Effect of moisture on cationic polymerization of silicone epoxy monomers

R. A. A. Upul Ranaweera,[1] Thomas P. Schuman,[1] Rongpeng Wang,[1] Bradley D. Miller,[2] Kathleen V. Kilway[2]

[1]Department of Chemistry, Missouri University of Science and Technology (Formerly: University of Missouri-Rolla) Rolla, Missouri 65409

[2]Department of Chemistry, University of Missouri-Kansas City, Kansas City, Missouri 64110

Correspondence to: T. P. Schuman (E-mail: tschuman@mst.edu)

ABSTRACT: Moisture in polymerization of a cationically cured silicone epoxy monomer blend is an important parameter that affects the resulting polymer properties. We report the kinetics of the cationic polymerization of epoxy monomers as a function of water concentration, directly quantified using Karl Fischer (KF) titration that was characterized using Fourier transform infrared (FTIR) spectroscopy and also the mechanical strength of resulting polymers via diametral tensile strength measurements. Methodology and results for a silicone epoxy monomer material were compared with the same methodology applied to a "control" monomer, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexyane carboxylate, for which moisture effects have been previously studied. Initially, an increase in moisture during cationic polymerization of epoxy caused increased rate (ROC) and degree of conversion (DOC) that for the silicone epoxy was followed by decreased DOCs for water contents approaching saturation, i.e., $[H_2O] \sim 0.19$ wt %. Further, the rate of conversion was also affected by the presence of moisture with a trend analogous to the DOC. Diametral tensile strength measurements found that small amounts of water present during polymerization caused small changes in tensile strength but found polymer strengths to be significantly decreased if initial water concentrations approached saturation or were in excess of saturation. Lower strengths corresponded with reduced rates of conversion and DOCs. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41831.
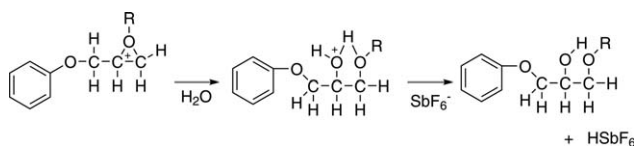
INTRODUCTION

Surprisingly, the effect of moisture content on cationic ring-opening polymerization does not appear to have been studied in great detail. There appears only limited research literature[1–6] where the effects of moisture on cationic polymerization are measured and even in these references moisture was quantified indirectly. According to Lühring and coworkers,[1] the effect of water and alcohols on the polymerization of epoxides with latent initiators has received little attention. Although it is well known that hydrogen donors should strongly influence cationic polymerization of monomers, the effect of moisture content on polymerization can be very important to the application especially when a resulting polymer is to be produced in a wet environment, e.g., as a dental or bone cement.

If the reaction is not directly initiated by carbocations formed by the decomposition of the initiator, a proton donor is required as co-catalyst for the formation of the initiating super acid.[1,7,8] As long as the environment is not anhydrous, e.g., the reaction is carried out in a humid atmosphere,[2] the amount of water naturally present in the monomer is high enough to function as a proton donor for the initiation. Furthermore, the presence of water or alcohol can influence the polymerization reaction through chain-transfer reactions from the positively charged end of the growing polymer chain, e.g., to alcohols forming an ether bond or to water where a pendant hydroxyl group is formed, and release of an initiating proton. The released proton initiates the growth of the next polymer chain. This is also called a "polymerization by activated monomer mechanism" and was examined with conventional initiators by Penczek et al.[1,9] Water and other proton donors thus serve multiple roles in cationic polymerizations and therefore can impact the properties of the resulting polymer dependent on concentration.[2,5,10–13] Depending on the type of epoxide used, the polymerization rate can be increased, such as for cycloaliphatic epoxides, or decreased, such as for glycidyl ether monomers.[6]

Additional Supporting Information may be found in the online version of this article.
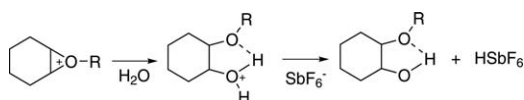© 2015 Wiley Periodicals, Inc.

Scheme 1. Chain-transfer reaction by water for the polymerization of glycidyl ether.

Scheme 3. The structures of SE monomer mixture and cycloaliphatic epoxy (EMEC) monomer. For IUPAC names of PHEPSI, CYGEP and EMEC, please refer to the Materials descriptions of the "Experimental" section.

With the advent of effective photo-initiator systems, such as diaryliodonium and trialrylsulfonium salts,[5,10,14,15] cationic photopolymerization has become a possible alternative to traditional free-radical photopolymerization systems with advantages of oxygen insensitivity and low toxicity and shrinkage.[5,16] Cationic polymerization of epoxides can be an alternative to the free-radical polymerization of acrylates.[6,17] Contrary to that of most free-radical chemistry, photopolymerization of epoxides is a living polymerization hence the curing has the potential to extend into regions which are not directly irradiated or exposed to UV light via the "dark reaction."[6,18] By the combination of UV and chemical curing, we sought to establish monomers whose polymerization reactions were less sensitive to oxygen and less toxic, hence can be used in biomedical applications.[19,20]
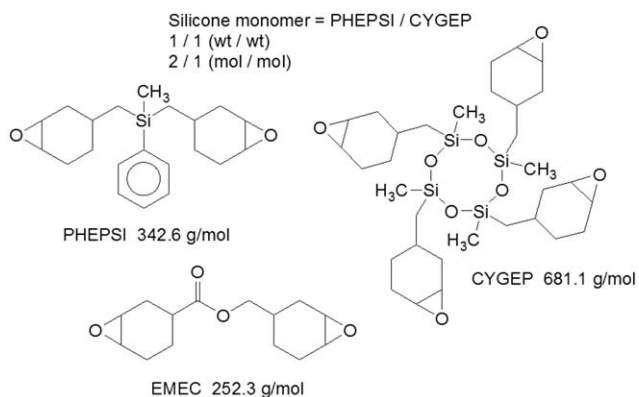
Previously, it has been shown with real-time infrared spectroscopy that for epoxides with exocyclic epoxide groups, the rate of polymerization was either minimally influenced by relative humidity, e.g., vinyl epoxide monomer, or was decreased by air humidity, e.g., glycidyl ether monomer.[1,2] On the other hand, for epoxide monomers with endocyclic epoxide groups, an increase in the rate of polymerization was observed with increasing air humidity.[2] For these studies, water concentrations in the polymerization mixtures were obtained through an indirect measurement of moisture, e.g., as a relative humidity in the surrounding environment to which the samples were exposed rather than as a measured concentration in the polymerization.

