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Nanophase Separation of Polymers Exposed to Simulated Bonding Conditions

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Abstract

Under *in vivo* conditions, there is little control over the amount of water left on the tooth during dentin bonding. As a result, it is possible to leave the dentin surface so wet that the adhesive actually undergoes physical separation into hydrophobic- and hydrophilic-rich phases. Using tapping mode atomic force microscopy/PhaseImaging technique, nanosized phases with worm-like features were found on the surface of model HEMA/BisGMA dentin adhesives cured in the presence of varying concentrations of water. The phase contrast became evident with the increase of water concentration in the initial adhesive formulation and varied with the ratio of hydrophilic/hydrophobic composition. Oversaturated water droplets of variable sizes may accumulate as micro-voids within the hydrophilic and hydrophobic polymer phases. The phase domains were also identified following ethanol-etching in combination with SEM/AFM techniques.

Keywords

dentin adhesive; atomic force microscopy; nanoheterogeneity; phase separated polymer; adhesion; dental/craniofacial material; nanomaterials/nanophase

INTRODUCTION

Water is a major interfering factor when bonding adhesives and/or composites to the tooth. Forty years ago, researchers were discussing the detrimental effect of water on bonding dental materials to the tooth and to date this problem has not been resolved.¹ Currently, more and more hydrophilic and/or ionic resin monomers are incorporated in contemporary dentin adhesives to enable them to bond to intrinsically wet dentin substrates.²⁻⁶ However, hydrophilic polymers absorb more water than more hydrophobic resins⁵; the consequence of this increased water sorption is accelerated degradation under wet conditions and lowered mechanical properties.^{4,7-9}

The addition of hydrophilic monomers in adhesive formulations can create other problems when bonding to wet dentin surfaces. For example, the addition of hydrophilic monomers, such as hydroxyethyl methacrylate (HEMA) reduces the mole fraction of water and therefore reduces the partial pressure of water (Raoult's law of partial pressures). As the partial pressure

of water drops it becomes more and more difficult to remove residual water from the demineralized dentin. Hydrophobic monomers, such as 2,2-bis[4(2-hydroxy-3-methacryloyloxy-propyloxy)-phenyl] propane (bisGMA), would resist diffusing into these sites where there is residual water.¹⁰⁻¹³

There have been reports of the sensitivity of our current adhesives to excess moisture, including reports of water-blisters in adhesives placed on over-wet surfaces¹⁴⁻¹⁶ and adhesive phase separation that leads to very limited infiltration of the critical dimethacrylate component.^{10, 11,17} In addition, water molecules that exist in the form of thermodynamically stabilized water clusters¹⁸ may form hydrogen bonds with hydrophilic functional groups of resin monomers. Results from our laboratory indicated that excess moisture prohibited the formation of an impervious, structurally integrated adhesive/dentin bond at the gingival margin of Class II composite restorations.^{19,20} *in vivo* aging studies have reported degradation of the adhesive/dentin bond at 1-year even when the bonded dentin was protected by enamel from direct exposure to the oral environment.⁸

The structure of methacrylate adhesives suggests a general mechanism for their chemical degradation in oral fluids. On prolonged exposure of the adhesive to oral fluids, water begins to penetrate the resin. Water initially enters the matrix by diffusion into loosely cross-linked or hydrophilic domains. The hydrophilic domain exhibits limited monomer/polymer conversion because of adhesive phase separation¹⁰ and lack of compatibility between the photoinitiator and hydrophilic phase.²¹ The poorly polymerized hydrophilic phase degrades rapidly in the aqueous environment. Resin elution continues to occur through the nanoleakage channels; water movement along the length and breadth of the adhesive/dentin interface becomes more rapid as transport pathways form relatively large water-filled channels.²²⁻²⁴ The previously resin-infiltrated collagen matrix is exposed and vulnerable to attack by proteolytic enzymes.^{25,26}

There has been limited investigation of the effect of water on the polymerization and mechanical properties of dentin adhesive resins.^{27,28} Similarly, the effect of initial water content on the detailed structure of crosslinked adhesive resins, formulated with hydrophilic and hydrophobic monomers, has received very limited attention. Questions such as crosslinking density heterogeneity and segmental distribution of degradation-susceptible regions have not been resolved. The degradation-susceptible regions may range in size from nanometers to micrometers, but these regions are potentially the sites for detrimental interaction between the external environment and the polymer matrix. Mapping and identifying these degradation-susceptible regions address important scientific questions and technologic challenges.

