

# Thermoplastic-Thermosetting Hybrid Polymer Systems as Gap-Filling Adhesives

SHAUL M. AHARONI and DUSAN C. PREVORSEK, *Chemical Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960*

## Synopsis

The most important requirement for a hot melt adhesive to perform well in gap-filling applications is the ability to yield or flow under shrinkage tension which develops in the adhesives during cooling, while maintaining a satisfactory bond to the substrate. In addition, such an adhesive must have a high room temperature viscosity and high green strength to effect an acceptable bond before curing. We found that the required combination of properties for the gap-filling applications can be achieved with interpenetrating networks of selected thermoset-thermoplastic polymers. The best results were obtained with systems consisting of an amorphous polyester and an epoxy blend. The properties of these adhesives depend on numerous variables. This study concerns the three composition variables which appeared particularly important in the performance of these adhesives: (1) epoxy-polyester ratio, (2) molecular weight of the epoxy system, and (3) the quality of dispersion.

## INTRODUCTION

The advantages of hot-melt adhesives in comparison with solvent-based or thermosetting adhesives are well known. Improved understanding of structure-property relationships in adhesive performance, new polymerization techniques and the necessity to avoid solvents as health hazards, etc., are some of the factors which contributed to the rapid penetration of hot melt adhesives in areas previously held by multicomponent systems.

There remains one major field of application which appears to be most suitable for a hot-melt adhesive. The most important characteristic of these applications is a constraint in dimensions, so that the joined surfaces cannot approach one another upon shrinkage of the adhesive inbetween them on cooling. A typical example of such a configuration is tubular adhesive joint between two concentric cylinders. The gap between the surfaces to be bonded was, in this case, maintained at about 5–7 mils.

In spite of considerable new knowledge in the chemistry and physics of adhesion, no inroads were made to date to solve effectively the problem of such configurations by means of hot-melt adhesives. The major problem of these adhesives is large contraction during cooling from the melt. This contraction frequently leads to a delamination of the joint surfaces with the application of stress.

The severity of thermally induced stresses which exist in such joints made with hot-melt adhesives can best be illustrated by comparing, in the following two examples, the performance of a standard lap shear joint and a tubular joint. (i) An aluminum-aluminum lap shear joint was prepared using a polyester hot-melt adhesive. The application temperature was about 220°C. After cooling the joint had a lap shear strength of ca. 700 psi at room temperature, and ca. 500 psi at –20°C. When the same adhesive was applied to a cylindrical joint of the same

