Toughening Epoxy Resins with Polyepichlorohydrin

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SYNOPSIS

Polyepichlorohydrin (PECH) rubbers were found to toughen epoxy resins based on the diglycidyl ether of bisphenol A (DGEBA) and cured with piperidine. The degree of toughening depends on the molecular weight of the PECH and on the curing temperature. Best toughening was achieved with PECH of the highest nominal molecular weight of 3400 (Hydrin 10 X 2). Hydrin 10 X 1 (nominal molecular weight 1700) did not toughen the epoxy resin unless bisphenol A was also added, whereas Hydrin 10 X 2 toughened it in the absence of bisphenol A. Curing resins containing bisphenol A and Hydrin 10 X 1 at 160°C resulted in a slightly more brittle resin than when cured at 120°C. In contrast, curing resins containing Hydrin 10 X 2 at 160°C gave a significantly tougher resin than when cured at 120°C. The effect of PECH rubbers on the T_g, modulus, and hot/wet properties is similar to that of carboxy-terminated butadiene–acrylonitrile rubbers (CTBN). Dynamic mechanical thermal analysis (DMTA) and scanning electron micrographs (SEM) of fractured surfaces show that the PECH separates as a discrete phase during curing. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Epoxy resins are one of the most important classes of thermosetting resins, but when cured are highly cross-linked and brittle. A number of approaches have been used to toughen epoxies or to reduce their brittleness including the addition of reactive rubbers and thermoplastics. Rubber toughening of epoxies was first investigated in the 1960s and work was reported describing the use of liquid carboxy-terminated butadiene–acrylonitrile rubbers (CTBN).[1,2] Since then, a large volume of work on the use of CTBN and other rubbers has been published.[3–18]

This paper is concerned with the use of polyepichlorohydrin (PECH) rubber to toughen epoxy resins based on the diglycidyl ether of bisphenol A (DGEBA). The structure of the reactants and the rubbers are shown in Figure 1. There appears to be no published reports of the use of PECH to toughen epoxy resins. Several patents[19–21] mention the use of PECH in epoxy resins, but no examples of such materials were given and no effect on toughening

reported. Another patent[22] describes a two-part epoxy resin in which PECH was used as a toughener in one part.

PECH has several potential advantages: The structure of PECH, with its pendent chloromethyl groups and terminal hydroxyl groups, gives great flexibility in the variation of the interactions that could be induced either by prereaction of the PECH or during the epoxy curing reaction. In addition, the absence of unsaturation in PECH in contrast to CTBN rubbers should result in greater stability at elevated temperatures.
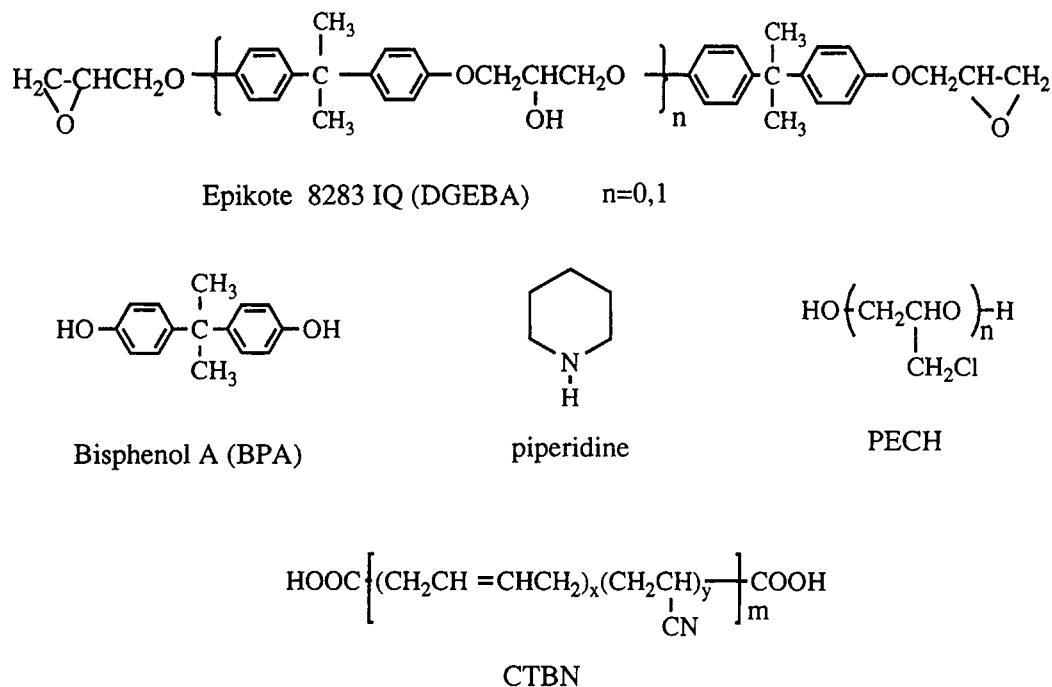
To provide a clear reference point, we have also cured epoxy resins with CTBN rubber under similar conditions to those for the PECH system. The morphology and fracture toughness of the CTBN systems were determined to provide a direct comparison with the epoxy/PECH samples.

