

# The Influence of Humidity on Surface Modulus of Photocured Epoxy Coatings

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Epoxy resins were cured via UV illumination in atmospheres of varying humidity levels. The chain-transfer reaction between the epoxy moieties and water molecules is described by the activated monomer mechanism. The physical effects of chain-transfer reactions mainly occur at the surface due to limited diffusion during the reaction. Force curves were obtained via atomic-force microscopy and used to determine the surface modulus of cured resins. A decrease in modulus was observed for resins cured in humid atmospheres.

## Introduction

Cationically cured epoxy coatings and adhesives are an important class of materials that serve as alternatives to the commonly used (meth)acrylate resins. Cationic polymerization is used in instances where inert gases or ultrahigh illumination intensities are not feasible because oxygen (which inhibits free-radical polymerizations) has no effect on cationic polymerization.<sup>1-3</sup> Although oxygen does not affect cationic polymerization of epoxy resins, humidity can and does.<sup>4-6</sup> Water, through the activated monomer (AM) mechanism,<sup>7</sup> acts as a chain-transfer agent (CTA) in epoxy systems, which results in lower polymer properties—specifically, reduced crosslink density and glass-transition temperature ( $T_g$ ).<sup>8</sup> If a formulation has been optimized for dry conditions and is then used

under humid conditions, the effects of water may negatively impact the performance of the material, even to the point of material failure. In this study, we used atomic force microscopy (AFM) to show the extent of damage humid curing conditions can have on the surface hardness of an epoxy resin. The surface of the cured materials will be impacted the greatest by atmospheric factors (water vapor in this case) because the surface interacts with the atmosphere directly, while the bulk of the resin is insulated from the atmosphere.

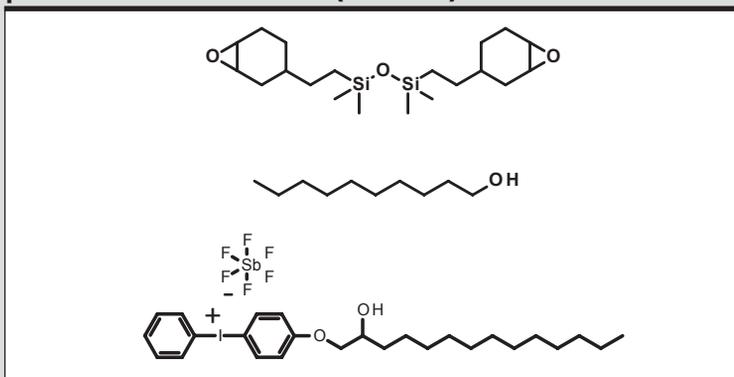
## Experimental

An epoxy silicone monomer (PC-1000, Polyset Company) was chosen for this study since it photopolymerizes quickly, resulting in polymers with a high crosslink density and  $T_g$ . The monomer was formulated with *n*-decanol (Sigma Aldrich) at concentrations such that the ratio of hydroxyl to oxirane rings was equal to 0.1. The alcohol was used as a chain-transfer agent to reduce the crosslink density and  $T_g$  of the neat resin to one that is less brittle and easier to handle. The photo-acid generator (PC-2506, Polyset Company) was formulated at 0.3 wt% relative to the resin mass (monomer + alcohol). All materials were used as received and are shown in Figure 1.

The liquid resins were poured into 1 mm deep, cup-style Teflon molds and placed inside an in-house fabricated

## FIGURE 1

Epoxy silicone monomer, PC-1000 (top); chain transfer agent, *n*-decanol (middle); and photoinitiator PC-2506 (bottom).



humidity control chamber fitted with a quartz window. The uncured resins were equilibrated in the humidity chamber for three minutes prior to photocuring. Polymer specimens were prepared using a 100-watt, high-pressure mercury lamp (Acticure® Ultraviolet/Visible spot-cure system, EXFO Photonic Solutions, Inc.). The UV light ( $300 \text{ nm} < \lambda < 450 \text{ nm}$ ), with an effective irradiance of  $50 \text{ mW/cm}^2$ ,

was directed at the sample through the quartz window for 400 seconds. In the first case, dry nitrogen gas was flowed through Drierite pellets and into the curing chamber. In the second case, the nitrogen gas was bubbled into saturated solutions of  $\text{NaSO}_4$ , resulting in the chamber equilibrating to 93% relative humidity at room temperature.

