Study on Relationship between Mechanical Properties and Particle Size Distribution for Polyhexamethylene Carbonate Diol Toughened Epoxy Resin

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ABSTRACT: The relationship between the mechanical properties and morphology of polyhexamethylene carbonate diol (PHMCD) toughened epoxy resin was investigated. The parameters describing the morphology (e.g., average diameter of particles and volume fraction of dispersed phase, etc.) were determined through SEM observation. It was observed that the particle size distribution changes from a unimodal distribution to a bimodal one and then to unimodal again with an increase in curing temperature. When it was cured at 120°C, an epoxy resin with a bimodal distribution of rubber particle size was obtained. The mechanical properties, especially the impacting strength, of the resin are the best because of the synergistic effect of the PHMCD particles. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 569–575, 1998

Key words: mechanical properties; particle size distribution; polyhexamethylene carbonate diol; toughened epoxy resin

INTRODUCTION

Epoxy resins are widely employed as the matrix for adhesive compositions. When cured, they become highly crosslinked amorphous thermoset polymers. This structure results in many useful properties, for example, high modulus, low creep, and excellent performance at an elevated temperature. However, the unmodified epoxies are relatively brittle polymers with poor resistance to cracking.

Some methods have been proposed to improve the toughness of epoxies. Therein, the most successful method is the addition of a suitable liquid rubber to the uncured epoxy resins and then controlling the polymerization reaction in order to achieve optimum phase separation.[1,2] The rubber-modified epoxy will exhibit a two-phase microstructure, which results in high toughness compared to an unmodified one.

The mechanical properties of rubber-modified epoxy resin depend on the morphological factors developed during the phase separation process, such as the total rubber content,[3] the volume fraction of the rubber phase, and the domain size and its distribution.[4] The domain size and its distribution can be controlled by changing the curing temperature.

Several types of reactive liquid rubbers were employed to toughen the epoxy resin. But the study of polyhexamethylene carbonate diol (PHMCD) as a toughening agent was not reported. PHMCD has low water absorption and high flexibility. In this article, the primary objective is to investigate the relationship between the distribution of rubber particle size and the mechanical properties of PHMCD toughened epoxy resin.

EXPERIMENTAL

Materials

The epoxy resin used in this study was a commercial diglycidyl ether of bisphenol A (DGEBA) provided

