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MICROSTRUCTURAL ENHANCEMENT OF DENTAL COMPOSITE AND CERAMIC MATERIALS BY PLASMA ETCHING

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Abstract

Radio frequency plasma etching of a selected number of dental materials, including glass filled polymeric composites, alumina reinforced ceramic, glass ionomer, and zinc oxide eugenol enhanced microstructural detail for scanning electron microscopy analyses. All four plasmas, argon, oxygen, carbon tetrafluoride (CF₄), and CF₄ + 4% O₂, proved effective, but the latter was the most effective. The etching of all materials, except the ceramic, was accomplished by the selective removal of a polymeric component. For the glass filled composites, this involved removal of the Bis-GMA matrix resin, leaving the filler particles in relief. For a microfilled composite, excellent delineation of the microfine particles contained within the prepolymerized polymer blocks was obtained, while for a hybrid composite, delineation of a bimodal particle distribution was revealed. For glass ionomer material, plasma etching enhanced the delineation between the silica gel lined unreacted glass particles and the polyacrylate matrix, as well as clearly defining regions in the matrix that were totally polysalt in nature. For a resin filled zinc oxide eugenol material, plasma etching removed the resin, leaving behind a porous material made-up of zinc oxide particles held together in a matrix partly composed of crystallites.

Key Words: Plasma etching, argon, oxygen, and carbon tetrafluoride plasmas, radio frequency electrical glow discharge, microstructure, microstructural enhancement, dental materials, dental composite, dental ceramic, glass ionomer, zinc oxide eugenol.

Introduction

Microstructural characterization by transmission or reflection microscopy of materials, including metals, ceramics, and polymers, usually requires special preparations prior to analysis. Optical contrast of the microstructural features of interest most often must be enhanced not only for routine qualitative analysis but even more so for quantitation techniques, such as digital image analysis. For homogeneous structures, features such as grain size, grain boundaries, grain orientation, and dislocation density may be of interest, while with heterogeneous structures multi phases, filler and reinforcement particles may also be of interest. Still other characteristics, such as porosity, inclusions, oxidation, corrosion and wear products, and nucleation sites, as well as microcracks, striation lines and other features resulting from stress cracking and fatigue processes can be of interest. Optical transmission microscopy frequently relies upon staining techniques for contrast enhancement. Reflected light microscopy may require methods of providing surface relief such as chemical/electrochemical etching, relief polishing, deposition of interference films, fractography, and polarization of radiation. Scanning electron microscopy may also require samples to be similarly treated. Transmission electron microscopy can be carried out only on extremely thin samples. Since thinning of samples is often a tedious process dependent upon sample composition and not always possible to carry out, the development of contrast enhancement techniques that are suitable for reflection microscopy (SEM and optical) and useful to the microstructural analyst are required. Plasma etching is one such technique.

Plasma etching can be defined [10] as a dry technique that utilizes an electrical discharge excited by a radio frequency field to produce chemically reactive species, including atomic, ionic, excited and ionized molecules, and free electrons from an appropriate gas at a low pressure. The etching effect is produced primarily due to the formation of volatile compounds from the highly reactive plasma species interacting chemically with the specimen surface. In contrast to inert ion sputter etching [1, 10, 11] which utilizes much higher

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Table 1. Materials Investigated.

Product Name	Material Type	Manufacturer
Vita High Ceram	Al ₂ O ₃ reinforced glass	Vident, Baldwin Park, CA
Herculite XR	glass reinforced resin [@]	Kerr, Romulus, MI
Silux Plus	glass reinforced resin [#]	3M, St. Paul, MN
Glass Ionomer Filling	glass ionomer [*]	Shofu, Japan
ZOE B & T Filling	zinc oxide eugenol ⁺	Caulk, Milford, DE

[@]hybrid composite, 78 wt % of sizes 1-5 μm (glass) and of less than 0.04 μm (colloidal silica); resin matrix is Bisphenol A glycidylmethacrylate (Bis-GMA).

[#]microfilled composite, 53 wt % of amorphous silica, 0.04 μm in size; matrix is Bis-GMA.

^{*}calcium aluminosilicate glass particles mixed with polyacrylic acid.

⁺zinc oxide and PMMA particles mixed with eugenol.

kinetic energies, plasma etching is intrinsically gentle.

