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## Synthesis and evaluation of novel siloxane-methacrylate monomers used as dentin adhesives

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### Abstract

**Objectives**—The objectives of this study were to synthesize two new siloxane-methacrylate (SM) monomers for application in dentin adhesives and to investigate the influence of different functionality of the siloxane-containing monomers on the adhesive photopolymerization, water sorption, and mechanical properties.

**Materials and method**—Two siloxane-methacrylate monomers (SM1 and SM2) with four and eight methacrylate groups were synthesized. Dentin adhesives containing BisGMA, HEMA and the siloxane-methacrylate monomers were photo-polymerized. The experimental adhesives were compared with the control adhesive (HEMA/BisGMA 45/55 w/w) and characterized with regard to degree of conversion (DC), water miscibility of the liquid resin, water sorption and dynamic mechanical analysis (DMA).

**Results**—The experimental adhesives exhibited improved water miscibility as compared to the control. When cured in the presence of 12 wt % water to simulate the wet environment of the mouth, the SM-containing adhesives showed DC comparable to the control. The experimental adhesives showed higher rubbery modulus than the control under dry conditions. Under wet conditions, the mechanical properties of the formulations containing SM monomer with increased functionality were comparable with the control, even with more water sorption.

**Significance**—The concentration and functionality of the newly synthesized siloxane-methacrylate monomers affected the water miscibility, water sorption and mechanical properties of the adhesives. The experimental adhesives show improved water compatibility compared with the control. The mechanical properties were enhanced with an increase of the functionality of the siloxane-containing monomers. The results provide critical structure/property relationships and important information for future development of durable, versatile siloxane-containing dentin adhesives.

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## Keywords

Siloxane-methacrylate; Dentin adhesive; Water miscibility; Dynamical mechanical property; Photopolymerization

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## Introduction

During the last 20 years, the primary motivation for changing the resin chemistry of restorative composites was to reduce the polymerization shrinkage[1]. The polymerization shrinkage occurs during the curing of the composite in the tooth cavity and may lead to the formation of marginal gaps. The silorane-based composite, introduced by 3M in 2007, exhibits the lowest polymerization shrinkage (1.4 vol %) of the current composite restorative materials [1, 2].

The hybrid monomer systems introduced by 3M contain both siloxane and oxirane structural units. The main benefits of these resins are the very low polymerization shrinkage, the good biocompatibility, the very low water solubility of the monomers, and low water sorption of the formed polymer networks[3–6]. This siloxane-based composite does not, however, exhibit the lowest polymerization stress[1, 2]. Other limitations, including increased exothermic effect (twice as high as dimethacrylate-based composites with similar filler load), the delay in establishing mechanical properties comparable to dimethacrylates, and the lower refractive index, have inhibited broad market acceptance of the silorane-based composite[1, 7, 8]. The lower bond strength of the silorane composite with commercial dentin adhesives[9] has raised concerns about the compatibility of these materials.

Siloxane-containing materials have been widely used as biomaterials in medical and pharmaceutical applications, due to their biocompatibility and low toxicity[10–13]. For example, polysiloxane has a high refractive index and can be used as the accommodating intraocular lens by the polymerization of siloxane-methacrylate monomers[14]. Siloxane-containing cross-linking agents are often used in drug delivery systems[15]. Moreover, in the presence of siloxane groups, the stability of restorative materials can be improved[16]. In this context, if siloxane groups could be incorporated into the dentin adhesive, it is expected that the durability of the dentin adhesives and compatibility with the silorane composite would be improved. However, polymers with siloxane groups are usually soft, and their mechanical strength may be low because of the flexibility of the siloxane groups[17–19]. Therefore, modification of siloxane with methacrylate to take advantage of both the stability of siloxane groups and good mechanical properties of methacrylates could be a solution.

The twofold objectives of this work were: 1) to synthesize and characterize two new siloxane-methacrylate monomers with four and eight methacrylate groups and 2) to investigate the influence of chemical structure of siloxane-containing monomers used in dentin adhesives on the following properties: degree of conversion, water miscibility, water sorption and dynamic mechanical properties. To our knowledge, this investigation marks the first study of siloxane-methacrylate monomers used in dentin adhesives. The results provide critical structure/property relationships for siloxane-methacrylate monomers and important

information for future development of durable, versatile siloxane-containing dentin adhesives.

## Materials and methods

### Materials

2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]-propane (BisGMA, Polysciences, Warrington, PA) and 2-hydroxyethylmethacrylate (HEMA, Acros Organics, NJ) were used as received without further purification, as monomers in dentin adhesives. Two siloxane methacrylate monomers (SM1 and SM2) were synthesized in our lab. The control adhesive resin consisted of HEMA and BisGMA with a mass ratio of 45/55. This control was used to compare with the experimental adhesive resins with HEMA / BisGMA / SM = 45/55-x/x (w/w) ratio. The control and experimental adhesives were also formulated with 12 wt % water to simulate bonding in the mouth. The concentration of water was based on the total final weight of the adhesive resin. Camphorquinone (CQ, 0.5 wt %), ethyl-4-(dimethylamino) benzoate (EDMAB, 0.5 wt %) and diphenyliodonium hexafluorophosphate (DPIHP, 1.0 wt %) were obtained from Aldrich (Milwaukee, WI, USA) and used as a three-component-photoinitiator system without further purification. 2,4,6,8-Tetramethyl-2,4,6,8-tetrakis (propyl glycidyl ether) cyclotetrasiloxane (TPGTS), Glycerol dimethacrylate (GDMA, assay 85%, mixture of isomers), ethyl acetate, boron trifluoride diethyl etherate ( $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ ), anhydrous magnesium sulfate ( $\text{MgSO}_4$ ), and all other chemicals were purchased from Sigma-Aldrich at reagent grade and used without further purification.

### Synthesis of Siloxane-Methacrylate (SM) monomers

2,4,6,8-Tetramethyl-2,4,6,8-tetrakis (propyl glycidyl ether) cyclotetrasiloxane (TPGTS, 10 g, 0.0143 mol), 2-hydroxyethylmethacrylate (HEMA, 10 g, 0.076 mol) or glycerol dimethacrylate (GDMA, mixture of isomers, 13.75 g, 0.06 mol) and ethyl acetate (EA, 100 mL) were mixed together. Boron trifluoride diethyl etherate (0.2 mL) was added into this solution. The reaction was allowed to continue at room temperature for about 12 h, and it was monitored by thin layer chromatography (mobile phase: dichloromethane / hexane, 50/50 wt %). The product-containing solution was washed with distilled water and dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed with a rotary evaporator at 35–40 °C. The process for the synthesis of the two siloxane methacrylate monomers (SM1 and SM2) is shown in Scheme 1. The yields of SM1 and SM2, which were colorless and viscous, were 92.4 and 95.0 %, respectively. The structure of the synthesized compounds (SM1, SM2) was confirmed using FTIR (Spectrum 400, Perkin-Elmer, Waltham, MA),  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (FT-400 MHz Bruker Spectrometer, DMSO as solvent) spectroscopies.

### Preparation of adhesive formulations

The preparation of the control adhesive formulations has been reported [20, 21]. As shown in Table 1, the control adhesive formulation (C0) consisted of HEMA and BisGMA with a mass ratio of 45/55 [21–23] which is similar to widely used commercial dentin adhesives. In the experimental adhesive formulations (E-SM), siloxane-methacrylates were used as comonomers to partially replace the BisGMA (Table 1). The siloxane-methacrylates were included at 5, 15, and 25 wt %. The abbreviations E1, E2, and E3 represent 5, 15, and 25 wt

% of either SM1 or SM2. Water at 12 wt % was added into C0, E3-SM1 and E3-SM2 to simulate the moist environment of the mouth. The composition of the three component initiator system was CQ (0.5 wt %), EDMAB (0.5 wt %) and DPIHP (1.0 wt %) with respect to the total amount of monomer[22, 24–27]. The resin mixtures were prepared in a brown glass vial. The solutions containing the monomers/photoinitiators were mixed for 48h at room temperature to promote complete dissolution and formation of a homogeneous solution.