The reasoning for differential influences of air humidity on the polymerization rate for different epoxide monomers is based on differences in the chain-transfer reactions carried out by water. In the case of the glycidyl ether transition state as a model for aromatic glycidyl ethers, both water protons are fixed in a five-membered ring at the positively charged end of the growing chain (Scheme 1).[1] Similarly, a model for endocyclic epoxy monomers applicable to this work is shown in Scheme 2, where transference of the proton to hexafluoroantimonate anion forming the corresponding acid is supported by computational modeling[5] as a possible mechanism for epoxide ring opening of cycloaliphatic ethers.

Variations in polymerization rate can be explained through hindrance of proton transfer and steric effects. Fixation or delocalization of positive charge can hinder release of a proton for starting a new chain reaction that leads to an observed retarda-

tion of the polymerization conversion with increasing humidity. On the other hand, Lühring and coworkers[1,2] explained an changes in polymerization rate as a function of humidity with the help of molecular modeling. They showed that small molecule nucleophiles, e.g., water, can attack from below or from the rear so that epoxide consumption occurs with a resulting protonated alcohol being sterically less hindered than the protonated epoxide, each with counterion, so that a second epoxide ring can more readily attack the protonated compound. A reduced steric hindrance of this partial step of the chain-transfer reaction can lead to acceleration of the polymerization rate with increasing humidity.

Here we explore the effect of moisture/water toward the polymerization of a silicone epoxy (SE) compared to a control, cycloaliphatic epoxy monomer[2] of analogous cycloaliphatic oxirane structure as a function of measured water concentration in cationically initiated systems (Schemes 3 and 4). Measuring the effect on monomer polymerizations can assist in understanding how to apply the monomer as a material in moisture-rich, e.g., dental implant or bone cement, environments. The control monomer is used as a comparator since previous polymerization data as a function of moisture concentration for this

Scheme 2. Chain-transfer reaction by water for the polymerization of a cycloaliphatic ether.
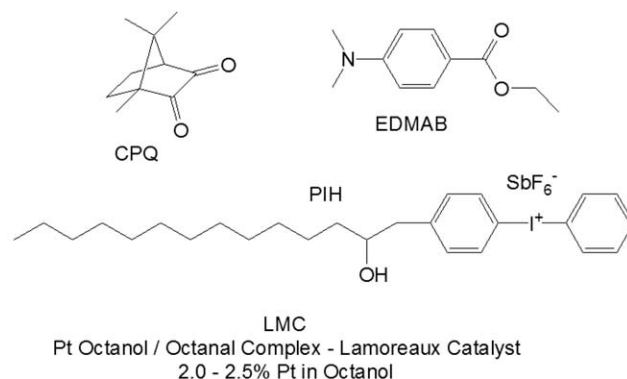
Scheme 4. The chemical structures of the dual-cure initiator system.[19,20] For IUPAC/common names of CPQ, EDMAB, PIH, or LMC, please refer the Materials descriptions of the Experimental section.

monomer exists.[1,2] We also seek to expand upon that prior work by providing quantitative moisture concentrations and mechanical properties data.

The concentration of moisture in the epoxy monomers was quantified using KF titrations, and real-time FTIR analyses were used to measure the kinetics of polymerization of SE through both reaction rate and degree of conversion (DOC). The changes in reactivity were further assessed by diametral tensile strength of the resulting polymers. Finally, we compared the results of SE monomers samples with those of cycloaliphatic epoxy, whose polymerization kinetics under influence of humidity was previously reported,[2] to show the differences in cationic curing behavior.

An initial increase in moisture from nearly anhydrous monomer during cationic polymerization of epoxies was found to increase the rate of conversion (ROC) and DOC that for the SE was followed by decreased DOCs for water contents approaching saturation, i.e., $[H_2O] \sim 0.19$ wt %. Further, the rates of conversion were also affected by the presence of moisture with trends that were analogous to the DOC. Diametral tensile strength measurements found that small amounts of water present during polymerization caused insignificant changes in tensile strength but found polymer strengths to be significantly decreased if initial water concentrations approached saturation or if, especially, were in excess of saturation. Lower strengths corresponded with reduced rates of conversion and DOCs. The effect of moisture on the cationic polymerization is not yet well-predicted by structural considerations and should be measured as described here for the specific epoxy system.

EXPERIMENTAL

Materials

HYDRANAL-Titrant 5 E, HYDRANAL-Solvent E, and infrared potassium bromide crystal windows (2×25mm) were purchased from Sigma-Aldrich Co. LLC. St. Louis, MO. Phenyl [p-(2-hydroxy-tetradecyloxy) phenyl] iodonium hexafluoroantimonate (IPH) was purchased from Sartomer Company, Exton, PA. Camphoroquinone (99%, CPQ) and ethyl 4-dimethylaminobanzoate (99+%, EDMAB) were purchased from Acros Organics. The SE monomers (bis [2-(3{7-oxabicyclo [4.1.0] heptyl})-ethyl] methyl-phenyl silane) (PHEPSI) and 2,4,6,8-tetrakis(2-(7-oxabicyclo [4.1.0] heptan-3-yl) ethyl)−2,4,6,8-tetramethyl-1,3,5,7,2,4,6,8-tetraoxatetra-silocane (CYGEP) (Scheme 3) were first synthesized,[19,20] purified, and then blended as a 50 : 50 by mass (0.146 : 0.073 by mole, respectively) mixture. Platinum-octanal/octanol complex (Lamoreaux's catalyst, LMC) was obtained from Gelest, Inc., Morrisville, PA. 3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate (EMEC) was obtained from Dow Chemical (as UVR 6110) and Aldrich Chemical. Deionized water (1 MΩ-cm) was used to prepare monomers of known water concentrations.

Chemical Characterizations

Fourier Transform infrared absorption spectra (FTIR) were measured with a Nicolet Nexus 470 spectrophotometer (Waltham, MA) in mid-IR region from 4000 cm^{-1} to 400 cm^{-1} with 16 scans each with 1 cm^{-1} resolution in KBr salt plates under a moisture and carbon dioxide free air purge. Diametral tensile testing was done with an Instron 4469 instrument with a 5 kN load cell. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 Thermogravimetric Analyzer with a scan rate of 10°C/min, scanning from 25 to 800°C. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q2000 differential scanning calorimeter with thermal scan rate of 10°C/min and temperature range from −30°C to 320°C.

