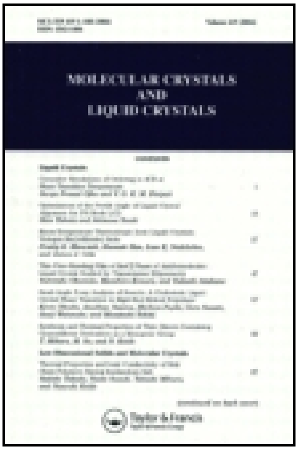

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Jinshu Yu [a][b], D. Zhou [a], W. Cai [a], S.-H. Park [b], T. J. Shin [b], W. Oh [b], S. W. Lee [b] & M. Ree [b]

[a] Dept. of Applied Chemistry, Harbin Institute of Technology, Harbin, Heilongjiang Province, 150001, People's Republic of China

[b] Dept. of Chemistry, BK-21 Functional Polymer Thin Film Group, Center for Integrated Molecular Systems, Polymer Research Institute, Pohang University of Science & Technology, San 31, Hyoja-dong, Pohang, 790-784, South Korea

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FT-IR Spectroscopic and Residual Stress Studies on Curing of Epoxy Resin Waterborne

JINSHU YU[1,2], D. ZHOU[1]*, W. CAI[1], S.-H. PARK[2], T.J. SHIN[2], W. OH[2], S.W. LEE[2] and M. REE[2]*

[1] *Dept. of Applied Chemistry, Harbin Institute of Technology,*
Harbin, Heilongjiang Province 150001, People's Republic of China and
[2] *Dept. of Chemistry, BK-21 Functional Polymer Thin Film Group,*
Center for Integrated Molecular Systems, and Polymer Research Institute,
Pohang University of Science & Technology, San 31, Hyoja-dong,
Pohang 790-784 South Korea

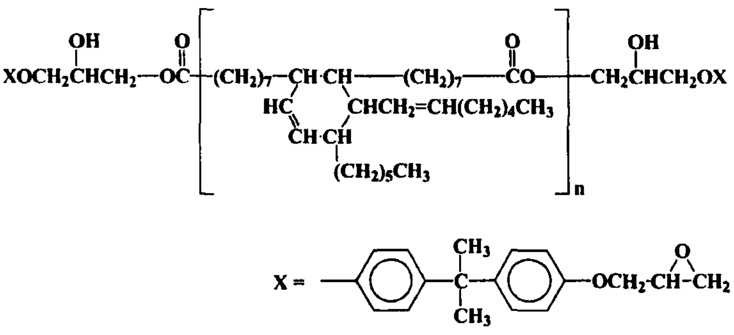
For an epoxy resin waterborne system mixed with a curing agent, butanone oxime blocked 4,4′-methylenediphenyldiisocyanate, curing-reaction-induced residual stress generation was in-situ measured in thin films adhered on silicon substrates. This measurement was carried out with varying composition as well as curing temperature, time and step. The residual stress was dependent upon the composition, the deblocking process of the curing agent and the curing condition. In addition, cured films were examined by FT-IR spectroscopy, differential scanning calorimetry, and thermogravimetric analysis.

Keywords: epoxy resin waterborne; blocked isocyanate; residual stress; deblocking reaction; curing reaction; network formation

INTRODUCTION

Epoxy resins are widely used as adhesive, laminating, and coating material owing to their excellent mechanical and thermal properties[1-2]. Epoxy resins are known to have a relatively low curing shrinkage[3-6].

However, this low shrinkage is still considered to generate residual stress which is sometimes high enough to cause cracks and to deteriorate weatherability and mechanical and electronic properties[6-7]. In the present work, the residual stress behavior of an epoxy resin waterborne in film was investigated with varying composition and curing condition.



A

FIGURE 1. Chemical structure of a modified epoxy resin waterborne (A) used in this study.

EXPERIMENTAL

A series of epoxy resin/curing agent solutions were prepared by mixing of epoxy resin A (4,000 $<M_n>$ and 17,400 $<M_w>$)[8] and butanoneoxime-blocked 4,4 ' -methylenediphenyldiisocyanate (b-MDI)[8-9] in various compositions. The mixtures were spin-cast on silicon wafers (76 mm diameter and ca. 380 μm thick) which were primed with 0.1% γ-aminopropyltriethoxysilane in water and soft-baked 60°C for 1 hr. For these soft-baked films, residual stress was in-situ measured using a residual stress analyzer made in our laboratory over various curing protocols[10-12]. Here, curvatures of the silicon wafers used were determined before use. In addition, FT-IR spectroscopic, thermogravimetric (TGA), and differential scanning calorimetric (DSC) measurements were carried out.

