Effect of Stirring on Morphology and Properties in a Catalyst Cured Epoxy System

CHING-SHIUN WU

Institute of Textile Engineering, Feng Chia University, Taichung, Taiwan 40724, Republic of China

SYNOPSIS

This article describes the effect of stirring on epoxy network morphology and physical properties. Several different mechanical stirrer speeds, from 45 rpm to 800 rpm, were employed for the mixing of diglycidyl ether of bisphenol A resin with 2-ethyl-4-methyl imidazole catalytic curing agent. The investigation indicated that the glass transition temperature, room temperature density, low temperature relaxation, tensile mechanical properties in the rubbery state, and nodular morphology are significantly affected by the stirrer speed used. Transmission electron microscopy has revealed that the extent of homogeneity for the dispersion of nodule domain in the low crosslinking matrix improved with increasing stirrer speed. However, an optimum stirrer speed condition is needed for achieving the most homogeneous system. In addition, it is shown that the room temperature tensile mechanical properties are independent of the mixing condition. This independence is ascribed to the fact that the glassy state mechanical properties are closely related to the intermolecular forces rather than to the network structure.

INTRODUCTION

Epoxy resins, with their outstanding characteristics, have been commonly used as the polymeric matrix in high performance composites employed in aerospace industries. In order better to design this very important class of material for engineering applications, a basic understanding of the influence of varying chemical and physical factors on the network structure and properties is required. Amid the extensive literature on the study of structure–property relations of epoxy networks, much of the work in the past two decades has concentrated on the polymerization conditions, such as stoichiometry and cure condition. However, there is very little mention of the effect of mixing efficiency on components. Moreover, we noted that most of the papers reporting on the study of epoxy network systems failed to describe the mixing processes used.

A mixing operation generally involves the introduction of raw materials and minor components such as plasticizers and fillers, which are inserted to improve the properties and appearance of the finished product. A mixing process is thus required to assure the required level of uniformity. This is an important consideration for the diffusion controlled epoxy system. In an epoxy system, the curing reaction can take place only when the reactants approach each other at less than a certain critical distance. This implies that, in the cure of epoxy resin, the curing agent molecules must diffuse to the nearest-neighbor shell of epoxy monomers. Therefore, we believed that inadequate mixing of both viscous and slowly diffused epoxy monomers and curing agents could lead to a locally high content of the curing agent and, hence, locally highly crosslinked particles are formed already before the reactants diffuse away to initiate the next neighbor reaction. Thus, the result of inadequate mixing in epoxy systems could conceivably affect the network structure and, therefore, the physical and mechanical properties of network system. In a previous article, Bell[1] has studied the mixing effectiveness of Epon 828 mixed with diethylene triamine (DETA) and Versamid 140 (polyamide), respectively, and has reported that the increased mixing effectiveness decreased the observed nodule size, raised the glass transition temperature, and increased the ultimate tensile strength in amine-cured resin. However, no T_g increase was observed in polyamide-cured resins, although the tensile strength improved with in-

creased degree of mixing. An extensive study was carried out by Ghaemy et al.[2] on triethylene tetramine (TETA) cured DGEBA resins using dinitrofluorobenzene stained sections and an ultraviolet light microscope. They used four different mixing procedures and they showed that inadequate mixing of epoxy resins with curing agents causes uneven curing; they further suggested that normal hand mixing is inadequate and that high speed mechanical stirring is necessary to produce uniform materials. Therefore, explanations of the controversy of the differences in size and the extent of inhomogeneities observed by previous workers,[3-8] may be traced to the nonoptimum condition of mixing.

In order to investigate the influence of the mixing condition on the glass transition temperature, bulk density, low temperature relaxation, tensile mechanical properties, and morphological structure, a mechanical stirrer with various speeds was employed in this study.