Karl Fischer Titration

The Karl Fischer (KF) titrations were carried out manually at room temperature using colorimetric end-point determination through an automatic, serialized/certified class A automatic buret with reservoir bottle. All chemicals were used as received. Glassware was baked at 220°C overnight and cooled under dry argon gas purge before use. The measurements followed ASTM D1364-02[21] and ASTM E203-08[22] standards for analysis of residual amounts of water in monomer samples. The KF titration is based upon the reduction of iodine by sulfur dioxide in the presence of water.[21] The general equation for the KF titration reaction is as follows:[22]

$$H_2O + I_2 + SO_2 + R'OH + 3RN \rightarrow (RNH)SO_4R' + 2(RNH)I \quad (1)$$

where RN = organic base, e.g., pyridine, and R'OH = a dry alcohol, such as methanol. From the quantity of sulfur dioxide and iodine titrant to yield a colorimetric iodine endpoint, the amount of water in the sample is calculated using eq. (1).

A minimum of three replicate titrations were carried out for ~ 1 g samples, e.g., the plain solvent as blank, a 1000 ppm water-in-THF standard, or epoxy monomer. When the titrated values varied significantly, additional replicates were carried out until good reproducibility was obtained. The equations used for the calculations are from ASTM E203-08 standard[22] with slight modification, as shown below.

$$\text{Water (wt \%)} = \frac{[A' \times F \times 0.001 \times 100]}{W} \quad (2)$$

For a 1000 ppm water-in-THF standard,

$$F = D \times \frac{E}{A} \quad (3)$$

The symbols for eqs. (2) and (3) are defined as follows: A' = milliliters of reagent required for titration of the SE sample; A = milliliters of reagent required for titration of the standard (for a 1000 ppm Water-in-THF standard); D = milliliters of water-in-THF standard required; E = milligrams of water per milliliter in the water-in-THF standard; F = water equivalent, in milligrams of water per milliliter of KF reagent; and W = grams of sample.

Measurements of Polymer Diametral Tensile Strengths

Diametral tensile strength cylindrical samples were first synthesized as described below. Then the diametral tensile strength of the polymer cylinders was then measured as a function of initial moisture concentration in monomer, whose details follow below. The reported diametral tensile strengths are an average

Table I. Component Ratios Used in SE Sample Preparation

Entry	Sample	Photoinitiators			LMC (g)	SE (g)	H_2O (g)
		PIH (g)	CPQ (g)	EDMAB (g)			
1	As-synthesized SE	0.060 (1.19 wt %)	0.020 (0.4 wt %)	0.002 (0.04 wt %)	0.016 (0.32 wt %)	4.902 (98.05 wt %)	0.000
2	As-synthesized SE + 1 wt %-H_2O	0.060	0.020	0.002	0.016	4.902	0.050
3	As-synthesized SE + 2 wt %-H_2O	0.060	0.020	0.002	0.016	4.902	0.100
4	Saturated-SE	0.060	0.020	0.002	0.016	4.902	0.000
5	Dried-SE	0.060	0.020	0.002	0.016	4.902	0.000
6	Ultra-Dried SE	0.060	0.020	0.002	0.016	4.902	0.000

Note: IPH = phenyl [p-(2-hydroxytetradecyloxy) phenyl] iodonium hexafluoroantimonate, CPQ = camphoroquinone, EDMAB = ethyl 4-dimethylaminobenzoate, LMC = Lamoreaux's catalyst, and SE = silicone epoxy monomers.

of those obtained from 10 specimens fabricated, for each material composition.

General Considerations for Preparations of SE Samples. The samples shown in Table I were prepared as follows: PIH (0.060 g, 1.19 wt %), CPQ (0.020 g, 0.4 wt %), EDMAB (0.002 g, 0.04 wt %) and SE (4.902 g, 98.05 wt %) were added to a scintillation vial and mixed with a spatula followed by LMC (0.016 g, 0.32 wt %) and mixing again with a spatula. The sample was allowed to dark cure for minimum of 1–3 days or more before the diametral tensile strength test. In the case of As-synthesized-SE + 1 wt %-H_2O sample, deionized water (50 μL, 0.050 g, 1 wt %) was added, and it was mixed again with a spatula before the addition of LMC. In the case of As-synthesized SE + 2 wt %-H_2O sample, deionized water (100 μL, 0.100 g, 2 wt %) was added and mixed again with a spatula before the addition of LMC. The water added samples were allowed to dark cure for 2–3 days.

The saturated SE was prepared by placing SE (4.902 g) in a scintillation vial with 2 mL of deionized water placed on top of the resin interface in the scintillation vial. The vial was capped, and it was allowed to stand for one week. After that time, the remaining water on top of the resin was decanted in order to obtain saturated SE.

Dry SE was prepared by first dissolving SE (∼10 g) in anhydrous toluene (10–15 mL), and then the solution was dried

under the vacuum suction of rotary-evaporator (∼3 h). The ultra-dried SE was prepared by dissolving SE (∼44 g) in anhydrous toluene (∼40 mL), distilling the contents with a Dean-Stark trap condenser attached to the flask azeotropically by removing toluene/moisture distillate, which was collected (2 × 20 mL). The distillation was continued until no toluene evolved (∼1 h). Then, the flask was allowed to cool to ∼50°C and dried under anhydrous vacuum suction in rotary-evaporator to remove the residual amounts of toluene (∼2 h).

General Considerations for Preparations of EMEC Samples. Three EMEC samples, dry-EMEC, as-synthesized-EMEC, and saturated-EMEC, were prepared similar to corresponding SE samples by replacing 4.902 g of SE with 4.902 g of EMEC and without Lamoreaux's catalyst (Table II). Then, the dried EMEC samples were irradiated for 120 s, as-synthesized EMEC samples were irradiated for 90 s, and saturated EMEC samples were irradiated for 40 s.

