Effect of the Structure of Silane-Coupling Agent on Dynamic Mechanical Properties of Dental Resin-Nanocomposites

Irini D. Sideridou, Maria M. Karabela

Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124, Hellas

ABSTRACT: This work was aimed at the study by dynamic mechanical analysis (DMA) of dental composites consisted of a Bis-GMA/TEGDMA (50/50 wt/wt) matrix and silica nanoparticles (Aerosil OX50) as filler, silanized with various silanes. The silanes used were 3-[(1,3(2)-dimethacryloyloxypropyl)-2 (3)-oxycarbonylamido] propyl-triethoxy-silane (UDMS), 3-methacryloxypropyl-trimethoxysilane (MPS), octyltrimethoxysilane (OTMS), blends of UDMS/OTMS (50/50 wt/wt), or MPS/OTMS (50/50 wt/wt). The total amount of silane was kept constant at 10% by weight fraction relative to the filler weight. The silanized nanoparticles were mixed with the dimethacrylate matrix (60% filler by weight fraction). The composites were light cured and tested by DMA for the determination of storage modulus (E'), loss modulus (E''), tangent delta (tan δ), and glass transition temperature (T_g). Measurements were performed in samples immediately after curing and samples stored in water at 37°C for 1, 7, 30, or 120 days. OTMS-composite in which OTMS does not form covalent bond with the dimethacrylate matrix showed lower elastic modulus both in dry and wet conditions. The ability of bifunctional UDMS for crosslinking was found not to increase the elastic behavior of the composite, as it was expected, compared with that of MPS-composite, because of the high amount of the silane used. After immersion in water the elastic modulus of OTMS-composite remained constant, while that of the other composites increased after 1 day and then remained constant up to 120 days. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 507–516, 2008

Key words: dental polymers; nanocomposites; photopolymerization; mechanical properties; DMA

INTRODUCTION

Most dental composites are composed of a polymeric matrix (continuous phase) prepared mainly by copolymerization of 2,2-bis[4-(2-hydroxymethacryloxypropoxy) phenyl]-propane (Bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA). They also contain inorganic fillers (dispersed phase) added to improve physical properties, such as abrasion resistance, strength, and hardness, and to reduce polymerization shrinkage and the thermal expansion coefficient.[1] The filler usually consists of glass, quartz, or ceramic particles of different compositions, sizes, and size distribution. Dental composites containing nanosized fillers reflect the growing interest in the dental community in nanostructured restorative materials.[2] Adhesion between the polymeric matrix and the inorganic filler is successfully achieved by the use of a silane coupling agent mainly the 3-methacryloxypropyltrimethoxysilane (MPS).[3] MPS is a bifunctional molecule capable of reacting with the dimethacrylate

monomers (Bis-GMA and TEGDMA) of the matrix via its methacrylate functional group and with the filler and itself by virtue of its methoxysilane groups. The overall degrees of reaction of the silane with the dimethacrylates by copolymerization, and with glass filler or with itself by siloxane formation, determine the efficiency of the coupling agent. The structure of the formed siloxane network depends mainly on the silane concentration. In many composites the structure of the siloxane network is characterized by a broad, more gradient like transition zone, that forms between the continuous and dispersed phases, that is more accurately referred to as interphase.[4] Although this interphase is the least abundant phase of the composite, it can have significant effects on the properties of composites. Compared with conventional composites containing microsized fillers, the effects of silane phase are more important in composites containing nanoparticles, since the nanoparticles have an exceptionally large surface area-to-volume ratio and require a higher degree of silanization than larger particulate fillers.[5,6]

Today MPS is the dominant silane in dentistry. Its adhesion promotion is usually sufficient, but its hydrolytic stability is of continuous concern. The

---

Correspondence to: I. D. Sideridou (siderid@chem.auth.gr).

oxane bond Si—O—Si that forms between the silane agent and the filler can be especially vulnerable to hydrolysis, because this covalent bond has significant ionic character.[4,7] The stability of the interphase in the oral environment and its ability to transfer stresses between the matrix and filler phases during mastication are especially significant properties for dental composites to have. Excellent matrix-to filler adhesion is needed for minimizing wear. Attempts to improve the hydrolytic stability of the matrix-filler interphase involve the use of silane coupling agents, which are more hydrophobic and flexible than MPS, such as the 10-methacryloxydecyltrimethoxy silane. It was found that the use of 10-methacryloxydecyltrimethoxy silane improved the stability of the composites in an aqueous environment.[8–10] However, the overall mechanical properties achieved with this silane bearing the flexible decyl spacer are worse than those attained with the silane possessing the propyl spacer.[11] Antonnucci et al. used various blends of MPS and n-octyltrimethoxysilane (OTMS) (Fig. 1) which is a hydrophobic but a nonreactive silane, without a methacrylate moiety that does not copolymerize with the dimethacrylates. They suggest that this dual silanization offers a number of potential advantages compared to silanization with MPS only. These advantages include improved uncured paste handling characteristics, higher double bond conversion during curing, improved durability in the aqueous oral environment, and lower polymerization stress due to the greater flexibility of OTMS compared to MPS.[5,6,12] Recently, the isocyanatopropyltriethoxysilane was tested and it was also found to be a potential coupling agent.[13] Another silane which shows promising results is the adduct of glycerol dimethacrylate and 3-(isocyanato)propyltriethoxysilane. This is a urethane dimethacrylate silane (UDMS) (Fig. 1) which has two methacrylate groups and therefore enable the preparation of crosslinked structures.[11] This has already been used as a coupling agent in the commercial hybrid filling material Definite®.[14]

This work is concerned with the study of the effect of various silanes on the dynamic mechanical properties of composites. The silanes used were MPS, OTMS, UDMS, and the blends of these silanes i.e., MPS/OTMS and UDMS/OTMS 50/50 wt/wt. The resin matrix was prepared by light-curing of Bis-GMA/TEGDMA mixture 50/50 wt/wt initiated by the system camphorquinone/ethyl-4-dimethylaminobenzoate. The filler was nanosized silica (Aerosil OX50). Dynamic mechanical analysis (DMA) was performed in samples immediately after curing and in samples stored in water at 37°C for 1, 7, 30, or 120 days.