Atomic force microscopy (AFM) used in the tapping mode with phase imaging technique is a powerful analytical tool for studying spatial heterogeneity at the nanometer scale. In tapping mode, the AFM probe oscillates such that there is only intermittent contact between the tip and sample surface. There are two types of tapping-mode images, that is, one known as the height image is a record of the change in the vertical displacement that is necessary to keep a fixed amplitude (through the feedback loop) and the other image known as the phase image is a record of the change in the oscillation phase lag relative to the cantilever response. This additional imaging capability has provided increased sensitivity to variation of the local viscoelastic properties in heterogeneous systems.

Our previous work using this novel technique showed that nanophase separated worm-like features is a general pattern of nonaqueous crosslinked resin containing hydrophilic HEMA and hydrophobic BisGMA bonded to each other.²⁹ The brighter features in the phase-contrast images may be associated with the densely cross-linked domain, and the darker features may

represent the loosely cross-linked domain. The nanoheterogeneity may be influenced by water. That is, water that is present within the environment during the polymerization reaction may influence the nanoscale morphology. Thus, the objective of this work was to understand the effect of water on the nanophase separation of polymerized experimental resin—HEMA/BisGMA mixtures photocured in the presence of water. With the advance of TMAFM, it is possible to provide direct spatial mapping of nanoscaled mechanically heterogeneous regions in multi-component polymer systems. Because the spatial resolution of TMAFM is superior to that of 2-D FTIR or other vibrational spectroscopic approaches, it is intended that the present study will serve to highlight the strengths of using this technique for the study of morphologic and phase features in heterogeneous dentin adhesives.

MATERIALS AND METHODS

The model resin consisted of hydroxyethylmethacrylate (HEMA, Acros Organics, NJ) and 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]-propane (BisGMA, Poly-sciences, Washington, PA) at ratios of HEMA/BisGMA 30/70; 45/55; 60/40 wt/wt. Distilled water at concentrations of 0, 5, 10, 16, and 20 wt % was selectively added into these neat resins. The following photoinitiators (all from Aldrich, Milwaukee, WI) were used in this study: camphorquinone (CQ), 2-(dimethylamino) ethyl methacrylate (DMAEMA), ethyl-4-(dimethylamino) benzoate (EDMAB) and diphenyliodonium hexafluorophosphate (DPIHP). The amounts of photosensitizer CQ, co-initiator amine and iodonium salt were fixed at 0.5 mol %, 0.5 mol % and 1.0 wt %, respectively, with respect to the total amount of monomer. The three-component photoinitiator system was more efficient and sensitive for HEMA/BisGMA co-polymerization than conventional two-component counterparts (unpublished data). The concentration of water was based on the total final weight of the model resin. Shaking and sonication were required to yield well-mixed resin solutions. A loss in clarity, as noted by visual examination, was interpreted as evidence of macro-phase separation. All the materials in this study were used as received.

The preparation of the cylindrical specimens, that were used in this investigation, has been described previously.²⁹ In brief, the model resins were injected into circular aluminum molds (ID 4.0 mm) and sealed with a cleaned cover glass. Each specimen was light-cured for 20 s using a dental curing light (Spectrum® 800, Densply, Milford, DE) operated at 550 mW/cm². After 24 h, the cover slips were carefully peeled off and the cylindrical specimens (4.0 mm diameter × 1.0 mm thickness) were stored in a vacuum at ambient temperature (24°C ± 2°C) for one week before microscopy observations. At least four specimens, that were free of air bubbles, were analyzed for each formulation.