Plasma etching techniques are well established in the semiconductor and integrated circuits industry to selectively etch away Si, SiO₂, Si₃N₄, and photoresist masks [2]. Some additional plasma processes are capable of etching Al, Al-Cu(2%), Ta, TaN, Ge, Mo, W, TiW, WSi₂, TiSi₂, CoSi₂, GaAs, Au, Pt, Cr, and InP [2, 9]. In polymeric biomedical applications, plasma surface modification is used for numerous purposes, some of which include chemical bonding, interfacial adhesion, surface cross-linking, charging, functionalization, reduction of protein deposits, and enhancement of hydrophobicity, biocompatibility, and wettability [6].

Plasma etching of materials solely for the purpose of enhancing microstructural features is not a new technique [10]. Some uses included microstructural analysis of carbon fibers and of natural and synthetic polymers, the latter which included demonstration of crystallinity and filler content. Oxygen plasma ashing and microincineration techniques found useful applications in revealing structure with biological tissue and plant matter [5, 7]. Still further applications have been used with ceramic and polymeric materials [4, 8]. Plasma etching in a CF₄ + 4% O₂ environment was found to be a superior metallographic technique for evaluating a ceramic composite composed of SiC whiskers in a matrix of Si₃N₄ and glass [4]. The Si₃N₄ was selectively attacked leaving the SiC and glass in relief. For polymethylmethacrylate (PMMA) resins, exceptional microstructural characterization of the prepolymerized beads from the polymerized matrix was obtained with an argon plasma [8]. Depending upon the etching time, the prepolymerized beads were either partially or totally etched from the surrounding and underlying matrix, which also developed its own etching pattern.

The purpose of this project was to apply similar plasma etching techniques as used previously by the authors with PMMA resins [8] to other types of dental materials, including ceramics, cements, and composite filling materials.

Materials and Methods

Table 1 summarizes the materials used.

Disk shaped samples, 10 mm in diameter by 5 mm thick, of all materials were processed according to manufacturers' instructions. For Vita Hi Ceram, this consisted of adding distilled water to the powder to form a slurry, inserting into a ground stainless steel mold with plungers, and placing in hydraulic press under 100 kg for 1 minute. The ejected samples were air dried under laboratory conditions for about 1 hour, followed by drying for 6 minutes in front of an open furnace (Huppert Challenger) at 800°C, firing in vacuum at 57°C/min to 1170°C, holding in air at 1170°C for 3 minutes, and bench cooling under laboratory conditions. For the glass filled resin composite materials, the viscous pastes were inserted into ring molds, lined on both top and bottom faces with mylar strips and cured for 2 minutes from both end faces with a visible light curing unit (Coe Light, Coe Laboratories, Chicago, IL). For both the glass ionomer and zinc oxide eugenol materials, the powder and liquid components were mixed according to instructions, inserted into ring molds, the end faces pressed between glass plates and secured with a clamp until the materials had set.

One face of all disc shaped samples was prepared for microscopy by grinding on wet silicon carbide abrasive papers to a grit size of 5 μm and followed by polishing with 1 and 0.05 μm alumina. For materials containing a softer matrix phase, which included the composites and zinc oxide eugenol, a 1 μm cerium oxide replaced the 1 μm alumina in the pre-final polishing step. The samples were sonicated in detergent, deionized-water rinsed, and dried with cold air from an air dryer.

The quality of all surfaces was first assessed by optical microscopy. Acceptable samples were subjected to plasma etching. Plasma etching was conducted with a glass barrel type radio frequency machine rated at 100 watt (model PDC-23G, Harrick, Ossining, NY). Prepared samples contained on a glass slide were inserted

into the chamber measuring 76 mm in diameter and 0.028 m³ in volume. The chamber was evacuated with a mechanical pump and at about 0.1-0.2 torr, a steady stream of argon, oxygen, carbon tetrafluoride (CF₄), or a combination of carbon tetrafluoride and oxygen gases was introduced. With the radio frequency current being emitted from coils surrounding the circular chamber, the plasmas became energized as revealed by an electrical glow within the chamber. Three power settings were available and used with the plasma machine, these being low, medium, and high and with etching times lasting for a duration of up to several hours. After an etching treatment, the temperature of the glass slide containing the samples felt moderately hot with the high power setting and only moderately warm with the medium power setting. The low power setting had little effect on the temperature.