The properties measured by the DMA are the storage modulus (E'), loss modulus (E''), loss tangent
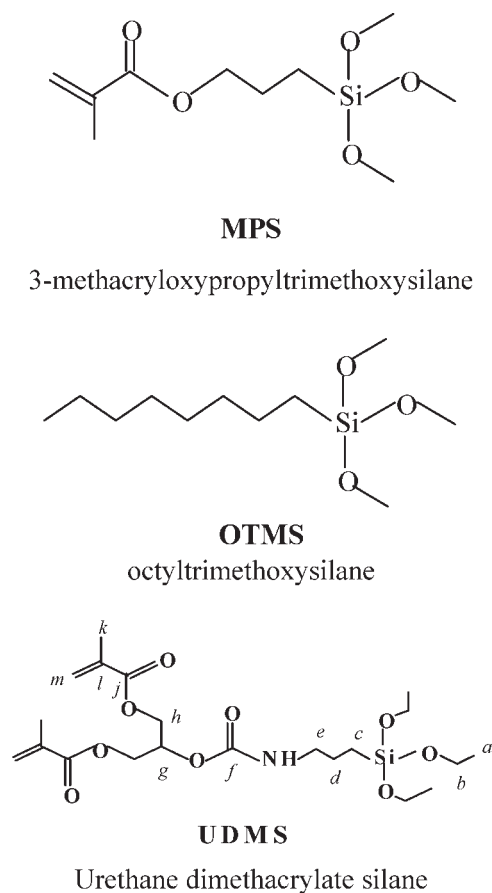

MPS
3-methacryloxypropyltrimethoxysilane

OTMS
octyltrimethoxysilane

UDMS
Urethane dimethacrylate silane

Figure 1 Chemical structure of silane coupling agents used in this study. They vary in the structure and reactivity of the organic moiety.

(tan δ), and glass transition temperature (T_g). The E' is an indicator of elastic behavior and reveals the ability of the composite to store elastic energy associated with recoverable elastic deformation. It is equivalent to the Young's modulus of an elastic solid. The E'' indicates the ability of the composite to dissipate mechanical energy through conversion into heat by molecular motion, being associated with unrecoverable viscous loss.

The ratio E''/E' defines the loss tangent often referred as tan δ. The lower the tan δ the quicker the composite will respond to load (more elastic like). The temperature at which the maximum of E'' or tan δ is observed is commonly defined as the T_g. The peak tan δ is the most prevalent criterion appearing in the literature. This is several degrees higher than the peak E''. It corresponds more closely to the transition midpoint, while the peak loss modulus more closely denotes the initial drop from the glassy state into the transition. In this respect the peak E'' value of T_g is similar to the value defined by the intersection of two tangents to the storage modules curve, one originating from the glassy region and the other from the transition region. ASTM D 4065 Practice for

determining and reporting dynamic mechanical properties of plastics, asserts that the temperature of the maximum loss modulus is the appropriate standard value. This is reasonable from a practical point of view, because the upper use temperature is the "softening" point. It is clear that by the transition midpoint (tan δ) the softening point has been exceeded.[15]

In dental polymeric material, the storage modulus and T_g are particularly important determinants of durability and clinical performance.

EXPERIMENTAL SECTION

Materials

Propylamine (99+%, Lot no 0.4419MS), cyclohexane (99+%, Lot no S22455-155), MPS (98%, Lot no 09426EC-265), and OTMS (Lot no 02327ED) used in the silanization of nanoparticles of silica were received from Sigma-Aldrich GmbH (Deisenhofen, Germany). The monomers used, i.e., Bis-GMA (Lot no 07210BB) and TEGDMA (Lot no 09004BC-275), were also provided from Sigma-Aldrich. The photoinitiator system was camphorquinone (CQ) (97%, Lot no: S12442-053) and ethyl-4-dimethylaminobenzoate (4EDMAB) (99+%, Lot no: 90909001) both from Sigma-Aldrich. The filler Aerosil OX50 (Degussa, Lot no.: 3155092345) was fumed amorphous silica with average specific surface area (BET) 50 (35–65) m^2/g and an average particle diameter of 40 nm. 3-isocyanatopropyltriethoxysilane was from ABCR GmbH and Co.KG (SII 6455.0) (Karlsruhe, Germany). Dibutyltin dilaurate (Metatin 812) (95%) (Lot no 13917HC-135) and glycerol dimethacrylate (85% mixture of isomers) were from Sigma-Aldrich (Lot no S32621-495) and hydroquinone (for synthesis > 99%) from Merck (Art 4610, 2606317).

All the materials used in this study were used as received without further purification.

Synthesis of the urethane dimethacrylate silane

UDMS was prepared from the reaction of 3-isocyanatopropyltriethoxysilane with glycerol dimethacrylate in the presence of hydroquinone and dibutylin dilaurate, following the method described in Ref. 14. The prepared silane was identified by FTIR spectroscopy (FTIR Spectrum One, Perkin–Elmer, resolution 4 cm^{-1}, 32 scans, 4000–1200 cm^{-1}). The peak at 2245 cm^{-1} attributed to the group NCO of 3-isocyanatopropyltriethoxysilane disappears when the silane reacts with glycerol dimethacrylate. UDMS was also identified by NMR spectroscopy (Bruker AM 300, internal standard: Me$_4$Si, solvent: CDCl$_3$). ^{1}H-NMR spectra were recorded at 300 MHz, while ^{13}C-NMR spectra at 75 MHz.

^{1}H-NMR: δ = 0.64 (t; 2H; CH$_2$Si), 1.23 (t; 9H; CH$_3$), 1.64 (m; 2H; CH$_2$), 1.95 (s; 6H; CH$_3$C=), 3.2 (m; 2H, CH$_2$NH), 3.8 (q; 6H; CH$_2$OSi), 4.29 (d; 4H; CH$_2$O), 5.3 (m; 1H; CHO), 5.6 (s; 4H; =CH$_2$) and 6.1 (br; 1H; NH).

^{13}C-NMR: δ = 7.6 (c), 18.1 (a,k), 22.9 (d), 43.3 (e), 58.3 (b), 62.8 (h), 69.1 (g), 126.1 (m), 135.6 (l), 155.1 (f), 166.6 (j).

Silanization of silica nanoparticles

The Aerosil OX50 silica nanoparticles were silanized following the method described in Ref. [5] using the silanes MPS, OTMS, UDMS, or the mixtures MPS/OTMS (50/50 wt/wt) and UDMS/OTMS (50/50 wt/wt). In all cases, the amount of silane was kept constant at 10% by mass fraction relative to silica.

The silica (5.0 ± 0.05 g), silane (0.55 ± 0.01 g), solvent (100 mL cyclohexane), and n-propylamine (0.1 ± 0.01 g) were stirred at room temperature for 30 min and then at 60°C ± 5°C for additional 30 min at atmospheric pressure. The mixture was then placed in a rotary evaporator at 60°C to remove the solvent and the volatile byproducts. The powder was then heated at 95°C ± 5°C for 1 h on the rotary evaporator, and finally dried at 80°C in a vacuum oven for 20 h.

