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EVOLUTION OF TRANSMISSION LOSS AND STRUCTURE IN EPOXY CURING

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1. INTRODUCTION

Communications, data storage or computation by manipulating the optical signals have the strong advantages over the traditional electronic circuits in regard to the data handling speed and capacity. Effective manipulation of the optical signals, however, requires materials of large nonlinear coefficients and of fast response time. Polymeric materials are one of the promising materials to meet the requirements for nonlinear optical (NLO) materials. The polymers also offer superior environmental stability, processibilty and the ability to tailor structure through the chemical synthesis. The simplest means of utilizing the polymers for second order NLO materials are by dissolving the organic chromophores or by incorporating the chromophores as the side units to the amorphous polymers such as PMMA, polycarbonate and polystyrene.. In order to minimize the relaxation of the poled chromophores, the amorphous polymers of high glass transition temperatures and the cross-linked epoxies or polyurethanes are used for the host matrices of NLO materials. In this case the optical transparency of the matrix polymer is one of the key parameters the material should possess. Especially in the cross-linking polymers the nonuniform distribution of the cross-links severely reduces the optical transparency, thus limit the use of cross-linking polymer matrix.

In this work we tried to investigate the transmission loss and the changes during the curing process of epoxy/EDA system. A UV-VIS spectrometer was utilized to monitor the structural changes and the optical transmittance changes simultaneously during the curing process.

2. RESULTS AND DISCUSSION

Epoxy used in this study was diglycidly ether bisphenol A (DGEBPA), molecular weight of 350 gmol-1 and ethylene diamine (EDA) for the curing agent. Epoxy was used without filtering but the EDA was purified through the distillation. Optical loss and the structural changes during the curing process were monitored through the UV-VIS spectrometer. To investigate the transmission loss due to the scattering loss originating from the structural inhomogeneity in the cured epoxy, the spectra were analyzed at the wavelength of 600-700 nm where the vibrational absorption can be avoided. The curing process, on the other hand, was monitored at the wavelength of 700 -1100 nm where the characteristic absorption peak of DGEBPA and EDA appears. Optical loss (dB/cm) of the specimens at each wavelength was then determined by the relation of = -10/L log I/Io, where L is the thickness of the sample and I/Io is transmittance measured at each wavelength.

UV-Vis spectra of the epoxy, epoxy/EDA and the cured Epoxy at 100 °C are compared in Figure 1. The spectrum of the pure epoxy shows flat absorption up to the wavelength of 680 nm and several absorption peaks thereafter. The flat portion of the absorption spectrum at 500-700 nm is composed of the absorption tail of the electronic transition and the Rayleigh scattering from the structural inhomogeneities. Several peaks at the near IR region arise from the vibrational absorption. The absorption peak at 1047 nm is, probably from the amine in the EDA compound. The epoxy /EDA mixture before curing shows extremely large transmission loss. The large loss is apparently due to the inhomogeneous mixing of the two components, resulting in the nonuniform structure and the high scattering loss. The inhomogeneity of the mixture appears to be lowered during the curing process. The transmission losses at 600 nm measured during the cure of the mixture at 1, 3, 5, 7 and 10 °C/min. are plotted against the temperatures in Figure 2. In the curves of 1 and 3 C/min, a huge initial drop in the transmission loss can be noted while other two curves of higher heating rate (5, 7 and 10 C/min) maintain the initial transmission loss before the curing begins. The slow heating rate apparently allowed the mixture homogeneous before the curing initiation, eventually leading to the cured epoxy with better structural uniformity. The epoxy cured at the higher heating rate of 5, 7 and 10 C/min show larger increment in the transmission loss during the curing process, resulting in a very high transmission loss. But the differences between the two curves of heating rate 5, 7 and 10 C/min are only marginal. The results manifest that the initial homogeneity of the mixture could be the main factor to control the structural uniformity and the optical transparency of the cured epoxy sample. In the curves of 5, 7 and 10 C/min a loss peak appear at 80, 90 and 100 C, respectively. These temperatures correspond to the temperatures of maximum curing in the DSC thermogram. Local thermal fluctuation due to the exothermic reaction probably cause such large increment of transmission loss. The changes of the absorption peak at 1047 nm, corresponding to the overtone of the amine absorption., represent the curing reaction. Therefore this peak was also utilized to monitor the curing process. Transmission loss changes of completely cured samples were measured at different temperatures under cooling and heating. The loss monotonically decreases as the temperature increases but the loss begins to increase near 105 C, which is believed to be the glass transition temperature as confirmed with the DSC curve. The changes in the transmission loss appears to be reversible and show the identical behavior under cooling. It is, however, unexpected to observe the decrease of the transmission loss with temperature below the glass transition temperature. The increase of thermal fluctuation is expected with the temperature increase and simultaneously the increase of scattering loss. It can be speculated that the loss due to the electronic transition might out run the small increment of thermal fluctuation effect.

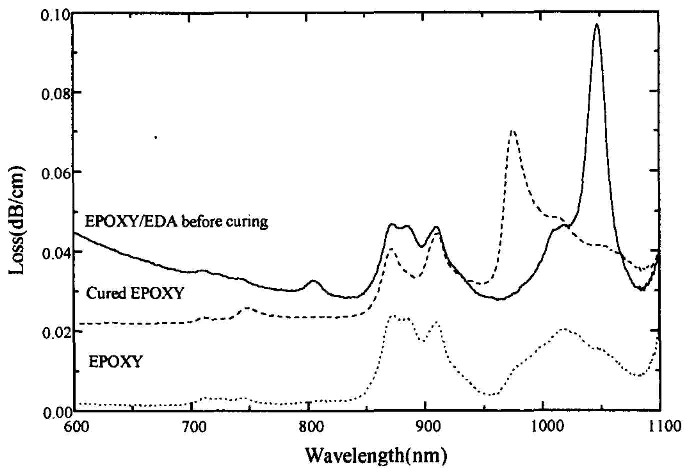

Figure 1. UV-Vis spectra of epoxy and epoxy/EDA before and after curing.

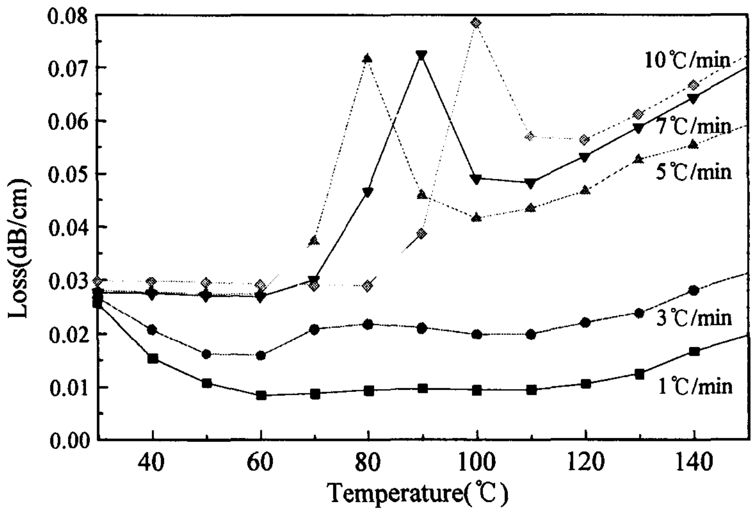

Figure 2. Transmission loss changes during the curing process at 600nm.