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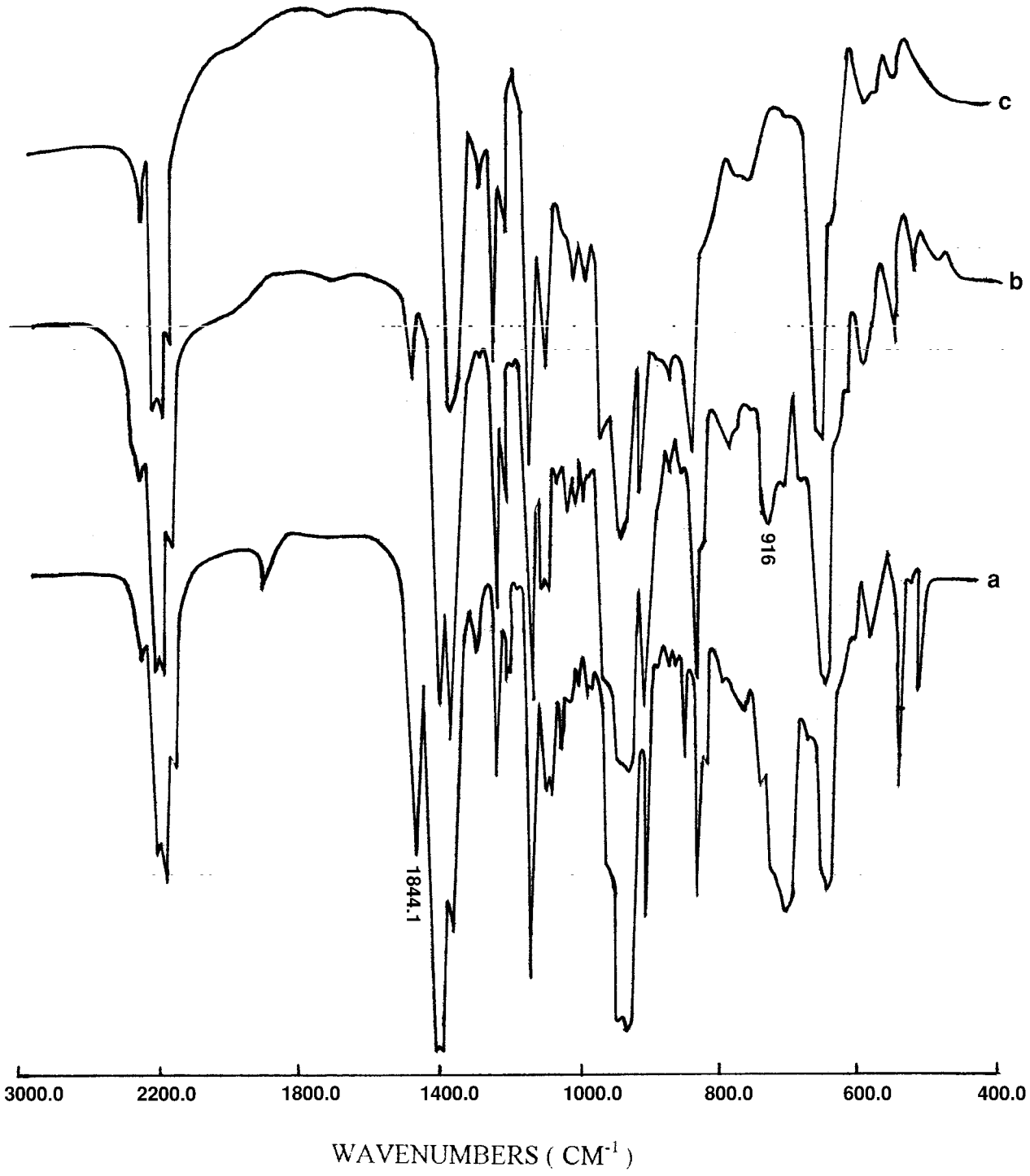

Figure 1 FTIR spectra of PHMCD toughened epoxy resin: (a) initial stage of curing, (b) gelation, and (c) finishing stage of curing.

by Jindong Chemical Factory, which has an epoxy equivalent of approximately 0.44 mol/100 g epoxy resin. Tetrahydrophthalic anhydride (THPA) was manufactured by the Jindong Co. PHMCD was made in our laboratory. Its molar mass is 2300 g/mol and the water content is below 0.1 w/w %.

Preparation of PHMCD Toughened Epoxy Resin

To prepare the PHMCD toughened epoxy, the curing agent (THPA) and PHMCD were added to the epoxy resin and mixed for 5–10 min. Then this mixture was degassed in a vacuum oven at 80°C. To

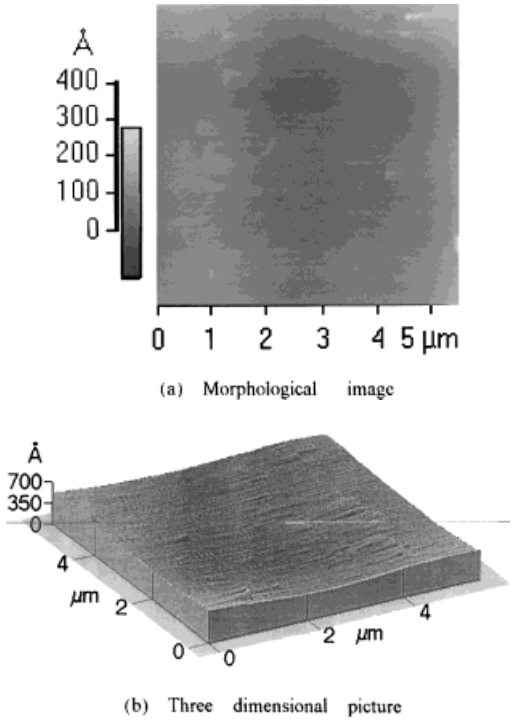

Figure 2 STM micrographs for untoughened epoxy resin.

observe the morphological change with curing temperature, the mixture was poured into a preheated mold and then cured at four different temperatures (90, 110, 120, and 130°C). Once the gelation occurred, the curing temperature was raised to 150°C and kept for 4 h. The following experiments on the microstructural and impact studies were conducted using specimens obtained from molded sheets of PHMCD-modified epoxy resin.