Fourier transform infrared (FT-IR) spectroscopy was used to qualitatively identify organic matter in samples of zinc oxide eugenol and the glass filled resinous materials. A Digilab FTS-7 (Biorad, Cambridge, MA) instrument was used. Powder samples were analyzed in a micro diffuse reflectance mode with a UMA 150 microscope. Samples of composite paste and of mixed cements were pressed into thin films between KBr plates and run in transmission within the optical bench of the spectrometer.

For scanning electron microscopy samples were mounted onto aluminum stubs, sputter coated with a thin film of gold, and examined in a Stereoscan 250 MK-2 (Cambridge, England) scanning electron microscope (SEM).

Results

Figures 1 and 2 present micrographs of alumina reinforced glass material in both the as-polished and in the as-polished plus CF₄/O₂ plasma etched conditions, respectively. The as-polished surface contains debris, while the plasma treated surface reveals excellent definition of both alumina particles as well as the glass matrix without debris remaining from the polishing procedure. Superior definition of interfaces between phases is also a feature of the plasma treatment.

Figures 3-6 present micrographs for Herculite XR composite. Figure 3 is the as-polished surface and Figures 4-6 correspond to plasma etching with CF₄/O₂, oxygen, and argon plasmas, respectively. The severity of etching and hence the definition of the microstructure is best with the CF₄/O₂ plasma, followed by O₂, and argon the least in that order. Evident with all three plasmas are two distinct particle morphologies, although distinction is least with the argon plasma.

Figures 7 and 8 present micrographs for Silux Plus composite in both the as-polished and in the CF₄/O₂ plasma etched conditions. The former surface appears to contain only filler particles of the order of several micrometers in size, while the latter surface reveals that these particles are made up of many more smaller