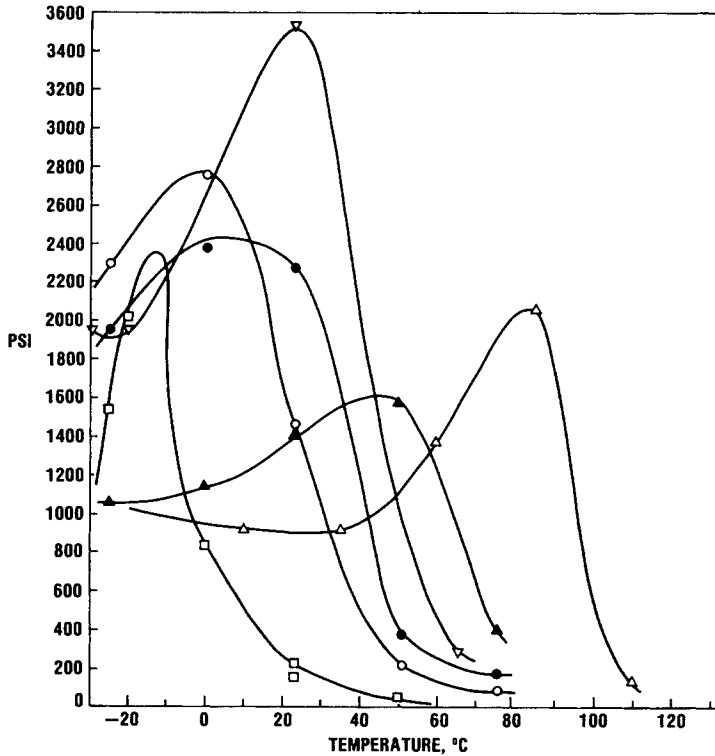


Fig. 1. Lap shear bond strength as a function of adhesive composition for the system Polyester A/epoxy. □ Polyester A, pure; △ epoxy blend, pure, cured; ○ 1:3 epoxy blend/polyester, cured; ● 1:1 epoxy blend/polyester, cured, phase separated; ▽ 1:1 epoxy blend/polyester, cured, solid solution; ▲ 3:1 epoxy blend/polyester, cured.

area, and the joint is cooled to  $-20^{\circ}\text{C}$ , the joint failed under no external stress because of cracking introduced by thermally induced stresses. (ii) A copolyester consisting of 60–40 terephthalic/isophthalic acid and ethylene glycol with a  $T_g$  of about  $70^{\circ}\text{C}$ , shows a lap shear joint strength of about 2200 psi at  $70^{\circ}\text{C}$  and room temperature strength of about 1000 psi. In the tubular type joint, however, the

TABLE I  
Lap Shear Strength of Several Adhesive Compositions

Code <sup>a</sup>	Procedure	Strength in psi at $23^{\circ}\text{C}$
I	"Solid solution"	2700
	melt blend	2050
II	"Solid solution"	1450
	melt blend	930
III	"Solid solution"	3580
	melt blend	2665
IV	"Solid solution"	2310
	melt blend	1930

<sup>a</sup> All adhesive systems are copolyester/epoxy blend preparations, each cured at its optimal temperature to its optimal duration.

TABLE II  
Ultimate Bond Strength at Various Temperatures, psi

Test	Temperature °C	System I	System II	System III
Green strength, lap shear joint	23	1260	1790	—
Optimal lap shear joint	-20	2820	2870	2200
Optimal lap shear joint	23	2950	2370	3760
Optimal lap shear joint	65	570	380	700
Optimal tubular joint	-20	1610	2050	—
Optimal tubular joint	23	1360	1130	1430
Optimal tubular joint	65	700	220	—

failure due to thermally induced shear cracks occurs already at room temperature.

The most important requirement for a hot-melt adhesive to perform well in these applications is the ability to yield or flow under the shrinkage tension which develops in the adhesives during cooling, while maintaining a satisfactory bond to the substrate. In addition, such an adhesive must have a high room temperature viscosity and high green strength to effect an acceptable bond before curing.

At the onset of this work it was found that the required combination of properties may be achieved by systems comprised of high molecular weight (*M*) polyester and an epoxy blend. The effects of three compositional variables on the performance of gap-filling adhesives were qualitatively studied: (a) epoxy-polyester ratio, (b) molecular weight of the epoxy ingredient, and (c) the quality of dispersion. In the following, the performance and characterization of the systems in question will be discussed.

## EXPERIMENTAL

The solvents, reagents, and crosslinkable polymers were used as received. The polyesters described in this study were all prepared by a common melt-condensation procedure.<sup>1</sup> Mechanical tests were performed in an Instron Testing

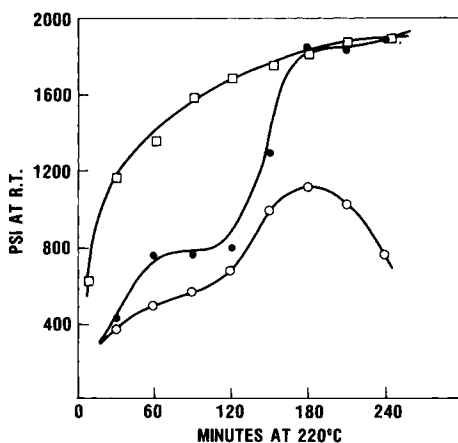


Fig. 2. Lap shear bond strength as a function of curing time for epoxy systems. ○ Phenoxy alone; ● 1:1 phenoxy/low-*M* epoxy; □ 2:1:1 phenoxy/intermediate-*M* epoxy/low-*M* epoxy.