Measurements

Micrographs were obtained for the clear surfaces of untoughened and PHMCD-toughened epoxy resins using a scanning tunnel microscope (STM, Park Scientific Instruments).

The scanning electron micrographs were obtained on fracture surfaces of PHMCD-toughened epoxies with a Hitachi 650X SEM. Cast specimens were fractured in liquid nitrogen and then coated with a thin layer of gold using a high vacuum gold sputterer.

The Fourier transform infrared (FTIR) spectra were obtained by means of a Nicolet 5DX FTIR spectometer. The mixture of epoxy, PHMCD, and THPA was analyzed on KBr disks.

The stress–strain tests were performed using

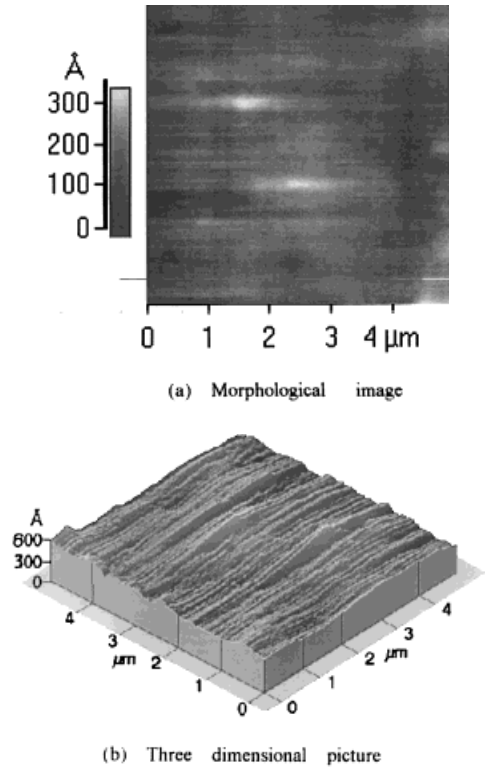

Figure 3 STM micrographs for PHMCD-toughened epoxy resin cured at 90°C.

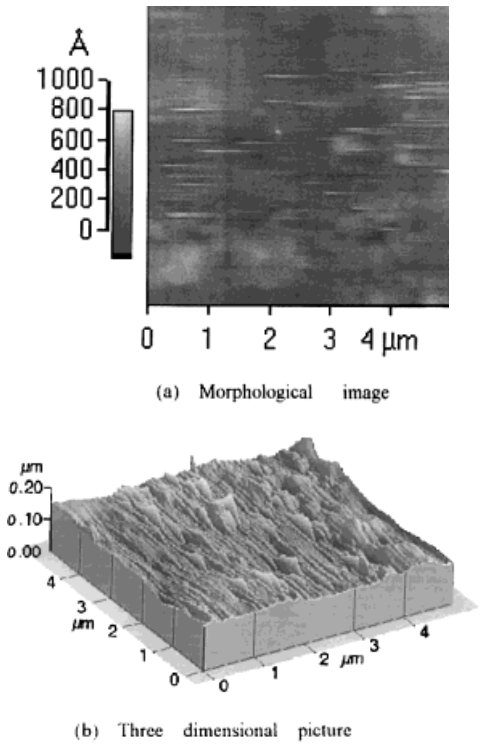

Figure 4 STM micrographs for PHMCD-toughened epoxy resin cured at 120°C.