EXPERIMENTAL

Materials

The diglycidyl ether of bisphenol A (DGEBA) (Epikote 8283 IQ) was obtained from Shell Chem-

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$$H_2C\text{-}CHCH_2O\text{-}\left[\text{-}\phenyl\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}\phenyl\text{-}OCH_2CHCH_2O\text{-}\right]_n\text{-}\phenyl\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}\phenyl\text{-}OCH_2CH\text{-}CH_2$$

Epikote 8283 IQ (DGEBA)   n=0,1

$$HO\text{-}\phenyl\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}\phenyl\text{-}OH$$

Bisphenol A (BPA)

piperidine

$$HO\left(CH_2\underset{CH_2Cl}{CHO}\right)_n H$$

PECH

$$HOOC\left[(CH_2CH=CHCH_2)_x(CH_2\underset{CN}{CH})_y\right]_m COOH$$

CTBN

Figure 1 Structure of chemical reactants and rubbers.

ical (Aust.) and used without purification. The CTBN rubbers (Hycar 1300 × 8 and Hycar 1300 × 13) and the PECH rubbers (Hydrin 10 × 1 and Hydrin 10 × 2) were obtained from B. F. Goodrich Chemical Ltd. (Aust.). Piperidine (BDH Chemical Ltd.) and bisphenol A (Dow Chemical Co.) were used without purification. Frekote 44 (Dexter Hysol) was obtained from Advanced Composites. Hexahydrophthalic anhydride was obtained from Aldrich Chemical Co. and hexahydro-4-methylphthalic anhydride from Chemicals Procurement Laboratories, College Point, NY.

Characterization of PECH Rubbers

Hydroxyl equivalent weight was determined using an acid-catalyzed acetylation procedure.[23] GPC

analysis was carried out at 30°C using a Waters 150-C ALC/GPC with Ultrastyragel columns. THF was used as the solvent. Molecular weights were calibrated with respect to polystyrene. A Hewlett-Packard 302B vapor pressure osmometer (VPO) was also used to determine molecular weights. Chloroform was used as the solvent. The results of these measurements are shown in Table I.

Curing Procedures

Bisphenol A (BPA 12.2 g) was added to Epikote 8283 (50.8 g) in a 100 mL round-bottom flask and the mixture heated on a rotary evaporator at 120°C/ 50 mbar for 20 min to give a clear solution of DGEBA containing 24 parts per hundred resin (phr) BPA. The solution was stored at 4°C.[14]

Table I   Properties of PECH Rubbers

Sample	Hydrin 10 × 1	Purified Hydrin 10 × 1	Hydrin 10 × 2
Nominal M_n[a]	1700	—	3,400
M_n by GPC	1600	3800	2,600
M_w by GPC	5600	7300	20,000
M_n by VPO	1800	3800	nd[b]
Hydroxyl equivalent weight	1340	1630	nd
Functionality (using M_n by GPC)	1.2	2.3	nd

[a] As reported by the supplier.[24]
[b] Not determined.

The above DGEBA/BPA solution (9.96 g) and PECH (0.99 g) was hand-mixed with a spatula for 5 min in a wide-mouthed resin vessel and then heated at 65°C with mechanical stirring for 5 min. The solution was then degassed at 65°C/20 mbar on a rotary evaporator for 1 h to give a clear solution. Piperidine (5 phr based on DGEBA) was added to the solution and stirred gently at 35°C with a spatula. The mixture was then transferred to heated stainless-steel molds with dimensions of 70 × 17 × 3 mm (for DMTA) that had been sprayed with Frekote 44 and a heated Teflon mold of dimensions 110 × 16 × 15 mm. After curing, the latter bar was cut into 6 cubes and machined to precise dimensions for fracture toughness measurements. The samples were cured in an oven at 120°C for 16 h and allowed to cool slowly.

A preparation in which the PECH was first end-capped with DGEBA was done as follows: A 20% methanolic solution of tetramethylammonium hydroxide was prepared by freeze-drying a sample of aqueous tetramethylammonium hydroxide (BDH Chemical) and redissolving in anhydrous methanol. A mixture of Epikote 8283 (40 g) and Hydrin 10 × 1 (4.0 g) was dissolved in methylene chloride (30 mL) and then a 20% methanolic solution of tetra-methylammonium hydroxide (0.5 mL) was added. The solution was heated slowly to 120°C on a rotary evaporator and then heated at 120°C for 5 h at 10 mbar. The temperature was increased to 160°C and maintained for 0.5 h to decompose the catalyst.[25] After cooling, piperidine (2.32 mL) was added and the samples cured as above.

A typical anhydride cure was done as follows: A mixture of Epikote 8283 (40 g) and hexahydro-phthalic anhydride (30 g) was heated at 70°C/10 mbar on a rotary evaporator until a clear solution formed and cooled. Benzyldimethylamine (0.3 mL) was added and the mixture degassed on a rotary evaporator at 50°C/20 mbar for 10 min and then poured into heated molds, cured at 120°/16 h, and allowed to cool slowly.

Reaction of PECH and Thioglycolic Acid

Hydrin 10 × 1 (9.3 g) was dissolved in dioxan (30 mL) and thioglycolic acid (Aldrich) (1.38 mL) and potassium hydroxide (2.25 g) dissolved in ethanol (10 mL) added. The mixture was refluxed for 2 h, cooled, and poured into a beaker of water (400 mL). Hydrochloric acid (1M, 50 mL) was added. The water was decanted from the precipitate, the precipitate washed with water, dissolved in acetone (25 mL), and poured into 0.001M hydrochloric acid to give a

precipitate that was left overnight to settle. The water was decanted off and the product dried under vacuum at 40°C to constant weight (6.3 g). The acid equivalent weight was measured by dissolving a sample (0.84 g) in acetone and titrating with 0.01N methanolic KOH using cresol red/thymol blue (1 : 3) as indicator and found to be 1860.

Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical properties were measured with a Polymer Laboratories DMTA with temperatures scanned from −100 to 200°C at 2°C/min. Samples were clamped in dual cantilever mode and scanned at a range of frequencies between 0.1 and 10 Hz. T_g values refer to the maximum in the tan δ measured at 1 Hz.

T_g values were also measured on a Mettler TA4000 differential scanning calorimeter (DSC). The T_g was taken as the midpoint value at a scan rate of 10°C/min.

Fracture Toughness

Fracture toughness data were obtained using small compact tension specimens of fixed dimensions (W = 12.7 mm; B = 10 mm) following the approach of Hinkley.[26] A natural precrack was introduced in each specimen by tapping a fresh razor blade placed in the root of a machined notch.[26,27] Specimens were loaded to failure at room temperature using an Instron Model 1185 universal testing machine and a displacement rate of 1.3 mm min^{-1}. Provisional Mode I critical stress intensity factors (K_q) were determined via the analyses provided in ASTM E399.[28] No attempt was made to validate the provisional values, though the chosen specimen thickness was considered sufficient to ensure that plane strain conditions were met.
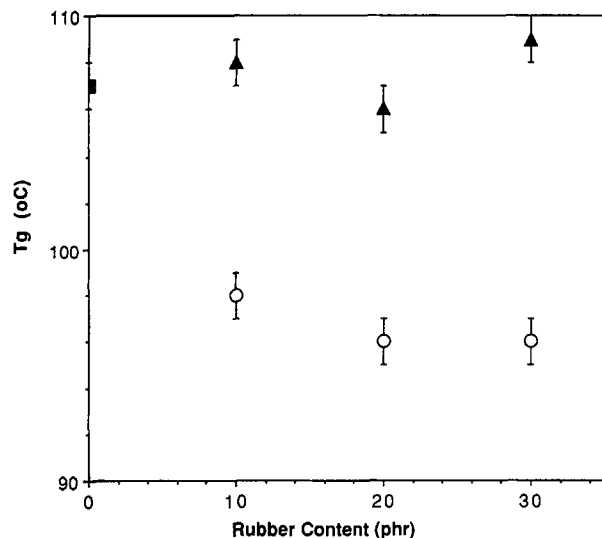
Hot/Wet Properties

Hot/wet properties were determined after soaking the samples in water at 71°C for 2 weeks, which was sufficient to achieve equilibrium absorption, since no change in water absorbed was found after soaking at 71°C for a further week. Accurate DMTA results for wet samples are difficult to obtain because the samples lose water during the DMTA measurement. The onset T_g was calculated by extrapolating the initial linear DMTA curve and the sloping curve where the modulus began to decrease as described by Barton and Greenfield.[29]
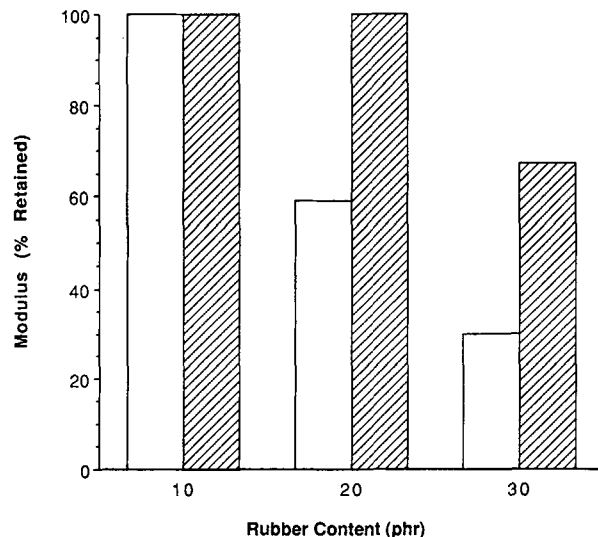
Morphological Observations

Scanning electron microscope (SEM) studies were carried out using a Cambridge Stereoscan 250 Mk III instrument. Failed compact tension specimens were mounted and gold-coated to allow fracture surface topographies to be examined. Morphological information was obtained from both backscattered and secondary electron images of carbon-coated polished cross sections. Image contrast was enhanced by treating specimens with alcoholic thiourea followed by heavy metal staining of the PECH using mercuric chloride.

RESULTS AND DISCUSSION

The toughness of a rubber-toughened epoxy depends on the morphology of the cured resin and this is related to the solubility of the rubber in the uncured system. After degassing, the DGEBA systems containing either CTBN rubbers or PECH rubbers were transparent, indicating solubility in the uncured epoxy. After curing, all samples containing rubbers and 24 phr of bisphenol A were opaque, indicating the formation of a second phase. On the other hand, samples containing BPA and no rubber and samples with no BPA and with or without rubber were all transparent with the exception of one sample to be discussed later. In these cases where transparent samples are produced, if rubber separates as a second phase, its size must be less than the wavelength of light.

Figure 3 Effect of rubber on the modulus (at T_g −30°C) of DGEBA/BPA/piperidine resins. The error in the modulus retained is ±10%: (□) CTBN (Hycar 1300 × 13); (▨) PECH (Hydrin 10 × 1).