Following photocuring, the specimens were stored in a drawer at

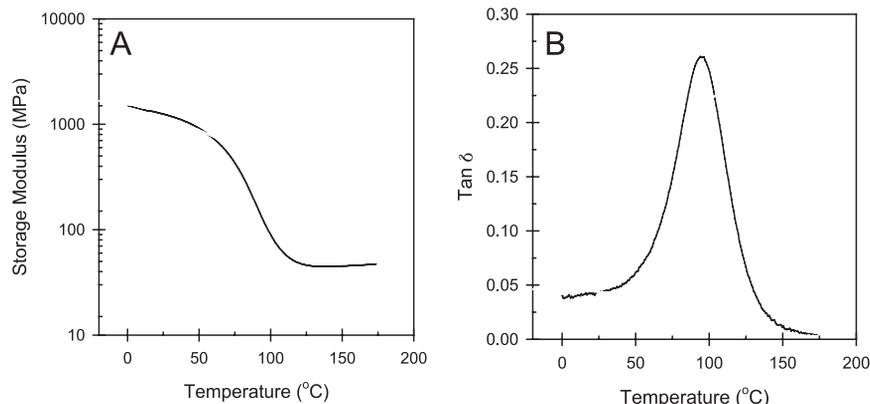
room temperature for two weeks and subsequently heated in a convection oven at  $125^\circ\text{C}$  for one hour and then  $175^\circ\text{C}$  for one hour; allowed to cool to room temperature; and removed from the mold for analysis. This annealing procedure was necessary to prevent continued epoxide reaction during dynamic mechanical analysis (DMA). The  $T_g$  of the polymer specimens was determined via DMA. The specimens were cut into  $0.3 \times 6 \times 15 \text{ mm}$  sections and fixed in a film-tension clamp. The temperature was ramped from  $-25$  to  $200^\circ\text{C}$  while oscillating the strain from 0 to 0.05% at a frequency of 1 Hz. The  $T_g$  was taken as the maximum of the tan delta profile.

Microsurface analysis was carried out using AFM. The elastic modulus of an AFM tip was calibrated by deflecting it against a clean glass slide. The polymer specimen was then imaged under coarse resolution conditions in order to find a flat, defect-free region. The defect-free region was indented by the cantilever 10 times per point, for a total of three points. The force applied to the sample was uniquely set for each

## FIGURE 2

Storage modulus (A) and tan delta (B) profiles of a photocured and annealed silicone epoxy formulation

The resin was cured under dry conditions, though humid conditions resulted in statistically similar profiles.



point (12.5, 10.0 and 8.5  $\mu\text{N}$ ). A high resolution image was then obtained of the indented area. The image was used to determine the penetration depth for each point.

## Results and Discussion

The effects of CTAs, including organic alcohols and water, in epoxy resins have been studied.<sup>8</sup> In general, increased concentration of CTA leads to increased conversion and maximum rate of polymerization with decreases in crosslink density and  $T_g$ .

The polymers prepared from epoxy-silicone monomer formulations are characterized as clear, colorless, highly crosslinked, hard and high  $T_g$  materials.<sup>9</sup> The tan delta maximum was approximately equal to  $\sim 90^\circ\text{C}$  and the approximate crosslink density, as measured from the rubbery modulus plateau at  $150^\circ\text{C}$ , was  $4.4 \times 10^3 \text{ mol/m}^3$  (see Figure 2).<sup>10, 11</sup> It can be expected that significant changes in the degree of cure and crosslink density of the material would be required in order for it to behave as a rubber at room temperature, as opposed to the glass-

like behavior it exhibits at full cure. These changes may be induced by the presence of humidity.

Water acting as a CTA decreases the crosslink density and  $T_g$  of a polymer, relative to the same polymer prepared under dry conditions.<sup>6</sup> The low solubility of water in epoxy resins, as well as the high viscosity and rapid photocuring of epoxy resins, limits the effects of high humidity to the surface and near-surface region. Using AFM, the relative surface hardness of cured epoxy resins was determined for specimens cured under dry and humid conditions, respectively, via indentation experiments (see Figure 3).

