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ABSTRACT

The effect of network changes on the surface and interface properties of amine-cured epoxy has been investigated. Samples of different crosslinked epoxies are prepared by mixing stoichiometrically pure diglycidyl ether of bisphenol A (n=0.03) with different ratios of 1,3-bis(aminomethyl)cyclohexane (terafunctional amine) and cyclohexylmethylamine (difunctional amine). All samples are cured in CO_2-free air. Both the film surface in contact with air and that in contact with the silicon substrate (the interface) are analyzed using atomic force microscopy (AFM) and nanoindentation. Small angle neutron scattering (SANS), attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, and contact angle measurements, are used to assist in the interpretation of AFM results. Substantial morphological and mechanical differences are observed between the surface and the interface for different crosslinked epoxies. The findings have strong implications on the wettablity, adhesion, and durability of amine-cured epoxies.

INTRODUCTION

Crosslinking is an important process in the film formation of coatings and the network structure of the coating is usually related to its application [1]. Changes in network structure invariably cause changes in the chemical, physical, and mechanical properties of a coating. Such changes can occur at surfaces and interfaces. Because surface and interface properties control the wettability, adhesion, and durability of coatings, the study of network effects on these properties is important for improving coating performance. However, little work has been reported on this subject. In this research, the effects of crosslink density on the chemical, mechanical and morphological properties of both surfaces and interfaces of epoxy coatings are investigated. The properties are characterized using AFM, nanoindentation, SANS, ATR-FTIR spectroscopy and contact angle measurements.

EXPERIEMNTAL*

Materials and specimen preparation

Highly pure diglycidyl ether of bisphenol A with weight per epoxy equivalent of 172 g/eq. was used. The curing agents used were mixtures of 1,3-bis(aminomethyl)-cyclohexane (BAC) and cyclohexylmethylamine (CMA). Samples of four different crosslinked epoxies were

prepared with stoichiometric blends of DGEBA with appropriate amine mixtures. The corresponding mole ratios of BAC to CMA for epoxy samples of E1000, E7525, E5050, and E2575 are listed in Table 1. For dynamic mechanical analysis, freestanding films of approximately 150 μm in thickness were made by molding the resins between two Mylar®-covered glass plates. For AFM and other measurements, the surface and interface samples were obtained from coated films applied on silicon substrates. These films were about 300 μm in thickness and were prepared in a CO_2- and H_2O-free glove box by a draw-down technique. All samples were cured at room temperature for 48 h, followed by post-curing at 130 °C for 2 h. The coated films were removed from the silicon substrates by cooling in liquid nitrogen, followed by peeling with tweezers. The face in contact with the silicon substrate is termed the interface, while the one exposed to air is the surface.

Dynamic mechanical analysis (DMA)

DMA was performed with a Rheometrics Solids Analyzer RSA II in the tensile mode at a frequency of 10 Hz. Temperature increment was 5 °C from 25 °C to 70 °C and 2 °C from 70 °C to 170 °C. Films having dimensions of 10 mm by 30 mm and thickness of about 0.15 mm were used.

Atomic force microscopy (AFM)

A Dimension 3100 Scanning Probe Microscope from Digital Instruments was operated in tapping mode to characterize the surface and interface morphology of epoxies with different crosslink densities. Commercial silicon microcantilever probes were used. Topographic and phase images were obtained simultaneously using a resonance frequency of approximately 300 kHz for the probe oscillation and a free-oscillation amplitude of 62 nm ± 2 nm. The set-point ratio ranged from 0.60 to 0.80. AFM was also used for nanoindentation tests using a diamond tip mounted on a stainless steel cantilever with the spring constant of (120 ± 10) N/m. The cantilever sensitivity was determined through measurements with a sapphire sample before and after the indentation tests. Three load levels were used to indent all the samples. For each load level, five force curves were obtained for epoxy surface and interface samples and ten for sapphire.