### Real-time conversion and maximal polymerization rate

Real-time *in situ* monitoring of the photopolymerization of the adhesive formulations was performed using an infrared spectrometer (Spectrum 400 Fourier transform infrared spectrophotometer, Perkin-Elmer, Waltham, MA) at a resolution of  $4\text{ cm}^{-1}$ [22, 25]. One drop of adhesive solution was placed on the diamond crystal top-plate of an attenuated total reflectance (ATR) accessory (Pike, GladiATR, Pike Technology, Madison, WI) and covered with a mylar film. A 40-s-exposure to the commercial visible-light-polymerization unit (Spectrum®, Dentsply, Milford, DE), at an intensity of  $550\text{ mW cm}^{-2}$ , was initiated after 50 spectra had been recorded. Real-time IR spectra were recorded continuously for 600 s after light curing began. A time-based spectrum collector (Spectrum TimeBase, Perkin-Elmer) was used for continuous and automatic collection of spectra during polymerization. Three replicates were obtained for each adhesive formulation. To determine degree of conversion, heavy water (deuterium oxide, 99.9%,  $\text{D}_2\text{O}$ ) (Cambridge Isotope Laboratories, Inc., Andover, MA, USA) was used in this study to reduce interference from the overlapping water peak at  $1640\text{ cm}^{-1}$ . The change of the band ratio profile ( $1637\text{ cm}^{-1}(\text{C}=\text{C})/1608\text{ cm}^{-1}(\text{phenyl})$ ) was monitored. DC was calculated using the following equation, which is based on the decrease in the absorption intensity band ratios before and after light curing. The average of the last 50 values of time-based data points is reported as the DC value at 10 minutes.

$$DC = \left(1 - \frac{\text{Absorbance}_{1637\text{ cm}^{-1}}^{\text{sample}} / \text{Absorbance}_{1608\text{ cm}^{-1}}^{\text{sample}}}{\text{Absorbance}_{1637\text{ cm}^{-1}}^{\text{monomer}} / \text{Absorbance}_{1608\text{ cm}^{-1}}^{\text{monomer}}}\right) \times 100\%$$

The maximal polymerization rate was determined using the maximum slope of the linear region of the DC-time plots[24, 28].

### Viscosity measurement

Brookfield DV-II +Pro viscometer with a cone/plate set up was used to measure the viscosity of the formulations at varying shear rate  $45\text{ s}^{-1}$  to  $75\text{ s}^{-1}$ . For each formulation viscosity of three samples was measured at  $25.0 \pm 0.2\text{ }^\circ\text{C}$ . The sample volume was kept constant to 0.5ml.

### Preparation of adhesive polymer specimens for property analyses

The preparation of polymer specimens for property analyses has been reported [28–32]. In brief, round beams with a diameter of 1 mm and a length of at least 15 mm were prepared by

injecting the adhesive formulations into glass molds (Fiber Optic Center, Inc., part no.: ST8100, New Bedford, MA). Fifteen specimens were prepared for each formulation. The samples were light polymerized with an LED light curing unit for 40s (LED Curebox, 200 mW/cm<sup>2</sup> irradiance, Prototech, and Portland, OR). The polymerized samples were stored in the dark at room temperature for two days to provide adequate time for post-cure polymerization. The samples were subsequently extracted from the glass molds. The resultant beam specimens were used for water sorption, dynamic mechanical analysis and microscale morphologic characterization.

### Water miscibility

Water miscibility is the property of the liquid monomer resin to mix with water, forming a homogeneous solution. In principle, the main focus is usually on the solubility of water in different formulations of the monomer resin. About 0.5 g of each neat resin was weighed into a brown vial, and water was added in increments of approximately 0.005 g until the mixture was visually observed to be turbid. The percentage of water in the mixture was noted ( $w_1$ ). The mixture was then back-titrated using the neat resin until the turbidity disappeared, and the percentage of water in the mixture was again noted ( $w_2$ ). Three samples were tested for each formulation and water miscibility of the liquid formulation was calculated as the average of  $w_1$  and  $w_2$ .

### Water sorption

The water sorption protocol has been reported [32]. In brief, water sorption was measured using cylindrical beam specimens (1 mm×15 mm). Five specimens were prepared for each adhesive formulation.

**Prewash**—Each beam specimen was weighed in air ( $m_{1dry}$ ) using an analytical balance with a resolution of 0.01 mg (Mettler Toledo, XS205 dualRange, Greifensee, Switzerland). The specimens were immersed in deionized water and stored at room temperature. The water was changed daily. After five days of prewash, the polymer specimens were allowed to dry in the vacuum chamber at 37 °C until a constant weight ( $m_{3dry}$ ) was obtained. The solubility during the prewash experiment was calculated as:

$$\text{Solubility}_1(\%) = 100 \frac{m_{1dry} - m_{3dry}}{m_{1dry}}$$

**Water sorption experiment**—After prewash, the dry beams were used in the following procedure. Each beam specimen was weighed in air ( $m'_{1dry}$ , the same value as  $m_{3dry}$  after prewash) using an analytical balance with a resolution of 0.01 mg (Mettler Toledo, XS205 dualRange, Greifensee, Switzerland). The specimens were then immersed in deionized water and stored at room temperature. At fixed time intervals (3, 7, 24, 48, 72, 120, 168 and 240 h), the polymer specimens were retrieved, blotted dry to remove excess liquid, weighed ( $m'_{2wet}$ ), and re-immersed in the water. After the data collection, the specimens were allowed to dry in the vacuum chamber at 37 °C until a constant weight ( $m'_{3dry}$ ) was obtained. The value (%) for mass change, solubility, and water sorption (since water uptake

and solubility occur simultaneously, the values of mass change and solubility were added together to provide the total water sorption) were calculated

$$\text{Mass change}(\%)=100\frac{m'_{2wet}-m'_{1dry}}{m'_{1dry}}$$

$$\text{Solubility}_2(\%)=100\frac{m'_{1dry}-m'_{3dry}}{m'_{1dry}}$$

$$\text{Solubility}(\%)=\text{Solubility}_1(\%)+\text{Solubility}_2(\%)$$

$$\text{Water sorption}(\%)=\text{Mass change}(\%)+\text{Solubility}_2(\%)$$

### Dynamic mechanical analysis (DMA)

As described [25, 28, 30–32], the viscoelastic properties of the dentin adhesives were characterized using DMA Q800 (TA Instruments, New Castle, USA) with a 3-point bending clamp. The cylinder beam specimens (1mm×15mm) were divided into two groups. The first group consisted of dry samples, which had been stored in the dark at room temperature for two days. These specimens were tested by a standard 3-point bending clamp. The test temperature was varied from 0 to 250 °C with a ramping rate of 3 °C/min, a frequency of 1 Hz, an amplitude of 15 μm, and a pre-load of 0.01 N. The second group consisted of wet samples, which were stored in the dark for two days to allow complete post-cure polymerization and then stored in distilled water at 37 °C for prewash. These samples were tested by 3-point bending, using a water submersion clamp[29]. The test temperature was varied from 5 to 80 °C with a ramping rate of 1.5 °C/min at a frequency of 1 Hz. The properties measured under this oscillating loading were storage modulus ( $E'$ ) and  $\tan \delta$ . The  $E'$  value represents the stiffness of a viscoelastic material and is proportional to the energy stored during a loading cycle. The ratio of loss modulus ( $E''$ ) to storage modulus  $E'$  is referred to as the mechanical damping, or  $\tan \delta$  (i.e.,  $\tan \delta = E''/E'$ ). The  $\tan \delta$  value reaches a maximum as the polymer undergoes the transition from the glassy state to the rubbery state. The glass transition temperature ( $T_g$ ) was determined as the position of the maximum on the  $\tan \delta$  vs. temperature plot. Five specimens of each adhesive formulation were measured under dry and wet conditions. The results from the five specimens per each formulation were averaged.

### Micro-X-ray tomography

The microscale morphologies of cylinder beams cured in the presence of 12 wt % water were observed using three-dimensional (3D) micro x-ray computer tomography (MicroXCT-400, Xradia Inc. Pleasanton, CA). Computer tomography (CT) facilitates viewing of an object in 3D and allows selection of virtual slices spaced by 1 μm, thus

illustrating the bulk structure of heterogeneous materials. The transmission x-ray imaging of the samples was performed using an x-ray tube with a tungsten anode setting of 50 KV at 8 W and an optical magnification of 20×[28]. The 3D images were constructed with the help of the software “XM Reconstructor 8.0” (Xradia Inc. Pleasanton, CA), using 1600 images taken at 12 s exposure time per image.

### Statistical analysis

The results were analyzed statistically using analysis of variance (ANOVA), together with Tukey’s test at  $\alpha=0.05$  (Microcal Origin Version 8.0, Microcal Software Inc., Northampton, MA).

## Results

### Characterization of the synthesized siloxane-methacrylates

The structures of the newly synthesized siloxane-methacrylate monomers (SM1 and SM2) were identified using FTIR and  $^1\text{H}$  NMR/  $^{13}\text{C}$  NMR spectroscopies. The FTIR spectrum is shown in Fig. 1A. The characteristic FTIR peaks for siloxane-methacrylates are:  $1718\text{cm}^{-1}$  (C=O stretching on OCO),  $1638\text{cm}^{-1}$  (C=C bending on methacrylate groups) and  $1259\text{cm}^{-1}$  (Si-CH<sub>3</sub> bending on cyclotetrasiloxane groups). The appearance of the –OH stretching band at  $3465\text{cm}^{-1}$  confirmed the formation of the new siloxane-containing monomer after the ring-opening reaction of epoxy groups. The  $^1\text{H}$  NMR/  $^{13}\text{C}$  NMR spectra of siloxane-methacrylates (Fig. 1B and 1C for SM1; Fig. 1D and 1E for SM2) show the chemical shifts, which confirm the desired structures. The methacrylate groups are supported by the presence of two singlets ( $\delta = 6.0$  and  $5.5$  ppm) on the  $^1\text{H}$ -NMR spectrum and by the peaks at  $135.9$  and  $126.1$  ppm in the  $^{13}\text{C}$ -NMR, assignable to the double bond of a methacrylate group.

