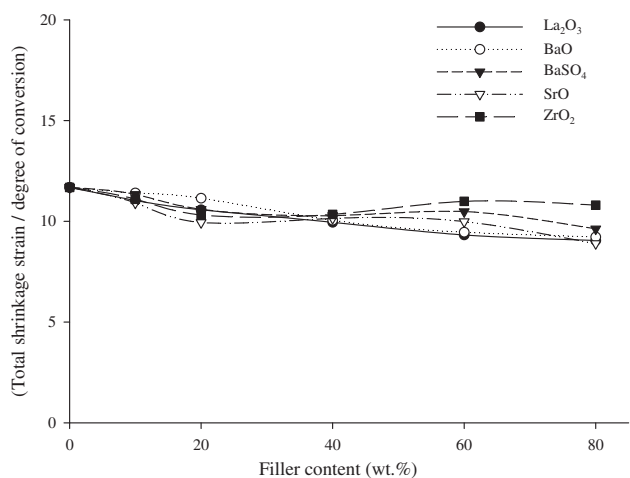


Figure 10 (Total shrinkage strain/degree of conversion) vs. filler content of composite (BisGMA/TEGDMA): (50/50), containing different opaque fillers.

conversion is not significant, whatever the loading of fillers in the composite is.

4. Conclusion

The results revealed that the fraction of opaque fillers had no significant effect on the shrinkage strain-rate and time at maximum shrinkage strain-rate but these two parameters are closely related to the monomer ratios and viscosity of the organic matrix. The shrinkage strain and DC evolve proportionally whatever the filler contents are whereas the monomer ratios affect more shrinkage strain than the degree of conversion and thus disturb the proportionality of these two properties. This work has confirmed that the shrinkage strain-rate of resin composites follows the same pattern as the polymerization reaction rate of di-functional monomers showing auto-acceleration and auto-deceleration, whatever the nature and the concentration of opaque fillers are.

The viscosity of monomer mixture is a very important variable in the kinetic behavior of resin composites as showed by the increase of shrinkage strain-rate with the increasing of the BisGMA content, whereas the time at maximum shrinkage strain-rate decreases.

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