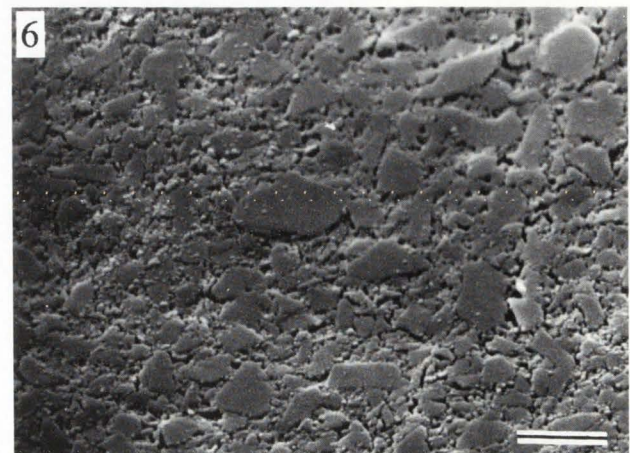
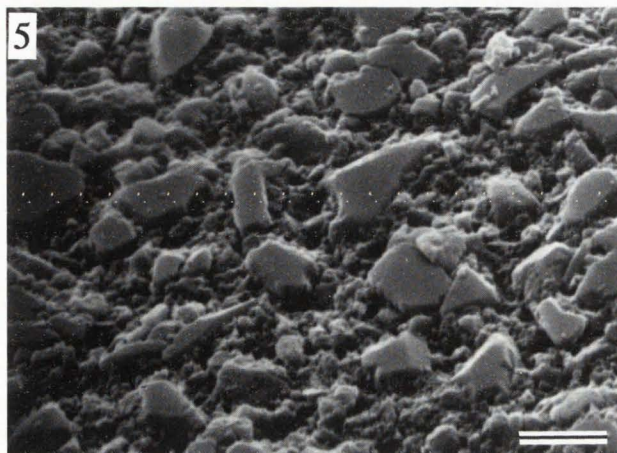
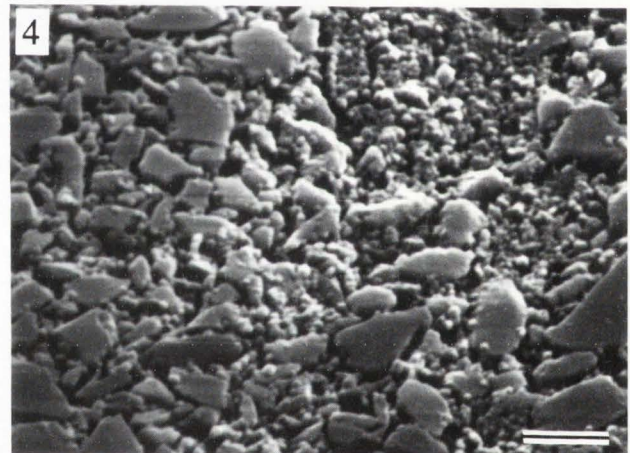
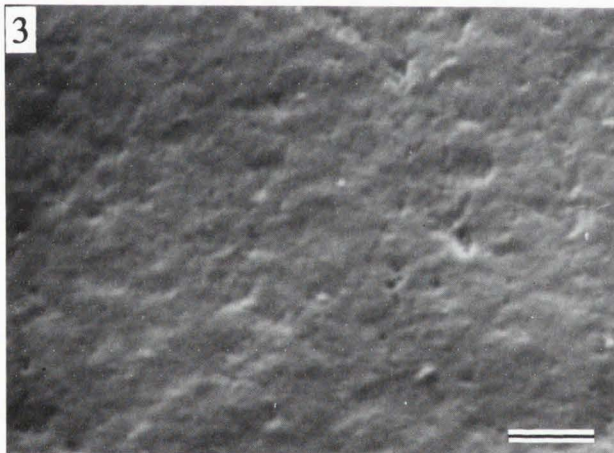
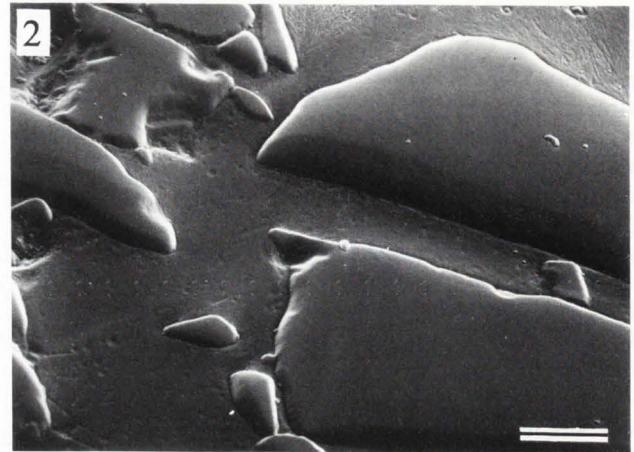
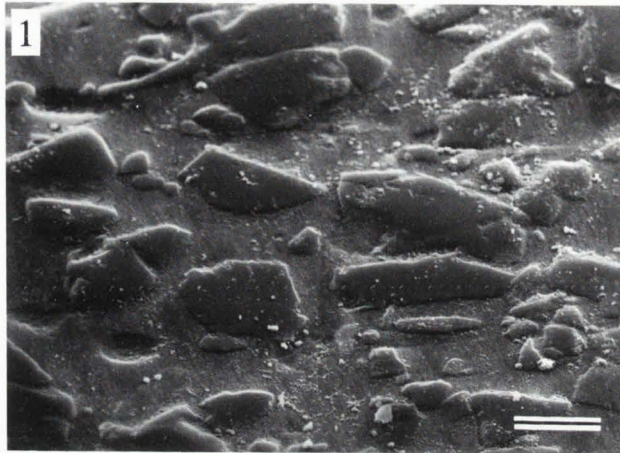
particles, as well as of their presence in the matrix. Surface treatment by etching in argon and oxygen plasmas also revealed these effects but not as well defined as shown in Figure 8.

Figures 9 and 10 present micrographs for glass ionomer material in both the as-polished and CF₄/O₂ plasma etched conditions. The as-polished surface does reveal some definition of structure, but nowhere as complete as with the plasma treated surface. The latter structure reveals sharp delineation of unreacted glass particles and clear definition of regions mainly occupied by acrylate matrix. As with the other structures, both argon and oxygen plasmas were not as effective as the CF₄/O₂ plasma.

Figures 11-12 present micrographs for zinc oxide eugenol material. The as-polished surface shown in Figure 11 reveals the fine particles of the unreacted zinc oxide in a matrix of reaction material and with much larger darker areas that correspond to PMMA. This latter component was identified as PMMA by micro FT-IR analysis. Figure 12 reveals the structure after an O₂ plasma treatment. It is evident the plasma treatment partially etched away the PMMA regions leaving craters in the surface. The depth of removal of this phase increased with the plasma etching time. Complete elimination was possible by etching for 1 hour in a plasma of CF₄/O₂. Also revealed along the walls of some of these craters are elongated crystals. The unreacted zinc oxide particles also appear to be sharpened by the plasma treatment.