### Degree of conversion, maximum polymerization rate, and viscosity of liquid adhesive resins

The degree of conversion was measured as a function of time for the control and the experimental adhesives using FTIR spectroscopy. As seen from Fig. 2 and Table 1, with the increase of weight content of SM, the degree of conversion decreased, especially for SM2 which contains eight methacrylate groups. The DC for SM1-containing adhesives was in the range of 63–65 %. For SM2-containing adhesives, the DC was in the range of 59–65 %. Samples polymerized in the presence of 12 wt % water (Control + 12 wt % water, E3-SM1 +12wt % water and E3-SM2 +12 wt % water) showed a higher degree of conversion (88.0 %, 91.4 % and 83.5 %, respectively) than those polymerized without water (C0: 65.2 %, E3-SM1: 63.6 % and E3-SM2: 59.0 %) (Table 1). In addition, the maximum polymerization rate decreased with the increase of SM content (Fig 2D), which should be attributed to the decreased viscosity of liquid resins (Fig 2E).

### Water miscibility

Fig. 3A and Table 1 show the results of the water miscibility experiment. For the control formulation, the water miscibility was 10.29 wt %. With an increase of the SM, the water miscibility increased. When there was 25% SM in the formulation, the water miscibility was

12.44 % (E3-SM1) and 11.60 % (E3-SM2), respectively. At the same weight content of SM, the water miscibility with SM1 was higher than SM2.

### Water sorption

Results showing the water sorption of dentin adhesive polymers containing SM are shown in Fig. 3B and Table 1. The water sorption values varied from 9.66 % to 12.53 % with the increase of SM1. For SM2, the water sorption values varied from 9.66 % to 11.45%.

### Dynamic mechanical analysis (DMA)

The results of DMA for the control and experimental polymers cured in the absence of water and tested under dry condition are shown in Fig. 4 and summarized in Table 2. As shown in Fig. 4A and 4B, the storage modulus ( $E'$ ) decreases with increase of temperature for all of the samples. The formulations exhibited similar storage modulus values at 37 °C. The experimental polymer networks showed higher storage modulus in the rubbery state than the control (Fig. 4D). At 180 °C, the storage moduli for SM1 and SM2 at 15 and 25 wt% SM content are statistically significantly greater ( $p < 0.05$ ) than the control. At the same weight content of SM, the storage modulus at 180 °C with SM2 was higher than SM1.

Representative  $\tan \delta$  curves of the control and the experimental adhesive polymers as a function of temperature are shown in Figures 4E and 4F. The height of the  $\tan \delta$  peaks and the corresponding full-width-at-half-maximum (FWHM) values are given in Table 2. The  $T_g$  value for the control is 153.8°C. The  $T_g$  values decreased from 149.9 °C (E1-SM1) to 133.8 °C (E3-SM1) with an increase in the content of SM1. In contrast, the  $T_g$  values of the SM2-containing adhesives increased from 152.6 °C (E1-SM2) to 161.1 °C (E3-SM2) with increased SM2 content. The  $\tan \delta$  peak heights of SM1 containing adhesives were similar with the control. In contrast, the  $\tan \delta$  peak height was significantly lower ( $p < 0.05$ ) for SM2-containing adhesives (E2-SM2 and E3-SM2) as compared to the control. The SM1-containing adhesives showed similar FWHM values (Table 2) as the SM content increased and there was no significant difference between experimental and control adhesives. However, SM2-containing adhesives showed increased FWHM values as the SM content increased (Table 2), and the FWHM values were significantly greater ( $p < 0.05$ ) than the control.

The results of DMA for the control and experimental polymers under wet condition are shown in Fig. 5 and summarized in Table 3. The storage modulus for all the samples decreased with increasing temperature, as shown in Fig. 5A and 5B. At 37 °C, with the exception of E1-SM2 (2067 MPa), the storage modulus values for the experimental formulations are significantly lower (996–1938 MPa) than the control (2106 MPa). At 70 °C, as shown in Fig. 5D, there is no statistically significant difference between the storage modulus values of the control and 5% SM1, 5% and 15% SM2. For the formulations with 15% SM1 (E2-SM1, 182 MPa), 25% SM1 (E3-SM1, 69 MPa), and 25% SM2 (E3-SM2, 327 MPa), the storage modulus values were significantly lower than the control (435 MPa). As shown in Table 3, the values of  $T_g$  in wet condition decreased with an increase in SM1 content and the  $T_g$  values for 15 and 25% SM1 are significantly lower than control. In contrast, for SM2-containing polymers, the  $T_g$  values were similar to the control for all the samples.

Fig. 6A and 6B and Table 4 show the results of DMA under dry conditions for the control and experimental adhesives cured in the presence of 12 wt % water. After two days of storage in darkness, the polymer specimens were removed from the glass molds and put into a vacuum oven at 37 °C for two weeks. At 37 °C the storage modulus value of E3-SM1+12 wt % water was significantly lower (3061 MPa) than the control containing water (3777 MPa) while there was no statistically significant difference between the storage modulus of E3-SM2 +12 wt % water and control. At 180 °C, the storage modulus of E3-SM2+12 wt % water was significantly greater (95MPa) than the control containing water (45 MPa). In contrast, at 180 °C there was no significant difference between E3-SM1 +12 wt % water (48MPa) and the control containing water (45 MPa). As shown in Fig. 6B, the T<sub>g</sub> value of (E3-SM1+12 wt % water) was significantly lower (132 °C) than the control containing water (162 °C), and the T<sub>g</sub> value of (E3-SM2 +12 wt % water) was similar (164 °C) to the control containing water (162 °C). The intensities of the tan δ peaks for the experimental formulations were significantly lower than the control. In addition, the FWHM values were significantly greater than the control.

### Micro-X-ray tomography

The internal morphology of the control and experimental adhesive polymers is shown in Fig. 6C, 6D and 6E. Voids are apparent in the micro-CT images (Fig. 6C) of the control formulation cured in the presence of 12 wt % water (pore size is from about 5.0 to 45.0 μm). In comparison, no voids were observed in the adhesive with 25 wt % SM1 (E3-SM1+ 12 wt % water) (Fig. 6D), and only a few voids (size is about 5.0 μm) appeared in the adhesive with 25 wt % SM2 (E3-SM2 + 12 wt % water) (Fig. 6E). In addition, both of the SM-containing adhesives were transparent after being cured in the presence of 12 wt % water.

### Discussion

Polymers with siloxane groups are usually soft because of the flexibility of Si-O bonds[17, 18] . The enhancement of mechanical properties is crucial for the development of siloxane-containing dentin adhesives. In the current study, two new siloxane-methacrylate monomers, SM1 and SM2, with four and eight methacrylate groups have been synthesized and characterized in order to understand the relationship between the mechanical properties and functionality of the siloxane comonomers.

In the absence of water, the additional functionalities of the new siloxane-methacrylates[33] appear to have contributed to the decreased degree of conversion with increased comonomer content in the experimental samples. However, the degree of conversion was significantly higher for samples cured in the presence of 12 wt % water as compared to samples cured in the absence of water. This difference reflects the enhanced mobility of reactive species in the lower viscosity water-containing solution[26, 28, 31] . The improvement in degree of conversion afforded by the lower viscosity water-containing solution was greater with adhesives containing SM1 and SM2 as compared to the control (Table 1); these results suggest increased tolerance of the wet environment of the mouth[28] . The maximum polymerization rate decreased with increasing SM content (Fig 2D). The decreased polymerization rate is likely associated with the lower viscosity of SM monomers (Fig 2E).

The results of the water miscibility experiments (Fig. 3A and Table 1) indicate that both of the SM monomers were more hydrophilic than BisGMA. These differences are reflected in the water sorption results with both SM-containing adhesives showing higher water sorption (Fig. 3B). At the same weight content of SM, the water miscibility with SM1 was higher than SM2. These results indicate that SM2 with eight methacrylate groups is more hydrophobic than SM1 with four methacrylate groups.