The AFM images were obtained using a Nanoscope IIIa scanning probe microscope (Digital Instruments, Santa Barbara, CA) operated in tapping mode under ambient conditions (24°C ± 2°C, 40% ± 5% RH) according to the techniques published previously.²⁹ In brief, a tapping mode etched silicon probe (Prod No.: TESPW, Veeco, Santa Barbara, CA) with a resonant frequency of about 245–265 KHz was used. The probes were 130–140 and 3.5–4.5 μm in length and thickness, respectively. Images were recorded in topographic (height) and phase modes simultaneously. Although graded amounts of water were used in the various model resins to induce phase separation, the images were made on water-free specimens. The set-point amplitude (A_{sp}) used in feedback control was adjusted to 90% of the tip's free amplitude of oscillation (A_0).

Images of each sample were recorded and analyzed with Nanoscope image processing software (5.30r2 version). In this study, the roughness values (R_a) of height images and phase-contrast images were analyzed with Nanoscope image processing software and based on a 1 μm × 1

μm^2 scan area. R_a is defined as the mean of the absolute values of the surface deviations measured from the mean plane at z_0 :

$$R_a = \frac{1}{M} \sum_i |(z_i - z_0)|$$

where $z_0 = 1/M \sum_i z_i$, M is the number of height values (nm) obtained from the height image or the number of phase values ($^\circ$) obtained from the phase image, z_i is the height or the number of phase values of the point i . Evaluation of R_a for surface under different conditions was used to compare the apparent topography or phase contrast. For all experimental groups, the differences between roughness values were evaluated using analysis of variance (ANOVA), together with the Tukey test at $\alpha = 0.05$.

Randomly selected specimens were subjected to 10 h ethanol etching. After vacuum-drying, the ethanol-etched specimens were directly imaged by AFM. For SEM analysis, the ethanol-etched specimens were mounted on aluminum stubs, sputter coated with 20 nm of gold–palladium and imaged at a variety of magnifications in a Philips XL30 ESEM-FEG (Philips, Eindhoven, Netherlands) at 5–15 kV.

RESULTS

As seen in Table I, the minimum water concentration that caused macro-phase separation in the mixture prior to photo-polymerization was determined. The relationship of water concentration, macro-phase separation and mixture formulation are as follows. Water concentration values of about 5, 10, and 16 wt % induce macro-phase separation in mixtures with a ratio of hydrophilic HEMA/ hydrophobic BisGMA at 30/70, 45/55, 60/40, respectively. The formulations of the model resin mixtures in the presence of different concentrations of water were designed on the basis of these values.

In Figure 1, the topographic images (left) along with the corresponding phase images (right) are shown for model resin surfaces cured in the absence or presence of water. The magnification of these images is indicated by the scan dimension, which is $1 \mu\text{m}$. Phase-contrast in the resin surface cured in the absence of water was barely discernible [Figure 1(a)]. However, co-continuous structure was seen in the resin surface cured in the presence of water. The higher parts in the topographic image show some corresponding features in the phase-contrast images, which look brighter [Figure 1(b)]. The width of the worm-like features are $\sim 15 \text{ nm}$ based on the phase-contrast images.

To assist in the identification of domains in the resin surface, the un-etched samples and ethanol-etched samples (made with HEMA/BisGMA 45/55) were imaged by SEM [Figure 2 (a,b)] and TMAFM [Figure 2(c,d)]. To reduce the potential of inducing irreversible damage in the polymer specimens, the SEM samples were imaged initially at low voltage (5 kV). Microdomains were not evident in the SEM images of the surfaces of un-etched specimens [Figure 2(a)]. In comparison, after ethanol etching the specimens presented with a rough surface [Figure 2(b)]. The rough surfaces of the etched specimens were clearly visible at higher voltages (15 kV). The width of the irregularities was $\sim 20 \text{ nm}$.