Discussion

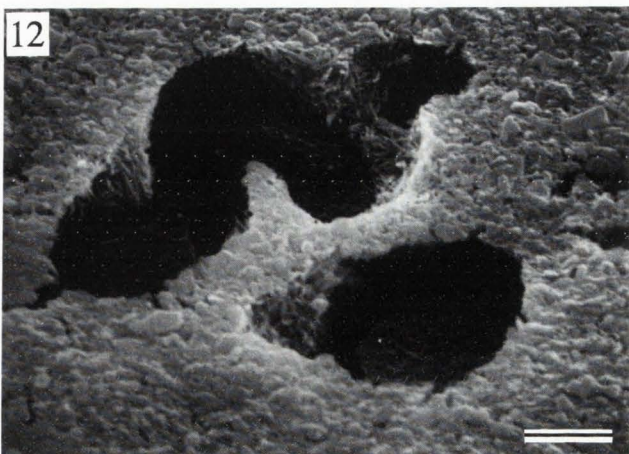
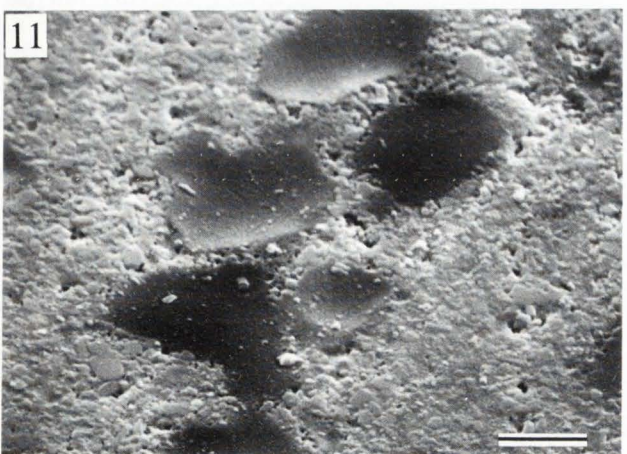
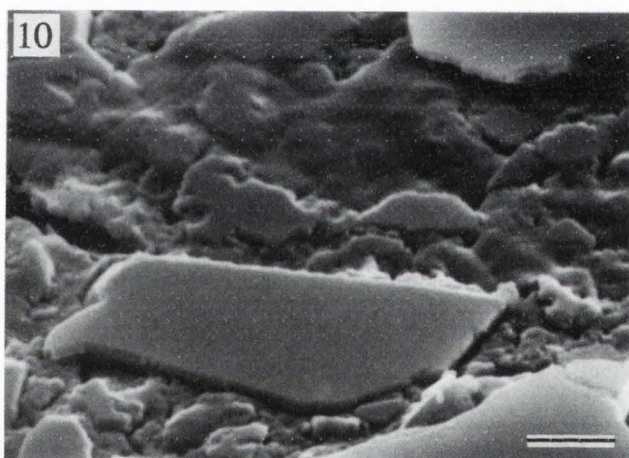
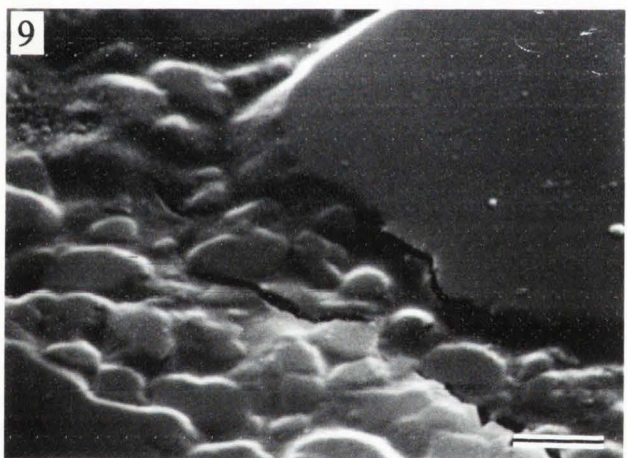
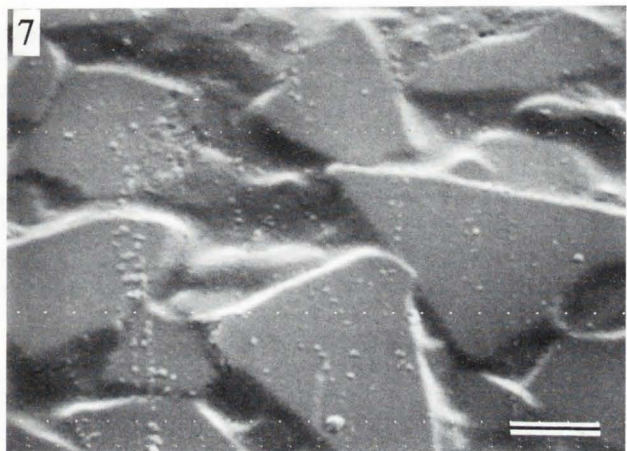
The usefulness of plasma etching with a diverse selection of dental materials has been shown. Except for the alumina reinforced glass ceramic material, enhancement of microstructure with all other materials occurred mainly through the selective etching or removal of phases or components that were polymeric in nature. The microstructure of both composites was enhanced by the selective removal of the Bis-GMA resin matrix leaving the glass filler particles in relief. For Silux Plus, this resulted in the detection of prepolymerized polymer blocks containing very finely dispersed filler particles. Without this selective removal of resin by etching, one would be lead to believe that this composite contained only much larger particle fillers. For Herculite XR, identification of a bimodal filler particle distribution, as well as the inclusion of prepolymerized polymer blocks was revealed. Due to the difference in the contrast of the filler particles produced by the plasma process, reasoning also suggests fillers with at least two different chemical compositions. For glass ionomer material, plasma etching selectively etched the polyacrylate matrix binding the unreacted glass particles overlaid with a silicious gel. This etching significantly improved detail between filler particles and matrix, apparently chemically reacting more with the silicious gel. For zinc oxide eugenol material, selective etching of the additive PMMA