Dynamic mechanical analysis provides information about the relaxation of molecular motions, which are sensitive to structure and variation in the stiffness of materials. Thus, this technique can be used to provide information on the properties of polymer networks, such as storage modulus and glass transition temperature [31, 32]. The values of the storage modulus at 180 °C are higher for the experimental as compared to the control adhesives, especially for the SM2-containing adhesives. The difference in storage modulus values at 180 °C between SM1 and SM2 reflects the higher entanglement of polymer networks with SM2 containing eight methacrylate groups. This indicates that more functionalities are beneficial for the storage modulus of these materials in the rubbery region[30–32].

The intensity of the maximum  $\tan \delta$  peak reflects the extent of mobility of the polymer chain segments as a function of temperature. When SM2, which contains eight methacrylate groups, was used as the comonomer, all the experimental adhesives showed lower  $\tan \delta$  peak heights than the control. At the same time,  $T_g$  increased with increased SM2 content, indicating more elastic behavior (i.e., more energy is stored in the material) and greater entanglement of polymer chains, which is consistent with the results of storage modulus.

The widths of  $\tan \delta$  peaks for the SM2-containing adhesives are greater than those of the control. The widths of the  $\tan \delta$  peaks indicate that the glass transition occurs over a wide temperature range. This broad glass transition can be attributed to heterogeneous networks, i.e. regions with different crosslink structure (highly crosslinked and less densely crosslinked regions), which results in broad distribution of mobilities or relaxation times. Generally, the wider  $\tan \delta$  peaks (higher heterogeneous networks) usually appears with increasing the crosslink density of the polymer networks[28–31, 33]. These results could be correlated with the storage modulus values in the rubbery region.

When SM1 containing four methacrylate groups was used as the comonomer the intensity of the maximum  $\tan \delta$  peak was similar to the control, indicating similar mobility of the polymer segments. The similar mobility of polymer segments for SM1-containing adhesives is associated with higher entanglement of polymer chains compared to control adhesives, since siloxane-containing polymers are usually softer and with higher mobility than polymethacrylates. Meanwhile,  $T_g$  decreased with increasing SM1 content due to the incorporated flexible siloxane groups[18].

The 3-point bending water-submersion clamp method was used in this study, which is expected to be representative of the wet environment of the mouth[31]. The lower storage modulus values at 37 °C for the experimental as compared to the control adhesives reflect the enhanced flexibility of the siloxane-containing polymer in the presence of water. At 70 °C, the polymers in wet conditions are in the rubbery state ( $T_g$  are shown in Table 3). The

storage modulus at 70 °C for SM1-containing adhesives is lower than SM2-containing adhesives (Fig. 5D), indicating the greater entanglement of polymer networks in the presence of SM2. With 5 % and 15 % SM2 as the comonomer, the storage moduli at 70 °C (479 and 438 MPa) are similar with the control (435 MPa) under wet conditions. It should be noted that the water sorption under wet conditions was increased in the presence of SM comonomer. With SM2 as the comonomer, the intensity of  $\tan \delta$  curves (Table 3) at 70 °C is much lower than control, indicating less mobility of polymer chains under wet conditions, which corresponds with the higher entanglement of the polymer network. In contrast, when SM1 was used as the comonomer,  $T_g$  decreased and intensity of  $\tan \delta$  curves at 70 °C increased. The results of DMA under wet condition indicate that the mechanical properties could be enhanced by increasing the functionality of siloxane-methacrylate monomers, even with more water sorption.

Comparing the DMA results under wet conditions to the results under dry conditions, the values of the storage modulus (Table 3) measured by the water-submersion clamp method were significantly less than those of dried samples measured by the standard clamp (Table 2). This difference is due to plasticization of the polymer in the wet environment[34, 35]. Water is responsible for plasticizing polymers in that it is attracted to polar groups in the polymer matrix and forms hydrogen bonds, resulting in reduced polymer chain interactions[31, 36]. It should be noted that water molecules enhance the mobility of the polymer chain segments by increasing free volume, thus increasing the flexibility of the materials. This increased-flexibility effect might be more severe for siloxane-containing materials because of the higher mobility (flexibility) of Si-O bonds.

The mechanical properties under wet condition could be maintained when SM2 was used as the comonomer. These results indicate that incorporation of SM monomer with more functionality is an efficient way to enhance the mechanical properties for siloxane-containing materials, even under wet conditions. Moreover, the enhanced performance in the presence of water could be beneficial in terms of the formation of a more uniform hybrid layer which should result in improved stress transfer and fatigue life of the dentin-adhesive interface[37, 38]. Therefore, these results provide important information for future development of siloxane-containing dentin adhesives.

Under *in vivo* conditions, water or saliva will be present during dentin bonding thus adhesives must undergo polymerization *in situ* in the presence of water or saliva. The results in Table 1 show that the degree of conversion for both of the SM-containing formulations can be significantly improved in the presence of 12 wt % water. This result is also in agreement with previous investigations reporting that the degree of conversion can be improved in the presence of water[24, 25, 27]. All of the experimental adhesives cured in presence of water showed higher rubbery moduli and lower  $\tan \delta$  peak heights than those of the control (Table 4, Fig. 6A and 6B). These results indicate greater entanglement of polymer networks with the experimental adhesives cured in the presence of water.

Water miscibility is another important issue for dentin adhesives. Less water miscibility will cause phase separation when monomer resins are cured in the wet, oral environment [28] leading to polymerized adhesive with a range of compositions and mechanical

characteristics [41]. This phase separation can inhibit the formation of a structurally integrated bond at the composite/adhesive/tooth interface[39, 40] . The control adhesives cured in the presence of 12 wt % water were not transparent, and voids were noted in the micro CT images (Fig. 6C). The voids indicate microphase separation when the control adhesive was cured in the presence of 12 wt % water. Voids at this water concentration are expected since the water miscibility of the control adhesive was 10.29 % (Table 1). In comparison, the experimental adhesives containing SM1 and SM2 with 12 wt % water are transparent after curing. No voids were noted in the micro CT images of the SM1-containing adhesives (Fig. 6D), although a small amount of voids appeared in the images of SM2-containing adhesives (Fig. 6E). This is related to the water miscibility value being 11.60 % when there is 25 % SM2 in the adhesives. However, the micro CT images offer a clear comparison of water miscibility. These results indicate both of the SM monomers could improve the water miscibility and decrease microphase separation in the presence of water.

The results in this paper indicate that siloxane-methacrylate monomers used in dentin adhesives could affect the water miscibility, water sorption and mechanical properties of the polymers. The mechanical properties of siloxane-containing polymers can be enhanced by increasing the functionality of monomers. The results elucidate critical structure/property relationships for siloxane-methacrylate monomers and provide vital information for future development of durable, versatile siloxane-containing dentin adhesives. Investigations regarding the durability and compatibility of these adhesives with silorane composite are ongoing.

## Conclusion

Two new siloxane-methacrylate monomers, SM1 and SM2, containing four and eight methacrylate groups, were synthesized and characterized. The degree of conversion, water miscibility, water sorption and dynamic mechanical properties of siloxane-containing dentin adhesives were examined. With more functionality, the degree of conversion decreased with an increase of the content of siloxane-methacrylate monomers. In addition, adhesives with newly synthesized SM monomers showed improved water miscibility. When formulated with 12 wt % water to simulate the behavior of these materials in the wet, oral environment, the degree of conversion and mechanical properties were improved as compared to the control adhesives. All experimental adhesives tested showed higher rubbery modulus than the control under dry conditions. Moreover, the mechanical properties under wet conditions for siloxane-containing materials were comparable with the control by incorporating SM monomer with more functionality, even with more water sorption. It is conceivable that the enhanced performance in the presence of water would be beneficial to the formation of more uniform hybrid layer which should result in improved stress transfer and fatigue life of the dentin-adhesive interface. Siloxane-methacrylate monomers show promise as a component of durable, water-compatible dentin adhesives.