EXPERIMENTAL

Synthesis of Epoxy Networks

Epoxy networks were synthesized based upon diglycidyl ether of bisphenol A (DGEBA), namely DER-332 ($n = 0$), supplied by Dow Chemical Co. The catalytic curing agent was 2-ethyl-4-methyl imidazole (EMI-24), obtained from BASF Wyandotte Corporation. This catalytic curing agent was effective when used in very small concentration. Only 3 phr of this reagent is required to gel epichlorohydrin bisphenol A type epoxy resins at 70°C.[9,10] In general, this catalyst can be used to reduce the cure time in manufacturing and to obtain a distinctive rate and degree of cure as compared with other catalytic curing agents.

The DER-332 and EMI-24 were mechanically mixed by a Teflon paddle stirrer at various speed (rpm) in an oil bath of 60°C for 5 min; the mixture was then cast in specimen molds and placed in a 60°C vacuum oven for 20 min to remove the bubbles. The cure schedule was 4 h in a preheated air oven at a temperature of 70°C, followed by postcuring at 150°C for 2 h, and finally slow cooling to room temperature.

Tensile Properties Test

In order to avoid complications due to the contamination with release agents that were used by many previous workers, and in order to avoid damage to the edges of the specimens as they are machined to the correct shape using a tensile specimen template, a Teflon mold was designed.

The Teflon mold was assembled in two steps: First, a 15 cm × 15 cm × 0.32 cm, highly polished, Teflon spacer with four dumbbell shaped openings and two similar Teflon sheets were pinned together by using five Teflon alignment pins. This assembly was then sealed around the three closed edges by wraping 2 mil thick aluminum foil around it. A 2.5 cm wide piece of aluminum foil was formed to a 45° bevel along the open edge to provide a full length funnel. Finally, the assembled Teflon mold was backed by two glass plates and clamped together using six heavy duty binder clips. The mold is easily assembled and disassembled. The dumbbell shaped opening spacer can be reused many times.

All stress–strain tests were performed on a Material Test System equipped with a 436 control unit, a 406 controller, a 410 digital function generator, and a 409 temperature controller. The measurements were made according to ASTM D638 type IV, with a gauge length of 25 mm and a crosshead speed of 5 mm/min.

Glass Transition Temperature Measurement

A DuPont 1090 thermal analyzer equipped with a 910 differential scanning calorimeter and a 1091 disk memory was employed. All tests were run in nitrogen atmosphere at a heating rate of 10°C/min. For calculation of T_g, data analysis was carried out with computer software provided by DuPont Instruments Inc. The temperature at the extrapolated onset, inflection, and end points were printed on the transition analysis report. The inflection temperature is somewhat dependent on the sample size. The extrapolated onset temperature is, in general, the most reproducible. Therefore, the extrapolated onset temperature is reported as the T_g in this study.

Density Determination

The water displacement method, as described in ASTM D792, was employed in the determination of the bulk density.

Thermally Stimulated Discharge Current (TSDC)

The relaxation processes were characterized by the TSDC technique. The TSDC spectra were run on the Electret Thermal Analyzer made by Toyo Seiki Seisaku-Sho. Gold-palladium metal was vacuum-deposited in a circle, 20 mm in diameter, on both

sides of the specimens (27 mm × 27 mm × 0.35 mm), using an SPI sputter coater. Specimens were polarized with an electric field of 10 kv/cm at temperature of 25°C for 20 min under dry nitrogen. The specimen chamber was then dipped into liquid nitrogen to cool down to −170°C with the electric field applied. The field was then removed and the depolarization current and temperature was recorded at a heating rate of 3°C/min.

Transmission Electron Microscopy

Nitrogen Ion Etching

It has been suggested that the ion etching of crystalline samples results in the preferential etching of the less ordered material, giving rise to observable surface details, which presumably are related to the bulk structure. For amorphous epoxy samples, one might expect similar preferential etching, based upon inhomogeneities in the local chemical structure (e.g., crosslink density).

The samples with fracture surface were exposed to nitrogen ions generated by a high frequency electric field in a vacuum of 80 μm using an induction heating generator (Lepel High Frequency Laboratories). The positive ions were accelerated toward the sample under a potential gradient of 300 volts d.c. Etching was conducted at low currents and the sample holder was cooled by liquid nitrogen during the period of exposure in order to avoid excessive heating and further degradation or cure reaction of the sample. Samples were etched continuously for 60 min.