As is commonly observed, Figures 2 and 3 demonstrate that both CTBN and PECH rubbers have a detrimental effect on the T_g and modulus of the cured epoxy. However, the effect of PECH is somewhat less severe than that of CTBN. The hot/wet properties (Figs. 4 and 5) are similar, except at the impractical level of 30 phr of PECH, where the equilibrium water content is much higher.
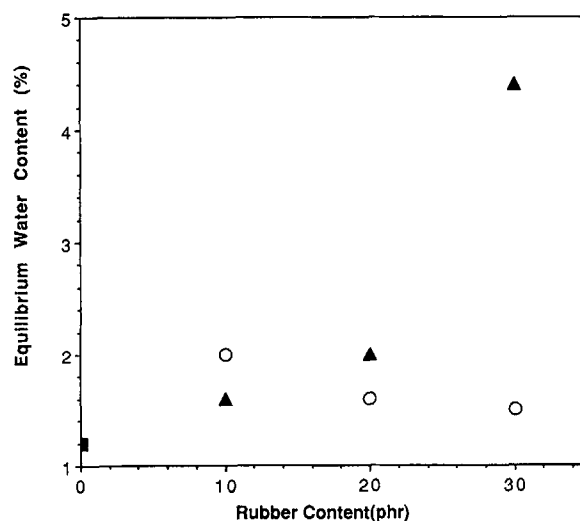

Figure 2 Effect of rubber on the T_g of DGEBA/BPA/piperidine resins: (■) no rubber; (▲) PECH (Hydrin 10 × 1); (○) CTBN (Hycar 1300 × 13).
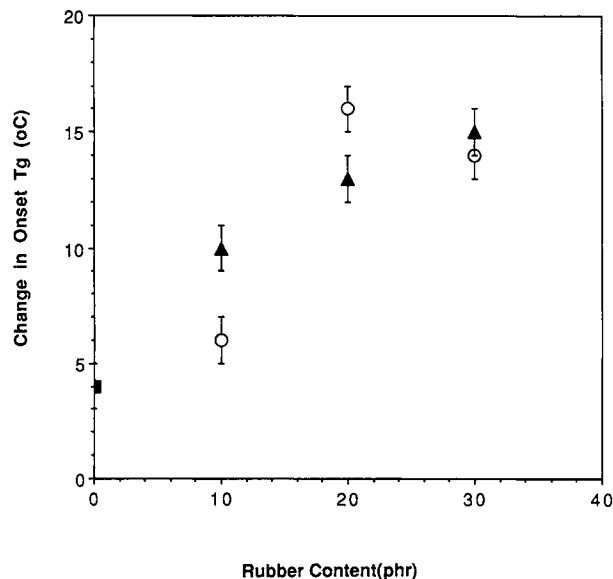

Figure 4 Equilibrium water content after 2 weeks at 71°C: (■) no rubber; (▲) PECH (Hydrin 10 × 1); (○) CTBN (Hycar 1300 × 13).

Figure 5 Change in the onset T_g after 2 weeks in water at 71°C: (■) no rubber; (▲) PECH (Hydrin 10 × 1); (○) CTBN (Hycar 1300 × 13).

DMTA Results

Figure 6 shows the low-temperature DMTA curves for the cured DGEBA resin with a β-transition temperature at about −60°C. The addition of CTBN resulted in a DMTA curve with an additional transition due to the T_g of the CTBN as reported by others.[30,31] Figure 7 shows the DMTA curves of samples containing PECH (Hydrin 10 × 1) with a peak at about −15°C, which increased in magnitude as the amount of PECH increased. Figure 8 shows that the addition of CTBN or PECH results in only a slight decrease in the β-transition temperature. As the amount of rubber increased, the T_g transition of the rubber became more intense and moved to higher temperatures. The T_g of the PECH increased less than that of the CTBN, which indicates that the PECH has less epoxy dissolved within it. The observation that the reduction in the T_g of the cured epoxy (Fig. 2) containing PECH is less than that for a cured epoxy containing CTBN indicates that less PECH is left dissolved in the epoxy after curing.
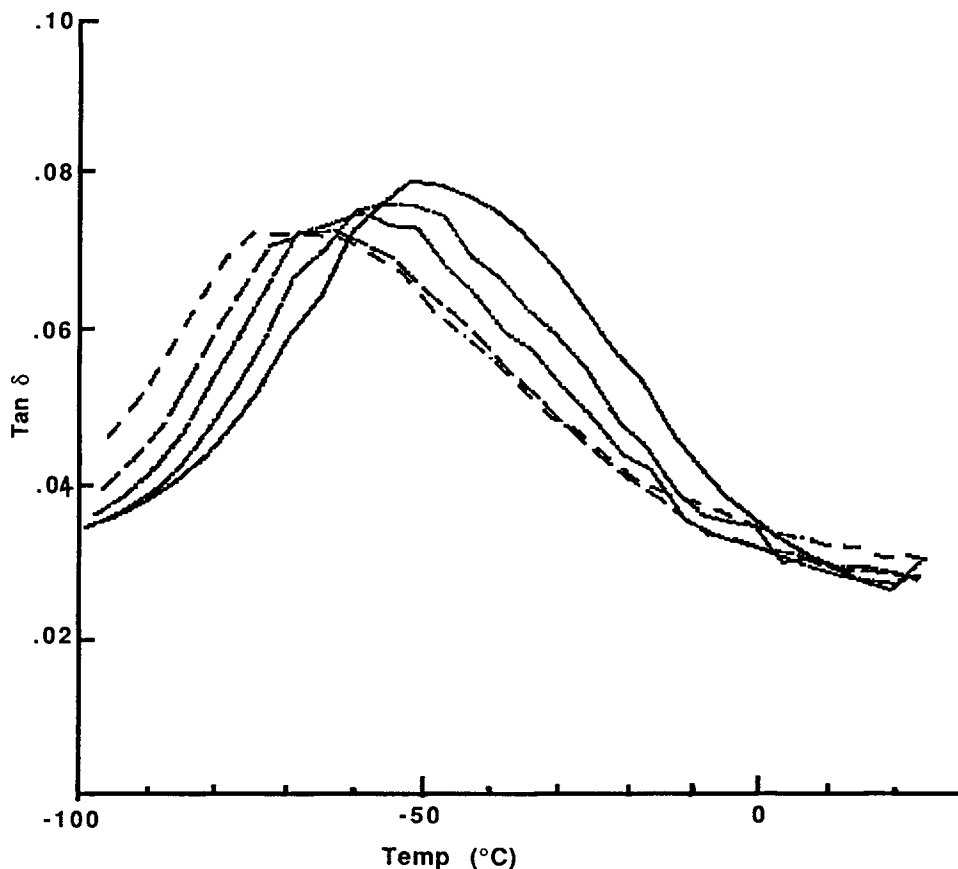