## Acknowledgments

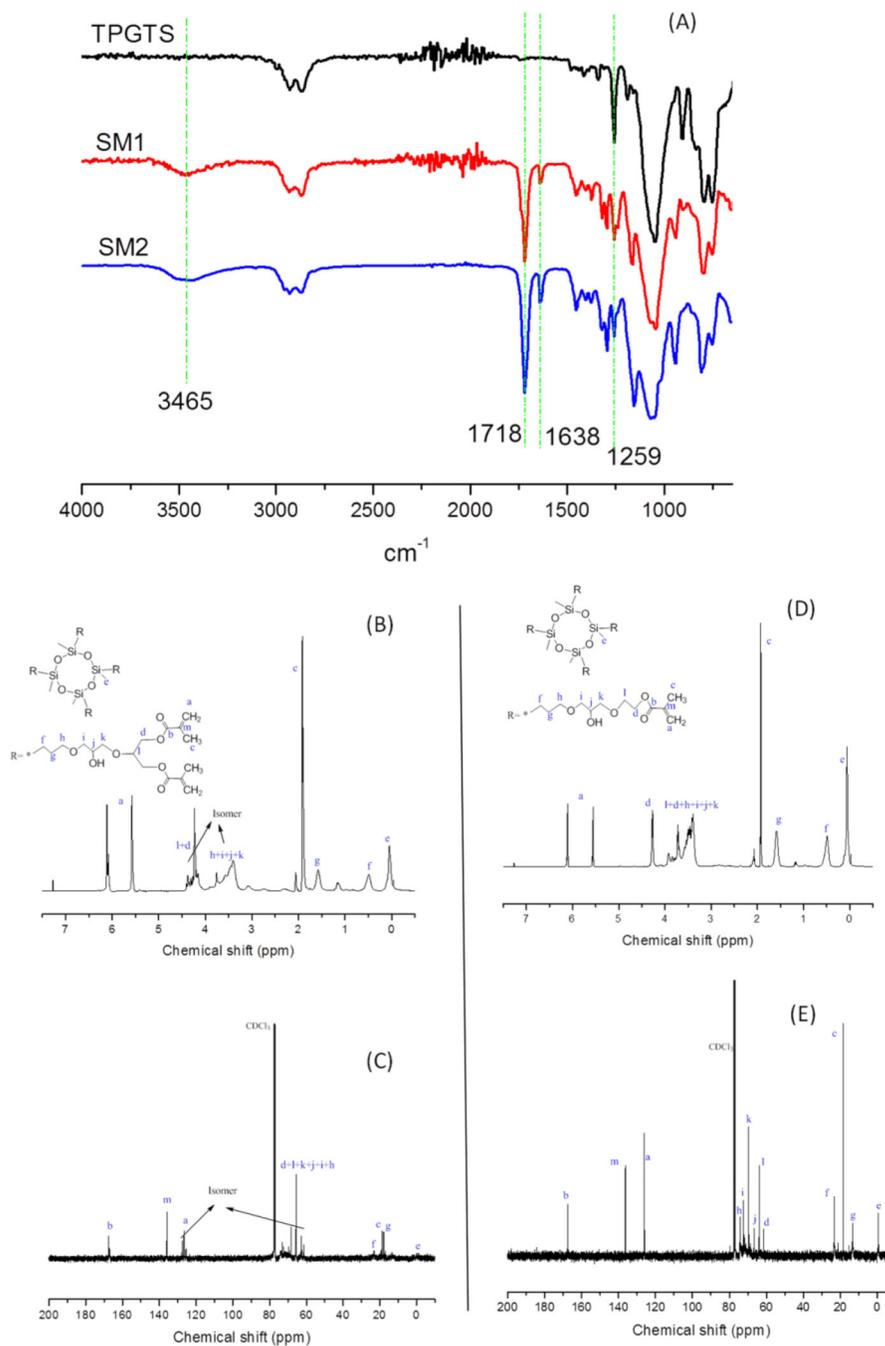
This investigation was supported by Research Grant: R01DE14392 and R01DE14392-08S1 and R01 DE022054 from the National Institute of Dental and Craniofacial Research, National Institutes of Health, Bethesda, MD 20892.

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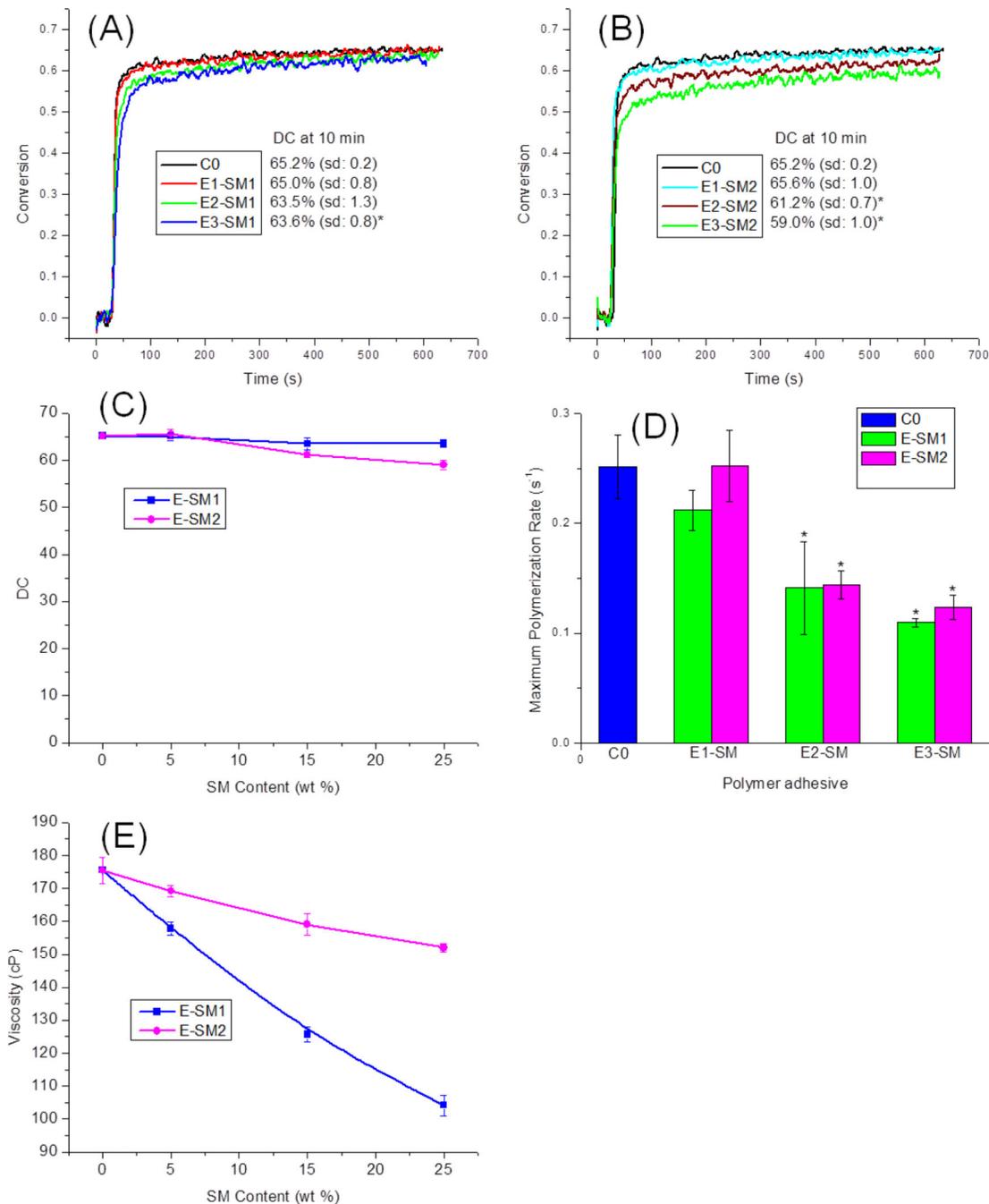
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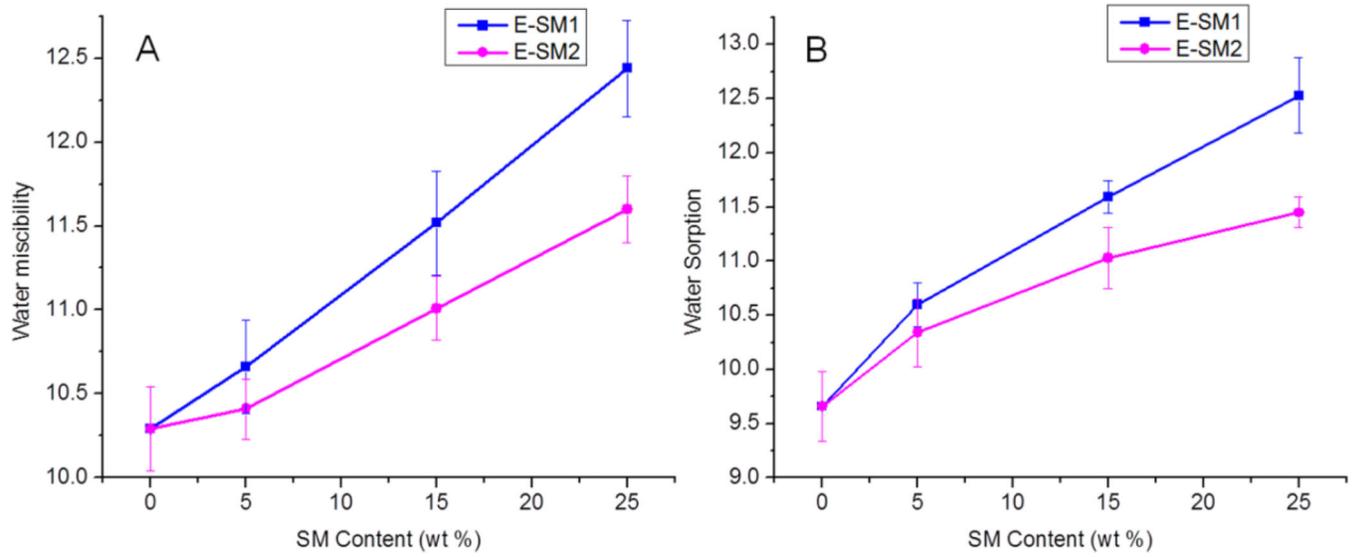


**Fig. 1.** 1A-FTIR spectra of TPGTS (starting material) and siloxane-methacrylates (SM1 and SM2). 1B and 1C-  $^1\text{H-NMR}$  (B) and  $^{13}\text{C-NMR}$  (C) spectra of SM1. 1D and 1E-  $^1\text{H-NMR}$  (D) and  $^{13}\text{C-NMR}$  (E) spectra of SM2.

