Rubber- and Thermoplastic-Toughened Epoxy Adhesive Films

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SYNOPSIS

Epoxy resins have been toughened using together two components: a liquid rubber (Hycar CTBN 1300x13) and a thermoplastic polymer (Phenoxy PKHH). Unsupported adhesive films have been obtained from blends. The effect of different curing cycles on morphology, fracture behavior, and adhesive strength has been studied, monitoring phase separation by dynamic mechanical analysis. The combination of the two moieties was found the most efficient toughening agent when a slow curing cycle was adopted. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The use of epoxy resins in high-performance structural materials is now a common practice, particularly in the field of adhesives and matrices for advanced composite for aerospace and electronic industries. Combined high-modulus and high-strength values at relatively high temperature make these materials suitable for demanding applications. However, the major drawback of cured epoxy resins is their brittleness. To improve this property, many studies have been carried out on the modification of epoxy resin by incorporation of a second component, usually a rubbery polymer, as, for instance, carboxyl-terminated butadiene–acrilonitrile liquid rubber (CTBN) or amine-terminated butadiene–acrilonitrile liquid rubber (ATBN).[1-8] The end groups present in such elastomeric moieties are able to react with the oxirane ring of epoxy resin, making the two phases chemically bound. Rubber-toughened epoxy resins are commonly prepared by curing the epoxy moiety in the presence of the liquid rubber.[1,2] A two-phase system is thus formed, where rubber particles are dispersed in the epoxy matrix. The compatibility level between modifier and epoxy as well as the curing rate determine the particle size and the interfacial bonding level. Fracture toughness of modified epoxy resins depends on these parameters and on the nature of the rubber component. The toughness enhancement by rubber modification is due mainly to the plastic deformation of the material at the crack tip and depends on the possibility of plastic deformation of the matrix during the fracture process.[9] Cross-linking density was found to have a great influence on toughening.[10,11] Practically, toughness exhibits a maximum for intermediate cross-linking densities.

In structural adhesive applications, both lap shear strengths and T-peel strengths are increased by addition of an appropriate amount of liquid rubber (30–40 phr), but shear strengths measured at high temperature (75–80°C) show only a limited or no effect.[12] This behavior is likely due to the fact that a fraction of the rubber can dissolve in the matrix, thereby depressing the T_g and Young's modulus of the adhesive system with respect to those of the pure epoxy resin. It is highly desirable to maintain at a good level such characteristics, which constitute crucial factors for performance under hot/wet conditions.

Recently, tough and ductile engineering thermoplastics have been experimented with in modifying epoxy resins.[13-20] Due to their high modulus and high T_g, the modulus and T_g of thermoplastic-modified epoxy resins will reach or even exceed the corresponding values of unmodified resin. Polyethersulfone (PES) and polyetherimide (PEI) have been used to modify trifunctional and tetrafunc-

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tional epoxies[13-15]; phenolic hydroxyl-terminated poly(ether sulfone) oligomers (PSF),[16] poly(ether ketone) (PEK),[17] poly(aryl ether ketone)s,[18] aromatic polyesters,[19] and liquid crystal polymers[20] have been also investigated. However, reduction in stiffness becomes significant only at temperatures near the T_g of the thermoplastic moiety.[13]

In this study, we tried to overcome the above problems by using both a liquid rubber and a thermoplastic polymer for toughening of epoxy resin. We fabricated adhesive films and measured their shear strength after curing cycles of different lengths. Glass transition temperatures, morphologies, and fracture surfaces of cured triphase systems were investigated.

EXPERIMENTAL

Materials

The following materials were used as received:

- Epikote 828 (Shell), consisting essentially of diglycidyl ether of bisphenol A (DGEBA).
- DDS (4,4'-diaminodiphenyl sulfone, Fluka) as curing agent.
- BF_3 (boron trifluoride, Fluka) as accelerator.
- Hycar CTBN 1300x13 (butadiene–acrylonitrile carboxyl-terminated rubber, Goodrich B.F.).
- Phenoxy PKHH (Union Carbide), a linear poly(hydroxyl ether) prepared by condensation of epichloridrine and bisphenol A.

