

MORPHOLOGICAL AND PHASE BEHAVIOR STUDIES OF UNIQUELY DERIVED SEMI-IPNS OF EPOXY AND POLYIMIDE

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Abstract: Interpenetrating networks (IPNs) of polyimide (PI) and epoxy were made by reaction of epoxy (DGEBA) with a polyamic acid (PAA). In addition, epoxy cured with monomeric hardeners (DDE and DDS) along with PAA were made to see changes in the morphology and glass transitions brought about the cure of the epoxy with the monomeric hardener. Due to "molecular interlock" of the individual polyimide molecules that was brought about by the PAA-epoxy reaction, systems cured with only PAA did not phase separate and only had one T_g . By dynamic mechanical analysis (DMA), it was confirmed that systems containing DDE or DDS along with PAA had two glass transitions, however for systems cured with only PAA, this was seen after long periods of postcure. PAA cured epoxy systems showed phase miscibility at all compositions.

Introduction

The concept of forming alloys of compatible polymers that have high moduli and glass transition values is currently an area of great interest. The formation of interpenetrating networks (IPN) of these molecules will allow for the fabrication of materials having unusual properties and morphologies. IPNs of polyimide (PI) and an epoxy resin (diglycidyl ether of bisphenol A) have been fabricated and characterized. The diepoxy chosen has the ability to react with the PAA, thus providing a unique hydrogen bond environment that inhibits molecular demixing. Employing a polyamic acid (PAA) that can both initiate epoxy cure of the epoxy and subsequently cyclize to become a high molecular weight PI is novel, for cure of an epoxy with a reactive polymer has not been addressed to any great extent(1). Since the PAA contains carboxyls, amides and amines as reactive groups, the implications on material morphology or glass transition behavior are not clear.

Due to unfavorable kinetics, linear polymers added in small percentages to epoxy have very little direct bonding to the epoxy and phase separation occurs due to the increase in molecular weight during the epoxy cure reaction.(2). We studied the morphology, phase stability and glass transitions of DGEBA cured with diaminodiphenylether (DDE) or diaminodiphenylsulphone (DDS) in conjunction with the polyamic acid.

Experimental procedure

Polyamic acid, as a 10 wt.% DMAc solution, was prepared by reacting stoichiometric

amounts of DDE and pyromellitic acid. To this was added, a DMAc epoxy solution (EPON 828, Shima Bocki Co.) with or without hardener (DDE or DDS) and mechanically stirred until the solutions became homogeneous. The systems are referred to as ratios, X/Y/Z, with: X = wt% EPON 828, Y = wt% PAA, Z = wt % DDE or DDS. The solutions were doctor bladed onto aluminum foil and cured for 2 hrs 125°C, 2 hrs 250°C, (noted: standard cure) to form films of varying thicknesses. As a postcure heat treatment, the films were subjected to 250°C for 96 hours (noted: post cured). Reactants and an example reaction are given in figure 1.

DMA was carried out on a Toyoseiki Rheovibron at 10Hz. The films examined with a scanning electron microscope (SEM) were fractured at -77°C and the fracture surfaces Ar plasma etched and coated with a osmium tetroxide (OsO₄). SEM was carried out with a JEOL SEM in secondary electron mode, using an accelerating voltage of 5kV. Magnification, composition and heat treatment of the samples are given in the figure legends

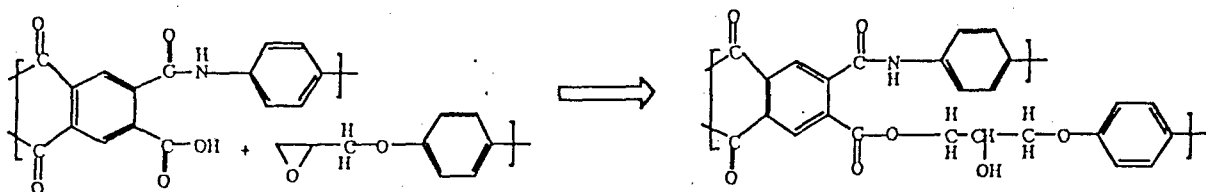


Figure 1. PAA carboxyl - DGEBA epoxide ring reaction

Discussion

Thermal Analysis

DMA

The interaction of the two polymers will have an effect on the glass transitions of one or both of the components because of semi-IPN formation. The amount of interaction, via reaction between the PAA carboxyl groups, amide groups, etc. and the epoxy determined the amount of influence on the T_g relaxation behaviors. Using a fixed curing schedule, variations in T_g are a consequence of (i) the extent of cure resulting from varying the X/Y/Z ratio, (ii) or the network morphology, or (iii) a combination of both of these effects.