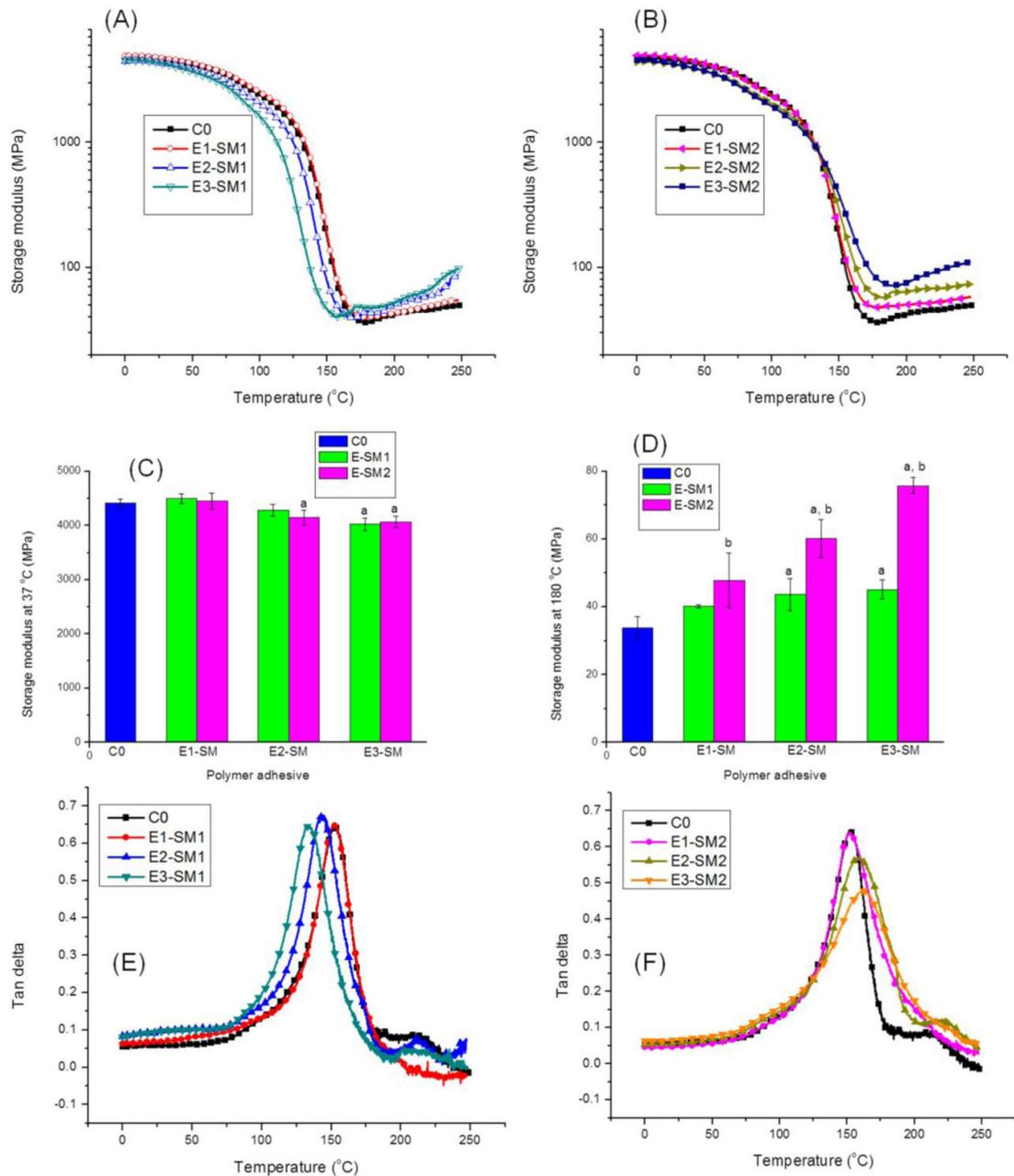


**Fig. 2.** Real-time conversion of adhesive resins with different weight contents of SM (A, B). The adhesives were light-cured for 40 sec at room temperature using a commercial visible-light-curing unit (Spectrum® 800, Dentsply, Milford, DE. Intensity was 550 mW/cm<sup>-2</sup>). Real-time IR spectra were continuously recorded for 600 s after light activation began. The comparison of DC for SM1 and SM2-containing system is show in C. The comparison of maximum polymerization rate is shown in bar figure D. N= 3 ± SD. \*Significantly (*p* < 0.05) different from the control (C0). Symbols: E1-SM, E2-SM and E3-SM represent 5, 15 and 25

wt % of SM content, respectively. Figure E shows the viscosity of liquid adhesive resins formulated with different weight content of SM.