Machine. All lap shear joints were between aluminum metal strips 1 in. wide and 0.071 in. thick. The strips were solvent wiped and the overlap was 1 in. Both these facts tend to reduce the psi values of the bond strength relative to the comparable ASTM test procedure D1002-64. The tubular joints were also of aluminum, with 1 in. depth and one inch circumference; exactly the same joint area as the lap shear joints. Electron micrographs,<sup>2,3</sup> wide-angle x-ray diffraction patterns<sup>4</sup> and thermograms<sup>5</sup> were obtained as is customary in the art. An extensive list of references pertaining to the methodology of various techniques used in this study may be found in the book of Manson and Sperling.<sup>6</sup>

Several polyester random copolymers were prepared and successfully incorporated in the polyester-epoxy mixtures. All these polyesters were amorphous or crystallized rather slowly to a low level of crystallinity.

The reagents employed in the polymerization of two typical copolyesters are as follows:

Polyester A: 0.37 moles dimethyl terephthalate, 0.16 moles dimethyl isophthalate, 0.03 moles dimethyl sebacate, 1.13 moles ethylene glycol, 0.03 moles poly(tetramethylene ether)glycol of  $M = 1000$ , and 0.103 moles resorcinol di( $\beta$ -hydroxyethyl)ether.

Polyester B: 0.34 moles dimethyl terephthalate, 0.16 moles dimethyl isophthalate, 0.25 moles dimethyl sebacate, and 1.70 moles ethylene glycol.

It was found that reasonable compatibility between the copolyesters and the epoxy blend was achieved only when the molecular weight distribution of the latter was extremely broad. The composition of one particularly successful epoxy blend is: 50 wt. % phenoxy (Union Carbide PKHH grade,  $M_w \cong 80,000$ ,  $M_n = 23,000$ ), 40% intermediate- $M$  epoxy (Ciba-Geigy Araldite 6099 grade  $M_w \sim 5000-8000$ ), and 10% low- $M$  epoxy (Ciba-Geigy Araldite 6010 grade  $M_w = 370-390$ ).

The intimate mixtures of copolyester with epoxy blend were prepared in the following manner: about equal amounts of the copolyester and the epoxy blend were separately dissolved with heating in a chlorinated solvent such as tetrachloroethane or dichloroethane to yield 10% solutions. Once fully dissolved, the warm solutions were mixed to yield a uniform, transparent, solution. The chlorinated solvent was removed from the intimate polymer mixture by one of two means: fast evaporation of the solvent off the heated solution under a forced air draft, or precipitation of the polymers by pouring the solution into a rapidly stirred large excess of petroleum ether.

The dried solid polymeric products were molded into films whose clarity was indicative of the copolyester-epoxy blend compatibility. Typical molding conditions were 140°C for up to 90 sec, with subsequent quick quench to room temperature. The usual film thickness was about 10 mils. From the films 1 in.<sup>2</sup> squares were cut and used to effect both the lap shear and the tubular joints. These were then cured at a temperature for a duration optimized for each system. The lap shear joints were tested according to ASTM test procedure D1002-64 with the exception that the overlap in our samples was 1 in. instead of the recommended  $\frac{1}{2}$  in. The tubular joints were tested in a procedure similar to ASTM D1002, taking into cognizance the fact that the joints are tubular and that the overlap per joint is 1 in.<sup>2</sup>.

## RESULTS

Several preliminary experiments have indicated that polyesters, homopolymers or copolymers, that usually possess a high degree of crystallinity, tend to crystallize and phase separate out of solution in epoxy-containing solvent or from the melt blend in epoxy. The strength of bonds prepared from such systems was remarkably low, and the bonds could be easily broken by hand.