Replica and Shadowing

In order to eliminate the artifacts and lower resolution produced in the two stage replica technique, one stage carbon–platinum replicas were made in this study. Specimens were prepared by shadowing the surfaces of etched samples with platinum–carbon at 30°, followed by the perpendicular deposition of a carbon film. Polyacrylic acid (PAA) solution was then placed on top of the C–Pt film and was allowed to dry for one day in a dessicator. The C–Pt replica, which adheres to the PAA, was removed by mechanical prying using tweezers. Finally, the PAA was dissolved in water by floating; the remaining carbon–platinum replica was picked up on a copper grid. All specimens were stored in a dessicator for at least 48 h prior to observation. This was to remove any absorbed moisture. An investigation was then undertaken to characterize the morphology of cured epoxy resins. This was done by using a JEOL 100C transmission electron microscope.

RESULTS AND DISCUSSION

Glass Transition Behavior and Bulk Density

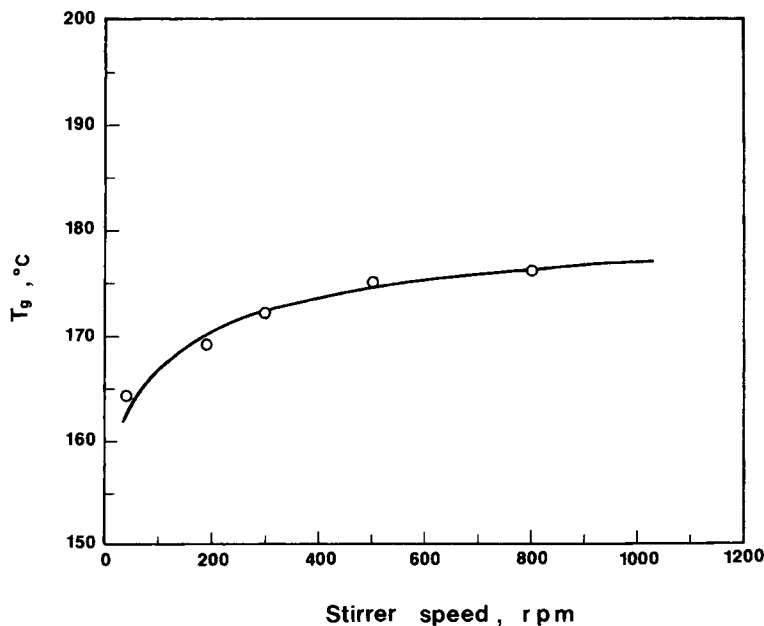Figure 1 shows the effect of stirring on the glass transition temperature. It is seen that the curve in

Figure 1 Effect of stirring on glass transition temperature of catalyst cured epoxy network.

Figure 1 shows two distinct stages: in the first stage the T_g increases more sharply with increasing stirrer speed up to 300 rpm, and then it increases slightly to reach a constant value. According to the results, a logarithm of the following equation can be derived from the data with correlation coefficient, $r = 0.99$:

$$T_g = 147.05 + 4.37 \ln V,$$

where V is the stirrer speed used other than $V = 0$.