The silanizated silica nanoparticles were identified by FTIR spectroscopy (resolution 4 cm^{-1}, 32 scans, 4000–1350 cm^{-1}). The spectrum of the silica nanoparticles showed absorption bands due to the surface silanol groups (Si—OH) which are principally of two types (a) free silanols which have a sharp infrared absorption band at 3740 cm^{-1} and (b) adjacent silanols which hydrogen-bond to each other and/or absorb water having a broad region centered around 3600 cm^{-1}. Silica also showed an absorption band at 1870 cm^{-1}, which is attributed to the siloxane linkages in the bulk of the silica and is unaffected by the surface treatment, and a band at 1630 cm^{-1} is due to the structure of the bulk silica. The ratio of the absorbances of the peak at 3740 and 1870 cm^{-1} was used to determine the effectiveness of silanization.[7] When the silica nanoparticles are silanized, the peak at 3740 cm^{-1} disappears. In addition two peaks appears, one at 1720 cm^{-1}, due to the free carbonyl (—C=O) stretching vibration, and another at 1470 cm^{-1} due to the double bond C=C of the methacrylate group. The peak at 1700 cm^{-1} characteristic of the carbonyl groups forming hydrogen bonds with the silica hydroxyls was almost completely overlapped by the strong peak at 1720 cm^{-1}.[16,17]

In the case of silica particles silanized with OTMS, the peaks at 1720 and 1470cm^{-1} do not appear, because OTMS does not have a methacrylate group.

Preparation of nanocomposites

The resin matrix consisted of Bis-GMA/TEGDMA mixture (50 : 50 wt/wt) which contained the photoinitiator system CQ (0.2 wt %) and 4EDMAB (0.8 wt %). Bis-GMA was first heated in an ultrasonic bath at about 40°C for 10 min and then TEGDMA containing the photoinitiating system was added. Then the silanized silica (60% mass fraction) was mixed with the resin by hand spatulation, as it is suggested in Refs. 5,6,12, and 18. Once the powder was completely wetted with the resin, the composite pastes were sheared against a glass surface using a Teflon spatula, until the pastes were semitransparent to assure maximum particle dispersion in the resin. The pastes were extremely consistent and air bubbles did not appear to be entrapped inside.

Dynamic mechanical analysis

For DMA tests, bar specimens were prepared by filling a Teflon mold (2 mm × 2 mm × 40 mm) with unpolymerized material, taking care to minimize entrapped air. The upper and lower surface of the mold was overlaid with glass slides, covered with a Mylar sheet to avoid adhesion with the unpolymerized material. The completed assembly was held together with spring clips and irradiated by overlapping, as recommended in ISO-4049, using a XL 3000 dental photocuring unit (3M Company). This source consisted of a 75-W tungsten halogen lamp, which emits radiation between 420 and 500 nm and has the maximum peak at 470 nm. This unit was used without the light guide in contact with the glass slide. Each overlap was light-cured for 80 s. The samples were irradiated on both sides. Then, the mold was dismantled and the composite was carefully removed by flexing the Teflon mold. Four specimen bars were prepared for each composite.

The bar-shaped specimens were divided into five groups of four samples each. The first group consisted of dry samples measured 1 h after preparation. During this time they were remained in a desiccator at 37°C ± 1°C in a dark environment. The second, third, fourth, and fifth group consisted of samples, which had been stored in distilled water at 37°C ± 1°C in dark for periods 1, 7, 30, and 120 days correspondingly. The samples of groups II–V were immersed in the water at 37°C ± 1°C immediately after curing.

DMA tests were performed on a Diamond dynamic mechanical analyzer (Perkin–Elmer instruments, technology SII) using a dual-cantilever clamp. A frequency of 2 Hz was applied (approximately average chewing rate) and amplitude of 10 μm. Also in the dry samples a frequency of 0.1 and 10 Hz was used; these frequencies were chosen because they represent a range of strain rates from close to "static" testing (0.1 Hz) to the upper limit of normal chewing frequency (10 Hz). A temperature range of 25 to 185°C at a heating rate of 2°C per min was selected to cover mouth temperature and the materials' likely glass-transition temperature (T_g). Storage modulus (E'), loss modulus (E''), and tangent delta (tan δ) were plotted against temperature over this period. After the DMA run was complete, the sample was allowed to cool naturally to room temperature and the values of E', E'', and tan δ at various temperatures were noted, as well as the T_g. Then the process was repeated with the same specimen and the "rerun" value for E', E'', tan δ, and T_g were determined. This method was used for each of the samples and the mean values calculated.

Statistical analysis

The values reported in all tables and figures represent mean values ± standard deviation of replicates. One-way analysis of variance (ANOVA) test, followed by a Tukey's test, for multiple comparisons between means to determinate significant differences was used at a significance level set at $P \leq 0.05$, for analysis of the experimental results.

RESULTS AND DISCUSSION

During the silanization of silica, the —OCH$_3$ groups are hydrolyzed to silanol groups by moisture contained in the cyclohexane used as solvent. Then the silanol groups condense with the surface hydroxyl groups of silica to form covalent bonds. The silanol groups on adjacent silanes can also condense with each other to form a polysiloxane network. In this network strong hydrogen bonds are also formed between the ester carbonyl groups of methacrylate moiety (MPS, UDMS), urethane groups (UDMS), and hydroxyl groups of the network, and also weak van der Waals interactions.

In all cases, the amount of the silane used was kept constant at 10% by mass fraction relative to silica, a ratio that was more than enough to completely cover the surface of the silica and to provide a durable interphase.