Preparation of Adhesive Films

Resin compositions, containing from 25 to 30 phr (parts per 100 parts of resin) of Phenoxy and from 10 to 20 phr of Hycar were prepared by the following standard procedure:

Phenoxy was dissolved in the epoxy resin by mixing for 2 h at 120°C; Hycar CTBN was then added to the homogeneous, clear, and transparent solution and mixed for 1 h; an opaque mixture was obtained, to which 20 phr of DDS were added in a fixed amount for all compositions. After 30 min, when DDS was completely dissolved and the mixture assumed an orange color, the temperature was lowered at 60°C, finally adding 1 phr of BF_3 and mixing for 15 min.

At room temperature, the obtained solids were only a little sticky and had a thermoplastic consistency. Using a press (5 ton/cm^2 at 60°C for 1 min), unsupported adhesive films were obtained.

In Table I, compositions of prepared adhesives are reported; all formulations are identified by two figures, $x.y$, where x corresponds to Phenoxy phr and y to CTBN rubber phr, respectively.

Cure Cycles

Sultan and McGarry[21] reported that a bimodal particle-size distribution is necessary to obtain a good toughening level of an epoxy matrix. This occurrence can be successfully reached by adjusting the length of the cure cycle. Thus, two different cure cycles were experimented with:

Table I Composition and Shear Strength of Adhesive Films

Adhesive[a]	Epon 828 (phr)	Phenoxy (phr)	Hycar (phr)	DDS (phr)	BF_3 (phr)	Cure Cycle (Type[b])	Shear Strength (N/mm^2)
25.10	100	25	10	20	1	Fast	14.1
						Slow	33.1
25.15	100	25	15	20	1	Fast	13.5
						Slow	32.1
25.20	100	25	20	20	1	Fast	12.3
						Slow	35.4
30.15	100	30	15	20	1	Fast	15.4
						Slow	40.1
30.20	100	30	20	20	1	Fast	10.0
						Slow	32.9

[a] The composition is referred to the phr of Phenoxy and Hycar, respectively, used.
[b] Cure cycles are discussed in the text.

Fast cure:

- Directly in an oven at 175°C for 75 min;
- From 175 to 210°C at 5°C/min;
- At 210°C for 30 min.

Slow cure:

- From room temperature to 175°C at 5°C/min;
- At 175°C for 75 min;
- From 175 to 210°C at 5°C/min;
- At 210°C for 30 min.

The effects caused by the different cure cycles on adhesive strength, transition temperatures, morphological structure, and fracture morphology were determined using the following techniques:

Adhesive Shear Strength

Single lap shear strengths were measured in accordance with ASTM D1002, using steel adherends (Fe P04) freshly pickled with a sulfonitric mixture.

Transmission Electron Microscopy (TEM)

Morphological–dimensional analysis was performed using a Philips EM300 TEM instrument. For observations, specimens were cut with an ultramicrotome (ULTRATOME III LKB) at room temperature; to better exhibit the phases present on the specimen, slices underwent to an oxidative treatment with vapors of a 4% aqueous solution of OsO_4 for several hours.