Figure 6 Low-temperature DMTA curves of a DGEBA/BPA/piperidine resin. Curves from left to right were obtained at frequencies of 0.1, 0.3, 1.0, 3.0, and 10 Hz, respectively.
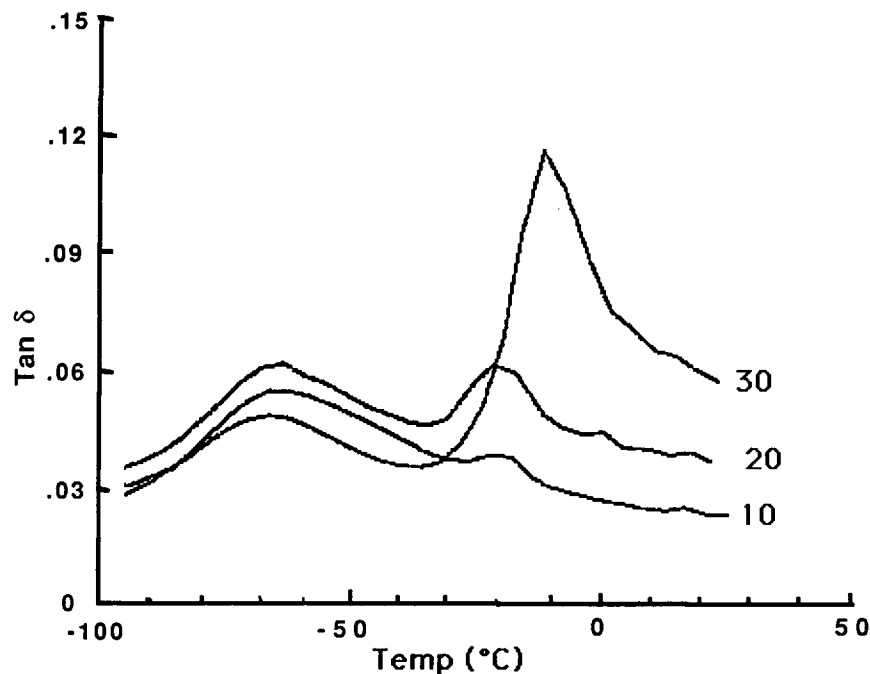
Figure 7 Low-temperature DMTA curves of DGEBA/BPA (24 phr)/piperidine (5 phr) resins containing PECH (Hydrin 10 X 1) at 10, 20, and 30 phr (based on DGEBA + BPA). Frequency, 1 Hz.

Fracture Toughness and Morphological Observations

Two different samples of PECH with nominal number-average molecular weights (M_n) of 1700 and 3400 were used in this study. However, GPC showed
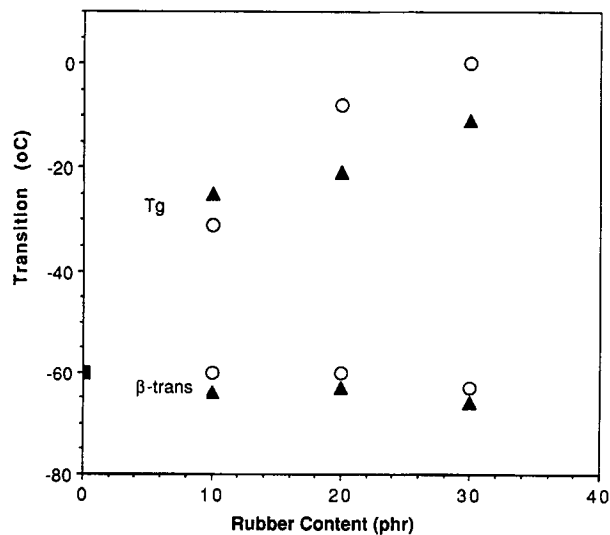
Figure 8 Effect of rubber on the low-temperature transitions of DGEBA/BPA/piperidine resins: (■) no rubber; (▲) PECH (Hydrin 10 X 1); (○) CTBN (Hycar 1300 X 13).

that both samples contained about 20% (w/w) of a very low molecular weight fraction (350–400). A "purified" version of Hydrin 10 X 1 was made by extraction with methanol, which reduced the level of the low molecular weight material to 1–5%. The properties of the PECH samples used are summarized in Table I. These values agree, in general, with other analyses of Hydrin 10 X 1 and Hydrin 10 X 2.[32]