A plot of the room temperature density of the epoxy network vs. stirrer speed is shown in Figure 2. The plot also reveals two distinct stages: the density decreases relatively rapidly as the stirrer speed is increased up to $ca.$ 300 rpm and then density tends to level off. This is rather surprising, since one would intuitively expect that the density would increase with the increasing T_g (i.e., lower free volume) due to increased stirrer speed. To explain this apparently anomalous behavior, Enns and Gillham[11] suggested that the lower density of the higher T_g epoxy network at room temperature is a consequence of the increase in free volume, which in turn is a result of the higher T_g material being further from equilibrium at room temperature. More recently, Morgan et al.[12] suggested that the room temperature density decreases with increasing crosslink density as a result of geometric constraints imposed on segmental packing by the network crosslinks. We propose schematic plots of specific volume vs. temperature for epoxy networks with 45, 300, and 800 rpm, as shown in Figure 3. For uncrosslinked polymers, the free volume decreases with decreasing temperature above T_g, with T_g occuring when the thermal constraints on molecular motion reach a given value. For un-
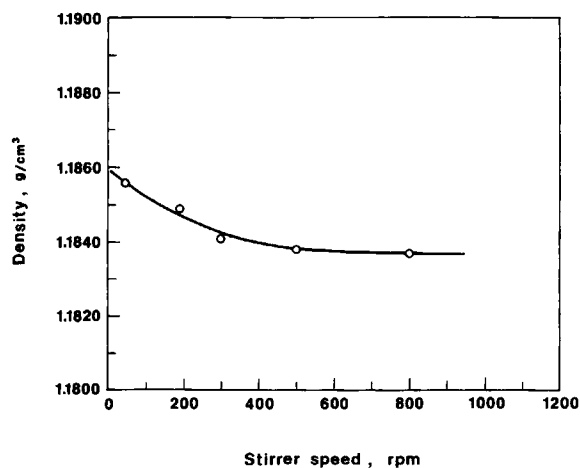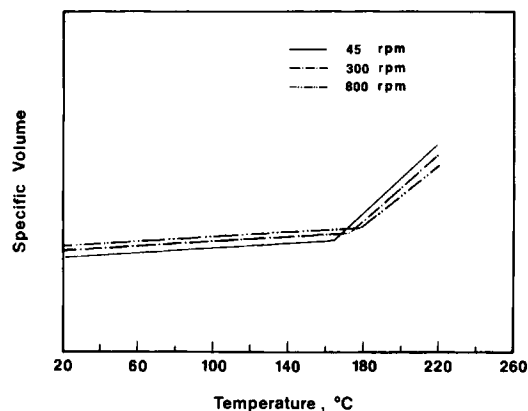

Figure 3 Schematic illustration of specific volume vs. temperature for epoxy network with different stirrer speeds.

crosslinked polymers, the thermal constraints can be considered in terms of the free volume, with T_g being described as an iso-free volume temperature. Samples of different polymers with different T_gs should level off at the same free volume as the samples are slowly cooled to room temperature. However, for crosslinked, amorphous polymers there are additional constraints on the segmental motion due to the crosslinks. Thus, though the higher crosslink density sample of a given polymer has a higher density above T_g, the additional crosslinking constraints, over and above the thermal constraint, can be expected to result in a higher T_g and a higher free volume in the glassy state than for a lower crosslink density sample. We propose T_g will occur when the total constraint, thermal plus crosslink, reaches a given value. For an equal cooling rate through the glass transition temperature, the specific volume lines will level off at a higher value of specific volume (i.e., higher free volume) for the more highly crosslinked sample, as indicated in Figure 3. This leveling off will result in a lower density at room temperature than for a less crosslinked sample.