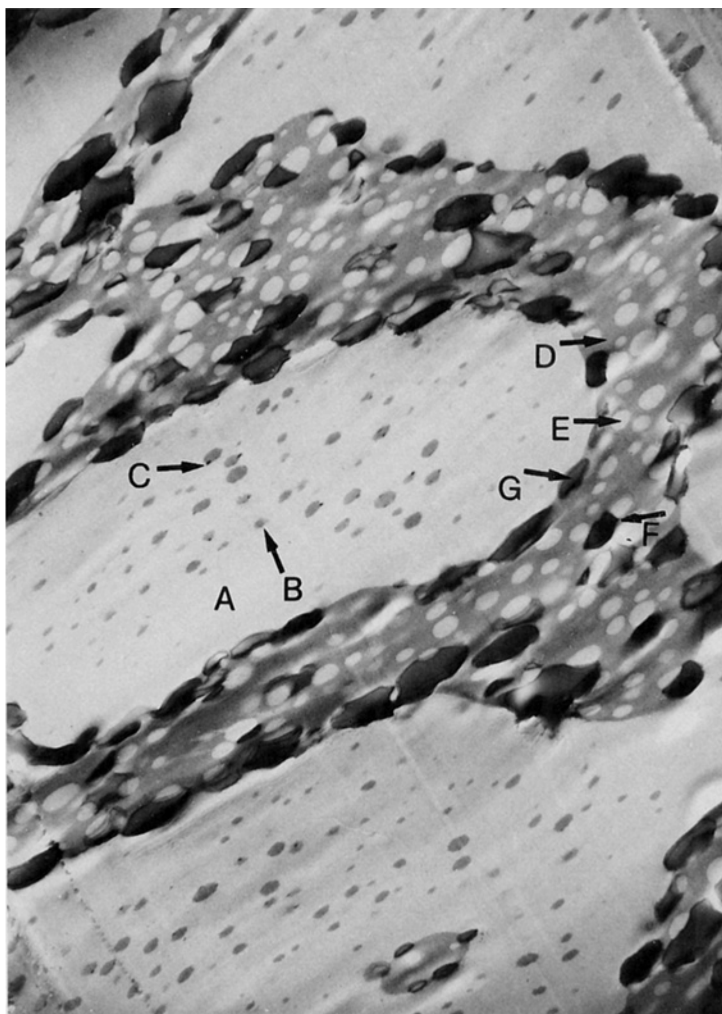

Figure 1 TEM micrograph of fast-cured adhesive 25.15 (magnification 6500×).

Scanning Electron Microscopy (SEM)

Scanning electron micrographs of fracture surfaces were obtained on a Cambridge Stereoscan 640 microscope, after sputter-coating with gold; cured specimens were fractured in liquid nitrogen.

Dynamic Mechanical Analysis (DMA)

DMA spectra were taken with a dynamic mechanical analyzer (Model 893, Dupont Instruments). Specimens (40 × 11 × 0.5 mm) were prepared by spreading a glass tape 8 cm long with a small amount of adhesive, previously kept at 50°C, to increase its fluidity. Specimens were stressed by oscillatory tension, with a constant oscillatory frequency of 1 Hz; a first scanning run was made to obtain cured materials, using the same cure cycle described above. An oscillatory amplitude of 0.4 mm was assumed for such experiments, whereas spectra of cured materials were recorded with an oscillatory amplitude of 0.3 mm.

RESULTS AND DISCUSSION

In Table I, lap shear strengths of joints after curing are reported. All joints cured following the slow cycle exhibited an adhesive strength much greater than those submitted to fast curing.

Morphological analysis on cured adhesives by TEM observations allowed us to determine the phase distribution in each system and the possible influence of the curing cycle length. Representative micrographs of adhesive samples after different cur-