SANS measurements

SANS experiments over the q range from 0.009 Å^{-1} to 0.138 Å^{-1} were carried out using the 8-m SANS instrument at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR). The incident neutron wavelength was $\lambda = 8$ Å with a wavelength resolution of $\Delta\lambda/\lambda = 0.15$. The scattered intensity was corrected for background and parasitic scattering, placed on an absolute level using a calibrated secondary standard and circularly averaged to yield the scattered intensity, I(q), as a function of the wave vector, q, where q = $(4\pi/\lambda)\sin(\theta/2)$ (θ is the scattering angle).

ATR-FTIR and contact angle measurement

Unless otherwise stated, the same experiment procedures were carried out as those described in Reference 2.

RESULTS AND DISCUSSION

Crosslink density

The networks were characterized in terms of the average molecular mass between crosslinks, Mc. The Mc values calculated from the dynamical mechanical storage moduli assuming the validity of the rubber elasticity theory [3] as

$$Mc = 3\rho RT/E_r' \qquad (1)$$

where E_r' is the storage modulus value in rubbery region, T is temperature corresponding to E', ρ is the network density at the test temperature, and R is the gas constant. Equation 1 assumes the network is ideal and all chains are elastically effective. A higher value of Mc corresponds to a less crosslinked network. As can be seen in Table 1, when the BAC/CMA ratio is changed from 100/0 to 25/75, a decreasing trend is observed for the crosslink density and glass transition temperature (Tg).

Table 1. Crosslink densities (ν_e) and some dynamic properties obtained from DMA for epoxies with different BAC/CMA ratios

Sample	E1000	E7525	E5050	E2575
BAC/CMA (mol/mol)	100/0	75/25	50/50	25/75
Tg (°C)	123 ± 1	111 ± 1	98 ± 1	84 ± 1
Tan(δ), max	0.49 ± 0.01	0.62 ± 0.04	0.94 ± 0.03	1.58 ± 0.09
$E_r' \times 10^7$ (Pa)	3.4 ± 0.1	1.9 ± 0.3	1.3 ± 0.3	0.6 ± 0.1
Mc (g/mol)	364 ± 16	650 ± 106	952 ± 211	1950 ± 188

Surface and interface properties

Morphologies of epoxy surface and interface samples were studied with AFM. In Figure 1, topographic and phase images of both surface (1a, 2a) and interface (1b, 2b) for two different crosslinked epoxies are shown. For both E1000 and E2575, the height and phase images of the interface exhibit greater contrast as compared to those of the surface, indicating that there are morphological differences between the surface and the interface. First, the interface is considerably rougher than the surface. Second, well-defined heterogeneous structures are observed for the interface but not for the surfaces. It should be mentioned that the silicon surface is essentially smooth and featureless as observed by AFM imaging. A two-phase microstructure, consisting of a bright matrix and relatively dark interstitial regions are observed in the interface phase images. This kind of heterogeneous structure is similar to those reported for other thermoset resins [2, 4]. Recently, such morphological differences between the surface and interface have also been observed for acrylic melamine and other epoxies in our laboratory [5].
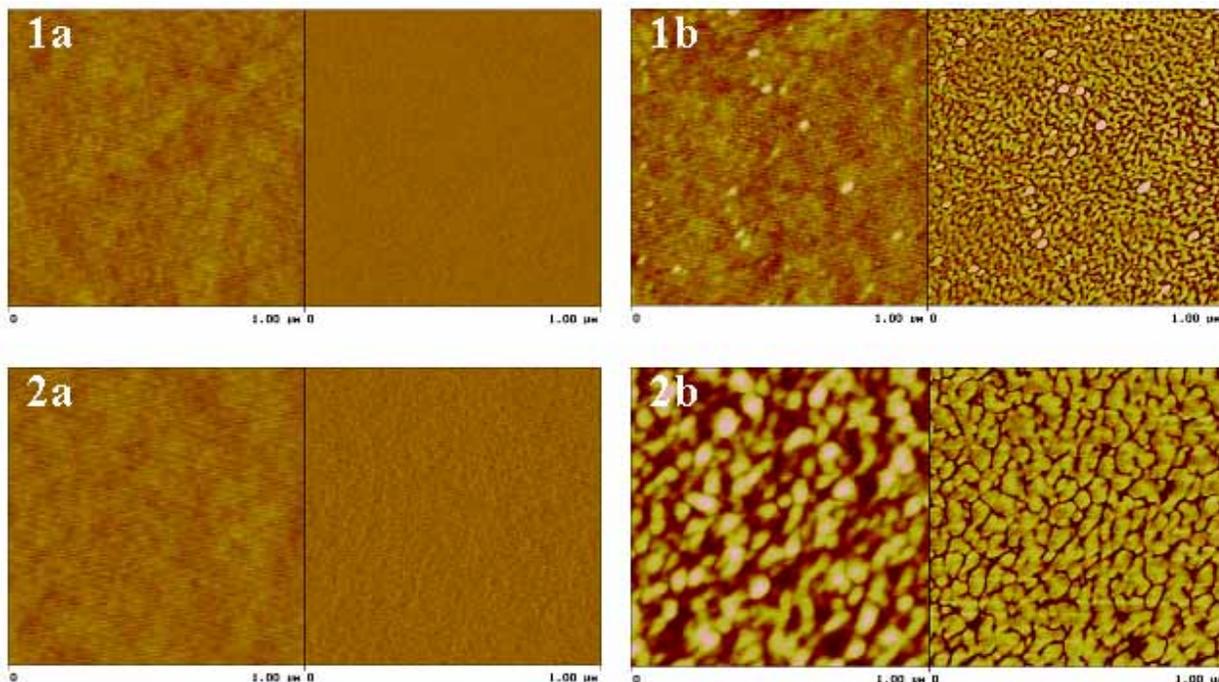
Figure 1. AFM height image (left) and phase image (right) of epoxy coatings applied on silicon substrates: (1a) E1000, surface; (1b) E1000, interface; (2a) E2575, surface; (2b) E2575, interface. Scan size is 1 μm × 1 μm. Contrast variations from white to black are 10 nm for the height images and 90° for the phase images.