The morphology of PECH-toughened resins was similar to that of CTBN-toughened resins with discrete rubber particles being observed during SEM examination of polished surfaces. Table II shows the average particle diameters from at least 40 observations of such micrographs. In bisphenol A-containing formulations other than that incorporating Hydrin 10 X 2 at a level of 15 phr, the separated rubber took the form of spheroidal particles of submicron size. The apparent size and number of separated particles increased with Hydrin level (Table II), as did the measured fracture toughness (Tables III and IV). Curing the formulation incorporating 15 phr Hydrin 10 X 2 at 120°C resulted in the formation of large spheroidal domains (up to 800 microns in diameter) of apparent phase inversion in addition to discrete submicron rubber particles. This morphology gave rise to the only instance of an increased Hydrin level, resulting in decreased

Table II Apparent Particle Diameters (μm) in Polished Specimens (DGEBA/BisphenolA/ Piperidine)

Rubber	phr	Particle Diameter (μm) When Cured at 120°C	Particle Diameter (μm) When Cured at 160°C
Hydrin 10 × 1	5	0.30	0.30
	10	0.60	0.65
	15	0.65	0.80
Purified Hydrin 10 × 1	5	0.50	
	10	0.50	
	15	0.70	
Hydrin 10 × 2	5	0.80	0.50
	10	0.90	0.80

Table IV Fracture Toughness of DGEBA Resins Cured with Piperidine (5 phr) at 160°C/6 h and 120°C/10 h

PECH (phr)	Kq (MPa m$^{1/2}$) With Bisphenol A (24 phr) Hydrin 10 × 1	Kq (MPa m$^{1/2}$) With Bisphenol A (24 phr) Hydrin 10 × 2
5	1.21 ± 0.07 (6)	2.40 ± 0.03 (6)
10	1.61 ± 0.10 (6)	2.58 ± 0.03 (6)
15	1.86 ± 0.11 (6)	2.62 ± 0.15 (3)

toughness within the range of formulations examined. Phase inversion did not occur when the formulation was initially cured at 160°C, although a number of large rubber particles (up to 200 microns in diameter) could be observed in addition to those of submicron size.

Tables III and IV show that Hydrin 10 × 1 is effective in toughening a DGEBA resin containing bisphenol A. Table III shows that the purified Hydrin 10 × 1 is a better toughener of a bisphenol A-containing DGEBA resin than is the unpurified material. Purification resulted in larger separated particles at a level of 5 phr and a greater number of particles of a similar size at 10 and 15 phr. Examination of respective fracture surfaces [Fig. 9 (a) and (b)] revealed that particle fracture took place with little attendant deformation in samples containing the unpurified material, whereas some dilation oc-

curred prior to rupture in those samples containing the purified material. The toughening effect of Hydrin 10 × 2 is much better still with only 5 phr (based on DGEBA + BPA), giving more than a 100% increase in the Kq value for a sample containing bisphenol A. The higher molecular weight Hydrin 10 × 2 produced larger particles than did Hydrin 10 × 1 for the same loading (Table II) and facilitated significantly larger and more numerous cavitation in fracture surfaces [Fig. 9(c)]. Only Hydrin 10 × 2 toughened the DGEBA resin without added bisphenol A. This was the only sample without bisphenol A and containing PECH that was opaque.

A comparison of the resins cured initially at 120°C (Table III) and at 160°C (Table IV) shows that the curing temperature affects the toughness, as has been observed by others. Increasing the cure temperature has been observed to greatly increase the toughness of DGEBA systems.[33,34] The average diameter of the dispersed particles has been reported to go through a maximum or increase as the cure temperature was increased.[35] Curing resins containing Hydrin 10 × 1 at 160°C (Table IV) compared

Table III Fracture Toughness of DGEBA Resins Cured with Piperidine (5 phr) at 120°C/16 h

PECH (phr)[a]	Kq (MPa m$^{1/2}$) No Bisphenol A Hydrin 10 × 1	Kq (MPa m$^{1/2}$) No Bisphenol A Hydrin 10 × 2	Kq (MPa m$^{1/2}$) With Bisphenol A (24 phr) Hydrin 10 × 1	Kq (MPa m$^{1/2}$) With Bisphenol A (24 phr) Hydrin 10 × 2	Kq (MPa m$^{1/2}$) With Bisphenol A (24 phr) Purified Hydrin 10 × 1
0	1.00 ± 0.07 (6)[b]		1.00 ± 0.2 (5)		
5		1.31 ± 0.05 (6)	1.32 ± 0.05 (6)	2.10 ± 0.10 (6)	1.41 ± 0.10 (8)
10	1.11 ± 0.15 (4)		1.66 ± 0.08 (5)	2.20 ± 0.07 (6)	1.87 ± 0.12 (5)
15			1.97 ± 0.07 (5)	1.94 ± 0.14 (5)	2.01 ± 0.10 (4)