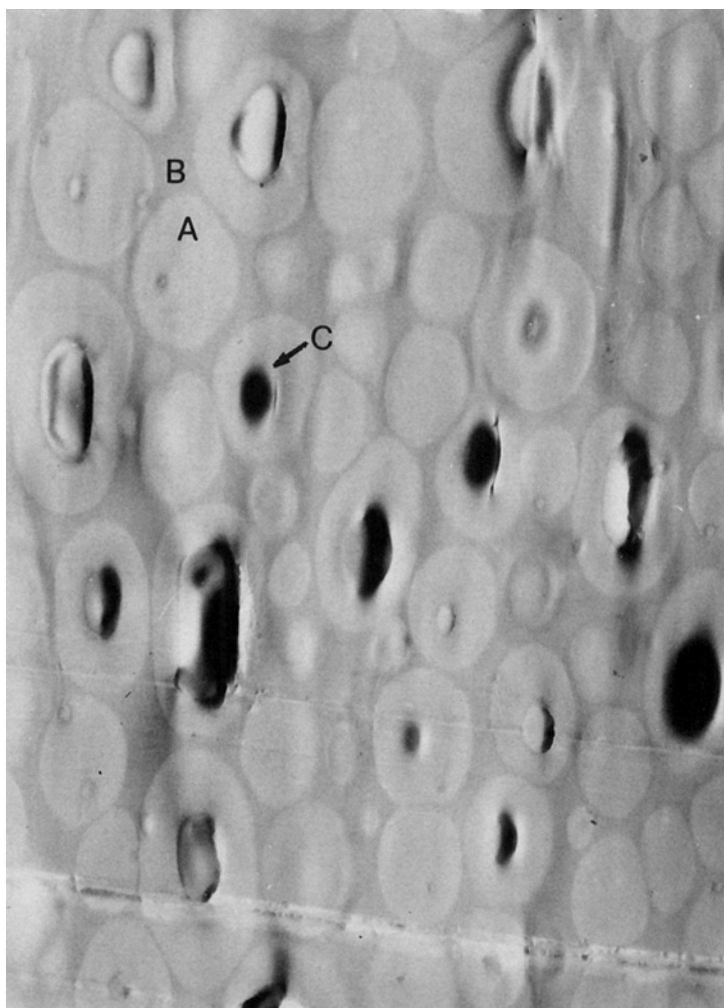

Figure 2 TEM micrograph of fast-cured adhesive 30.15 (magnification 10,000×).

ing cycles are shown in Figures 1–5. For the interpretation of TEM micrographs, it is necessary to take into account that the three main moieties (epoxy, Phenoxy, and rubber) react differently with OsO_4, assuming a different contrast in TEM micrographs.[22,23] In particular, the rubber phase, containing a high amount of insaturation, becomes dark (strong interaction) while Phenoxy remains light (weak interaction). Epoxy has an intermediate behavior, its contrast also being influenced by its role as a solvent of another moiety. A further criterion for phase identification is done by material composition: Extended phases (matrix or very large domains) should be constituted by epoxy, which is the dominant moiety in the mixture (at least 67% by weight, i.e., 100 to 50 phr).

Mixtures containing 25 phr of Phenoxy, i.e., 25.10, 25.15, and 25.20, cured by the fast cycle, show large light gray areas that correspond to the Phenoxy-rich epoxy resin (labeled A in Fig. 1, adhesive 25.15). In such areas, rubber-rich epoxy particles (dark gray, d = 0.1–0.5 μm, labeled B) and rubber particles (black globules, d = 0.05–0.1 μm, labeled C) are visible. Near this Phenoxy-rich epoxy phase, a second separated phase is present (dark gray, labeled D), likely constituted by a rubber-rich epoxy phase, in which both Phenoxy particles (light gray, d = 0.2–0.8 μm, labeled E) and rubber globular domains (black, d = 0.7–1 μm, labeled F) are visible. The Phenoxy-rich epoxy phase and the rubber-rich epoxy phases are interconnected and perfectly separated; at their interface, large rubber domains (black, d = 1–1.5 μm, labeled G) are present. By increasing the rubber concentration from 10 to 20 phr, an increase of dimension of particles, rather than of their number, is observed.