Tensile Mechanical Properties in Glassy and Rubbery States

Figure 4 shows a plot of the effect of stirring on the room temperature mechanical properties. It is obvious from the figure that the tensile strength, Young's modulus, and ultimate elongation were found to be independent of the effect of mixing. These constant tensile mechanical properties imply that at room temperature (glassy state) the strength of interaction between the entities is unaffected by
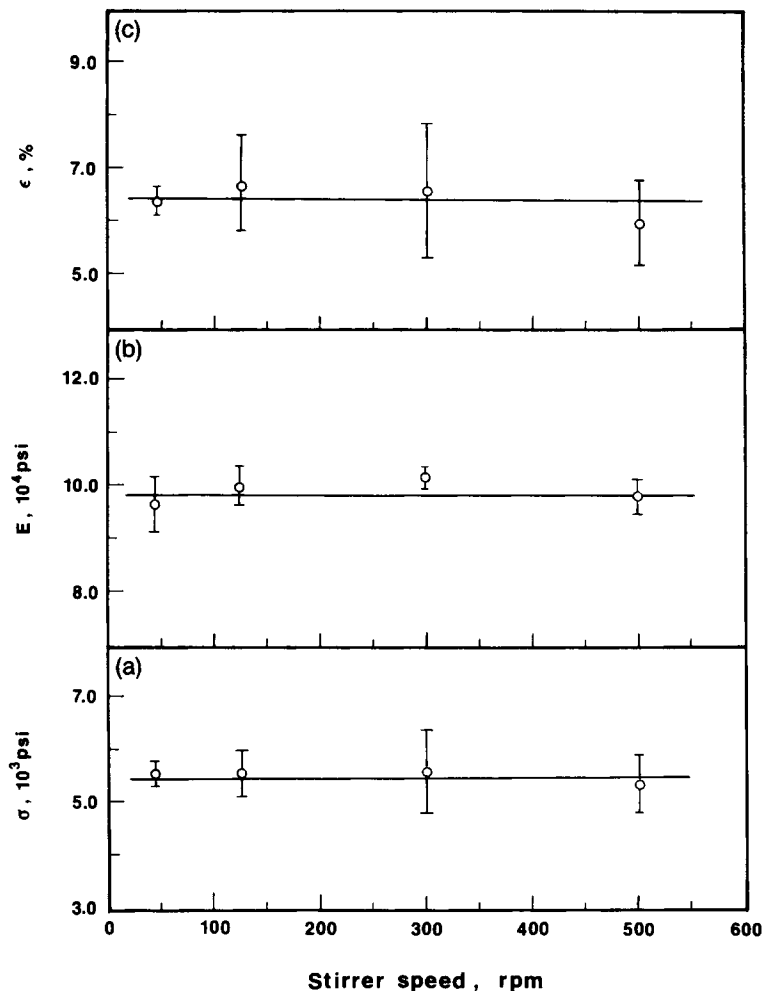

Figure 2 Effect of stirring on the room temperature density of catalyst cured epoxy network.

Figure 4   Effect of stirring on the tensile mechanical properties in the glassy state (25°C).
(a) tensile strength, (b) Young's modulus, (c) ultimate elongation.

the degree of crosslinking, which in turn is the result of increasing stirrer speed (i.e., increasing T_g). In fact, the mechanical properties in the glassy state are determined primarily by the strength of intermolecular forces and not by the strength of the covalent bonds of the polymer chain.[13] The intermolecular forces include dispersion forces, dipole forces, and hydrogen bonding. Since most polymers have only the relatively weak dispersion and dipolar forces, their mechanical properties in the glassy state are nearly similar. However, strongly polar polymers with a lot of hydrogen bonding should have higher mechanical properties.

The tensile mechanical properties in the high temperature region (rubbery state), as a function of the effect of stirring, are shown in Figure 5. The measurement of tensile strength, Young's modulus, and ultimate elongation were conducted at a temperature of 210°C.

As seen from Figure 5 (a) and (b), both the tensile strength and Young's modulus in the rubbery state show a significant increase with increasing stirrer speed of up to 300 rpm. Then the tensile strength and Young's modulus gradually tend to level off. Moreover, the dependence of the ultimate elongation on the effect of mixing is shown in Figure 5 (c). The figure shows a similar trend in that the elongation decreases as stirrer speed is increased, but elongation reaches a constant value at 300 rpm.

A comparison with the room temperature data indicate that, at room temperature, no trend can be observed as an effect of stirring. In the rubbery state, however, we find that the tensile strength and Young's modulus increase with increasing stirrer speed. Therefore, one may conclude that above T_g the tensile mechanical properties of epoxy network are closely correlated with the extent of homogeneity. However, these correlations are restricted if
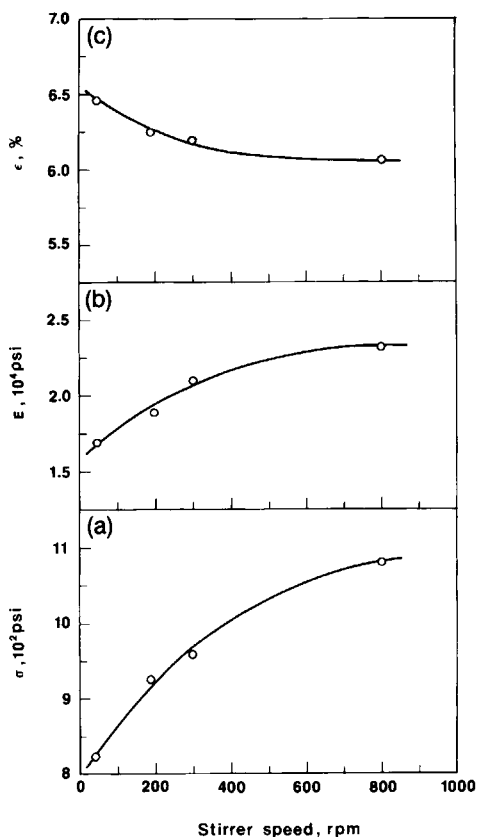
Figure 5 Effect of stirring on the tensile mechanical properties in the rubbery state. (a) tensile strength, (b) Young's modulus, (c) ultimate elongation.