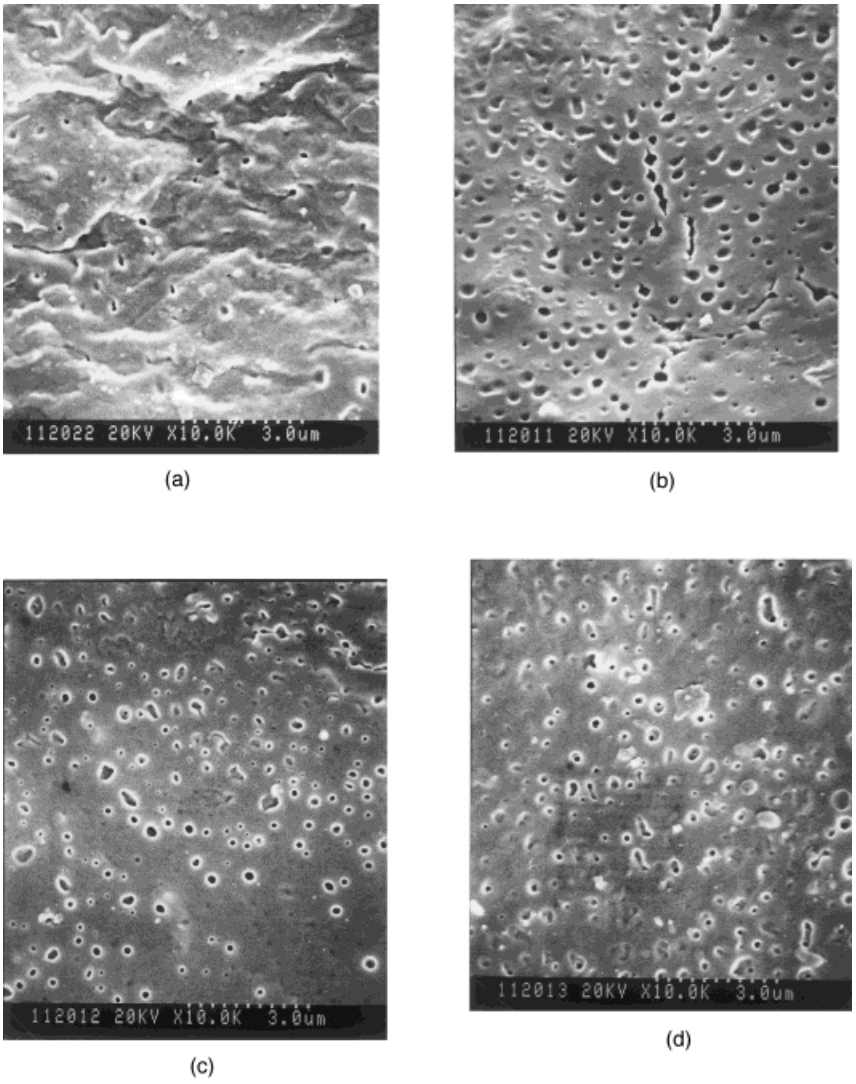

Figure 5 SEM micrographs of PHMCD toughened epoxy at different curing temperatures: (a) 90°C, (b) 110°C, (c) 120°C, and (d) 130°C.

an Instron DL-1000B mechanical tester. The crosshead speed was kept at 10 mm/min and the testing temperature was held at 25°C.

The unnotched impact test was carried out by using an XCJ-90 impacting tester to obtain the toughness value of the resin at a high strain rate.

RESULTS AND DISCUSSION

IR Analysis

Figure 1 displays the FTIR spectra for the curing process of the epoxy. The epoxy resin is characterized by 916 cm^{-1} for $-CH(O)-CH_2$ For THPA, a strong absorption band at 1844.1 cm^{-1} for the anhydride group is observed (see curve a). During the cure reaction, the bands at 916 and 1844.1 cm^{-1} decayed (curve b) and then disappeared (curve c), which implies that $-CH(O)-CH_2$ has reacted completely and the amount of THPA was suitable.

The STM micrograph and its corresponding three-dimensional image for untoughened epoxy resin are shown in Figure 2. The surface roughness of untoughened epoxy sample is less than 5 nm. The smooth surface is seen in the three-dimensional picture. When PHMCD was added into epoxy, phase separation is observed (see Figs. 3, 4). Figure 3 and Figure 4 show the surface morphological images and three-dimen-

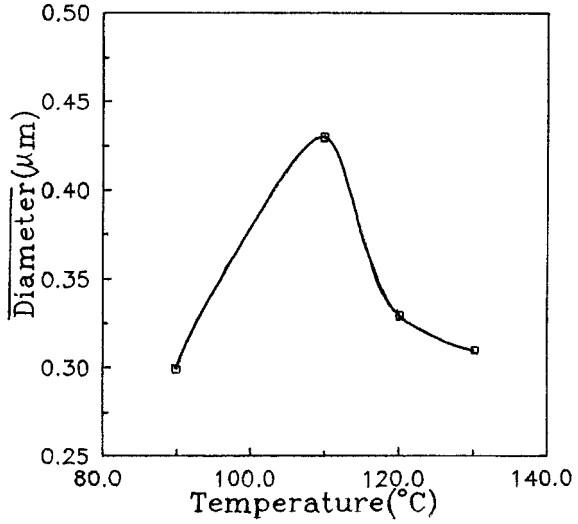

Figure 6 Average diameter of PHMCD particles, $\overline{D}$, as a function of curing temperatures.