TMAFM phase images showed the heterogeneous contrast of the surface regardless of whether the specimen was ethanol-etched. It is usually found that, the higher parts (including the irregularities) in the topographic image show some corresponding features in the phase-contrast images, which looks brighter [Figure 2(d)]. This means the rougher ($p < 0.01$) etched surface shows a similar phase pattern with that of non-etched surface. The roughness values (R_a) of phase-contrast image were also calculated; these values represent the degree of heterogeneity

of the two contrasted phases (Figure 3). Thus, the phase-contrast degrees were calculated and there is no significant difference ($p > 0.05$) between the values of these specimens. Based on the phase images, the width of the worm-like phase was around 15 nm.

The effect of water concentration in the adhesive formulation was studied. Figures 4-6 show the phase-contrast images of model adhesives cured with different ratios of HEMA/BisGMA (30/70; 45/55; 60/40 wt/wt) and concentrations of water ranging from 0 to 20 wt %, as described above. The specimens cured in the presence of low water concentration (below the minimum values) usually show transparency and may not show any defects under optical microscopy. Our TMAFM data show nanosized heterogeneity in copolymers of hydrophilic HEMA and hydrophobic BisGMA cured in the presence of water. The overall effect was an increase in heterogeneity with an increase in the water concentration, that is, the phase contrast is more evident with an increase in water in the initial adhesive formulation.

The roughness values (R_a) of phase-contrast images were calculated to provide a representation of the degree of heterogeneity of the two contrasted phases (Figure 7). It is found that the higher the water concentration in the resin formulation, the larger degree of heterogeneity showing more contrasted phases. It is noted that phase contrast increased rapidly when the water concentration was oversaturated in the initial resin formulation. In contrast, the phase contrast of the polymerized resin decreased with an increase in the ratio of HEMA/BisGMA. For example, it is found that, although not clearly evident in the image, phase contrast could be detected in the resin with higher BisGMA content (HEMA/BisGMA 30/70) even when this resin was cured in the absence of water [Figure 4(a)]. In comparison, there was no detectable phase-contrast in the resin with lower BisGMA content (HEMA/BisGMA 60/40) even when the resin was cured in the presence of 5 wt % water [Figure 6(a,b)].

It is noted that the phase images of these specimens were carefully obtained from the area without voids or defects on the topographic images, so that the calculated degree of phase-contrast could be comparable. Actually, there were numerous visible voids identified on the topographic images of the over-saturated specimen [one example, resin surface morphology of B-16% is shown in Figure 8(a)]. These voids were round/oval and ranged in diameter from 60 to 400 nm. The AFM images [Figure 8(b)] of one small area ($2 \mu\text{m} \times 2 \mu\text{m}$) show voids with diameters ranging from 60 to 100 nm. These areas looked darker in the phase-contrast images.

DISCUSSION

Clinicians must routinely attempt to bond to naturally wet substrates such as caries-affected dentin³⁰ or deep dentin.³¹⁻³⁴ Bonding to these clinically relevant substrates is a formidable challenge.^{20,34-36} The water content of caries-affected dentin has been reported to be 2.7 times greater than that of normal dentin.³⁰ In deep dentin, 22% of the surface area is exposed tubules while exposed tubules account for 1% of the surface area of dentin close to the DEJ.³⁷ The large increase in surface area attributable to tubules means that in deep dentin, pulpal fluid will contribute additional moisture to that already present within the demineralized dentin matrix. In deep dentin, the surface can be wetted by the upward movement of fluid droplets from dentin tubules to the adhesive layer.³⁸

Demineralized dentin has been characterized as 30% collagen and 70% water.^{39,40} With wet bonding techniques, the channels between the demineralized dentin collagen fibrils are filled with water, solvent, conditioner, and/or oral fluids.^{40,41} The only mechanism available for adhesive resin infiltration is diffusion of the resin into whatever fluid is in the spaces of the substrate and along the collagen fibrils.