the epoxy network is characterized at room temperature.

Low Temperature Relaxation Behavior

Figure 6 shows the TSDC spectra as a function of stirrer speed. Three relaxation peaks found in the figure correspond to those reported by Pangrle, Wu, and Geil.[14] The β peak, which occurred at $-114°C$, did not seem to change in position with increased stirrer speed, but the peak height was reduced. The γ peak, at $-141°C$ with a stirrer speed of 45 rpm, shifted to slightly higher temperature with 800 rpm; no quantitative measurement of changes in peak height with increased stirrer speed were possible. The β' peak at $-80°C$ shows a more pronounced shoulder as the stirrer speed increased. In the previous paper[14] the authors have reported that the peak height of the β relaxation has been ascribed to the number of crosslink junctions in the internodular matrix, while the β' peak has been ascribed to the number of crosslink junctions in the nodular domains. It thus becomes apparent that there is a decrease in the number of crosslink junctions in the internodular matrix as the stirrer speed increased. The number of crosslink junctions in the nodular domains increased, however, resulting in an increase in the β' relaxation strength with increasing stirrer speed.
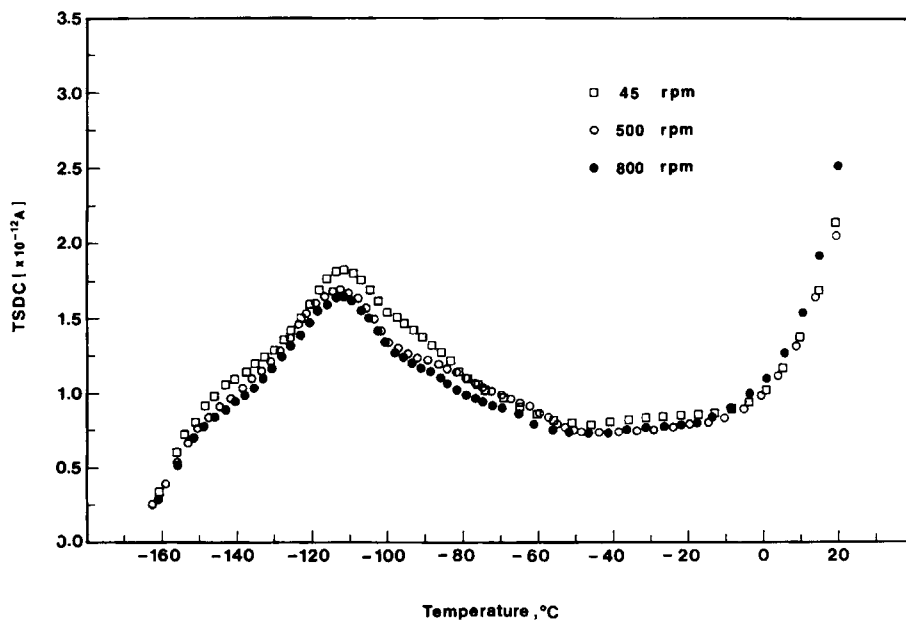