Figures 1 and 2. Scanning electron micrographs of alumina reinforced glass material in the as-prepared condition without plasma etching (**Fig. 1**), and with CF_4/O_2 plasma etching for 1 hour at high power setting (**Fig. 2**). Bars = $10\ \mu\text{m}$ (**Fig. 1**); $4\ \mu\text{m}$ (**Fig. 2**).

Figures 3 to 6. Scanning electron micrographs of Herculite XR glass filled polymeric material in the as-prepared condition without plasma etching (**Fig. 3**); with CF_4/O_2 plasma etching for 30 minutes at low power setting (**Fig. 4**); with O_2 plasma etching for 30 minutes at low power setting (**Fig. 5**); and with Argon plasma etching for 30 minutes at low power setting. Bars = $1\ \mu\text{m}$.

Plasma Etching of Dental Materials



Figures 7 and 8. Scanning electron micrographs of Silux Plus glass filled polymeric material in the as-prepared condition without plasma etching (**Fig. 7**) and with CF_4/O_2 plasma etching for 30 minutes at low power setting (**Fig. 8**). Bars = $1\ \mu\text{m}$ (**Fig. 7**); $2\ \mu\text{m}$ (**Fig. 8**).

Figures 9 and 10. Scanning electron micrographs of glass ionomer material in the as-prepared condition without plasma etching (**Fig. 9**) and with CF_4/O_2 plasma etching for 30 minutes at low power setting (**Fig. 10**). Bars = $1\ \mu\text{m}$.

Figures 11 and 12. Scanning electron micrographs of zinc oxide eugenol material in the as-prepared condition without plasma etching (**Fig. 11**), and with O_2 plasma etching for 30 minutes at low power setting (**Fig. 12**). Bars = $2\ \mu\text{m}$ (**Fig. 11, 12**).

resin particles occurred leaving craters scattered across the surface. Elongated crystallites were revealed protruding from the walls of the craters. These crystallites were products of the setting reaction.

The results from this project, along with results from a previous report [8], have shown the usefulness of plasma etching for polymeric containing dental materials. The previous project emphasized PMMA denture resins, including a high impact resin containing a rubbery component and carbon fiber reinforced resin.

Removal of polymeric material can be referred to as etching, microincineration, or even partial ashing. Whatever the terminology used, it has been shown that the very outermost surface layers of polymeric materials being submitted to a plasma process are altered [3, 12]. For PMMA exposed to an H₂O saturated argon plasma, a two step mechanism including reduction of various functional groups and H₂O adsorption has been proposed (3). Isotactic PMMA shows a greater degree of surface modification than the atactic form.