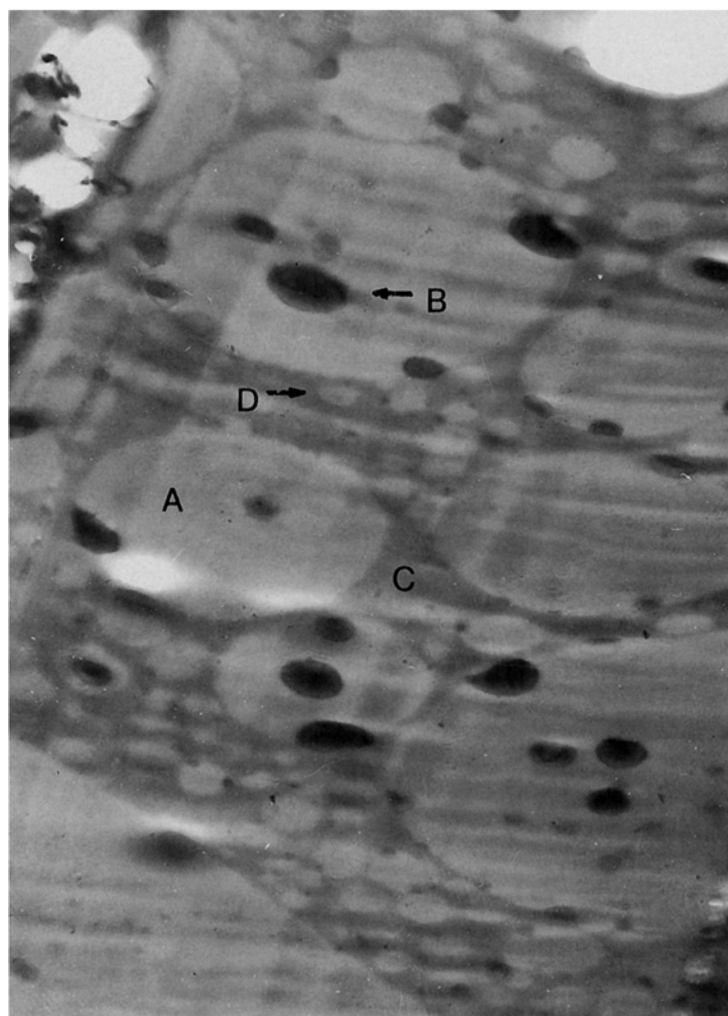

Figure 3 TEM micrograph of slow-cured adhesive 25.20 (magnification 10,000×).

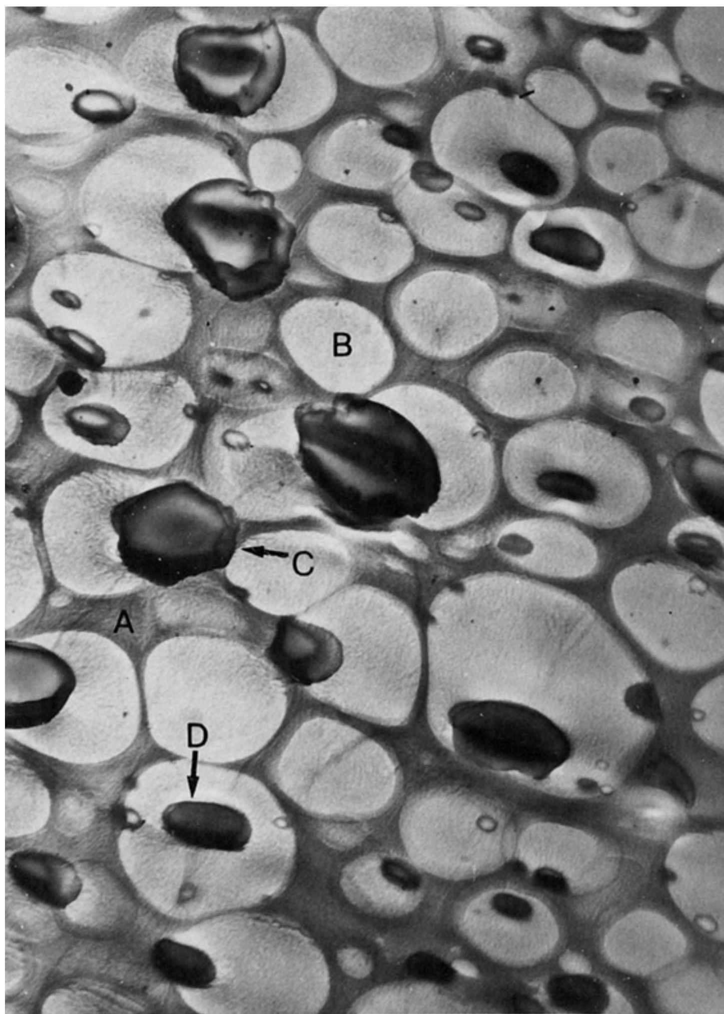

Figure 4 TEM micrograph of slow-cured adhesive 30.20 (magnification 10,000×).

Mixtures containing 30 phr of Phenoxy, i.e., 30.15 and 30.20, show a different morphology when cured following the fast cycle. Phenoxy-rich epoxy particles, assuming a light gray color (d = 0.5–2.0 μm, labeled A in Fig. 2, adhesive 30.15), are immersed in the rubber-rich epoxy matrix (dark gray color, labeled B). Rubber domains (d = 0.5–1.0 μm, labeled C) are localized into the A phase, forming a core-shell structure; no free rubber particles are observed.