Diametral Tensile Strength Measurement Detail. The resulting polymeric cylinders were aged for 7 days at ambient temperature. The scintillation vial solids were removed and cut into disks with a diameter ∼0.50–0.60 inches and a thickness of ∼0.25–0.50 inches before analysis. Load was applied vertically on the lateral portion of the cylinder at a crosshead speed of 1.0 mm/min, producing tensile stresses perpendicular to the vertical plane passing through the center of the specimen (see Figure 1).[23,24]

Table II. Component Ratios Used in EMEC Sample Preparation

Entry	Sample	Photoinitiators			EMEC (g)	H_2O (g)	Irradiation time (sec.)
		PIH (g)	CPQ (g)	EDMAB (g)			
1	Dried-EMEC	0.060	0.020	0.002	4.902	0.000	120
2	As-synthesized EMEC	0.060 (1.20 wt %)	0.020 (0.4 wt %)	0.002 (0.04 wt %)	4.902 (98.35 wt %)	0.000	90
3	Saturated-EMEC	0.060	0.020	0.002	4.902	0.000	40

Note: IPH = phenyl [p-(2-hydroxytetradecyloxy) phenyl] iodonium hexafluoroantimonate, CPQ = camphoroquinone, EDMAB = ethyl 4-dimethylaminobenzoate, and EMEC = (3,4-epoxycyclohexyl) methyl-(3,4 epoxycyclohexyl) carboxylate.
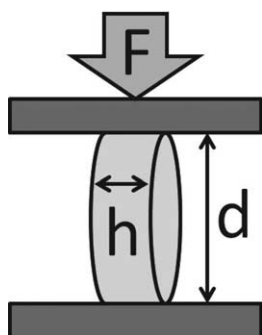
Figure 1. Schematic diagram showing the orientation of the disks made out of the samples in the instrument during the diametral tensile strength test.

After each diametral tensile strength test, the fracture load (F) in Newtons (N) or kilo-Newtons (kN) was recorded, and the diametral tensile strength (σ, megaPascal, MPa) was calculated as follows:

$$\sigma = \frac{2F}{\pi dh} \qquad (4)$$

where F = applied force, d = diameter of the cured disks, h = height (thickness) of specimens, and π = 3.1416.

Polymerization Kinetics Analysis
The polymerization DOC (α) can be calculated as:[5]

$$\alpha = 1 - \left[\frac{A(t)}{A(0)}\right] \qquad (5)$$

where $A(t)$ = the absorbance at a given time and $A(0)$ = the absorbance at the first measurement, in this case acquired at $t \sim 3$ min.

Kinetics Analysis of SE Samples Using FTIR
The composition of each sample was prepared according to Table I. A background was taken of a clean KBr salt plate. The scan resolution was 1 cm^{-1}, and the number of scans taken at for a given measurement was 16 scans. A thin layer of the sample was placed on a clean KBr disk, and spectra were measured at 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 min., 1 h, 1.25 h, 1.5 h, 1.75 h, 2 h, 2.25 h, 2.5 h, 2.75 h, 3 h, 4.5 h, 5 h, 5.5 h, 6 h, 6.5 h, and 7 h. Reaction time (t_o) was started upon addition of LMC, which was the last component added to each SE sample.

To ensure resin polymerization was complete, we analyzed the DOC of the polymerization of the SE using FTIR spectroscopy. The DOC was calculated for each polymer sample using a polymerization dependent peaks of SE at 884 cm^{-1} (oxirane ring opening) and 1208 cm^{-1} (cyclic ether formation), which were normalized as a ratio to the internal standard peak of SE at 1259 cm^{-1} (Si-O in ring), analogous to analyses by Eick at al.,[20] who had utilized 883 cm^{-1} peak against 1258 cm^{-1} absorbance. The DOC was calculated as the difference in the normalized absorbance ratios versus unpolymerized resin that represented the normalized absorption ratio at no (0%) polymerization.

Rate constants were obtained by fitting data points using Igor Pro software (WaveMetrics Inc.) onto the following equation,

$y(t) = y(0) + A_1.\exp \quad (-k_1 t) + A_2 \quad \exp \quad (-k_2 t)$, where: $y(t)$ = absorbance at time t; $y(0)$ = absorbance at 3 min; A_1, A_2 = constants; k_1 = faster rate constant (for reaction times less than $\sim$100 min); and k_2 = slower rate constant (at longer reaction times, not reported). The dual rate constant equation fitting did not yield separate long reaction time rate constants for saturation excess moisture SE samples or EMEC sample kinetics.

General Considerations for Preparation of EMEC Samples for Kinetics Analysis Using FTIR. The sample compositions were prepared according to the Table II following FTIR methodology of SE polymerization. The bulk sample was irradiated for 60 s, and immediately afterward, a thin layer was placed on a KBr disk to obtain FTIR absorption measurement. Then FTIR was measured after 5, 10, 15, 20, 25, 30, and 60 min. The DOC was calculated for each polymer sample using a polymerization dependent peak of EMEC at 1083 cm^{-1} (oxirane ring opening), which was compared to an internal standard peak of EMEC at 1730 cm^{-1} (C=O stetch). Hartwig et al.[2] carried out similar analyses during their work, utilizing the 1100 cm^{-1} and 1740 cm^{-1} peaks. The DOC was calculated as a difference in normalized absorbance ratios, for the 3511 and 1083 cm^{-1} bands versus absorbance at 1730 cm^{-1} of the samples, at time t compared to the same absorbance ratios for unpolymerized resin that represented no (0%) polymerization.

RESULTS AND DISCUSSION

Moisture Concentration
ASTM E203[2,22] standard test method was used to determine moisture/water via volumetric KF titration. Although the literature has reported that effects of moisture/water/relative humidity on cationic polymerization and kinetics exist, to our knowledge there has been no report utilizing a quantitative measurement of water concentration in the monomer versus the aforementioned indirect methods of moisture concentration, e.g., humidity exposure. Monomers in this work were prepared to have varying concentrations of water present from very low water concentration (see Tables III and IV below) to saturation to in excess of saturation. The water concentrations were prepared and assessed by KF titration and subjected to cationic polymerization initiation with assessment of polymerization kinetics, degree of cure, and subsequently polymer tensile and thermal characterizations.

Silicone Epoxy (SE) Monomer Samples. The amount of moisture present in the SE samples is shown in Table III and Supporting Information Figure S1. Through the azeotropic removal of water, the amount of moisture in the SE monomer was reduced significantly as compared to as-synthesized material.

Table III. Summary of Karl Fischer Titration Results for SE Samples with Average Water Concentration in Units of Weight Percent

Sample	Average water concentration (wt %)
Ultra-dried SE	0.0291 ± 0.0057
Dried-SE	0.1029 ± 0.0082
As-synthesized SE	0.1781 ± 0.0165
Saturated-SE	0.1932 ± 0.0133

Table IV. Summary of Karl Fischer Titration Results for EMEC Samples

Sample description	Average water concentration (wt %)
Ultra-dried EMEC	0.0374 ± 0.0060
As-synthesized EMEC	0.0516 ± 0.0071
Saturated- EMEC	1.0006 ± 0.0064

The as-synthesized SE sample was found to have nearly the same amount of moisture as the saturated SE sample.