Figure 6 Effect of stirring on TSDC spectra of catalyst cured epoxy network.
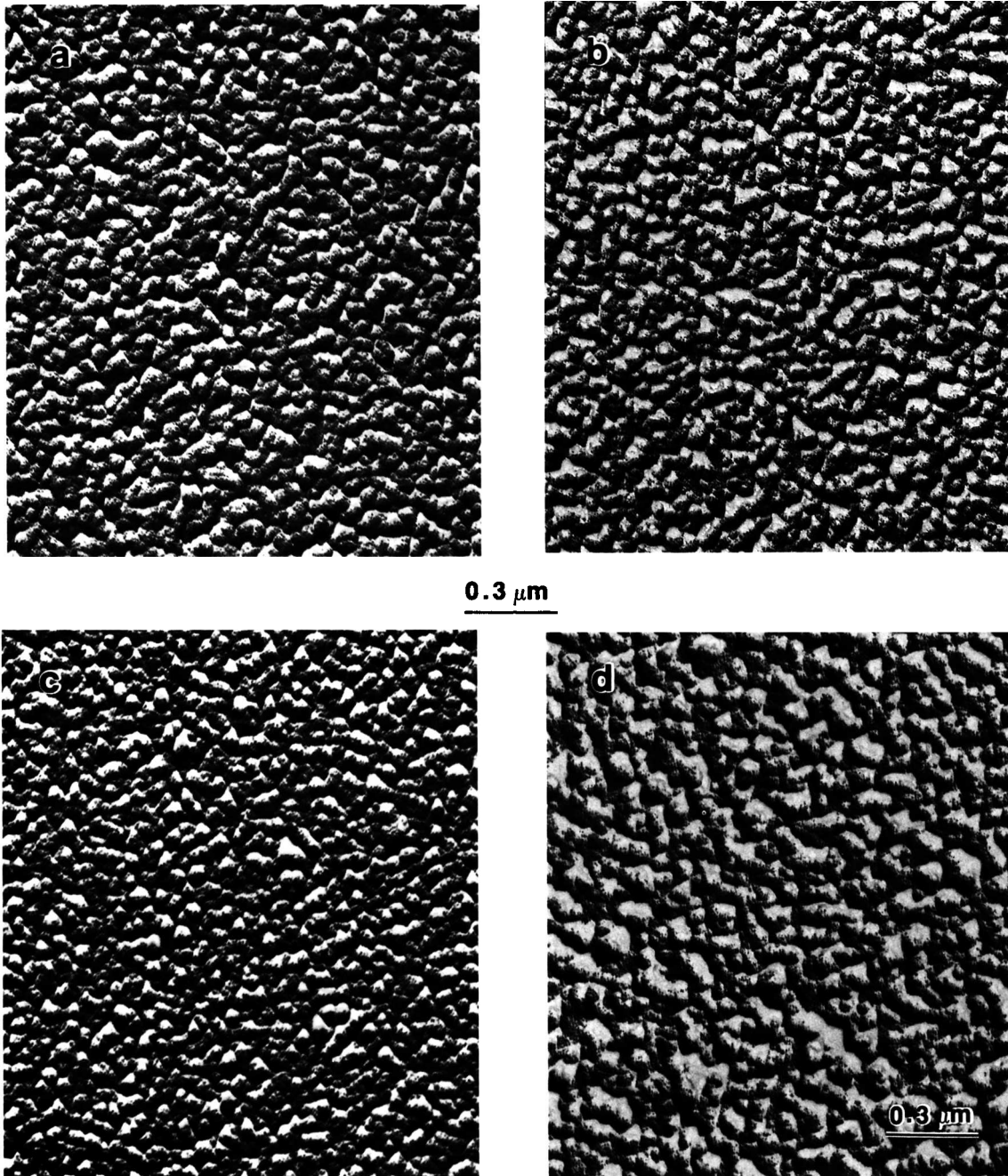
0.3 μm

Figure 7   TEM micrographs of replicas of ion-etched tensile fracture surface for catalyst cured epoxy networks having different stirrer speeds. (a) 45 rpm, (b) 190 rpm, (c) 300 rpm, (d) 800 rpm.