Turning to the slow curing cycle, relevant changes in morphology occurred. In samples containing 25 phr of Phenoxy, i.e., 25.15 and 25.20, the interconnected structure is not yet observed; the Phenoxy-rich epoxy phase (light gray, labeled A in Figure 3, adhesive 25.20) is separated in spherical domains, having a diameter up to 7.5 μm and more; into them, rubber particles are observed (black, d = 0.05–0.15 μm, labeled B). Such large domains are immersed in a rubber-rich epoxy phase (dark gray, labeled C), where small Phenoxy-rich epoxy particles (light gray, d = 0.5–2.0 μm, labeled D) are also visible. Adhesives containing 30 phr of Phenoxy, i.e., 30.15 and 30.20 (Fig. 4, adhesive 30.15), cured following the slow cycle showed a simplified morphology. Phenoxy particles (light gray, d = 1–5 μm, labeled B) and rubber domains (black, d = 0.5–3 μm, labeled C) are separated from the epoxy matrix (labeled A). Phase separation is good; however, some rubber particles (d = 0.3–1 μm, labeled D) are still included in the Phenoxy globules, forming a core–shell structure. Adhesive 30.20 showed the core–shell structure in a more extensive way, due to the higher rubber content.

Since it was apparent that phase separation increased in the opposite sense of the fastness of curing cycle, a very slow cycle was carried out on samples 30.15 and 30.20, adopting the following thermal profile:

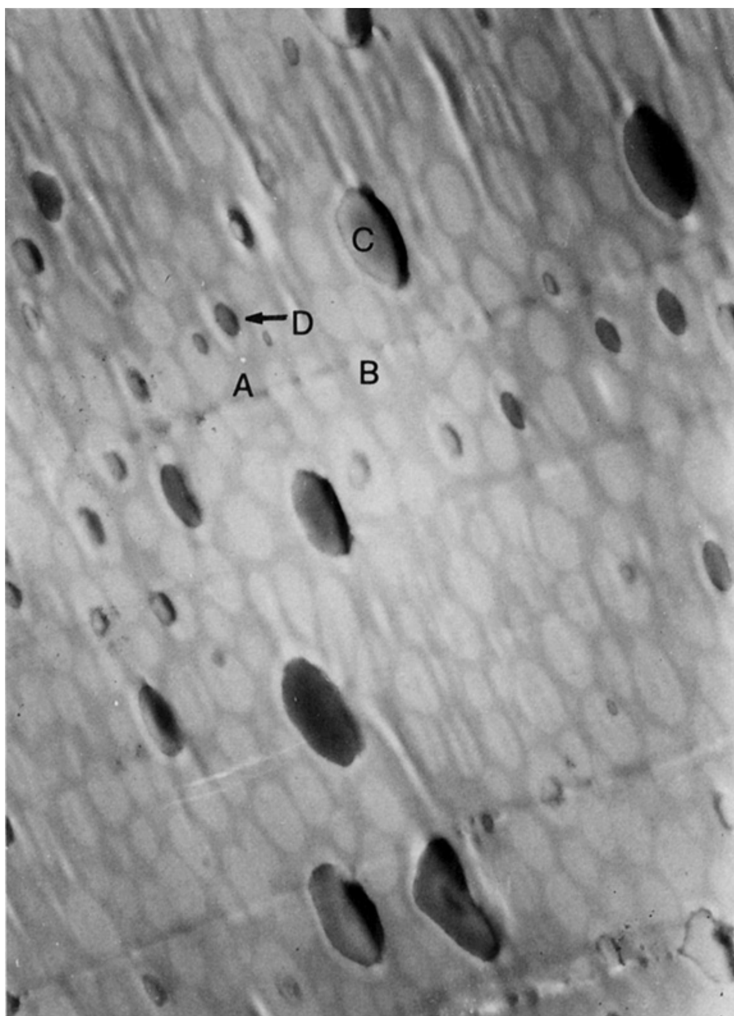

Figure 5 TEM micrograph of very slow cured adhesive 30.15 (magnification 10,000×).

- From room temperature to 175°C at 0.5°C/min;
- At 175°C for 75 min;
- From 175 to 210°C at 5°C/min;
- At 210°C for 30 min.

As expected, the above cycle caused a complete phase separation of Phenoxy and rubber particles (Fig. 5); the Phenoxy-rich epoxy phase (light gray, d = 0.8–1.6 μm, labeled B, adhesive 30.15) and the most of rubber particles (dark gray, d = 0.2–2.2 μm, labeled C) appear completely separated from the epoxy matrix, labeled A; only a very small number of rubber particles are still included in the Phenoxy-rich epoxy phase (dark gray globules, d = 0.05–0.25 μm, labeled D), giving rise to a core–shell structure.