The amount of silane (g) to obtain a minimum uniform coverage of the filler particles (X) is given by the following equation[5,16]:

$$X = (A/\omega)f$$

In which A is the surface area of the filler ($=50$ m^2/g), ω is the surface coverage per gram of silane, and f is the amount of silica (g). In the case of MPS, it was found[17] that each silane molecule covers 1.11 nm^2 of filler and the surface area coverage per gram
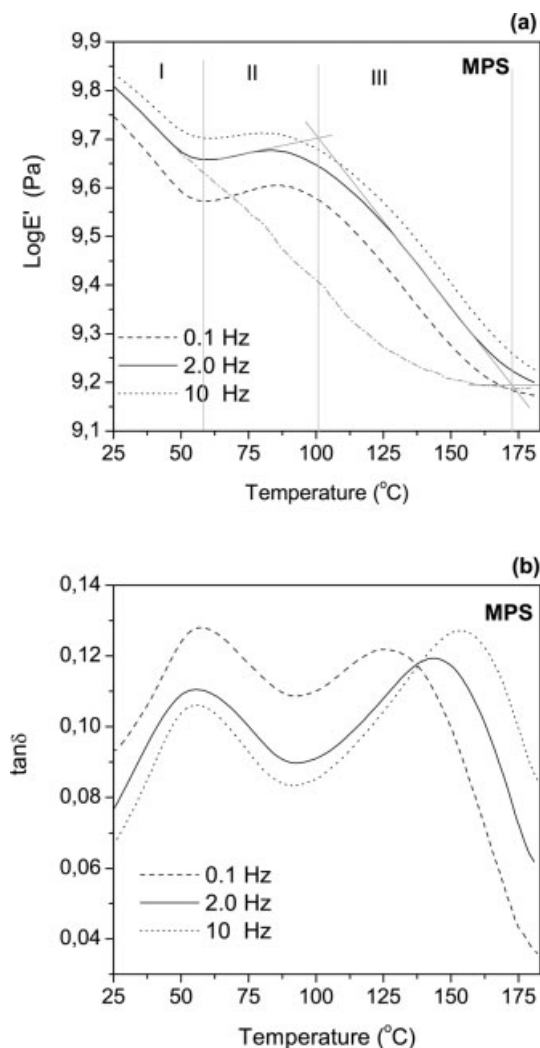
Figure 2 Curves of log storage modulus (E') (a) and tan δ (b) versus temperature at three frequencies for MPS-composite.

loosely adsorbed (physisorbed). The absence in the FTIR spectra of the silanized silica of a peak at 1700 cm^{-1}, characteristic of a hydrogen bonded C=O group and indicative of existence of a monolayer of silane on silica,[17] confirms the view that, the adsorbed silane forms multilayers.

Dynamic mechanical properties of samples after light curing

Figure 2–4 displays log storage modulus (E') and tan δ versus temperature curves obtained respectively, for MPS-composite, OTMS-composite, and UDMS-composite at three frequencies 0.1, 2.0, and 10 Hz. Analogous curves were obtained for MPS/OTMS-composite and UDMS/OTMS-composite.

The log E' versus temperature curve showed in all cases two sudden decreases between 25 and 50°C and 85–170°C, which correspond to two glass
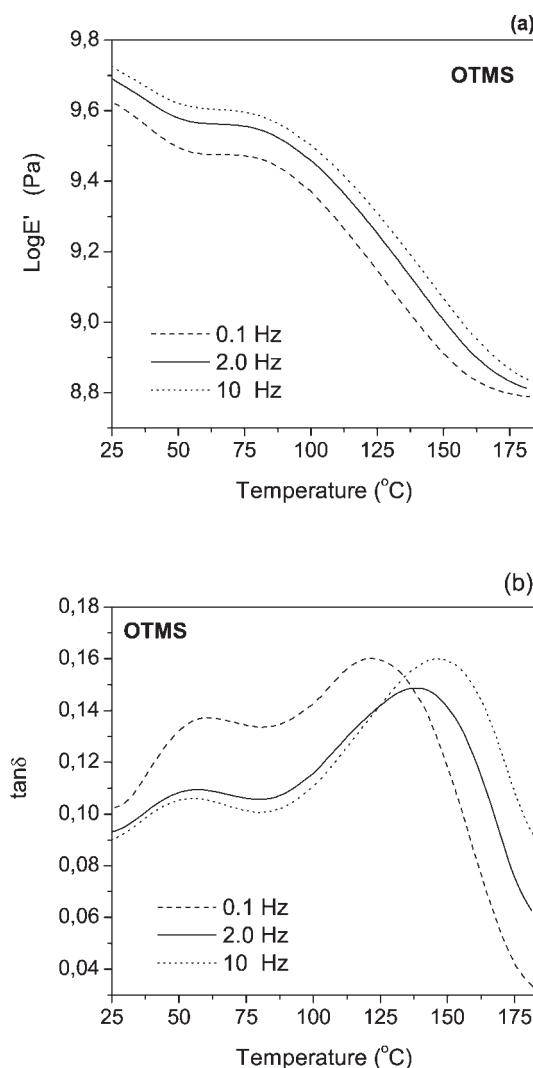

of MPS is ω = 2525 m^2/g. According to the above equation, 5.0 g of silica OX50 require 0.1 g of MPS (2% MPS by mass fraction) for minimum uniform coverage. As far as the OTMS is concerned, the filler surface area covered per this silane molecule will be about the 2% by mass, because its molecular weight (234.4) is close to that of MPS (248.3). The UDMS has much higher molecular weight, so the required amount for the minimum coverage of the filler should be lower than 2% by mass. Therefore, the silane amount used in this study (10% by mass) was more than enough to completely cover the surface of the silica.

Since the amount of silane used to cover silica was greater than that theoretically needed for mono-molecular coverage and the particles were not washed, it was expected that, the silica nanoparticle interphase consists of multiple layers of silane molecules both covalently bonded (chemisorbed) and

Figure 3 Curves of log storage modulus (E') (a) and tan δ (b) versus temperature at three frequencies for OTMS-composite.

TABLE I
Glass Transition Temperatures (T_g) of Nanocomposites After Light-Curing During the First and Second Run in DMA