sional images for the epoxy resins toughened by PHMCD and cured at 90°C (Fig. 3) and 120°C (Fig. 4), respectively. Contrasted to Figure 2, there is a noticeable roughness in Figure 4. It can be seen from the three-dimensional images in Figure 3(b) and Figure 4(b) that hill-like PHMCD moieties with various height are distributed on the flat surface of epoxy matrix. The surface of epoxy resin cured at 120°C is much more rougher than that cured at 90°C. It can be assumed from the STM micrographs that adding PHMCD, the microstructure of epoxy can be changed and it will be different under different curing temperatures.

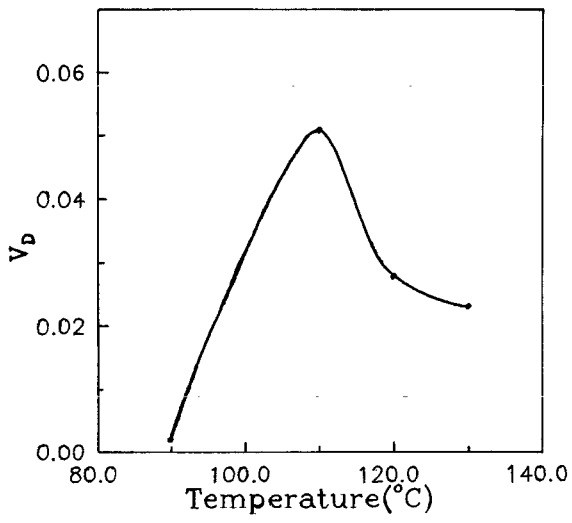

Figure 7 Volume fraction of PHMCD, V_D, as a function of curing temperatures.

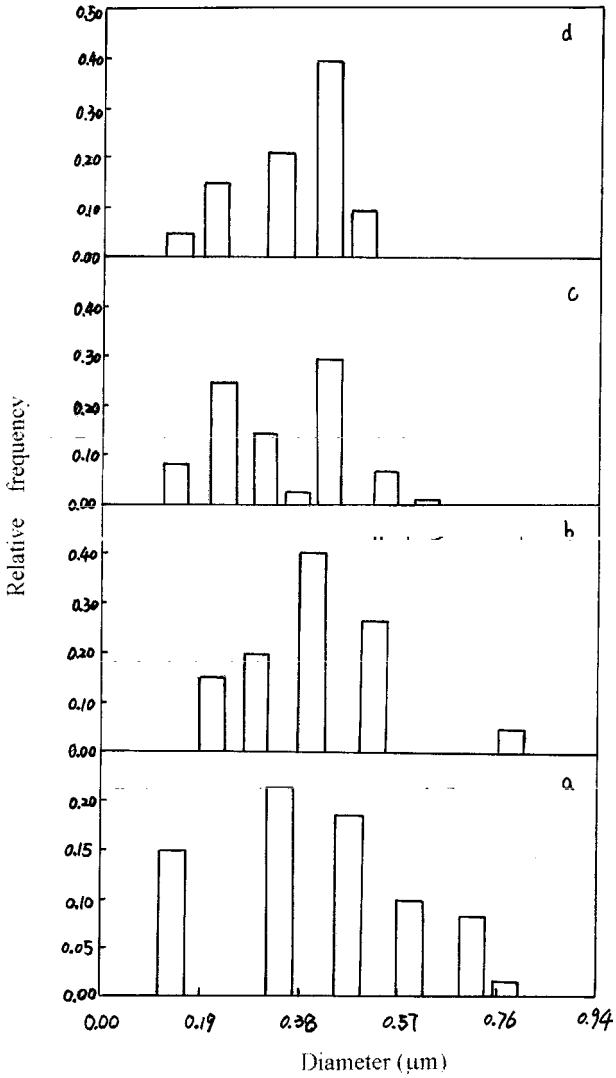

Figure 8 Particle size distribution for PHMCD-toughened epoxy resin cured at different temperatures: (a) 90°C, (b) 110°C, (c) 120°C, and (d) 130°C.