Among the commercially available dentin adhesives, the most widely used are adhesives based on cross-linked glassy polymers prepared from a combination of hydrophobic monomers, such as dimethacrylate—BisGMA, and hydrophilic monomers, such as HEMA.⁴² A previous study from our laboratory presented the first direct spectroscopic evidence of micron-sized phase separation in a commercial HEMA/BisGMA adhesive at the interface with wet demineralized dentin.^{10,13} Raman spectra collected from the phase-separated adhesive indicated that the composition of the particles and surrounding matrix material was primarily BisGMA and HEMA, respectively.^{10,13} Phase separation in conjunction with partitioning of the adhesive components inhibits not only the formation of an integrated collagen/polymer network, but suppresses adhesive infiltration throughout the width of the demineralized dentin matrix and the subjacent, intact dentin.

Tay et al.⁴³ have reported the phenomenon known as “nanoleakage” within the adhesive and hybrid layer. The nanoleakage was detected using silver nitrate staining and SEM analysis. The authors claimed that the microvoids were most likely attributable to areas where water was incompletely removed from the resin–dentin interfaces. Regardless of the mechanism responsible for nanoleakage, the spaces identified by ammoniacal silver nitrate are not nanoleakage in its original definition,⁴⁴ but more likely represent microphase separation of copolymers containing hydrophobic and hydrophilic resin domains. The domains would be represented by the more hydrophobic “hard-chain segments” and the more hydrophilic “soft-chain segments”.⁴⁵ This indirect assessment of adhesive heterogeneity is limited by the difference of silver deposits in water and in hydrophilic resin domains with variable hydrophilicity. Thus, the spotted pattern does not adequately reflect the size and pattern of the real phase features.

In this work, we noted nanoscale phase separation even for visibly void-free polymerized adhesives. The nanoscale phase separation may be associated with solubility differences of polymer/monomer and the incompatible nature of hydrophilic/hydrophobic components.

The model crosslinked copolymer used in this work presented a mixture of modern hydrophobic component (BisGMA) and hydrophilic component (HEMA and water); the composition was based on conventional dentin adhesives.^{10,46} Commercial adhesives were not selected as experimental objects, because of the unknown complex composition, that is, commercial adhesives routinely include a wide variety of additives, which may interfere with the control, identification and imaging analysis especially at the nano level. It is noted that we use neat resin without volatile solvent to simulate bonding conditions within the aqueous oral environment. When a solvated comonomer mixture has been applied to wet dentin, a neat resin will be left contaminated by varying amounts of water that seeped into the comonomers as the solvents were being evaporated.

The water concentration introduced into model resin formulation was controlled to maintain visually homogeneous specimens prior to photopolymerization. This approach simulated the situation in which the homogeneous resin confronts the threshold of water absorption. For example, before the photopolymerization, 10 wt % water is the limit of macroscopic separation for resin mixture (HEMA/BisGMA 45/55). For the mixture without water, HEMA is a good solvent for BisGMA, so a relatively homogeneous solution could be formed; as a consequence, the specimens synthesized using this mixture would have a low degree of heterogeneity. With the increase of water concentration, the synthesized resins would have a very different nanostructure (Figure 1). Water is a good solvent for HEMA but a nonsolvent for BisGMA. Given that water may also be a good solvent for hydrophilic oligomer, for example, poly (HEMA)-rich segments, these segments would be highly nanophase separated from poly (BisGMA)-rich segments on mixing with water. In the course of nanophase separation, water and poly(HEMA)-rich segments are associated with each other to form hydrophilic domains,

whereas poly (BisGMA)-rich segments form their own domains. This nanophase separated structure is permanently locked in by crosslinking copolymerization.

Water may cause the plasticization of the hydrophilic domains and lower the degree of crosslinking. Thus, the degree of phase contrast between the two domains would increase with the water concentration in the hydrophilic domain due to the softer material that is formed. When the water content in the monomer system was oversaturated, the water was likely to form clusters that functioned like microvoids, [Figure 8(a)], even when the mixtures were shaken thoroughly prior to polymerization. In addition, the existence of oversaturated water may pull more hydrophilic monomer/oligomer from hydrophobic domain and this may increase the cross-linker concentration in the hydrophobic domain. This means that the hydrophobic domain becomes stiffer and the hydrophilic domain softer, causing increased phase contrast between these two domains.