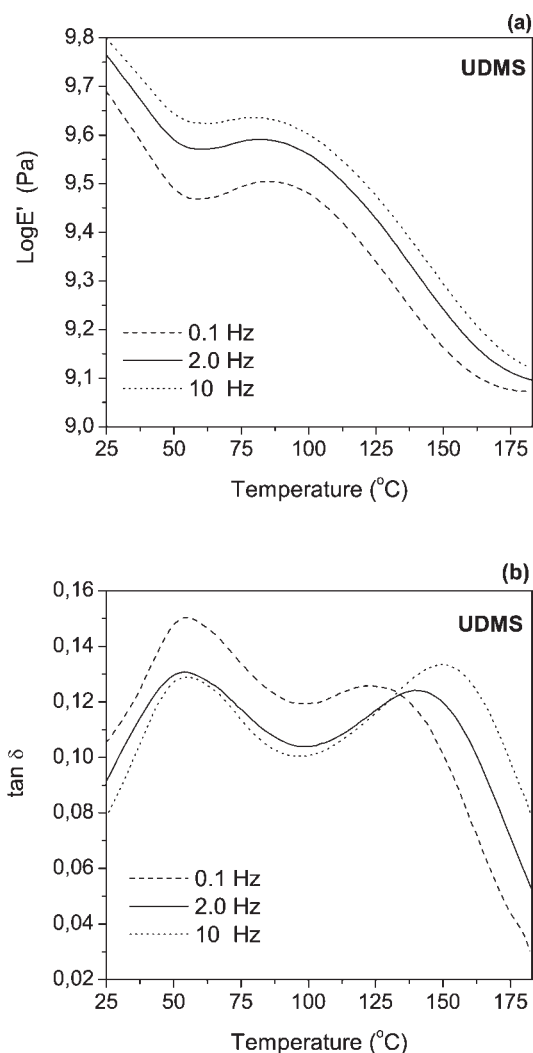| Type of silane	T_{g1} (°C)			T_{g2} (°C)		
	0.1 Hz	2 Hz	10 Hz	0.1 Hz	2 Hz	10 Hz
1st Run						
MPS	56.6	55.3	55.14	125.8	142.9	154.0
OTMS	60.5	57.5	55.6	120.8	137.8	146.0
MPS/OTMS	60.5	59.2	59	121.1	134.9	145.9
UDMS	55.2	53.9	55.4	120.9	139.4	150.9
UDMS/OTMS	56.5	53.6	53.5	122.2	139.4	149.2
2nd Run						
MPS	–	–	–	140.9	144.5	152.7
OTMS	–	–	–	131.2	143.4	149.8
MPS/OTMS	–	–	–	127.3	141.1	149.1
UDMS	–	–	–	129.1	141.1	150.9
UDMS/OTMS	–	–	–	129.4	143.1	151.1

Figure 4 Curves of log storage modulus (E') (a) and tan δ (b) versus temperature at three frequencies for UDMS-composite.

transition regions. In the corresponding tan δ versus temperature curve two separate and distinct peaks were observed assigned to two T_gs. The trend of two apparent T_g values have also been observed in room-temperature-cured vinyl ester resins[19,20] and has attributed to additional cure of the sample when the temperature is being scanned in the DMA. Two T_gs were also observed in the tan δ curve of UDMA/TEGDMA resin,[21] a Bis-GMA resin,[22] a UDMA resin,[23] and in two commercial light-cured resin composites[24,25]; in all these cases the two T_gs were attributed to the additional thermal cure occurring in the middle of the first glass transition.

As shown in Figure 2(a), the curve of log E' can be divided into three temperature regions obtained by intersecting tangential lines: first glass transition (I), thermal reaction (II), second glass transition (III). The onset of the first glass transition occurs below 25°C. As the temperature increases the log E' continues to decrease rapidly until it reaches a minimum at about 50°C. Further increase in temperature produces a gradual increase in the log E', which is indicative of additional cure. The increasing log E' reaches a maximum value at about 85°C and then begins to decrease rapidly as the additional cure is completed. The decreasing region above 85°C is due to the glass transition of the new material which has been created. Above 175°C the new material becomes rubbery.

In the incompletely cured specimen, by irradiation at room temperature, the glass transition I was disturbed by the thermal reaction. In Figure 2(a) the dashed curve in log E' is drawn assuming that there is no thermal reaction in the transition region. If this is the case, one can decide T_g with accuracy from the corresponding tan δ peak as usual at about 50°C.
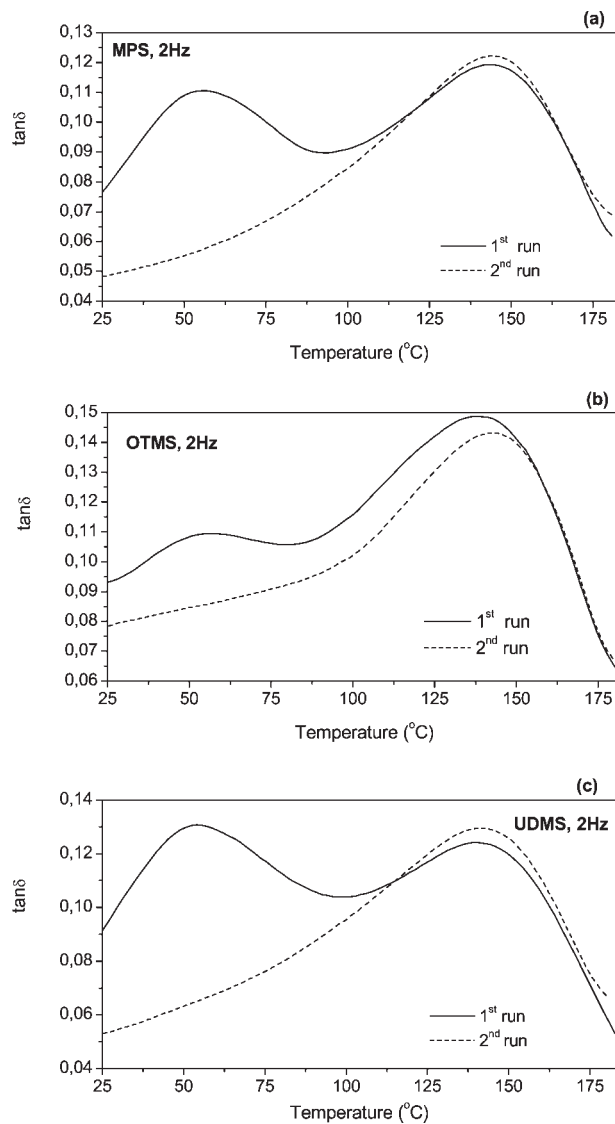
Figure 5 Tan δ versus temperature from DMA at 1st and 2nd run for frequency 2 Hz in (a) MPS-composite; (b) OTMS-composite; and (c) UDMS-composite.

The values of T_g of composites at various frequencies are presented in Table I. The first T_g at 54–60°C is independent of the composite and frequency and the second T_g is at 121–126°C for 0.1 Hz and higher 146–154°C for 10 Hz. The T_g at high frequency is higher than that determined at low frequency because the rate of molecular motion (or molecular relaxation) will not catch up with the higher test frequency until the polymer sample reaches a higher temperature.