In both the dry-cured and humid-cured materials, indentations formed from 12.5 and 10.0  $\mu\text{N}$  forces produced similar penetration depths for each sample; while the indentation resulting from the 8.5  $\mu\text{N}$  force was two to three times more shallow than those from the two higher forces. However, the surfaces of the humid-cured material were sufficiently softened such that the permanent indentation depth was approximately double that of the

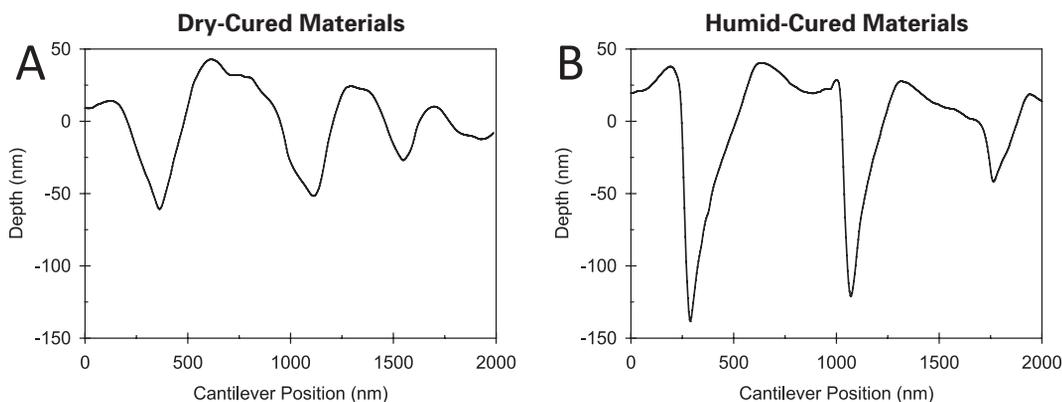
dry-cured material indentations. The increased indentation depth suggests that the humid-cured polymer surface was much softer relative to the dry-cured material. The available water reduced the crosslink density of the material at the surface via chain-transfer reactions, which resulted in a softer surface.

Another qualitative relationship to surface hardness is found in the shape of the force curves obtained during the indentation procedure.<sup>12</sup> Similar to stress-strain profiles, steep curves indicate a high modulus (hard surface) and shallow curves indicate a low modulus (soft surface). The force curves in Figure 4 display a distinct difference between the surface modulus of the humid-cured and dry-cured materials, despite the bulk properties of the polymer specimens being similar. The surface is affected by humidity because the water vapor is initially sorbed on the resin surface. The water may then diffuse into the depths of the resin but much more slowly due to the high viscosity of epoxy resins. Therefore, the highest

## FIGURE 3

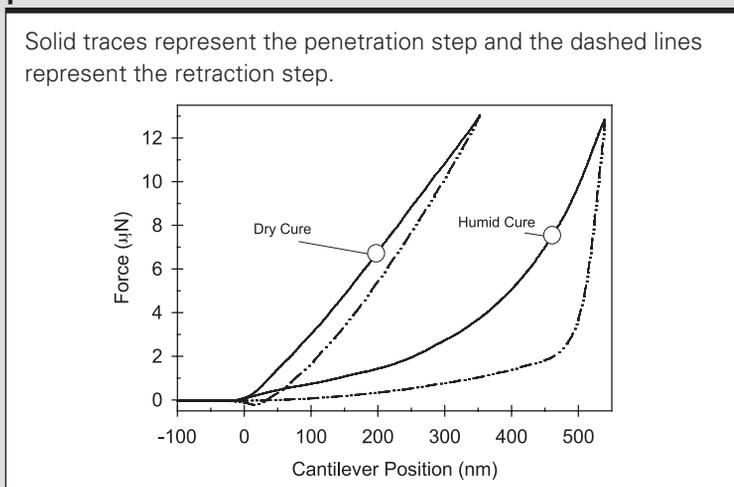
### Indentation and surface imaging of crosslinked epoxy silicone materials

Cross sections of the polymer specimens after indentation procedure were acquired. Dry-cured materials are represented in A and humid-cured materials are represented in B. Indentations were obtained by applying 12.5, 10.0 and 8.5  $\mu\text{N}$  from left to right.



## FIGURE 4

### Force curves obtained during the indentation procedure via AFM



concentration of water is at the surface; and the greatest impact water has on physical properties is observed at the surface.

### Conclusions

The effects of humidity on the bulk polymer properties of crosslinked materials based on photocured epoxy silicone monomers were negligible. AFM was used to determine qualitatively the surface hardness of the polymers when cured under dry and humid atmospheres. The apparent surface modulus and, therefore, hardness were impacted negatively when cured in a humid atmosphere. The decrease in properties (namely,  $T_g$  and crosslink density) due to humidity is explained by the AM mechanism, whereby water at the air-formulation interface acts as a CTA and reduces the crosslink density in the surface layer of the cured material relative to polymers cured under dry conditions. Further work is needed to characterize fully this impact of humidity on surface properties of cationically cured epoxy resins, including quantifying the depth

of polymer affected and the property gradients across that depth.

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