EMEC Samples. The amounts of moisture present in the EMEC samples were measured with values shown in Table IV to compare results for SE samples with literature results and to benchmark the commercially available EMEC as a standard. We found that azeotropic removal of water from commercial EMEC using toluene only slightly reduced water concentration and indicated the commercially available EMEC was mostly dry. However, in comparison to SE samples, the amount of moisture observed for the water-saturated EMEC samples was ∼20 times higher than as-synthesized EMEC. The comparison of saturated-SE and the saturated-EMEC samples showed that saturated-EMEC had a moisture content about five times higher than the saturated SE.

Diametral Tensile Strength
SE Polymer Diametral Tensile Strength. A comparison of average diametral tensile strengths of the SE samples showed that the driest SE polymer samples produced the highest strengths of 9.4 and 9.1 MPa, respectively (Table V and Supporting Information Figure S2). The as-synthesized-SE to saturated-SE samples, which had similar water concentrations, also had similar average diametral tensile strengths. As the amount of water in the sample was increased to near saturation in the monomer, the average diametral tensile strength began to decrease significantly. At highest water content, the polymers were rubbery/plastic materials, hence they did not fracture elastically upon increasing the compressive force. Diametral tensile strength results showed that the materials failed at lower tensile strengths upon increasing the water content/moisture content in monomer during polymerization toward saturation when above a certain water concentration threshold, about 0.1 wt %.

Table V. Diametral Tensile Strength Results as a Function of Water Concentration for SE Samples

Sample	Average diametral tensile strength (MPa)
Ultra-Dried SE	9.40 ± 1.23
Dried-SE	9.13 ± 1.77
As-synthesized SE	6.10 ± 1.83
Saturated-SE	6.03 ± 1.09
As-synthesized SE + 1 wt % Water	3.08 ± 0.58
As-synthesized SE + 2 wt % Water	1.85 ± 0.19

Table VI. Diametral Tensile Strength Results as a Function of Water Concentration for EMEC Samples

Sample	Average diametral tensile strength (MPa)
Dried-EMEC	22.04 ± 1.16
As-synthesized EMEC	22.26 ± 0.60
Saturated-EMEC	11.72 ± 2.73

When the water saturation concentration was exceeded, it produced yet worse mechanical strengths through formation of a heterogenous material. Under magnification, the additional water was observed as micrometer sized pockets of water within the cured polymer matrix. The increase of the water amount beyond the solubility limit during polymerization produced very significantly reduced mechanical performance and should be particularly avoided.

Diametral Tensile Strength for UV-Cured EMEC. Comparison of average diametral tensile strength of the EMEC samples showed that the dried-EMEC and as-synthesized EMEC polymer samples produced the highest strengths of 22.0 and 22.2 MPa, respectively (Table VI).

Commercially available, as-synthesized EMEC and dried-EMEC polymerized monomer samples had similar strengths that were consistent with KF results that showed similar water concentrations. As the amount of water in the sample was increased to near saturation in the EMEC monomer, the average diametral tensile strength began to decrease significantly. Diametral tensile strength results revealed that the materials tended to have lower tensile strengths upon increasing the water content/moisture content present during polymerization toward saturation, reducing the strength by nearly half the strength obtained with dry monomer.

The decrease in strength found for EMEC polymer when made of water-saturated monomer was similar to results for the SE monomer. The reader should recall that saturated water concentration was 10-fold higher in EMEC than in SE monomer. Also, similar to SE samples, exceeding the water saturation concentration produced further reductions in mechanical strength through formation of heterogeneous material.

FTIR Kinetics
Kinetics for SE Samples. Absorption peak ratios of functional groups associated with polymerization, e.g., 884 cm^{-1} representing ring-opening of C—O in epoxy ring, against an unchanging functional group absorption, e.g., 1259 cm^{-1} in curing siloranes,[19,20] were calculated for each material (see Supporting Information Figures S3 and S4) to normalize changes in absorption. Analyses of the peak ratios at 884 cm^{-1} to estimate DOC and ROC indicated that as-synthesized SE + 1 wt %-water sample had the slowest ROC (Table VII). The second slowest ROC was observed for a water-saturated SE monomer sample. On the other hand, depletion of the epoxy ring was fastest in the slightly lower water concentration as-synthesized-SE sample.

Table VII. Degree and Rate of Conversion (DOC and ROC, Respectively) Measured During Polymerization of Different SE Samples Based Normalized Absorption Loss at 884 cm^{-1}

Sample	Normalized DOC after 1 h	Normalized DOC after 7 h	Rate constant in first 1 h ± error (×10^{-3} min^{-1})	Rate constant after first 7 h ± error (×10^{-3} min^{-1})
Ultra-dried SE	7.44	17.27	15.3 ± 4.6	2.6 ± 2.5
Dried-SE	9.03	17.90	21.7 ± 3.1	2.3 ± 2.1
As-synthesized SE	9.02	14.79	101.9 ± 11.7	8.7 ± 0.9
Saturated-SE[a]	5.58	15.38	7.01 ± 0.29	7.0 ± 0.3
As-synthesized SE + 1 wt %-water[a]	4.99	12.56	3.2 ± 0.3	3.2 ± 0.3

Rate of decay was constant over 7 h polymerization time.

The dried-SE sample of moderate water concentration had the second highest ROC.

Except for the as-synthesized SE sample, the absorbance peak ratio very slightly increased at the beginning of measurements before the ratio decreased for all other samples, which we think was due to some viscous flow of the resin sample on the KBr salt plate before viscosification upon cure. Interestingly, ultra-dried SE samples had less ROC and less DOC compared to dried-SE samples indicating that the polymerization rate and DOC were nearly optimized for a dried-SE sample of moderate water concentration in monomer, whose polymer also demonstrated good mechanical strength.

While monitoring polymerization by FTIR, we observed a growth of a new peak at 1208 cm^{-1} corresponding to a C─O stretch of cyclic ether formation. DOC measured using the 1208 cm^{-1} band also showed the greatest DOC for the dried-SE sample followed by DOC for the saturated-SE sample (Table VIII). The next highest DOC for the peak at 1208 cm^{-1} was for the ultra-dried SE, followed by the as-synthesized SE + 1 wt %-water sample and the as-synthesized SE sample. While high monomer conversions for a dried-SE sample were perhaps expected with its moderate moisture concentration, a very low DOC for as-synthesized-SE sample was not, unless it somehow resulted in a different distribution of products compared to other sample compositions as measured by the 1208 cm^{-1} band.