The T_g for each sample was redetermined after cooling down from the first determination. In this 2nd run the first T_g was disappeared and the second T_g was appeared at about the same temperature [Table I, Fig. 5(a–c)]. This behavior shows that the first T_g is due to the partially light-cured at room temperature sample and that additional curing occurs during the DMA experiment as the temperature is raised.
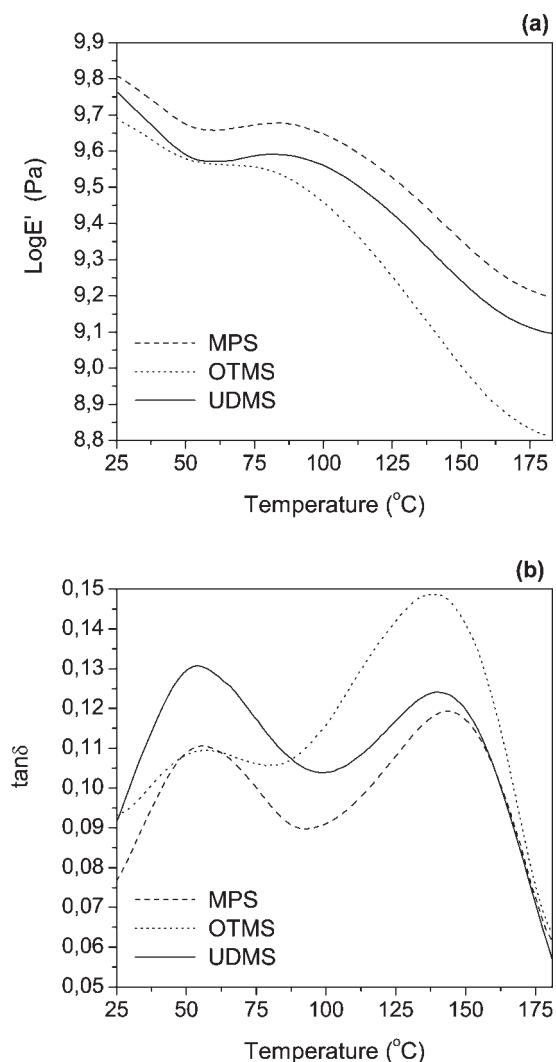
This value is about 25°C higher than the cure temperature (room temperature) in accordance with the finding observed for the curing of epoxy resins that the T_g is 20–70°C higher than the curing temperature and for the curing of a diacrylate that the T_g is 70°C higher than the curing temperature.[19]

For all composites the storage modulus increases as the frequency increases [Figs. 2(a), 3(a), and 4(a)]. The first maximum peak in the tan δ is independent of frequency, while the second peak moves to higher temperatures with increasing frequency [Figs. 2(b), 3(b), and 4(b)]. An analogous behavior has been also reported for neat Bis-GMA resin[22] and for light-cured at room temperature dental composites,[25] indicating that the first transition is not a thermodynamically stable transition.

Figure 6 Log storage modulus (E') versus temperature (a) and tan δ versus temperature (b) for the MPS-composite, OTMS-composite, and UDMS-composite for frequency 2Hz.

TABLE II
Values of the Storage Modulus (E') [GPa] at 37°C for Five Composites After Immersion
in Water for a Certain Time (days) [mean ± SD]*, $n = 4$

Type of silane	0 day	1 day	7 days	30 days	120 days
MPS	4.97 ± 0.32[a]	5.88 ± 0.45[c,A]	6.91 ± 0.50[A]	6.01 ± 0.10[e,A]	6.13 ± 0.49[g,A]
OTMS	3.97 ± 0.28[b,B]	4.41 ± 0.33[B]	4.11 ± 0.01[B]	4.81 ± 0.41[B]	4.89 ± 0.63[h,B]
MPS/OTMS	4.63 ± 0.35[a,b]	5.85 ± 0.49[c,C]	5.42 ± 0.26[d,C]	5.57 ± 0.05[f,C]	6.28 ± 0.80[g,h,C]
UDMS	4.50 ± 0.34[a,b]	5.90 ± 0.76[c,D]	5.53 ± 0.21[d,D]	5.82 ± 0.43[e,f,D]	6.07 ± 1.19[g,h,D]
UDMS/OTMS	4.44 ± 0.60[a,b]	6.01 ± 0.60[c,E]	5.65 ± 0.19[d,E]	5.35 ± 0.08[f,E]	5.53 ± 0.36[g,h,E]

* Common corresponding lowercase letters in a given column indicate no significant difference ($P > 0.05$). Common corresponding uppercase letters in a given row indicate no significant difference ($P > 0.05$).

The values of E' and tan δ determined during the 2nd run after cooling down from the first determination, showed generally a significant increase in elastic modulus and a decrease in tan δ for all specimens.

In Figure 6 the curves of log E' and tan δ are compared for the studied composites. The values of log E' for MPS-composite are higher for all temperatures, followed by the values of UDMS-composite and finally by OTMS-composite. Also the tan δ values of MPS-composite are lower than those of UDMS-composite. The lower the loss tangent, the quicker the material will respond to load (more elastic like) returning faster to its original shape, whereas the higher it is the higher the amount of energy lost as heat (more viscous like). Thus the ability of bifunctional UDMS for crosslinking seems not to increase the elastic behavior of the composite, as it was expected, compared with that of MPS composite.

The composition and structural arrangement within the polysiloxane interphase impacts its interaction with the resin matrix and hence the chemical reactivity between the methacrylate groups of silane with the methacrylate groups of the resin matrix. This interaction forms the basis of the interpenetrating network theory of silane reinforcement.[26] Studies with γ-aminopropyltriethoxysilane and epoxy resin have shown that their reactivity with each other is dependent upon the extent of condensation of the silane interphase. This result is due to decreased dif-

fusion of the resin into the polysiloxane network at increased condensation.[27] On the other hand, a study of the influence of MPS content on the degree of conversion of methacrylate groups of Bis-GMA/TEGDMA composites showed that the higher the silane content the lower the degree of conversion.[18] It was found that when large amount of silane is used the most of the methacrylate functionality within the silane interphase is in a nonreactive environment. A highly condensed silane interphase seems to limit mobility of the silane methacrylate and hence its reactivity with the dimethacrylate monomers. Based on these literature data we could suggest that in our work the UDMS formed a more condensed silane interphase than MPS, which limited the copolymerization of the silane methacrylate groups with the dimethacrylate monomers and did not improve the dynamic mechanical properties of the corresponding composite by crosslinking, as it was expected. The amount of silane which is used seems to play an important role and most probably the use of lower amount of silane than that used in this work will give better results.