When amorphous polyesters or copolyesters were mixed with epoxy, the large majority phase separated upon cooling from the melt or upon the removal of the solvent. Here, again, the mechanical strength of the bonds was low, in the order of 250–400 psi. Several copolyesters, all tending in the pure form towards very low levels of crystallinity and having very low rates of crystallization, were found, nonetheless, to be able to form intimate mixtures with epoxy. These intimate mixtures showed marked improvement in their bond performance, as compared with the separating blends described above, yielding bond strengths several orders of magnitude larger (up to 3760 psi at room temperature) than the latter mixtures. Among the highly performing intimate mixtures it was found that mixtures in the range of 40:60–60:40 copolyester/epoxy yielded the best performance. Mixtures richer in copolyester tended to be relatively soft and the bonds yielded at low ultimate strengths, in the range of 1400–1600 psi at room temperature. Mixtures richer in epoxy (epoxy content higher than 60:40 epoxy/

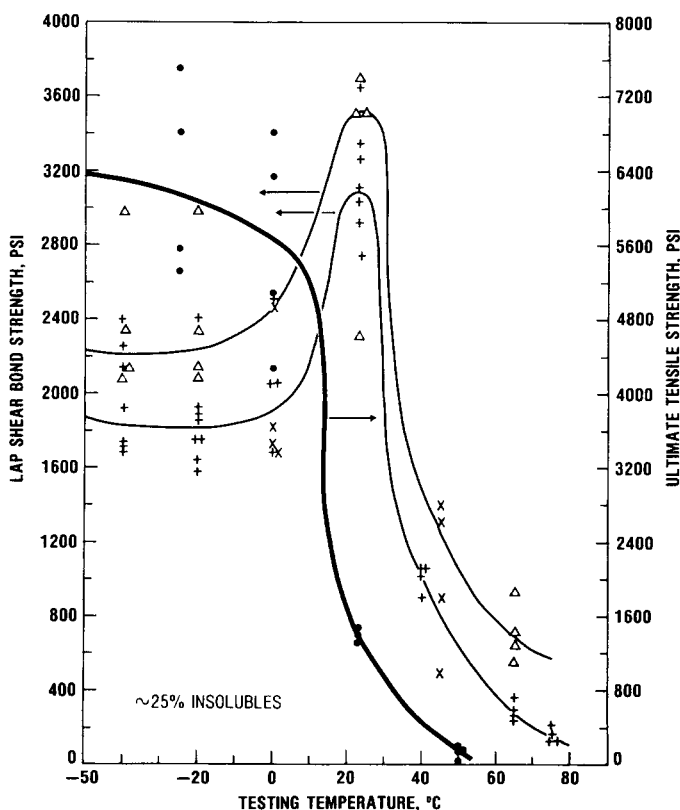


Fig. 3. Lap shear bond strength and ultimate tensile strength of the adhesive system as a function of testing temperature. Low level of crosslinking, ~25% insolubles. ● +45 min cure; ×75 min cure; Δ 90 min cure.