Because the specimens were imaged after long-term vacuum storage, most of the free water (not bound water) on the specimen surface/subsurface should have evaporated. (The specimens without vacuum storage were not easily imaged probably due to vapor movement during the probe operation). The area of microvoids would be more associated with neighboring hydrophilic domains in the cross-linked network. Also, the corresponding regions in the phase-contrast image were dark due to lower stiffness [Figure 8(b)]. The diameter of the microvoids was quite variable. We theorize that the formation of these voids is due to the agglomeration of tiny water molecules driven out from the nanosized hydrophilic phase when polymerization occurred and the solubility changed. This means that the domains included water droplets, hydrophilic and hydrophobic phases, all at the nanoscale. Large sized water droplets (up to 400 nm diameter) may be coalesced from small ones during the polymerization. Of course, these may not be the huge water droplets, which existed before the polymerization of specimens in the presence of oversaturated water; the diameter of these droplets ranged from 2 to 30 μm depending on the specimen preparation protocol (not shown). Whatever the size of the droplets, these water droplets may be sites where internal micro-stresses accumulate leading ultimately to crack initiation. Based on our current understanding of bond failure, a void-free adhesive layer is beneficial for bond integrity, especially in the long term.

The water concentration in the resin formulation is a main factor that influences the phase contrast. Without water in the resin formulation, the phase contrast could not be detected, except in the case of a model resin cured with high BisGMA content. This exception may be due to a very dense cross-linked network. It is easily understood that the phase contrast of model resin cured in the presence of the same concentration of water, decreased with the ratio of HEMA/BisGMA (Figure 4). When the mixture was oversaturated with water, the tiny water droplets driven out from the hydrophilic phase would be attracted to the neighboring hydrophilic oligomer during the polymerization. The phase contrast will increase because of the larger area occupied by the hydrophilic oligomer as compared to the hydrophobic phase that will be represented by a hard, dense crosslinked network.

It should be kept in mind that the surface topography/phase features usually do not represent the bulk properties. However, in this investigation, the phase features of smooth sample surface cured under cover glass were similar with the bulk characteristics. This unique technique for sample preparation was based on the substrate selection⁴⁷: Neither too hydrophilic nor too hydrophobic thus, reducing the effect of the substrate on phase formation during the cross-linking reaction. We have shown this substrate effect in our previous work.²⁹

To further identify the domains, after ethanol-etching, the subsurface micro-domains were imaged and compared with the surface. A solvent-based method in combination with AFM was recently used to study chemically-heterogeneous polymer surface.^{48,49} The changed

morphological roughness and unchanged phase contrast led us to the proposed mechanism that is shown in Figure 9. It should be mentioned that the round particles plotted in this scheme do not represent the real shape of contrasted phases. If the hypothesis of phase contribution is correct, it is expected that after ethanol-etching the loosely cross-linked phases experienced preferential dissolution (swelling extraction) as compared with the hydrophobic phases. It is expected that the regions that experienced dissolution consisted of partially polymerized, low molecular weight, low-crosslinked materials; whereas the irregularities are representative of densely cross-linked structures, which could resist the ethanol etching. This means the hydrophobic phases representing hard, dense crosslinked network will be slowly swollen in the ethanol, compared with the hydrophilic phases. On the basis of this scheme, the distance of separated particles on the top surface will be larger than the space between adjacent phases. This may explain why the SEM images show irregularities with widths larger than those of the worm-like contrasted phase features.

Recognizing the existence of nanophases and their multitude of phase types allows a systematic exploration of a large number of new materials. Investigators have only begun to recognize the importance of these nanolevel phase structures. Because water is present on the dentin surface during adhesive application and polymerization, it is crucial to know the phase properties of polymerized adhesives in water. These phase structures contribute to the heterogeneity of the material. The more heterogeneous a material, the more likely it will have a significantly weaker structure in some regions. It is likely that during function, stress will concentrate at the boundary of the two contrasted phases and material deterioration may initiate at these sites of stress concentration.⁵⁰ Thus, these phase structures may play a critical role in determining the integrity and durability of the adhesive/dentin bond under stresses that occur within the oral environment.