Dynamic mechanical properties of samples after light curing and immersion in water at 37°C for 1, 7, 30, or 120 days

In the literature authors do not always agree about the effect of water storage on mechanical properties of composites, as there were conflicting trends of

TABLE III
Values of the Loss Modulus (E'') [GPa] at 37°C for Five Composites, After Immersion in Water
for a Certain Time (days) [mean ± SD]*, $n = 4$

Type of silane	0 day	1 day	7 days	30 days	120 days
MPS	0.50 ± 0.03[a,A]	0.40 ± 0.05[c,B]	0.47 ± 0.02[d,A,B]	0.42 ± 0.00[f,B]	0.37 ± 0.03[g,B]
OTMS	0.38 ± 0.02[b,C]	0.38 ± 0.01[c,C]	0.35 ± 0.00[e,C]	0.38 ± 0.04[f,C]	0.34 ± 0.04[g,C]
MPS/OTMS	0.48 ± 0.04[a,D]	0.41 ± 0.04[c,D,E]	0.36 ± 0.02[e,E]	0.37 ± 0.01[f,E]	0.41 ± 0.06[g,D,E]
UDMS	0.48 ± 0.06[a,b,F]	0.45 ± 0.06[c,F]	0.39 ± 0.01[e,F]	0.45 ± 0.06[f,F]	0.44 ± 0.10[g,F]
UDMS/OTMS	0.40 ± 0.07[a,b,G]	0.45 ± 0.07[c,G]	0.45 ± 0.01[d,G]	0.43 ± 0.03[f,G]	0.38 ± 0.02[g,G]

* Common corresponding lowercase letters in a given column indicate no significant difference ($P > 0.05$). Common corresponding uppercase letters in a given row indicate no significant difference ($P > 0.05$).

TABLE IV
Values of Tangent Delta (tan δ) (×10^3) at 37°C for Five Composites, After Immersion in Water for a Certain Time (days) [mean ± SD]*, $n = 4$

Silane type	0 day	1 day	7 days	30 days	120 days
MPS	101 ± 2[a]	69 ± 2[b,A]	67 ± 2[c,A]	69 ± 1[f,A]	61 ± 2[h]
OTMS	98 ± 9[a,B]	86 ± 1[B,C]	87 ± 3[d,B,C]	78 ± 2[g,C,D]	70 ± 5[h,i,D]
MPS/OTMS	106 ± 4[a]	70 ± 1[b,E]	67 ± 3[c,E]	65 ± 2[f,E]	65 ± 5[h,i,E]
UDMS	108 ± 4[a]	75 ± 5[b,F]	71 ± 4[c,e,F]	76 ± 7[f,g,F]	72 ± 3[i,F]
UDMS/OTMS	102 ± 8[a]	74 ± 2[b,G]	80 ± 4[d,e,G]	80 ± 5[g,G]	68 ± 4[h,i,G]

* Common corresponding lowercase letters in a given column indicate no significant difference ($P > 0.05$). Common corresponding uppercase letters in a given row indicate no significant difference ($P > 0.05$).

increase and decrease over time. According to Gladys et al.[28] the Young's modulus increased slightly during the first month and then showed a slight decrease to reach a steady state. Ferracane et al.[29] reported that composites showed a slight but significant decrease in their modulus after immersion in water for 30 days and reached a plateau at 6 weeks. Drummond et al.[30] noticed a significant decrease in the modulus of elasticity after aging in water for 6 months. Sabbagh et al.[31] found an increase of composites moduli between 24 h and 1 month and a relative stability up to 6 months.

It is known that storage of composites in water at 37°C will induce some post cure, water sorption, and solubility and that the magnitude of each effect depends on the composite composition. Post cure increases the storage modulus. On the contrary water acts as a plasticizer and decreases with time the modulus. However with time the material loses its own plasticizer through solubility. These three effects superimposed and the precise behavior of each material depends on its composition.

Our results about the effect of water on elastic modulus at 37°C are shown in Table II.

MPS-composite showed an increase of elastic modulus after 1 day immersion in water which remained constant up to 120 days. OTMS-composite did not show any difference, while MPS/OTMS-composite showed an increase of elastic modulus after 1 day immersion in water, which remained constant up to 120 days, as in the case of MPS-composite. UDMS-composite showed an increase of elastic modulus after 1 day in water, which remained constant up to immersion 120 days. The same behavior showed also UDMS/OTMS-composite.

It is interesting to note that OTMS-composite in which OTMS does not form covalent bond with the dimethacrylate matrix showed lower elastic modulus both in dry and wet conditions. After immersion in water the elastic modulus of OTMS-composite remained constant, while that of the other composites increased after 1 day and then remained constant.

The effect of immersion in water on the loss modulus (E'') and the tan δ is presented correspondingly in Tables III and IV.

The dry composites showed at 37°C statistically the same loss modulus and the OTMS-composite a lower value; after immersion in water for 120 days the loss modulus of MPS-composite was decreased, while for all other composites remained statistically the same. More characteristic is the effect of water on tan δ at 37°C (Table IV). MPS-composite shows a significant decrease of tan δ after 1 day and then also after 120 days. OTMS-composite showed a decrease after 30 days and the other composites a decrease after 1 day.

Figure 7 shows the effect of water on tan δ at all temperatures for MPS-composite. The shape of curves show that post curing occurs during immersion in water mainly up to 7 days. Analogous results were obtained and for the other composites. The samples remained in water for 7, 30, or 120 days showed one peak that is one T_g. The effect of immersion time on T_g is shown in Table V.

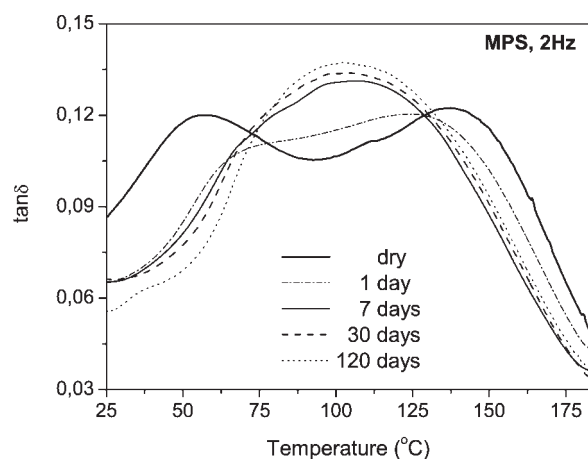Water acts as a plasticizer of the resin matrix and decreases the T_g, analogously to the absorbed water

Figure 7 Effect of immersion time in water at 37°C on tan δ for MPS-composite at 2 Hz and 25–175°C.