In systems of Y, Z > 0 there are two distinct T_g values, for the epoxy and PI, at about 200°C and 375°C (Figure 2).

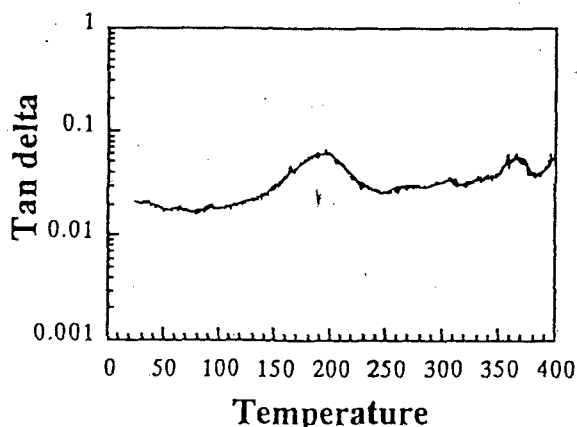


Figure 2. DMA of 50/38/12 (standard cure) showing two T_g s

This indicates a lack of interaction between the epoxy network and the polyimide when $Z > 0$, and the degree of phase segregation between the PAA rich domains and the epoxy. Conversely, when $Z = 0$, the position of the epoxy T_g peak increases slightly with Y due to an increase in the crosslink density resulting from greater amounts of PAA - epoxy interaction.

At $Y = 50, Z = 0$ there is virtually no PI T_g peak due to the large amounts of mechanical molecular interlock of the PAA by the epoxy. At higher temperatures and lower PAA/EPON ratios, there is the appearance of a slight PI T_g peak at approximately 380°C due to molecular detachment from the epoxy network. When $Z = 0$, the epoxy T_g peaks are quite broad due to incompletely crosslinked epoxy in all systems (Figure 3a). Due to molecular interlock, in these systems the PI peak does not appear except at high PI% or post curing times (Figure 3b).

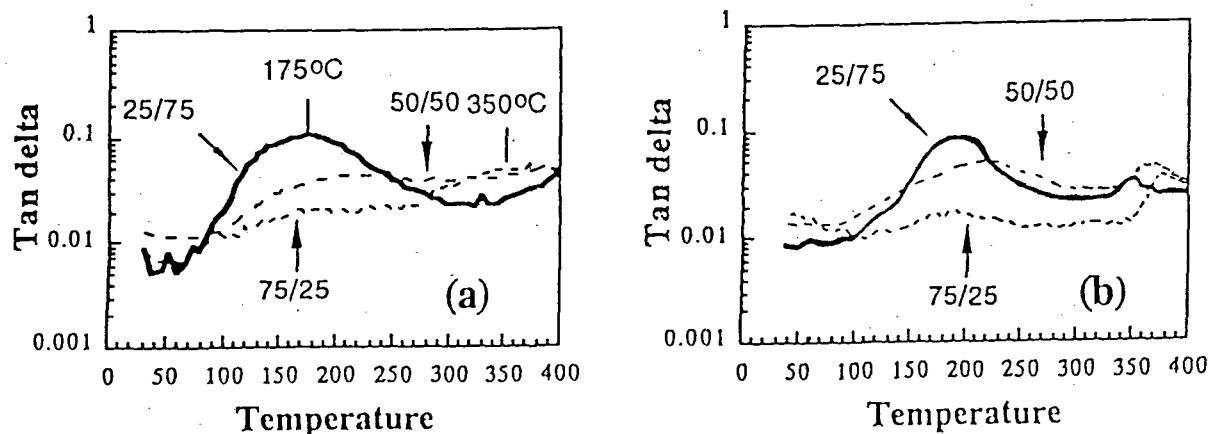


Figure 3. DMA of PAA cured epoxy systems X/Y (a) standard cure (b) post cure

The separation of the PI from the epoxy network due to the closure of the imide ring accounts for these observed phenomena. The lack of a large PI relaxation at 350°C , when $Z = 0$, is caused by restriction of cyclization of PAA resulting in few fully imidized PAA molecules. Thus, the PAA is molecularly "locked" becoming an integral part of the epoxy network, at high X values. The hindered polyimide appears as a small T_g peak.