The long-term stability of bonding, in particular to dentin, remains questionable.^{51,52} A factor known to promote bond degradation is long-term water exposure. Bond deterioration by water storage might be caused by degradation of regions with low crosslinking, insufficiently cured materials and microvoids. Thus, understanding the factors that contribute to nanoscale heterogeneity is vital to our ability to develop durable dentin adhesives.

The use of neat resins instead of solvated resins represents idealized conditions.⁵³ It is anticipated that the use of solvated resins will create non-homogenous regions with uncontrollable voids, or increased polymer chain mobility, making these polymers more susceptible to water sorption. Further work should be carried out to characterize the polymer structure of these solvated resins with the novel PhaseImaging techniques.

CONCLUSION

Because the wetness of bonded surfaces varies with dentin structure, that is healthy as opposed to caries-affected, dentin depth and the presence of residual rinse water, it is important to understand the influence of water content on polymer formation in situ. We have shown in this paper that nanophase separation is a general feature of cross-linked polydimethacrylate photocured in the presence of water. Nanophase separation effects tend to disappear only at much lower water concentration and crosslinking density. The brighter features in the phase-contrast images may be associated with the densely cross-linked domains, and the darker features may present loosely cross-linked domains. Under oral conditions, it is likely that these phases will swell and degrade by different amounts and rates. These differences will ultimately have a negative impact on the integrity of the material and its ability to tolerate the chemical and mechanical challenges present in the mouth.

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Figure 1. TMAFM images of crosslinking polymer surface cured in the absence or presence of water: (a) without water (b) with 8 wt % water. Resin formulation: HEMA/BisGMA 45/55. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 2.

SEM and TMAFM images of un-etched and ethanol-etched specimens. (a) SEM, unetched; (b) SEM, etched; (c) AFM, un-etched; (d) AFM, etched. Resin formulation: HEMA/BisGMA 45/55, water concentration 8 wt %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3.

The calculated roughness values for the topographic and phase contrast AFM images of un-etched and ethanol-etched specimens. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4.

Effect of water concentration on the TMAFM phase-contrast images. Resin formulation: HEMA/BisGMA 30/70. (a) A-0%; (b) A-5%; (c) A-10%; It is noted that these phase images were carefully obtained from the area without voids or defects on the height images. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5.

TMAFM phase images of model adhesive cured with different concentrations of water. (a) B-0%; (b) B-5%; (c) B-10%; (d) B-16%; Resin formulation: HEMA/BisGMA 45/55. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 6.

TMAFM phase images of model adhesive cured with different concentrations of water. (a) C-0%; (b) C-5%; (c) C-10%; (d) C-16%; (e) C-20%; Resin formulation: HEMA/BisGMA 60/40. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 7. Effect of water concentration on the calculated phase-contrast. The formulations of resin A, B, C contained HEMA/BisGMA with different mass ratios: 30/70; 45/55 and 60/40, respectively.

Figure 8.

AFM images of model adhesive cured in the presence of 16 wt % water. (a) topographic image of a large surface area (10 μm × 10 μm) showing numerous voids; (b) topographic (left) and phase image (right) of a small area (2 μm × 2 μm). Resin formulation: HEMA/BisGMA 45/55.

Figure 9.
Schematic illustration of ethanol-etched changes of TMAFM images.

TABLE I

Water Concentration Values that Cause Macro-Phase Separation of Mixtures of Monomers/Water and the Composition of the Experimental Adhesives Used in this Study

Sample	Ratio of HEMA/BisGMA (wt/wt)	Water Concentration Limit (wt %)	Adhesives Made with Different Concentrations of Water (wt %)
A	30.0/70.0	5	A-0%; A-5%; A-10%
B	45.0/55.0	10	B-0%; B-5%; B-10%; B-16%
C	60.0/40.0	16	C-0%; C-5%; C-10%; C-16%; C-20%