[a] phr is parts per hundred DGEBA or DGEBA plus biphenol A where bisphenol A is used.
[b] Number in parentheses is number of test samples.
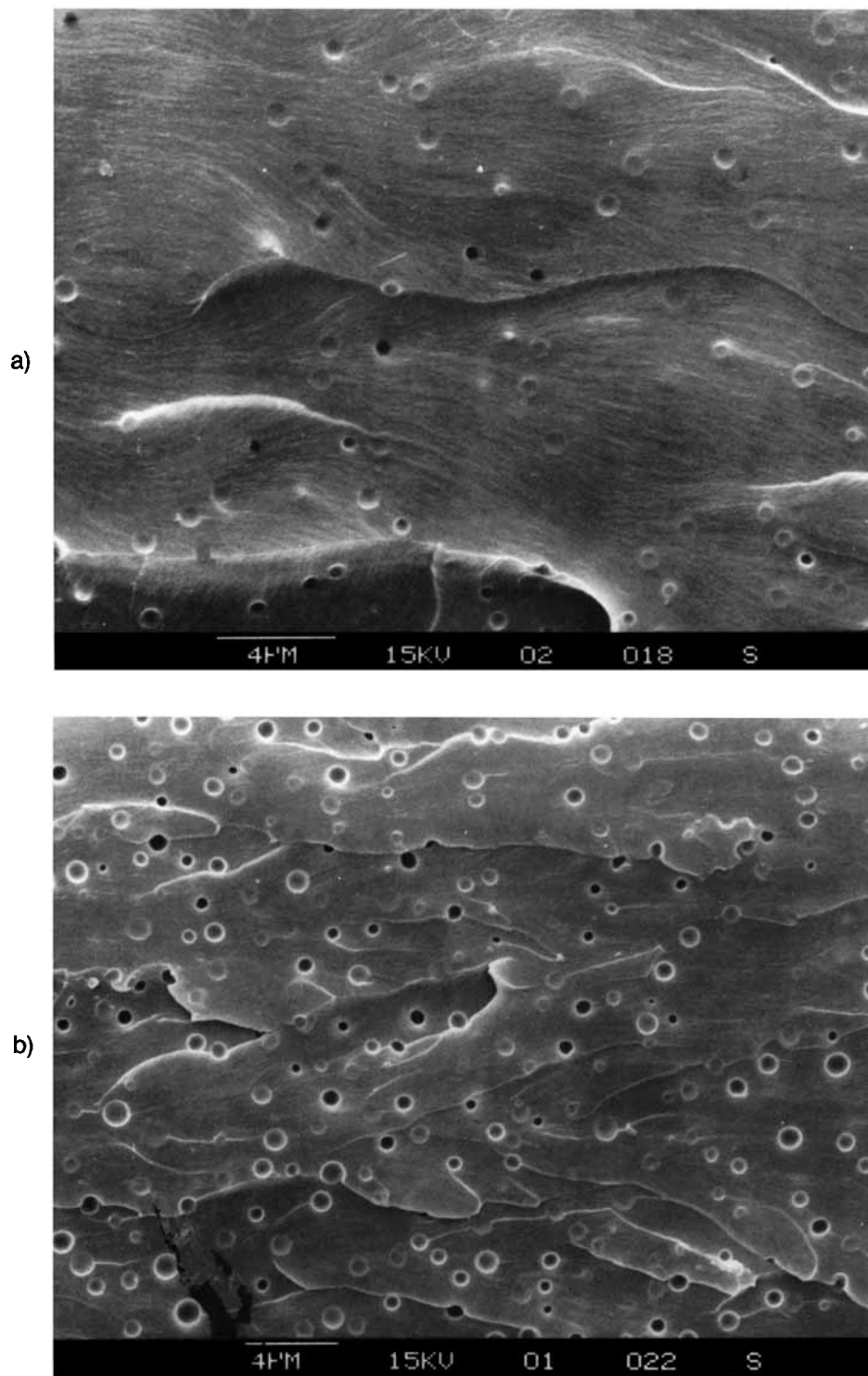
Figure 9 Scanning electron micrographs taken in the slow crack growth region of compact tension specimen fracture surfaces of DGEBA/bisphenol A (24 phr)/piperidine (5 phr) samples containing 10 phr of rubber and cured at 120°C/16 h: (a) Hydrin 10 × 1; (b) purified Hydrin 10 × 1; (c) Hydrin 10 × 2. Crack propagation is from left to right.
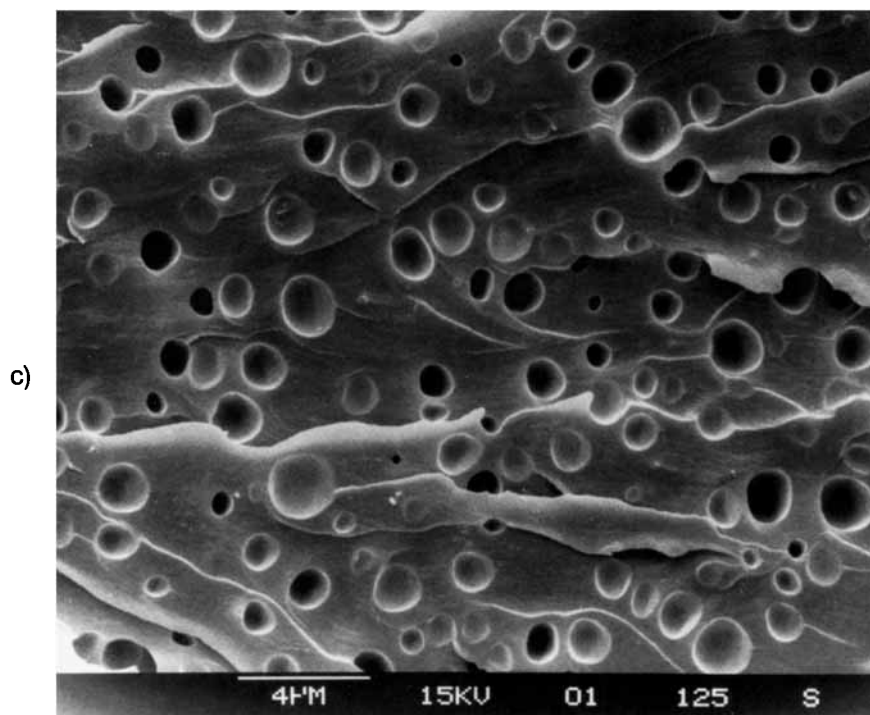
c)