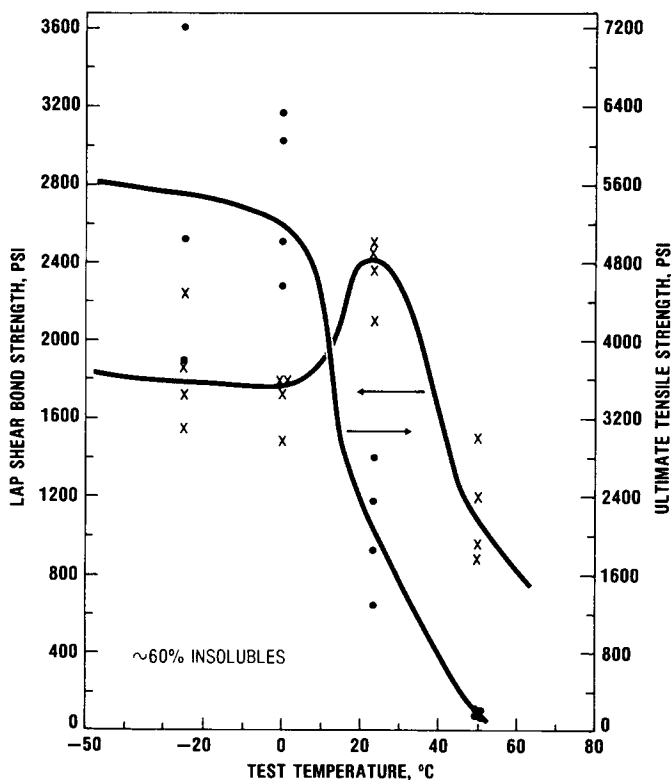


Fig. 4. Lap shear bond strength and ultimate tensile strength of the adhesive system as a function of testing temperature. Medium level of crosslinking, ~60% insolubles. ● ×45 min cure.

copolyester) tended to become brittle and the bonds failed at ultimate strength of about 1500 psi in a brittle fashion.

The following results are limited, therefore, to copolyester/epoxy compositions revolving around 50:50, unless specified otherwise.

Results of lap shear bond strength of changing adhesive composition are plotted in Figure 1 as a function of the testing temperature. It is obvious that each composition passes through a strong maximum in its bond strength value. Thermal scans of the cured materials indicate that the glass transition temperature  $T_g$  of each composition is in excellent correspondence with the peak in lap shear bond strength of the particular composition. The data in Figure 1 belong to the pure polyester A, described in the Experimental section, whose  $T_g = -15^\circ\text{C}$ , and to the epoxy system described therein, whose  $T_g$  after curing is  $85^\circ\text{C}$ . In the term "curing" we mean only exposure to heat in the absence of amine or other crosslinking agents; whenever added, their addition, will be specifically mentioned.

Comparison of the same 1:1 composition of polyester A/epoxy blend exhibiting, on one hand, the behavior of a solid solution and, on the other, revealing minute phase separation, indicates that at room temperature (the  $T_g$  of both samples was  $27^\circ\text{C}$ ) the "solid solution" sample has a lap shear bond strength much higher than the "phase separated" sample. This observation was found to be true for all the systems tried: the more uniform the material, on a microscopic level, the better is its performance relative to its nonuniform counterpart. A performance