Polymerization kinetics showed that the dried-SE sample had very high DOC in first 60 min, e.g., ~80%, indicating that moderate moisture favored initiation and fast propagation early in the polymerization. In comparison, the saturated-SE sample showed similar DOC to as-synthesized-SE, which are of similar monomer water concentration. The as-synthesized-SE + 1 wt %-water sample began polymerization very slowly but appeared to gradually increase in reactivity, exhibiting a higher dark reaction ROC for the 1208 cm^{-1} peak after 7 h among all samples with a rate constant of 4.0 ± 0.7 min^{-1}.

The DOC at 1208 cm^{-1} was lowest for the as-synthesized-SE sample and the as-synthesized SE + 1 wt %-water samples during first hour of curing. This result indicates an inhibition by deactivation of PIH initiator by hydrolysis, which is similar to what Cai and Jessop observed during their study,[5,25] and participation in propagation by moisture/water in the two later samples. The lower DOC after short time of polymerization for as-synthesized SE sample and as-synthesized SE + 1 wt %-water samples suggested that water/moisture content in the sample affected the initiation step, resulted in inhibition of initiation by excess water or reduced the efficiency of the initiation. The dried-SE sample exhibited a higher DOC at shorter polymerization times indicating that it underwent polymerization with less inhibition or increased rates of initiation by water-associated species.

Cai and Jessop[5] observed the epoxide induction period increased with the increasing water concentration when only cationic initiator was present. We observed a similar trend, where epoxide induction period followed the order (at 884 cm^{-1}): As-synthesized SE + 1wt %-water < As-synthesized SE < Saturated-SE < Ultra-dried SE < Dried-SE samples, respectively. For Ultra-dried SE and the Dried-SE samples, we

Table VIII. Degree and Rate of Conversion (DOC and ROC, Respectively) Measured During Polymerization of Different SE Samples Based on Normalized Absorption Gained at 1208 cm^{-1}

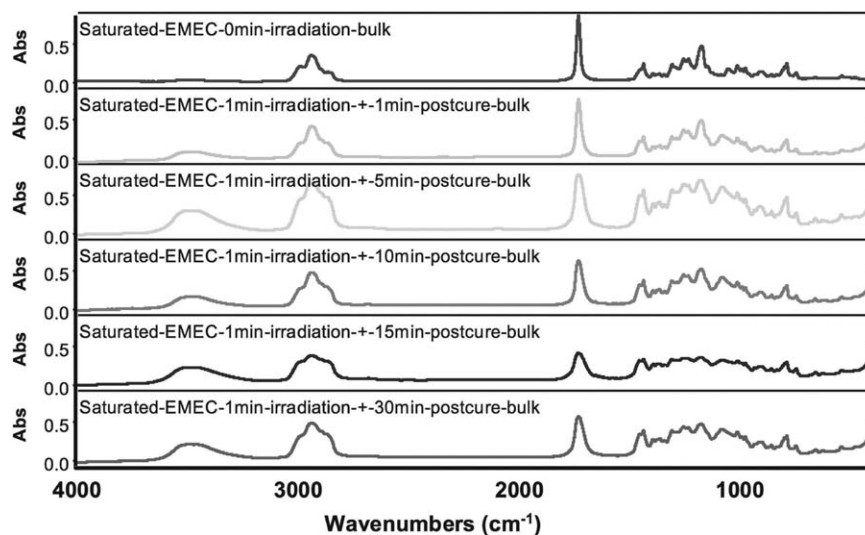| Sample	Normalized DOC after 1 h	Normalized DOC after 7 h	Rate constant 1 h ± error (×10^{-3} min^{-1})	Rate constant after first 7 h ± error (×10^{-3} min^{-1})
Ultra-Dried SE	43.7	94.1	15.6 ± 2.4	2. 3 ± 5.7
Dried-SE	80.2	132.3	24.0 ± 1.9	2.4 ± 2.6
As-synthesized SE	24.4	52.6	22. 6 ± 1.2	1.4 ± 1.4
Saturated-SE	27.7	83.9	19.3 ± 1.2	1.5 ± 0.8
As-synthesized SE + 1 wt %-water	11.9	67.3	39 ± 13 (50–120 min)	4.0 ± 0.7

Figure 2. The growth of ─OH peak at 3500 cm^{-1}, growth of formed ether vibration at 1100 cm^{-1} and broadening of 1730 cm^{-1} vibration during the irradiation of EMEC.

hypothesize that the polymerization rate was better optimized with Dried-SE of moderate water concentration than in Ultra-dried SE. This observation indicates that an optimum amount of moisture provided fast initiation and early propagation of the polymerization but that lower or higher amounts of water resulted in inhibition either through sluggish initiation or chain transfer with degradation of the initiator, respectively.

The FTIR absorbances of normalized spectra for three different EMEC samples at 3511 cm^{-1} and 1083 cm^{-1} after time "t" ($t = t$ min) with respect to the absorbance before irradiation ($t = 0$ min) showed that the absorbance initially increased with respect to time and afterwards became constant (see Figure 2 below and Supporting Information Figure S5). We monitored the change in absorbance of FTIR peaks at 3511 cm^{-1} and 1083 cm^{-1}, which correspond to absorption bands of the ─OH group (after ring opening of epoxy group during the polymerization) and the formed ether group, respectively. We used the internal ester carbonyl peak at 1730 cm^{-1} as an internal standard for peak normalization. The peaks reached the maximum DOC within 30 min for all three samples (Tables (IX–XI)). Analyses of normalized spectra showed that the saturated-EMEC sample had the highest normalized DOC indicating that higher moisture concentration corresponded with a higher DOC. This result was analogous to the result of Hartwig et al. for the same monomer material.[2] However, they presented their work in terms of the relative humidity exposure and not a water concentration in monomer.