Table 2. Contact angles (θ)**,** surface free energy (γ) and polarity (X^p) of surface and interface of different crosslinked epoxy coatings

Epoxy		θ_{H2O} (°)	θ_{CH2I2} (°)	γ (mJ/m^2)	X^p
E1000	S	76.0 ± 0.6	37.5 ± 0.6	42.6 ± 0.8	0.13 ± 0.01
	I	73.0 ± 1.8	37.3 ± 1.0	43.5 ± 0.7	0.16 ± 0.02
E7525	S	76.8 ± 2.1	36.0 ± 1.3	43.0 ± 0.8	0.13 ± 0.02
	I	73.5 ± 1.2	43.3 ± 1.2	41.3 ± 0.6	0.19 ± 0.02
E5050	S	77.4 ± 1.5	37.3 ± 2.7	42.3 ± 1.1	0.12 ± 0.02
	I	74.6 ± 0.6	51.8 ± 1.8	37.9 ± 0.7	0.23 ± 0.02
E1000	S	72.9 ± 4.4	38.3 ± 3.7	43.5 ± 2.1	0.18 ± 0.06
	I	69	37	44.9	0.2

S: surface; I: interface. [a]Sample was too small to perform replicate measurements.

As can be seen in Figure 1, the sizes of the bright nodules in the phase image of the interface are larger for the low crosslinked E2575 compared to the high crosslinked E1000. This observation   implies that the crosslink density may have an influence on the microstructure of the interface, though no obvious effects were observed on the surface.

The differences between the surface and the interface of the epoxy coatings are probably due to surface enrichment and interface interaction and confinement. The polarity results obtained from contact angle measurements (Table 2) have provided evidence for such a hypothesis. For each epoxy, the polarity of the interface is higher than that of the surface, indicating that the air

surface of coatings could be covered with a thin layer of lower surface-free energy material. Additionally, the surface polarity appears independent of network variation while the interface polarity increases with decreasing crosslinking.