However, for postcured $Y > 0, Z = 0$ systems, the PI relaxation once again appears at 350°C and the epoxy relaxation at $150\text{--}200^\circ\text{C}$ narrows. This confirms that the PI becomes less attached to the epoxy network but the crosslink density of the epoxy network is increased. However, this is unobservable by SEM due to the inability of the PI in the semi-IPN to diffuse through the surrounding epoxy network to form separate distinct phase.

Morphology

SEM

As seen in many studies of various epoxy systems, the relaxations of the system are dependent on morphology.(3) Since the morphologies of non-stoichiometric systems are similar to stoichiometric systems, we only studied stoichiometric or systems deficient in hardener.

The complex phase behavior in X/Y/Z systems lead us to draw some general conclusions. All $Z > 0$ systems phase separated. This is attributed to the early establishment of the epoxy network and the segregation of the PAA molecules by the epoxy network at low degrees of conversion. However, for $Z = 0$, phase separation did not occur. Phase stability is brought about by immobilization by the large three dimensional epoxy structures that form around the individual PI/PAA molecules. This "molecular interlock" phenomenon accounts for the restriction of the phase separation of the two polymers and the stability of the homogeneous mixture formed.(4)

In $Y, Z > 0$ systems the largest inhomogeneities of epoxy rich and polyimide rich regions formed for larger Z . The comparatively high reaction rates of the monomeric hardening agents versus that of the polyamic acid-epoxy reaction establishes a crosslinked

epoxy phase with very little ring opening occurring due to polyamic acid-epoxy reaction contributions. Reaction rate difference will cause phase separation to occur in the early stages of cure and the morphologies of the systems will be decided at low degrees of conversion.

Finally, even with postcuring there is no change in phase morphology (Figure 4). For $Z=0$ phase separation did not occur due to molecular lock stabilizing the single phase structure formed during the early curing stages. This also accounts for the lack of morphology seen in these systems, since the individual PAA molecules are an intrinsic part of the crosslinked epoxy network and can not diffuse through the network to form a separate phase.

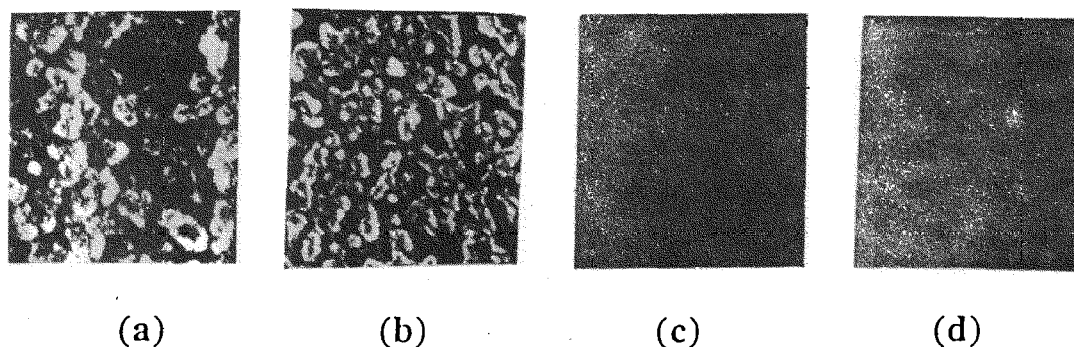


Figure 4. SEM of a) 50/37/13 standard cure b) a, post cured, c) 40/60 standard cure, d) c, post cured (magnification=50,00x, 1cm=200nm)

Conclusions

Because of phase segregation $Y, Z > 0$ systems, there were two T_g peaks. Systems where $Y=0$, those cured exclusively with PAA only one T_g peak appears. The lack of a PI T_g peak when $Z=0$ and short heat treatment times, makes the case for the freezing and interlocking of molecular movement of the polyimide by the epoxy. After long times of post cure at high temperatures, molecular detachment of the PI from the epoxy network upon cyclization occurs and a PI T_g becomes evident. The morphology and the position and breadth of the T_g peak when $Y, Z > 0$ is determined by the amount of DDE or DDS. The early establishment of a three dimensional network in these systems led to phase separation of the components early in the reaction sequence resulting in two distinct T_g peaks for the epoxy network and the PI. In systems cured by only PAA, the mixtures did not phase separate and formed what we term "molecularly interlocked" interpenetrating networks. These systems had only one T_g peak after the standard cure, but displayed two for the polyimide after extended times of post cure. Formation of a semi-IPN, wherein one of the components is a three dimensional network while the other phase forms a molecularly separate linear reinforcement, occurred to a greater extent in the systems cured exclusively with PAA than when monomeric hardeners (DDE, DDS) were present.

References

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