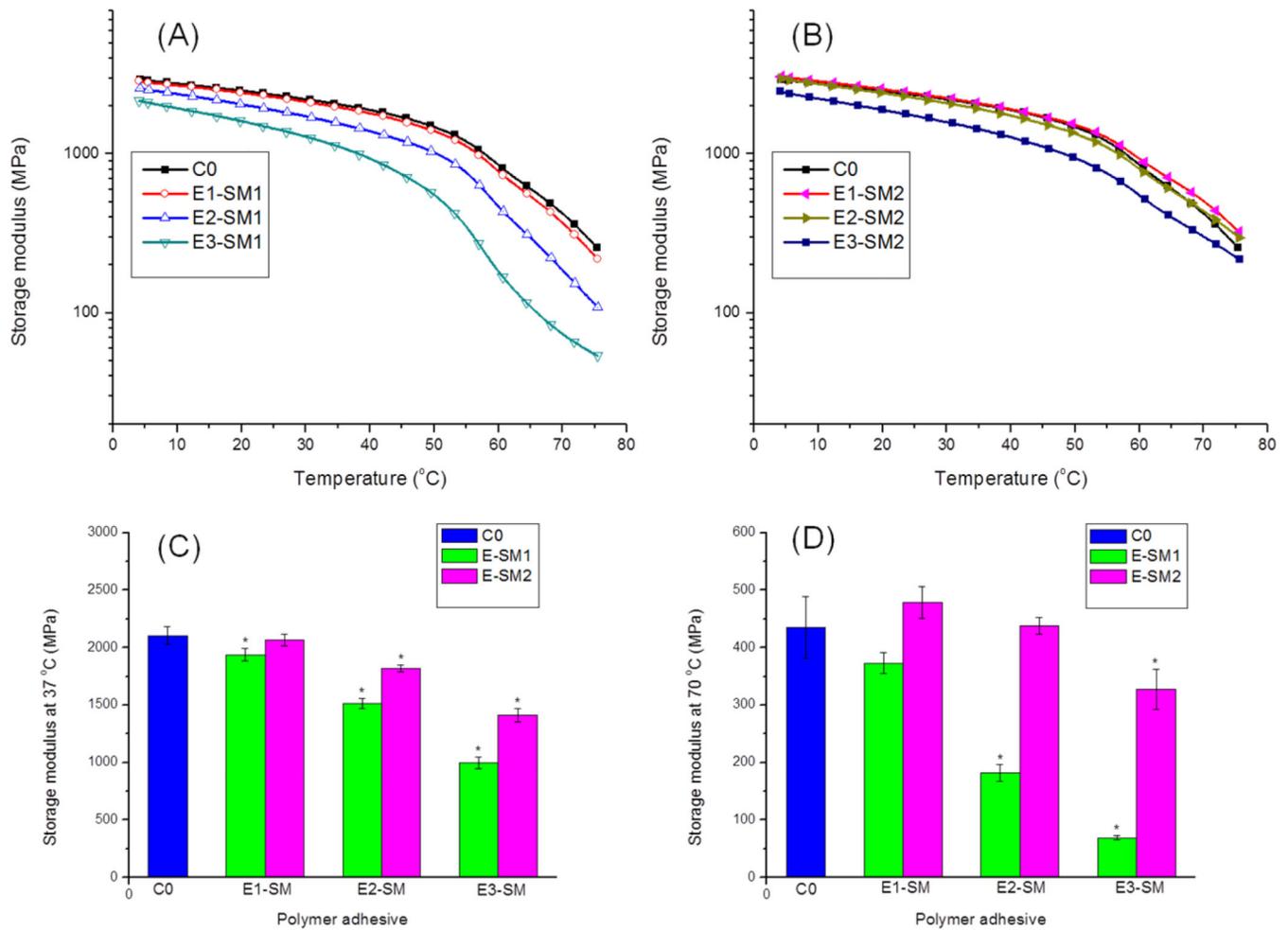


**Fig. 3.** (A) Water miscibility and (B) water sorption of monomer resins with different weight contents of SM.

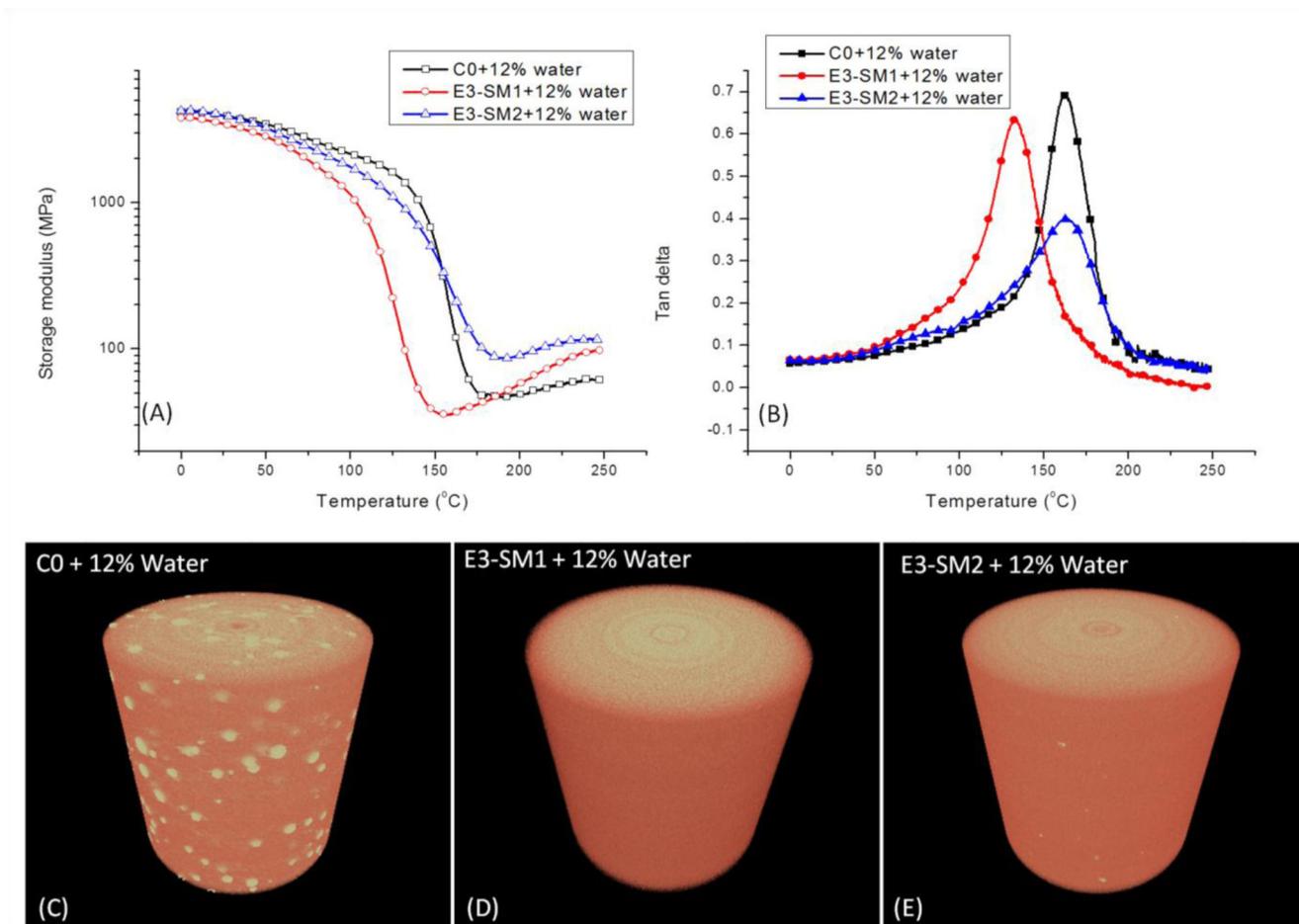


**Fig. 4.** DMA under dry condition: Comparison of the storage modulus versus temperature curves for experimental adhesives (A: SM1-containing; B: SM2-containing) with those of the control adhesive (C0). The comparison of storage modulus at 37 and 180 °C is shown in bar figure C and D, respectively. <sup>a</sup> Significantly ( $p < 0.05$ ) different from the C0; <sup>b</sup> Significantly ( $p < 0.05$ ) different from the E-SM1 with the same SM content. Representative  $\tan \delta$  versus temperature curves for SM1 (E) and SM2 (F) containing polymers with different weight

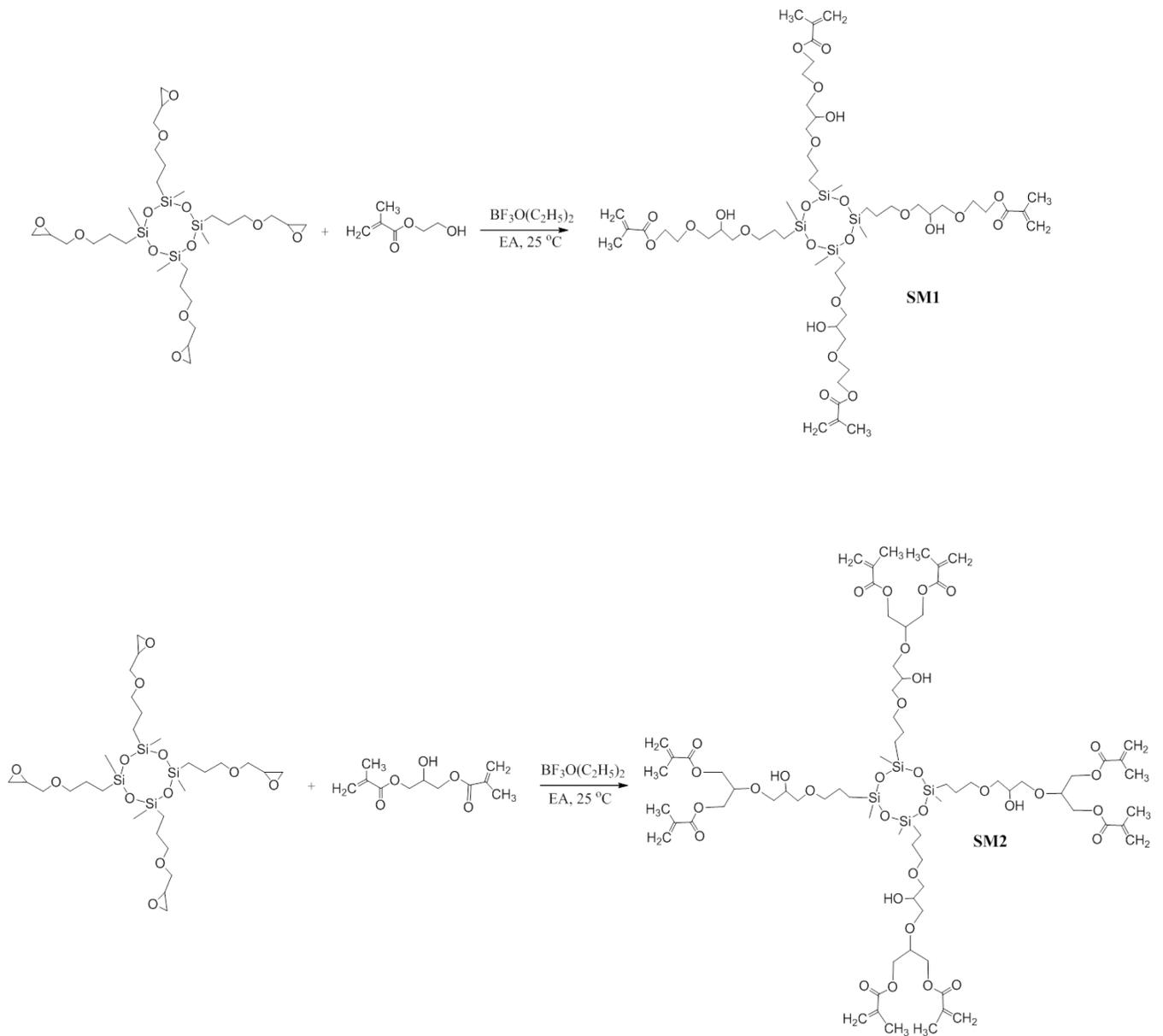
content. Symbols: E1-SM, E2-SM and E3-SM represent 5, 15 and 25 wt % of SM content, respectively.