Figure 9 (continued from the previous page)

to 120°C had little observable effect on the particle size (Table II), but resulted in a slightly more brittle resin (Table III). In contrast, curing resins containing Hydrin 10 × 2 at 160°C resulted in slightly smaller but more numerous particles and a significantly tougher resin than when cured at 120°C. The higher initial cure temperature gave rise to larger cavitation in the fracture surfaces.

The increased toughness is not due to a change in the molecular weight between cross-links—which is known to affect toughness.[36,37] The molecular weight between cross-links (M_c) was calculated from the modulus (E_r) at $T_g + 50°C$ using the equation[38,39]

$$M_c = \frac{293\rho}{\log(E_r/3)}$$

where E_r is the modulus in MPa and $\rho = 1.18$ g cm^{-3}, and found to be independent of the amount of rubber in the 0–30 phr range and of the nature of the rubber (either CTBN or PECH), when allowance was made for the presence of the rubber using the Ishai–Cohen model.[40]

During the curing reaction, DGEBA could react with the terminal hydroxyl groups of the PECH and the piperidine could react with the chloromethyl groups of PECH. From the results in Table V, it would appear that any of the former types of reactions are disadvantageous as far as toughening is concerned since prereacting the PECH with DGEBA gave a more brittle resin. Although CTBN requires its terminal carboxylic acid groups to react with the DGEBA for significant toughening,[14] the introduc-

Table V Fracture Toughness of DGEBA Resins Cured with Piperidine (5 phr) at 120°C/16 h

		Kq (MPa m$^{1/2}$)	
Rubber	phr	No Bisphenol A	With Bisphenol A (24 phr)
None		1.00 ± 0.07 (6)	1.00 ± 0.20 (5)
Hydrin 10 × 1/thioglycolic acid	7.3		1.07 ± 0.10 (6)
Hydrin 10 × 1/DGEBA	10.0	0.65 ± 0.08 (6)	1.53 ± 0.02 (6)
Hydrin 10 × 1	10.0	1.11 ± 0.15 (4)	1.66 ± 0.08 (5)

Table VI   Fracture Toughness of DGEBA Resins Cured with Anhydrides

Curing Agent[a]	Bisphenol A	Rubber	phr	Appearance	Kq (MPa m$^{1/2}$)
HHPA[b]	0	—	—	Transparent	0.60 ± .09 (5)
HHPA	0	Hycar 1300 × 8	10	Hazy	1.08 ± .09 (6)
HHPA	0	Hydrin 10 × 1	10	Transparent	0.64 ± .05 (6)
4MeHHPA[c]	24	—	—	Transparent	0.69 ± .05 (6)
4MeHHPA	24	Hycar 1300 × 8	10	Opaque	1.06 ± .10 (6)
4MeHHPA	24	Hydrin 10 × 1	10	Transparent	0.78 ± .10 (4)

[a] Plus a small amount of benzyldimethylamine.
[b] Hexahydrophthalic anhydride.
[c] Hexahydro-4-methylphthalic anhydride.

tion of about one carboxylic acid group into PECH by reaction with thioglycolic acid surprisingly destroyed PECH's ability to toughen the DGEBA resins (Table V). We are unable to offer a satisfactory explanation for this result. The extent and effect of any reaction between the PECH and piperidine has not been resolved. The fact that PECH is much less effective at toughening DGEBA resins cured with anhydrides (Table VI) indicates that such reactions may be important. However, CTBN is also much less effective at toughening anhydride-cured resins (Table VI). Therefore, the PECH may be a less effective toughener of the anhydride-cured resins for the same reason that CTBN is less effective and not because it has less opportunity to chemically react with the DGEBA via an initial reaction with the piperidine.

In conclusion, it has been found that PECH rubbers initially dissolve in epoxy resins and then separate during cure to form submicron rubber particles that result in the toughening of the epoxy resin. Based on the effect on the T_g of the PECH particles and the T_g of the cured epoxy, the cured epoxy is less soluble in the PECH particles and the PECH is less soluble in the cured epoxy than is CTBN. The use of a PECH rubber of twice the molecular weight greatly increased the toughness. Similarly, curing a resin containing this rubber at 160°C compared with 120°C further increased the toughness, whereas curing a resin containing the lower molecular weight PECH at the higher temperature slightly decreased the toughness. In general, as the amount of PECH content was increased, the particle size and the number of particles increased as determined by SEM studies of stained and polished surfaces. However, the increase in the particle size was small compared to the increase in the toughness. In contrast, the degree of cavitation and the size of the cavitated sites in the fractured surfaces usually increased dramatically as the toughness increased.

Nevertheless, it has not been possible to determine a direct structure–toughness relationship from these results and further work is needed. Other authors have indicated that they are also doing further work.[41] Since the toughness depends on the complex interplay between many factors such as the matrix, particle, and interphase composition, the interfacial bond strength and the particle size and the particle-size distribution, it would be surprising for a direct correlation to exist between just particle size and toughness.

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