The order of DOC for three EMEC samples were Ultra-Dry EMEC ≤ As-synthesized EMEC < Saturated-EMEC. The DOC for as-synthesized EMEC and ultra-dry EMEC were similar although the ultra-dry sample had less DOC. The KF titration data showed these samples had somewhat similar moisture contents. The spectra in Figure 2 show that a shoulder or peak broadening was formed at low wavenumber side of the ester carbonyl band at 1730 cm^{-1}, which is consistent with Hartwig et al. observations.[2] This shoulder is characteristic for hydroxyl esters and is caused by associative interaction of hydroxyl proton with the ester carbonyl group. This observation also supports the formation of hydroxyl groups during polymerization as confirmed by the formation of ─OH group vibrations around 3500 cm^{-1} region.[2]

In comparison of SE and EMEC samples, we observed that an increase of moisture content during cationic polymerization significantly increased the DOC for EMEC. For SE samples, the DOC initially increased but then were decreased in DOC as a function of increasing moisture concentration. The reason as to why the analogous epoxy structures display differences in polymerization kinetics, degree of cure, and mechanical strength in response to moisture concentration in the monomer during cationic initiation is not clear. Differences in cure behavior were clearly demonstrated for non-analogous epoxy structures in previous literature reports.[1,2] Hartwig et al. concluded that differences in chain growth or chain-transfer reactions of epoxide groups are affected by the different chemical environment and

Table IX. Normalized Rates of Conversion (ROC) for EMEC Samples

Sample	Rate constant (×10^{-3} min^{-1}) with respect to 3511 cm^{-1} peak	Rate constant (×10^{-3} min^{-1}) with respect to 1083 cm^{-1} peak
Ultra-Dried EMEC	4.5	13.1
As-synthesized EMEC	5.7	12.8
Saturated-EMEC	626	1099

Table X. Degree of Conversion (DOC) of Different EMEC Samples Based on 3511 cm^{-1} Peak

Sample	Normalized DOC after 1 min	Normalized DOC after 30 min
Ultra-Dried EMEC	3.7	10.0
As-synthesized EMEC	5.3	13.8
Saturated-EMEC	34.6	94.9

are the reason for different reaction behavior. For instance, the curing behavior of the siloxy cycloaliphatic epoxies versus the cycloaliphatic epoxy ester may be influenced by different hydration structures of the siloxy groups versus ester groups in the two monomers. Siloxanes are known to have strong water repulsion properties,[26] and the SE monomer had a five-fold lower equilibrium, saturated water concentration than EMEC (Table III versus Table IV).

TGA Analyses

We carried out TGA analyses of the SE and EMEC polymer samples in order to determine the decomposition temperatures of each sample (Table XII and also Supporting Information Figures S6 and S7). The TGA analyses showed that nearly all the SE samples had 1st decomposition temperatures between 379 and 392°C. The onset temperature appeared to be slightly decreased with increasing moisture during polymerization with the exception of as-synthesized SE. The decrease in onset decomposition temperature with the increase of moisture could be due to less strong polymer crosslink networks in for samples with more water and lower DOC. However, all samples had onset temperatures >320°C, and peak decomposition temperature increased with moisture concentration. A lower onset temperature is thus likely related to increased evolution of moisture from the polymer, perhaps with added influence of a lower crosslink network density.

The TGA analysis showed that nearly all the EMEC samples had higher onset decomposition temperatures than SE polymers between 373 and 376°C. The peak decomposition temperatures of EMEC samples were similar to but higher than the SE samples and were very slightly, perhaps insignificantly, decreased with increasing moisture concentration during polymerization. No significant correlation between thermal decomposition and DOC or ROC was observed.

DSC Measurements

Thermal phase transition properties were measured by DSC to determine glass transition temperature (T_g) of the epoxy polymer

Table XI. Degree of Conversion (DOC) of Different EMEC Samples Based on 1083 cm^{-1} Peak

Sample	Normalized DOC after 1 min	Normalized DOC after 30 min
Ultra-Dried EMEC	16.3	34.2
As-synthesized EMEC	28.7	42.6
Saturated-EMEC	57.6	97.1

Table XII. Decomposition Temperatures of Different SE Samples Measured Using TGA

Sample	Onset temperature (°C)	Peak decomposition temperature (°C)
Ultra-Dried SE	332.12	379.7
Dried-SE	325.71	384.13
Saturated-SE	333.85	391.86
As-synthesized SE	342.45	388.77
As-synthesized SE + 1 wt %-H$_2$O	325.91	388.37
As-synthesized SE + 2 wt %-H$_2$O	329.56	390.39
Dried-EMEC	373.54	408.6
As-synthesized EMEC	374.82	407.87
Saturated-EMEC	376.18	407.76

samples (Table XIII and also see data in Supporting Information Figures S8 and S9 for SE and EMEC samples, respectively). However, we did not observe a resolved T_g for either SE or EMEC polymer samples due to the presence of reaction exotherms. The exothermic events provided evidence of further polymerization reactions upon heating, indicative of remnant DOC.

One exothermic event was present upon heating the SE samples. Two exotherm transitions for EMEC samples were observed indicating different reaction/cross-linking mechanisms and reactivity for SE versus EMEC samples. Even after the initial heating cycle of the 1st DSC scan, a broad T_g transition suggested a widely distributed cross-link density that prevented reporting of T_g. Examination of the residual reaction enthalpy for each sample showed that more residual reaction was correlated with an increase of initial moisture concentration in the SE monomer but reaction enthalpy was decreased for EMEC samples of higher water concentration. These results showed that there was less DOC for samples with higher water content for SE monomer, where the lower residual enthalpy was correlated to higher initial DOC. The EMEC DSC results indicated that there was less residual reaction enthalpy for EMEC samples with higher initial water content that also correlated with higher measured DOC, respectively. In this way, the EMEC curing behavior as a function of water concentration was different and somewhat opposite to that of the SE samples. While both SE and EMEC were initially improved in ROC, DOC and of lower residual enthalpy with increasing water concentration in the monomer, SE samples became less reactive and of lower ROC, DOC and of higher residual cure enthalpy at water concentrations in the monomer approaching saturation with water. On the other hand, EMEC was accelerated in DOC and of reduced residual reaction enthalpy by increased water concentrations up to and including saturation with water. Water-saturated EMEC polymer had approximately 5x more water per volume than the water-saturated SE samples.