Dynamic mechanical spectra of pure moieties (epoxy resin, Phenoxy, and CTBN rubber) have been collected together with those of several adhesives: 25.15 (fast curing), 30.15 (fast and slow curing), and 30.20 (fast, slow, and very slow curing). Transitions observed in the tan delta curves are collected in Table II, whereas some representative spectra are reported in Figure 6.

The unmodified epoxy resin gives a broad loss peak at 150°C, corresponding to its glass transition; Phenoxy shows a sharp peak at 105°C, again corresponding to the T_g. The rubber shows a very small peak around 0°C.

DMA spectra of cured blends show generally three peaks, corresponding approximately to those of unmixed components, and confirming the tendency to phase segregation during the curing process. The CTBN rubber peak is generally very small, whereas Phenoxy and epoxy peaks are more intense. The latter two are normally well separated in the tan delta curve; however, in a limited number of cases,

Table II Transitions of Adhesive Films from DMA Spectra

Sample	Curing Cycle	Transitions (°C)		
		Hycar	Phenoxy	Epoxy
Pure components	—	−10	105	150
25.15	Fast	−4	105	144
30.15	Fast	−3	112	139
30.15	Slow	−5	110	141
30.20	Fast	—	105	130
30.20	Slow	−4	102	130
30.20	Very slow	2	100	128

the peak of the thermoplastic moiety appears as a shoulder of that of the thermoset. As reported in Table II, the T_g values are marginally affected by composition and curing cycle. Variations observed can reflect the presence of limited amount of other components dissolved in the considered phase, as suggested in the interpretation of TEM micrographs. A systematic dependence upon composition and curing cycles was not found. The effect of curing cycle length is well described by the sequence of DMA spectra reported in Figure 6 for adhesive 30.20. Fast curing originates a tan delta curve where the Phenoxy peak is a shoulder of the broad epoxy peak. By slackening the curing process, in agreement with TEM observations, separated peaks are progressively obtained.

SEM examination of surfaces of adhesive 30.15 fractured at liquid nitrogen temperature are reported in Figure 7. A close examination of the fast cured sample [Fig. 7(a)] shows a rough surface, likely due to phase separation, confirming that the material is heterogeneous. The fracture surface of slowly cured sample [Fig. 7(b)] appears rougher and less brittle than the previous one; some plastically deformed material and crack branching (fracture planes located at different heights) are observed as well as several small holes, which were attributed to the dilatational deformation of the elastomer particles and shear yielding of the surrounding matrix. These observations agree well with TEM (Fig. 4), where an increase of separated rubber particles was observed. Finally, the fracture surface of the very slowly cured sample [Fig. 7(c)] is much rougher than the previous ones, revealing extensive shear yielding associated with holes of few micrometers and crack branching. The whole series of SEM observations suggests an increase of toughness connected to the increasing of cure cycle length.

CONCLUSIONS

This work has demonstrated that an epoxy matrix can be efficiently toughened by addition of both a thermoplastic and a rubber, obtaining a bimodal distribution of particles; this result is reached by acting on the cure cycle length. In fact, the key of an efficient toughening in resin blends seems to be a good phase separation, which was obtained by curing the blends following a slow cycle.

Fast-cured adhesives containing 25 phr of Phenoxy showed a phase separation of the spinodal type, leading to a single lap shear strength lower than 14 N/mm^2; in this case, the large areas observed at TEM appear insufficient to toughen the epoxy matrix.

Fast-cured adhesives containing 30 phr of Phenoxy gave again a single lap shear strength lower than 15 N/mm^2; TEM micrographs revealed that rubber particles are completely included in the Phenoxy-rich epoxy phase, forming a core–shell structure: With this particular morphology, it is likely that the rubber cannot develop its action. In fact, the absence of the rubber phase from the interface of epoxy–Phenoxy does not offer opposition to the crack propagation.