The STM micrographs of PHMCD toughened epoxy under different curing temperatures are shown in Figure 5. They reveal the presence of two-phase morphological feature in the system. This result agrees with that of STM. The micrographs were magnified in order to estimate morphological parameters. About 150 particles of dispersed phase were measured for each sample. The distribution of particle diameters was determined directly from the diameters on the magnified SEM micrographs. The number average diameter ($\overline{D}$) is defined as[5]:

$$\bar{D} = \sum nD / \sum n \qquad (1)$$

where n is the number of particles having a diam-

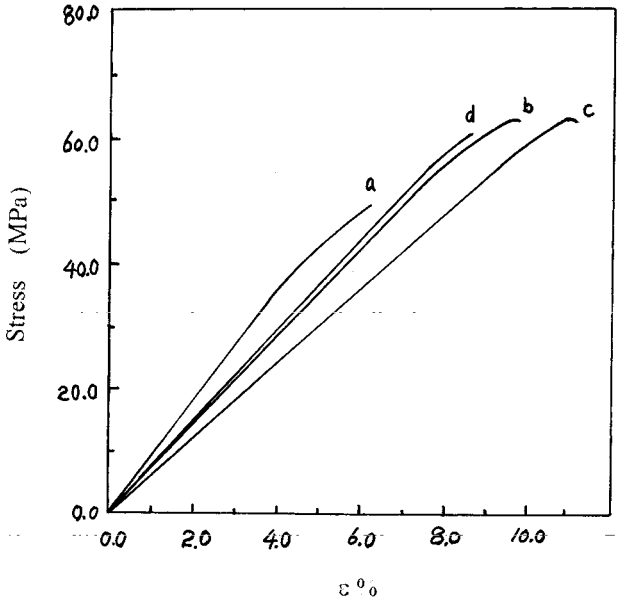

Figure 9 Curves of stress–strain for PHMCD-toughened epoxy resin cured at different temperatures: (a) 90°C, (b) 110°C, (c) 120°C, and (d) 130°C.

eter of D. The volume fraction of the dispersed phase (V_D) may be calculated as follows[5]:

$$V_D = \pi/4(\sum nD^2/A_T) \qquad (2)$$

where A_T is the area of micrographs under analysis. Equation (2) assumes that the volume fraction is an isotropic property. Hence, values measured in the micrograph plane are the same as those in the real volume.

Figure 6 displays the average diameter of dispersed particles as a function of the curing temperatures. It is found that the resin cured at 110°C would form the largest rubber particles with a number average diameter of about 0.43 μm. But the resin cured under other temperatures would form smaller particles. This fact suggests that the rate of phase separation is faster than the curing rate at a temperature lower than 110°C, but the curing rate becomes faster than the phase separation rate under temperatures higher than 110°C. Figure 7 shows the volume fraction of the dispersed phase (V_D) versus the curing temperatures. The maximum of V_D is at 110°C also.

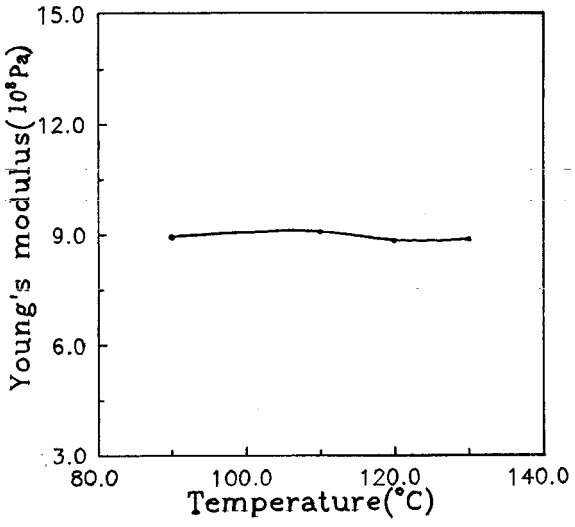

Figure 10 Dependence of Young's modulus on curing temperatures.