The differences in reactivity between the two epoxy monomers as a function of moisture concentration are rather surprising

Table XIII. Post-Curing Temperatures and Enthalpies of Different SE Samples Measured Using DSC

Sample	Onset (P_o)/°C	P(max)/°C	Residual ΔH (J g^{-1})
Ultra-Dried SE	93.1	168.6	95.4
Dried-SE	97.5	168.4	64.5
As-synthesized SE	69.9	150.5	100.3
Saturated-SE	74.1	132.1	102.7
As-synthesized SE + 1 wt %-H_2O	63.6	139.0	120.5
As-synthesized SE + 2 wt %-H_2O	64.3	125.6	183.5
Dried-EMEC	60.2/102.4	74.2/130.9	57.2
As-synthesized EMEC	60.0/98.0	74.0/125.8	52.8
Saturated-EMEC	56.7103.7	70.7/128.2	54.3

Note: ΔH is the integral of heat flow per mass of sample.

since the monomers share a common epoxy ring structure. The polymerization mechanism difference in the cycloaliphatic ester vs. cycloaliphatic silicone monomers could be due to different hydration structures, e.g., that might influence the location of the superacid anion at lower versus higher water contents, or differential repulsion of water by the silicone segments at higher water contents versus by the carbon ester group. For instance, the silicone segments could be causing microseparation of the epoxy and water domains. Such separation may affect deprotonation of the alcohol group and deactivation during chain-transfer reaction.

Bisphenol A (glycidyl) epoxy monomer reaction was decelerated by increasing water concentrations that was proposed to be a differential reactivity for transfer of a proton during polymerization.[1,2] The molecular modeling of Hartwig *et al.* was practically limited to the epoxy group itself and, even then, was inadequate to explain the observed differences in behavior between cycloaliphatic groups. Both SE and EMEC possess identical 3,4-epoxycyclohexyl monomer structures and only have different joining chemical structures, silicon/siloxy based versus ester, respectively. While a differential hydration or phase separation phenomena appears likely, it remains unclear why the monomers polymerize so differently under influence of moisture.

CONCLUSIONS

We chemically quantified the moisture concentration present in SE monomer samples and EMEC samples using KF titration. A series of samples was prepared to be from nearly dry to saturated in moisture content and the effect of moisture on their polymerized mechanical properties and cationic polymerization rates were measured. Despite that both monomers possess the same general 3,4-epoxycyclohexyl oxirane structure, their sensitivity to moisture during polymerization was found to be quite different.

The diametral tensile strength tests indicated that the diametral tensile strength was initially unchanged upon increasing moisture concentration as compared with dry samples but was subsequently decreased by pre-polymerization moisture concentrations approaching saturation in the monomer for both SE and EMEC polymers. The FTIR kinetic studies showed that

with an initial increase in moisture content, the typical trend was an increase of polymerization degree and rate of conversion (DOC and ROC, respectively) for both monomers. However, higher water concentrations decreased ROC and DOC for SE monomer as the moisture concentration approached saturation. This result is similar to those earlier reported for bisphenol A glycidyl epoxy monomers, whereas polymerization DOC and rate were only accelerated by increased water concentrations for EMEC samples. Thus, the effect of moisture on the cationic polymerization is not well-predicted by epoxy group structural generalizations and should be measured as described above for the specific epoxy system.

REFERENCES

1. Hartwig, A.; Koschek, K.; Lühring, A. In Adhesion; Wiley-VCH Verlag GmbH & Co. KGaA: **2006**, p 205.

2. Hartwig, A.; Schneider, B.; Lühring, A. *Polymer* **2002**, *43*, 4243.

3. Baschek, G.; Hartwig, G.; Zahradnik, F. *Polymer* **1999**, *40*, 3433.

4. Cai, Y.; Jessop, J. L. P. *Polymer* **2006**, *47*, 6560.

5. Cai, Y.; Jessop, J. L. P. *Polymer* **2009**, *50*, 5406.

6. Hartwig, A. *Int. J. Adhes. Adhes.* **2002**, *22*, 409.

7. Timpe, H. J.; Schikowsky, V. J. *für Praktische Chem.* **1989**, *331*, 447.

8. Pappas, S. P. *Prog. Org. Coat.* **1985**, *13*, 35.

9. Jenkins, A. D. *Polym. Int.* **2000**, *49*, 1729.

10. Fouassier, J. P. In Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications; Hanser-Gardner Publications: New York, NY, **1995**.

11. Crivello, J. V.; Acosta Ortiz, R. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 2298.

12. Sangermano, M.; Malucelli, G.; Morel, F.; Decker, C.; Priola, A. *Eur. Polym. J.* **1999**, *35*, 639.

13. Lin, Y.; Stansbury, J. W. *Polym. Adv. Technol.* **2005**, *16*, 195.

14. Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci.: Polym. Chem. Ed.* **1979**, *17*, 977.

15. Crivello, J. V. In Initiators—Poly-Reactions—Optical Activity, Vol. *62*; Springer: Berlin Heidelberg: **1984**, p 1.

16. Weiss, P. *J. Polym. Sci.: Polym. Lett. Ed.* **1983**, *21*, 310.

17. Decker, C.; Moussa, K. *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 3429.

18. Jenkins, A. D. *Polym. Int.* **2000**, *49*, 1729.

19. Melander, J. R.; Weiler, R. A.; Miller, B. D.; Schuman, T. P.; Kilway, K.; Day, D. E.; Velez, M.; Eick, J. D. *J. Biomed. Mater. Res., Part B: Appl. Biomater.* **2012**, *100*, 163.

20. Eick, J. D.; Barragan-Adjemian, C.; Rosser, J.; Melander, J. R.; Dusevich, V.; Weiler, R. A.; Miller, B. D.; Kilway, K. V.; Dallas, M. R.; Bi, L.; Nalvarte, E. L.; Bonewald, L. F. *J. Biomed. Mater. Res. Part B: Appl. Biomater.* **2012**, *100B*, 850.

21. In Standard Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method); ASTM International: West Conshohocken, PA, **2012**, p 1.

22. In Standard Test Method for Water Using Volumetric Karl Fischer Titration; ASTM International: West Conshohocken, PA, **2008**, p 1.

23. Della Bona, Á.; Benetti, P.; Borba, M.; Cecchetti, D. *Brazil. Oral Res.* **2008**, *22*, 84.

24. Anusavice, K. J. In Phillips's Science of Dental Materials, 11th ed.; W. B. Saunders: St. Louis:, MO, **2003**.

25. Hartwig, A.; Harder, A.; Lühring, A.; Schröder, H. *Eur. Polym. J.* **2001**, *37*, 1449.

26. Zhang, W.; Okubayashi, S.; Badura, W.; Bechtold, T. *J. Appl. Polym. Sci.* **2006**, *101*, 4140.