Electron Microscopy

Figure 7 shows the electron micrographs for samples with ion etched tensile fracture surfaces. It appears that the sample having the stirrer speed of 45 rpm has densely packed nodules with an average size of approximately 70 nm. The sample with the higher stirrer speed of 190 rpm exhibited widely spaced, less closely packed, small nodules with an average size of 65 nm. However, as the stirrer speed increased to 300 rpm, particularly noteworthy is the sample that exhibited smaller nodules of an average size *ca.*

50 nm, but the sample was dispersed in a more homogeneous internodular matrix. It seems that the 300 rpm sample provides a more homogeneous system (i.e., increasing mixing effectiveness). With increasing stirrer speed of up to 800 rpm, however, a marked difference in morphology was observed as shown in Figure 7 (d). It shows that the nodules seem to aggregate into larger supernodules at a stirrer speed of 800 rpm. But, as compared with the overall volume fraction of the internodular matrix, it seems to remain the same as that of the 300 rpm sample. From the figure it can be seen that the average nodule size is 95 nm for the sample with stirrer speed of 800 rpm.

It is somewhat surprising that the system homogeneity decreased and that the nodule size increased when stirrer speed increased from 300 rpm to 800 rpm. One would intuitively expect that the higher stirrer speed would increase shear forces, which are not only the major resistence to moving a stirrer, but also provide the mechanism for moving the fluid, thereby reducing the dispersed phase particle size. In general, however, the vessel geometry, impeller shape, and operating speed have already been mentioned as primary factors that affect the uniformity of a mixed system.[15] In our mechanical mixing system, we used a flat bottom flask as a mixing vessel and a Teflon paddle as a impeller. This assembly may produce a flow pattern in which the liquid flows parallel to the path described by the vessel. In this type of flow, the fluid discharges from the agitator into the surroundings and its entrainment in the impeller is small. Transfer in the vertical direction is insignificant. Mixing is only effected by eddying near the periphery of the stirrer arm. The mixing effect may be lowest when the rotational velocity of the liquid attains the same value as that of the stirrer. This may be the case of the sample with stirrer speed of 800 rpm, which leads to the system with the largest nodule size.

Based on the results, therefore, we claim that the high value of T_g can be attributed to the increase in crosslink density of the internodular matrix, which creates a more homogeneous system occurring with an increase in stirrer speed. However, as the stirrer speed is increased up to 300 rpm, the crosslink density of the matrix reaches a constant value and the T_g and free volume of density then, in turn, tend to level off.

CONCLUSIONS

Our present morphology and property results reveal a good correlation with the stirrer speed. It is be-lieved that control of the mixing process during sample preparation is important so as to obtain a homogeneous system that is tractable.

The effect of stirring may be summarized as follows:

1. The glass transition temperature increases with stirrer speed in the DGEBA/EMI-24 mixing system. The high value of T_g can be attributed to an increase in the crosslink density in the matrix because of the creation a more homogeneous system.
2. Decreasing density at room temperature as the stirrer speed increases (i.e., T_g increases) is attributed to the additional crosslinking, which adds molecular constraints to the thermal constraints. Thus, a higher free volume at T_g can be expected to remain in the glassy state as the sample is slowly cooled through glass transition temperature.
3. The room temperature tensile properties for the present epoxy system are independent of the extent of mixing. This independence is ascribed to the fact that the glassy state properties are closely related to the intermolecular forces rather than to the network structure.
4. In the rubbery state, the tensile strength and Young's modulus increased with increasing stirrer speed, while the ultimate elongation decreases as the stirrer speed increases.
5. The TSDC spectra have indicated that the low temperature relaxation behavior is affected by the stirrer speed. The peak height of the β relaxation decreased with increasing stirrer speed. This decrease is due to the decrease in the number of crosslink junctions in the internodular matrix as the stirrer speed increased. The number of crosslink junctions in the nodular domains, however, increased, resulting in an increase in the β' relaxation strength with increasing stirrer speed.

In summary, the variation in morphology and properties of this catalyst-cured epoxy system with the extent of mixing emphasizes the need to specify the processing conditions when describing the measurements of their properties.

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