Microstructure study using SANS

Figures 2a and 2b represent the SANS data for epoxy bulk samples of E1000 and E5050 after soaking in deuterated acetone. For Dry bulk samples, only incoherent scattering background is observed due to no neutron contrast in both E1000 and E5050. After soaking in d-acetone, the solvent diffused into and swelled the voids and/or the low crosslinked regions and enhanced the neutron contrast of the heterogeneous regions in the network. An upturn is seen in the relatively low q region (ca. q <0.03 Å) from E1000 in Figure 2a suggests the existence of a well-ordered microdomain. The value of the peak position can be related to an average predominant domain size, d, as d=2π/q, The domain size estimated from the predicted peak position (see insert in Figure 2a) is approximately 50nm, which is well consistent with the nodules size obtained from the AFM. The time dependence of the scattering profiles indicates the peak tends to shift to a lower q position with a longer soaking time. Because the lower q will
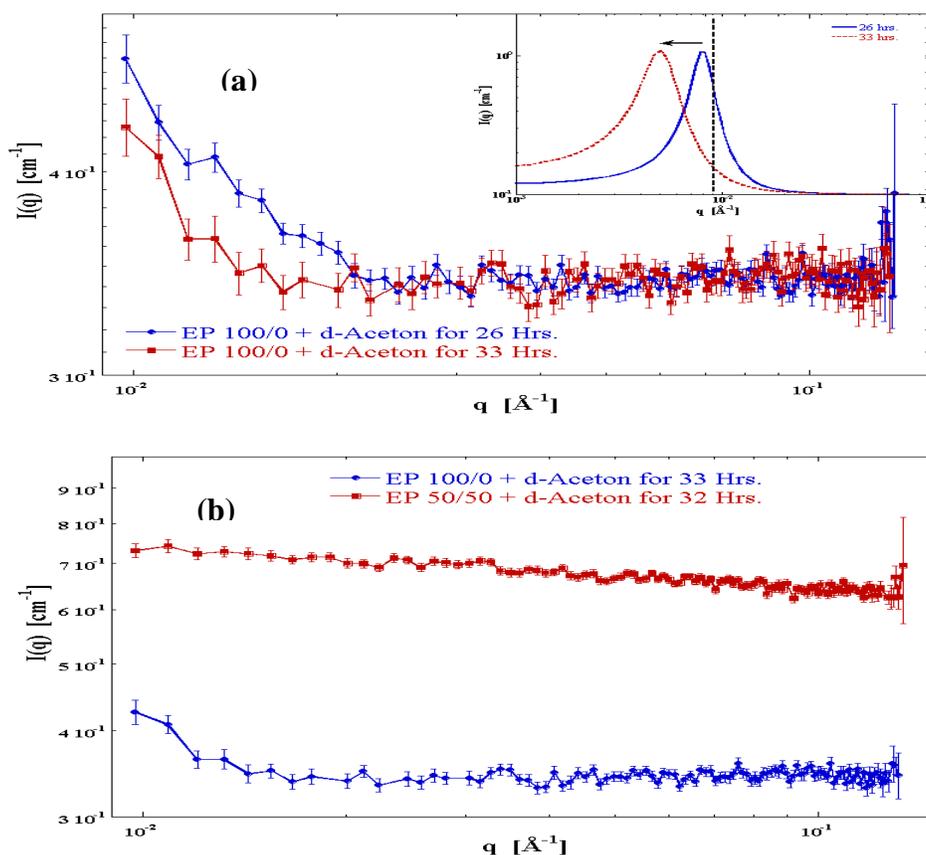

Figure 2. Small angle neutron scattering profile of (a) E1000 bulk sample as a function of soaking time in deuterated acetone and (b) E1000 and E5050 bulk samples soaked in deuterated acetone for about 32 h.

result in a larger domain size, this observation is consistent with the swelling of the network with the time. However, no peak was observed in the scattering profile for E5050 after soaking 32 h in Figure 2b, it implies a larger sized domain distributed in the network, which corresponds to a very low q value. The above SANS data from the bulk samples are consistent with the heterogeneous microstructures observed from the interface samples using the AFM.

Further studies on this topic are being conducted with nanoindentation and ATR-FTIR. The results will be presented.

SUMMARY

Effects of network changes on the surface and interface properties of amine-cured epoxy have been investigated by AFM, nanoindentation, ATR-FTIR and contact angle measurements. Results have shown a strong influence of crosslink density on the surface and interface properties of epoxies. Substantial morphological and chemical differences are also observed between the coating surface and interface. The SANS data are confirmed the existence of a heterogeneous microstructure for epoxy network.

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