TABLE V
Values of Glass Transition Temperature (T_g) (°C) for Five Composites, After Immersion
in Water for a Certain Time (days) [mean ± SD]*, $n = 4$

Silane type	0 day	1 day	7 days	30 days	120 days
MPS	136.2 ± 0.9[a]	123.1 ± 1.8[b]	106.7 ± 0.1[c,A]	104.9 ± 0.1[d,A]	103.5 ± 1.9[e,A]
OTMS	134.4 ± 1.9[a]	117.0 ± 0.1[b]	109.9 ± 0.5[c,B]	111.2 ± 1.1[B]	111.3 ± 2.0[B]
MPS/OTMS	132.5 ± 3.7[a]	122.5 ± 1.1[b]	105.7 ± 0.2[c,C]	102.9 ± 0.9[d,C]	101.7 ± 3.8[e,C]
UDMS	130.1 ± 0.9[a]	122.8 ± 1.5[b]	102.2 ± 0.4[c,D]	100.7 ± 2.8[d,D]	98.4 ± 4.3[e,D]
UDMS/OTMS	129.7 ± 1.8[a]	118.8 ± 3.0[b]	108.7 ± 0.2[c,E]	102.6 ± 4.0[d,E]	103.9 ± 2.0[e,E]

* Common corresponding lowercase letters in a given column indicate no significant difference ($P > 0.05$). Common corresponding uppercase letters in a given row indicate no significant difference ($P > 0.05$).

amount. All composites showed significant decrease of T_g up to 7 days which then remained constant.

Also it is interesting to note that, after immersion for 120 days in water, the T_g of OTMS-composite with the more hydrophobic OTMS is higher than the T_g of the other composites which is statistically about the same.

CONCLUSIONS

The ability of bifunctional UDMS for crosslinking did not increase the elastic behavior of the composite. Most probably the UDMS formed a more condensed silane interphase than MPS which limit the copolymerization of the silane methacrylate groups with the dimethacrylate monomers. The amount of silane which is used plays an important role and the use of lower amount must be tested. OTMS-composite in which OTMS does not form covalent bond with the dimethacrylate matrix showed lower elastic modulus both in dry and wet conditions. After immersion in water the elastic modulus of OTMS-composite remained constant, while that of the other composites increased after 1 day and then remained constant.

References

1. Craig, R. G.; Powers, J. M., Eds. Restorative Dental Materials, 11th ed.; Mosby: St. Louis, MO, 2002; p 231.
2. Moszner, N.; Klapdohr, S. Int J Nanotechnol 2004, 1, 130.
3. Matinlinna, J. P.; Lassila, L. V. J.; Özcan, M.; Urpo, A. Y.; Vallittu, P. K. Int J Prosthodont 2004, 17, 155.
4. Antonucci, J. M.; Dickens, S.; Fowler, B. O.; Xu, H. H. K.; McDonough, W. G. J Res Natl Inst Stand Technol 2005, 110, 541.
5. Wilson, K. S.; Zhang, K.; Antonucci, J. M. Biomaterials 2005, 26, 5095.
6. Wilson, K. S.; Antonucci, J. M. Dent Mater 2006, 22, 995.
7. Chen, T. M.; Brauer, G. M. J J Dent Res 1982, 61, 1439.
8. Antonucci, J. M.; McDonough, W. J.; Schutte, C. L.; Moon, C. K. Polym Prepr 1995, 36, 821.
9. McDonough, W. J.; Antonucci, J. M.; Dunkers, J. P. Polym Prepr 1997, 38, 112.
10. McDonough, W. J.; Antonucci, J. M.; Dunkers, J. P. Dent Mater 2001, 17, 492.
11. Klapdohr, S.; Moszner, N. Monatsh Chem 2005, 136, 21.
12. Wilson, K. S.; Allen, A. J.; Washburn, N. R.; Antonucci, J. M. J Biomed Mater Res A 2007, 81, 113.
13. Matinlinna, J. P.; Lassila, L. V. J.; Kangasniemi, I.; Vallittu, P. K. J Dent Res 2005, 84, 360.
14. Mozner, N.; Völkel, T.; Von Clausbruch, S. C.; Geiter, E.; Batliner, N.; Rheinberger, V. S. Macromol Mater Eng 2002, 287, 339.
15. Chartoff, R. P.; Weissman, P. T.; Sircar, A. In Assignment of the Glass Transition; Seyler, R., Ed.; ASTM: Philadelphia, 1993; p 90.
16. Liu, Q.; Ding, J.; Chambers, D. E.; Debnath, S.; Wunder, S. L.; Baran, G. R. J Biomed Mater Res 2001, 57, 384.
17. Söderholm, K. J. M.; Shang, S. W. J Dent Res 1993, 72, 1050.
18. Halvorson, R. H.; Erickson, R. L.; Davidson, C. L. Dent Mater 2003, 19, 327.
19. Cook, W. D.; Simon, G. P.; Burchill, P. J.; Lau, M.; Fitch, T. J. J Appl Polym Sci 1997, 64, 769.
20. Herzog, B.; Gardner, D. J.; Lopez-Anido, R.; Goodell, B. J Appl Polym Sci 2005, 97, 2221.
21. Lee, J. K.; Choi, J.-Y.; Lim, B.-S.; Lee, Y.-K.; Sakagushi, R. L. J Biomed Mater Res Part B: Appl Biomater 2004, 68, 216.
22. Clarke, R. L. Biomaterials 1989, 10, 549.
23. Lee, J. K.; Kim, J. Y.; Lim, B. S. Polym J 2003, 35, 890.
24. Sideridou, I. D.; Karabela, M. M.; Vouvoudi, E. Ch. Dent 2008, 24, 737.
25. Enami, N.; Söderholm, K. J. M. Dent Mater 2005, 21, 977.
26. Plueddemann, E. P. Present Status and Research in Silane Coupling Agents. Interfaces in Polymer, Ceramic and Metal Matrix Composites; Elsevier: New York, 1988; p 17.
27. Culler, S. R.; Ishida, H.; Koening, J. L. J Colloid Interface Sci 1986, 109, 1.
28. Gladys, S.; Van Meerbeek, B.; Braem, M.; Lambrechts, P.; Vanherle, G. J Dent Res 1997, 76, 883.
29. Ferracane, J. L.; Hopkin, J. K.; Condon, J. R. Dent Mater 1995, 11, 354.
30. Drummond, J. L.; Botsis, J.; Zhao, D.; Samyn, D. J Oral Sci 1998, 106, 661.
31. Sabbagh, J.; Vreven, J.; Leloup, G. Dent Mater 2002, 18, 64.