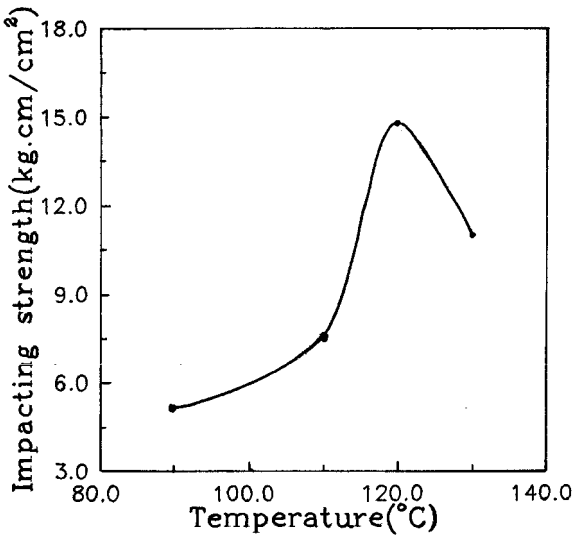

Figure 11 Plot of impacting strength vs. curing temperatures.

The variation of particle size distribution with the curing temperatures is shown in Figure 8. The range of particle size distribution is wider at a lower temperature than that at 110°C. However, it becomes narrower under the temperatures over 110°C. It is interesting to observe the following phenomena: the distribution appears as a bimodal one when epoxy resin is cured at 120°C. But if it is cured under other temperatures (90 or 130°C), the distribution will be unimodal. These phenomena are different from those of Sang et al.,[1] where the particle size distribution moves from bimodal to unimodal when the curing temperature rises.

Mechanical Properties

Figures 9 and 10 show the stress–strain curves and the Young's modulus curve, respectively. The Young's moduli of the resins obtained under different curing temperatures are almost the same. For the stress–strain behavior of PHMCD-tough-

ened epoxy resin, there are two features worth noting. One is the stress at break, and the other is the elongation at break. In this work, the maximum elongation at break and the maximum stress at break both appear for epoxy resin cured at 120°C. This indicates that the toughened systems with the bimodal rubber particle size distribution can dissipate more strain energy through higher values of stress and elongation. Therefore, they are more resistant to breakage through the formation of a localized shear yeilding.[6]

The results of the impact test are displayed in Figure 11. The value for PHMCD-toughened epoxy resin cured at 120°C achieves a maximum. This phenomenon can be attributed to cavitation at the particle–matrix interface and shear yielding in the matix.[7] Based on this mechanism, in the bimodal rubber particle distributed epoxy resin, much more stress will concentrate on the equators of the large particles and the small particles, which are distributed in between the large ones, may tend to enhance the shear yielding. Thus, the interaction gives rise to a synergistic toughening effect of the bimodal rubber particle distributed epoxy resin system.

CONCLUSIONS

Investigation of the relationship between mechanical properties and particle size distribution in PHMCD-toughened epoxy resin reveals that as the curing temperature increases, the particle size distribution is changed from unimodal (90°C) to bimodal (120°C) and then to unimodal (130°C) again. The mechanical properties are best when the epoxy is cured at 120°C because of the bimodal distributed rubber particles. The synergistic effect of these particles gives rise to the increment in the toughness in PHMCD-toughened epoxy resin.

REFERENCES

1. C. K. Sang, B. K. Moon, and H. J. Won, *Polymer,* **36,** 2189 (1995).
2. S. Henry and Y. Hsich, *Polym. Eng. Sci.,* **30,** 493 (1990).
3. L. J. Manzione, J. K. Gillham, and C. A. McPherson, *J. Appl. Polym. Sci.,* **26,** 907 (1981).
4. J. A. Kinioch and D. C. Huston, *J. Mater. Sci. Lett.,* **5,** 1207 (1986).
5. D. Verchere, J. D. Pascault, H. Sautereau, S. M. Moschiar, C. C. Riccardi, and R. J. J. Williams, *J. Appl. Polym. Sci.,* **42,** 701 (1991).
6. D. S. Kunz, P. W. R. Beaumont, and M. F. Ashby, *J. Mater. Sci.,* **15,** 1109 (1980).
7. A. J. Kinloch, S. J. Shaw, D. A. Tod, and D. L. Hunston, *Polymer,* **24,** 1341 (1983).