RESULTS AND DISCUSSION

Curing agent/epoxy resin mixture in solution was made with various compositions over 1/10 - 15/10 (= b-MDI/A epoxy resin, weight ratio). The thermal deblocking reaction of b-MDI curing agent occurs around 118°C so that all the soft-baked films on silicon substrates were cured as follows. The film sample was heated to 175°C with a rate of 2.0 K/min, soaked for 30 min at the temperature, and finally cooled back to room temperature with a rate of 2.0 K/min. This curing process was done under N_2 flow. During the curing process, residual stress was in-situ monitored. For the compositions of ≤ 3/10, no residual stress was generated in the film. This is resulted from a relatively high mobility in the film which has a low degree of crosslinks formed under the presence of relatively small amount of the curing agent. In contrast, for the mixtures of ≥ 4/10 composition, residual stress started to build up during the cooling process after cure (see a typical stress-temperature profile in Figure 2). Level of the generated residual stress was increased with increasing the loading of curing agent over the composition range of 4/10 - 8/10 and then turned to decrease with further increasing curing agent loading. Here, the highest residual stress was 8.0 MPa at room temperature. For the residual stress-temperature profile measured during the cooling process, glass transition temperature (T_g) of the resultant epoxy resin film was estimated. T_g raised to 93°C, depending on the loading of curing agent. Its variation with composition exhibited a similar trend as that of the stress variation with composition. The T_g and

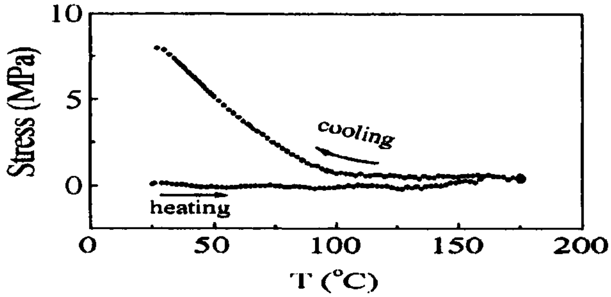


FIGURE 2. Residual stress-temperature profile measured *in-situ* during curing and subsequent cooling process: A 10.0 μm thick film of 8/10 (= b-MDI/A, weight ratio) composition was used.

stress increment are caused by the immobilization of molecules and its enhancement via the network structure formation of epoxy resin with the curing agent loaded.

In addition to the composition, the residual stress generation in the film was further dependent on cure temperature. For the 8/10 mixture film cured over 125-300°C, stress built up in a range of 0-19.2 MPa. Stress began to build up for the film cured at ≥150°C and reached to a maximum value, 19.2 MPa for one cured at 200°C, then turning to decline for films cured at >200°C. For the 4/10 composition, residual stress started to generate at >150°C and increased with increasing cure temperature, showing a maximum value, 5.9 MPa at 250°C. Overall, the cure temperature causing a maximum stress value is shifted to low temperature region as the loading of curing agent increases.

The cured epoxy resin films were further examined by FT-IR spectroscopy, DSC and TGA. Figure 3 shows typical FT-IR spectra of a film of curing agent/epoxy resin mixture before and after curing. The dried film reveals vibrational peaks of –O-H (3420, 1029, 1016 cm^{-1}) and -epoxy ring (1121, 916 cm^{-1}) from the A component and also of

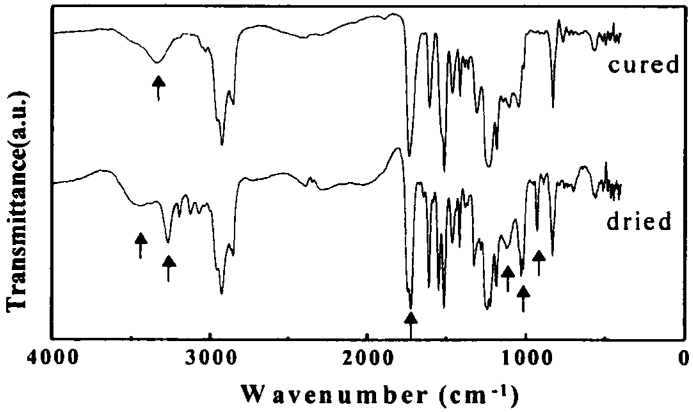


FIGURE 3. FT-IR spectra of films of 4/10 (= b-MDI/A, weight ratio) composition before and after cured at 175°C for 30 min.

>N-H (3264 cm^{-1}), -N=C< (927 cm^{-1}), and >C=O (1722 cm^{-1}) from the b-MDI curing agent component. These characteristic peaks appeared with a highly reduced intensity or disappeared for the cured film. Instead, the cured film newly shows vibrational characteristics of >N-H (4322 cm^{-1}) and >C=O (1735 cm^{-1}), indicative of urethane linkages. These results indicate that the epoxy adduct A and curing agent components react together through the curing process at 175°C. The curing reaction was further confirmed by DSC analysis. As mentioned earlier, the deblocking reaction of b-MDI curing agent was determined to occur over 107-125°C, and the deblocked butanone oxime started to evaporate at >130°C. And its reaction with the epoxy adduct occurred over the range of 107-145°C. In addition, the thermal stability of cured epoxy films were examined by TGA: the thermal degradation started at 251°C.

CONCLUSION

The curing of epoxy adduct **A** with b-MDI was studied by FT-IR and DSC. The curing reaction took place mainly over the range of 107-125°C at which the deblocking reaction occurred. Residual stress generated by the curing reaction was measured dynamically and understood with considering of composition and curing condition. The residual stress in the film was caused mainly by the immobilization of and T_g increase of epoxy resin molecules via network formation.

Acknowledgements

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