For Vita High Ceram, the only material without a resinous component, plasma etching still greatly benefitted the quality of the microstructure, even though much longer times and a higher power setting were required. Except for the loose particle debris, not much material was removed by the plasma process. Volatilizing particle debris, delineation of the interface between alumina particles and glass matrix, and an overall sharpening of the alumina particles were the main improvements.

The CF₄ plus 4% oxygen plasma was most effective in etching the various materials. Although the CF₄/O₂ plasma was not utilized in the previous project [8], an argon plasma over proved better than an oxygen plasma with the materials from that project. Longer times were required with the argon and oxygen plasmas as compared to the CF₄/O₂ plasma in this project. As shown with Herculite XR, different effects can be shown with the different plasmas. Therefore, the CF₄/O₂ plasma may not necessarily be the plasma of choice.

The usefulness of plasma etching with other types of dental materials needs to be investigated. Materials of interest include the light cured glass ionomers, numerous other glass filled polymeric materials, porcelain, mica reinforced glass ceramics, dentin, enamel, and others. The usefulness of other gaseous plasmas also needs to be investigated.

Conclusions

1. All four plasmas, argon, oxygen, CF₄, and CF₄ plus 4% O₂ have merit for delineating detail prior to microstructural analysis of a variety of dental materials by scanning electron and optical microscopies. For most materials, the CF₄/O₂ plasma proved most effective.

2. Plasma etching of composite filling materials delineates the glass fillers from the matrix. Distinctions

can be made between single or multi type filler composites. Characterization of the prepolymerized filler blocks in the microfilled composites is also easily accomplished.

3. Plasma etching of a resinous-containing zinc oxide eugenol material preferentially etches away the additive PMMA particles leaving a pore-filled material of unreacted zinc oxide particles in reaction matrix. Elongated needle-like crystals were easily detected after the plasma treatment.

4. Plasma etching of glass ionomer sharpens the clarity of the interface between the unreacted glass particles and polyacrylate matrix, as well as delineating regions in matrix that are totally polysalt in nature.

5. Plasma etching of alumina reinforced ceramic volatilizes retained polishing debris, delineates interface between alumina particles and glassy matrix, and sharpens the clarity of alumina particles and matrix.

Acknowledgement

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Discussion with Reviewers

D.R. Hull: Did you examine the possibility of distinguishing microstructural features using backscattered electron (BSE) imaging? My guess is that it might show the structure of the zinc oxide eugenol material because of the average atomic number difference between zinc oxide and PMMA. For the other materials average atomic numbers appear to be very similar and it might not be as useful.

Authors: We use BSE imaging during most of our routine microstructural analysis. You are correct, BSE imaging of the zinc oxide eugenol material is able to reveal differences in contrast between the PMMA additive component from the zinc oxide eugenol material. For the glass filled composites, contrast differences are usually not detected if only a silica-containing glass is used. However, contrast differences have been detected with some composites that contain heavier elements within the glass phase. For these composites, BSE imaging is useful.

D.R. Hull: Results for Silux Plus were very dramatic. You comment that the larger features are "prepolymerized polymer blocks" containing fine filler particles. Is the prepolymerization done by the manufacturer?

Authors: The submicrometer size filler particles, of the order of 0.04 μm and less are polymerized with Bis-GMA resin into larger blocks, of the order of several micrometers, by the manufacturers. These polymer blocks are then admixed with unpolymerized Bis-GMA resin and diluents to form a paste. For light cure material, the paste also contains an initiator which activates the polymerization upon exposure to visible light. For chemically cured material, another paste containing catalyst is mixed with the first paste to activate polymerization.

D.R. Hull: We have found that you can retain unetched portions of the sample by covering it with a high temperature resistant tape, Mystik 9710. We have used this tape for etching times up to 4 hours in $\text{CF}_4 + 4\% \text{O}_2$ at 100 watts power. This allows imaging of both unetched and etched portions at the same time in the SEM. You also retain both conditions if additional microscopy needs to be performed.

Authors: So far we have not used tape or any other means to preserve the as-polished condition during the plasma etching process. Thank you for your suggestion, we will try this technique in future etching procedures. The advantages are evident as you mention. In order to prevent any confusion, the high temperature resistant tape, that you mention, is needed not for its high temperature resistance but likely for its ability to continually adhere to the surface throughout the whole plasma process and protect the surface from the plasma. As we know, one advantage of the plasma etching procedure is the elimination of the use of higher temperatures. Temperatures only slightly raised above ambient are usually encountered.