Slow-cured adhesives showed an optimum morphology and an efficient phase separation. On joints

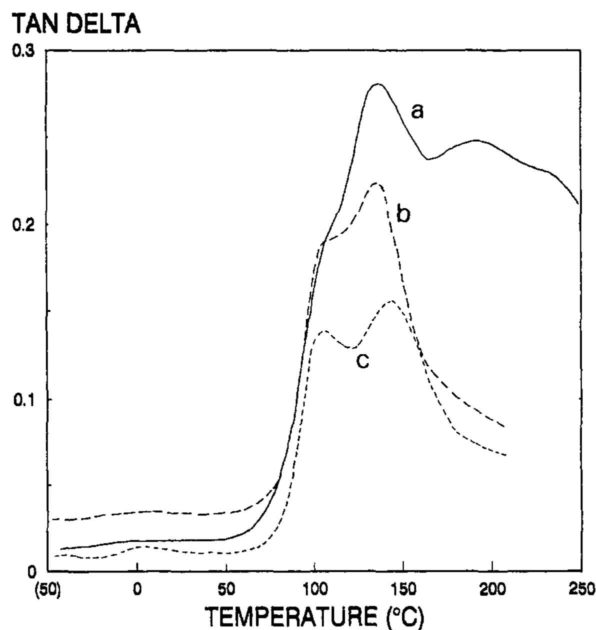

Figure 6 DMA spectrogram of adhesive 30.20 (a) after fast, (b) slow, and (c) very slow curing cycle.

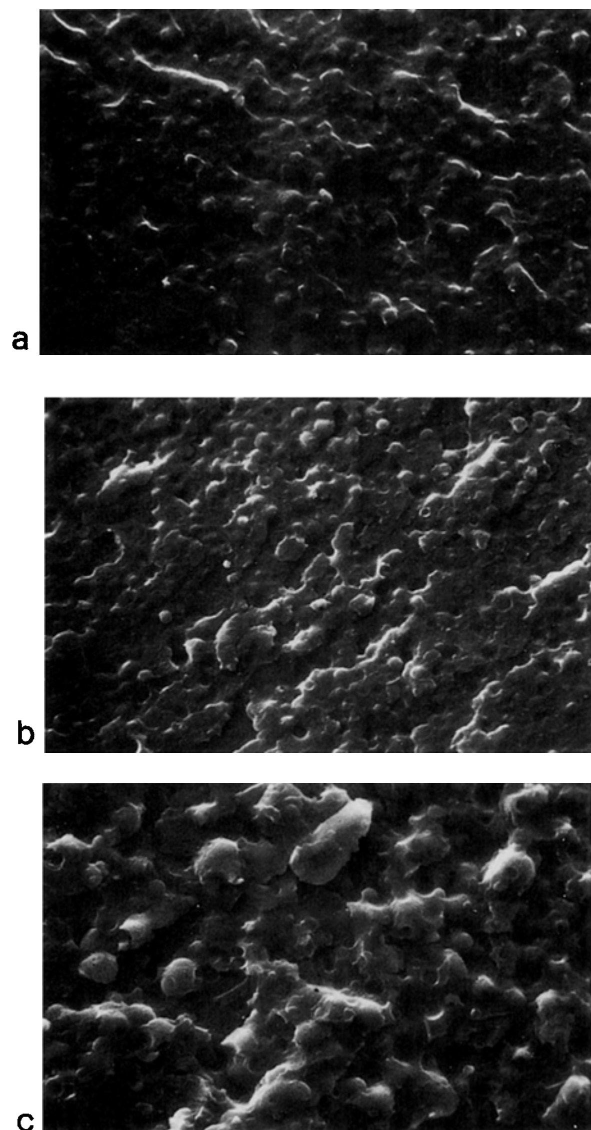

Figure 7 SEM micrographs of fracture surfaces of adhesive 30.15: (a) after the fast-curing cycle; (b) after the slow-curing cycle; (c) after the very slow curing cycle (magnification 700×).

made with these materials, a single lap shear strength up to 40 N/mm^2 was measured. In this case, the rubber could separate from the matrix before the occurrence of gelation, giving rise to an interesting triphase system.

Further studies are necessary to establish the influence of composition and cure cycle on other mechanical properties like peel strength and to check possible improvements of high-temperature behavior.

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