**Fig. 5.** DMA under wet condition: Comparison of the storage modulus versus temperature curves for experimental adhesives (A: SM1-containing; B: SM2-containing) with those of control adhesive (C0). The comparison of storage modulus at 37 and 70 °C were shown in bar figure C and D, respectively. Symbols: Symbols: E1-SM, E2-SM and E3-SM represent 5, 15 and 25 wt % of SM content, respectively. \*Significantly ( $p < 0.05$ ) different from the C0.



**Fig. 6.** (A) and (B) show the results of DMA under dry condition for the resins in the presence of water: (A) Storage modulus versus temperature curves for experimental adhesives with the control adhesive (C0); (B) Representative  $\tan \delta$  versus temperature curves for SM-containing polymers. (C), (D) and (E) show the 3D images of the control (C), 25 wt % SM1 containing (D) and 25 wt % SM2 containing (E) adhesives cured in the presence of 12 wt % water. The morphologies were observed using three-dimensional (3D) Micro XCT (Xradia Inc. Concord, CA). Symbols: C0+ 12 wt % water, E3-SM1+12 wt % water and E3-SM2+12 wt % water represent the C0, E3-SM1 and E3-SM2 formulations had 12 wt % water added.



**Scheme 1.**  
Synthesis scheme for new siloxane-methacrylate monomers.

**Table 1**

Adhesive formulation, degree of conversion, water miscibility and water sorption

Samples	HEMA (wt %)	BisGMA (wt %)	SMI (wt %)	SM2 (wt %)	Water (wt%)	Conversion (%)	Water Miscibility (%)	Water Sorption (%)
C0	45	55				65.2 (0.2)	10.29 (0.25)	9.66 (0.32)
C0 +12 wt% water	45	55			12.0	88.0 <sup>a</sup> (2.6)		
E1-SM1	45	50	5			65.0 (0.8)	10.66 (0.28)	10.60 <sup>d</sup> (0.20)
E2-SM1	45	40	15			63.5 (1.3)	11.52 <sup>a</sup> (0.31)	11.59 <sup>a</sup> (0.15)
E3-SM1	45	30	25			63.6 (0.8) <sup>a</sup>	12.44 <sup>a</sup> (0.29)	12.53 <sup>a</sup> (0.35)
E3-SM1 +12 wt% water	45	30	25		12.0	91.7 <sup>d</sup> (1.7)		
E1-SM2	45	50		5		65.6 (1.0)	10.41 (0.18)	10.34 <sup>d</sup> (0.31)
E2-SM2	45	40		15		61.2 <sup>a,b</sup> (0.7)	11.01 <sup>a,b</sup> (0.19)	11.03 <sup>a,b</sup> (0.28)
E3-SM2	45	30		25		59.0 <sup>a,c</sup> (1.0)	11.60 <sup>a,c</sup> (0.20)	11.45 <sup>a,c</sup> (0.14)
E3-SM2 +12 wt% water	45	30		25	12.0	83.5 <sup>e</sup> (2.0)		

<sup>a</sup> Significantly (p<0.05) different from the corresponding control.

<sup>b</sup> Significantly (p<0.05) different from the corresponding E2-SM1.

<sup>c</sup> Significantly (p<0.05) different from the corresponding E3-SM1.

<sup>d</sup> Significantly (p<0.05) different from the corresponding E3-SM1.

<sup>e</sup> Significantly (p<0.05) different from the corresponding E3-SM2.

Table 2

DMA data for control and experimental adhesives cured in the absence of water and tested under dry conditions

Sample	Storage modulus at 25 °C (MPa)	Storage modulus at 37 °C (MPa)	Storage modulus at 180 °C (MPa)	Tg (°C) <sup>a</sup>	Height of tan $\delta$ peak	Full-width-at-half-maximum values of tan $\delta$ peak (°C) <sup>b</sup>
C0	4590 (81)	4411 (76)	33.7 (3.3)	153.8 (0.7)	0.64 (0.01)	33.7 (1.2)
E1-SM1	4697 (94)	4493 (90)	40.1 (0.5)	149.9 (1.7)*	0.65 (0.01)	34.3 (1.1)
E2-SM1	4508 (109)	4279 (108)	43.6 (4.7)*	144.1 (0.8)*	0.65 (0.02)	35.6 (2.4)
E3-SM1	4284 (124)*	4022 (118)*	45.1 (2.9)*	133.8 (0.7)*	0.64 (0.01)	37.9 (1.4)
E1-SM2	4671 (148)	4448 (145)	47.8 (8.2)	152.6 (2.5)	0.66 (0.02)	44.0 (4.4)*
E2-SM2	4366 (152)*	4144 (143)*	60.2 (5.7)*	157.9 (2.2)*	0.57 (0.02)*	49.6 (0.7)*
E3-SM2	4308 (101)*	4069 (100)*	75.8 (2.4)*	161.1 (1.0)*	0.47 (0.01)*	58.5 (3.9)*

Values are mean ( $\pm$  standard deviation) for n = 5 in each group.

\* Significant (p<0.05) difference from Control C0.

<sup>a</sup>The glass transition temperatures (Tg) values of the polymer networks were taken to be the maximum of the tan  $\delta$  versus temperature curve determined using a dynamic mechanical analyzer.

<sup>b</sup> Full-width-at-half-maximum values of tan  $\delta$  peak were analyzed by Gauss fit (Fit single peak) using Microcal Origin Version 8.0 (Microcal Software Inc., Northampton, MA).

DMA data for control and experimental adhesives cured in the absence of water and tested under wet conditions

**Table 3**

Sample	Storage modulus at 25 °C (MPa)	Storage modulus at 37 °C (MPa)	Storage modulus at 70 °C (MPa)	Tg (°C) <sup>a</sup>	Intensity of tan δ at 70 °C
C0	2491 (87)	2106 (76)	435.4 (53.6)	57.6 (0.2)	0.40 (0.00)
E1-SM1	2320 (67)*	1938 (56)*	373.1 (17.9)	57.3 (0.2)	0.40 (0.00)
E2-SM1	1888 (39)*	1514 (43)*	182.1 (14.9)*	56.4 (0.2)*	0.48 (0.01)*
E3-SM1	1385 (55)*	996 (52)*	69.3 (4.2)*	53.3 (0.5)*	0.45 (0.01)*
E1-SM2	2461 (62)	2067 (145)	478.6 (27.4)	57.7 (0.3)	0.36 (0.02)*
E2-SM2	2211 (47)*	1820 (31)*	438.2 (14.4)	58.1 (0.3)	0.34 (0.01)*
E3-SM2	1794 (75)*	1411 (56)*	327.5 (34.6)*	57.4 (0.1)	0.33 (0.00)*

Values are mean (± standard deviation) for n = 5 in each group.

\* Significant (p<0.05) difference from Control C0.

<sup>a</sup>The glass transition temperatures (Tg) values of the polymer networks were taken to be the minimum of the Deriv. storage modulus versus temperature curve determined using a dynamic mechanical analyzer.

DMA data under dry conditions for control and experimental adhesives cured in the presence of 12 wt% water and tested under dry conditions

**Table 4**

Sample	Storage modulus at 25 °C (MPa)	Storage modulus at 37 °C (MPa)	Storage modulus at 180 °C (MPa)	Tg (°C) <sup>a</sup>	Height of tan $\delta$ peak	Full-width-at-half-maximum values of tan $\delta$ peak (°C) <sup>b</sup>
C0+12 wt% water	4000 (119)	3777 (103)	45.1 (2.9)	162.4 (0.3)	0.70 (0.01)	33.4 (0.7)
E3-SM1+12 wt% water	3350 (127)*	3061 (120)*	48.2 (7.0)	132.6 (0.4)*	0.63 (0.01)*	43.9 (2.7)*
E3-SM2+12 wt% water	3938 (162)	3653 (73)	95.2 (4.1)*	163.8 (0.7)	0.42 (0.02)*	56.9 (2.9)*

Values are mean ( $\pm$  standard deviation) for n = 5 in each group.

\* Significant ( $p < 0.05$ ) difference from Control C0.

<sup>a</sup>The glass transition temperatures (Tg) values of the polymer networks were taken to be the maximum of the tan  $\delta$  versus temperature curve determined using a dynamic mechanical analyzer.

<sup>b</sup> Full-width-at-half-maximum values of tan  $\delta$  peak were analyzed by Gauss fit (Fit single peak) using Microcal Origin Version 8.0 (Microcal Software Inc., Northampton, MA).