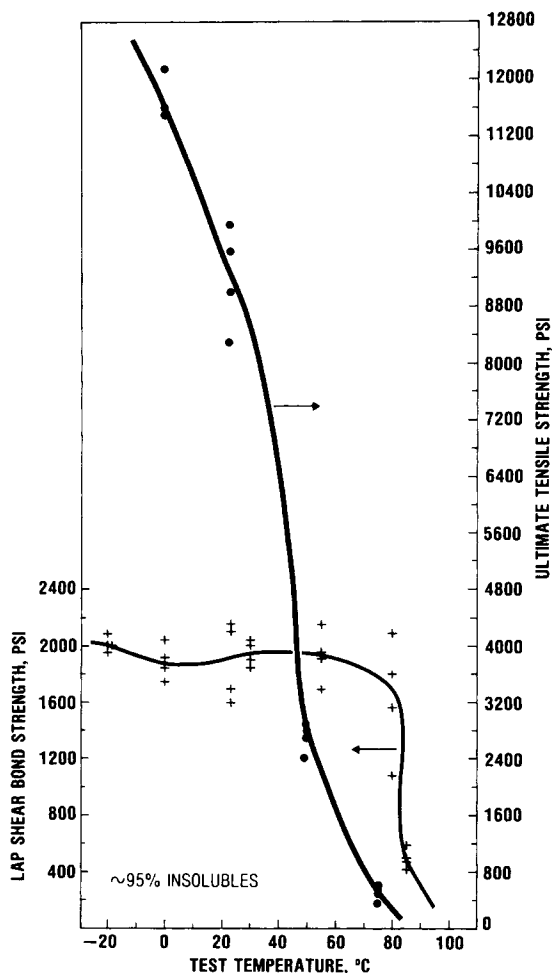


Fig. 5. Lap shear bond strength and ultimate tensile strength of the adhesive system as a function of testing temperature. High level of crosslinking, ~95% insolubles. ● +75 min cure.

comparison between several systems prepared by melt blending and according to our procedure is given in Table I.

Other systems, less compatible than the system polyester A/epoxy blend discussed above, show a significantly lower maximum bond strength, and a narrower composition range in which reasonable bond strengths, of the order of 2000 psi, are obtainable.

In instances where the polyester tends to crystallize out of the mixture, the lap shear bond strength of the corresponding joint falls to the order of 500 psi, significantly lower than the strengths of the bonds effected with either of the pure polyester or epoxy components.

Even though the adhesive systems described above performed much better in the lap shear and the fixed-gap tubular joints, their performance in the fixed-gap configuration was not as good as in the lap-shear joints. This is, of course, due to the fact that in the former configuration the bonded substrates can not approach one another during the cooling of the adhesive, thus increasing the internal stresses around microheterogeneities in the adhesive layer and reducing its ultimate strength.

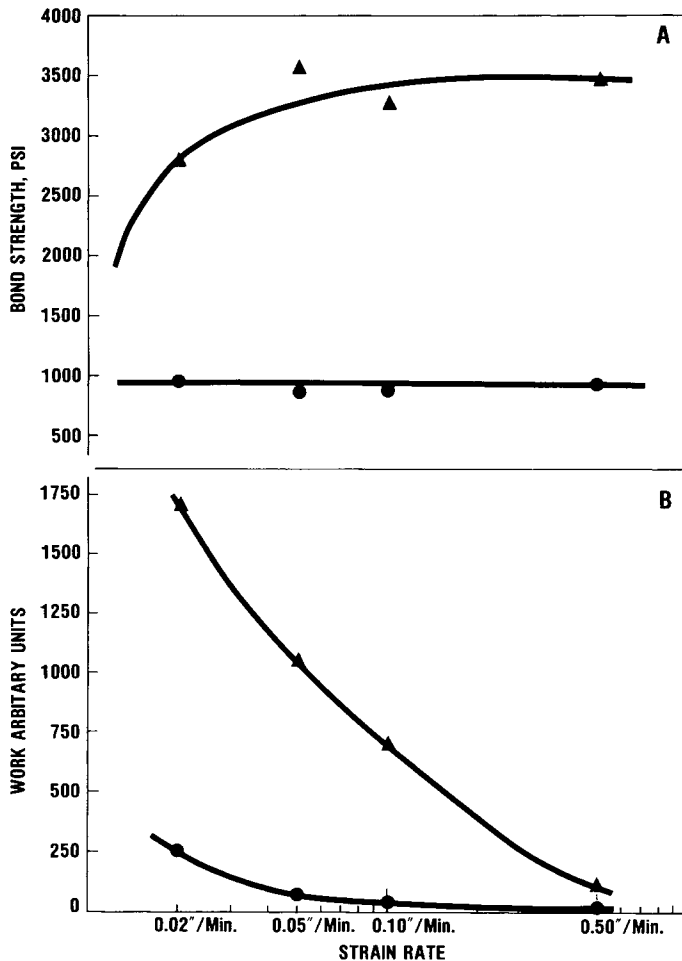


Fig. 6. Strain rate dependence of (A) bond strength, and (B) work to break, of epoxy blend, cured (●) and copolyester/epoxy blend, cured (▲).

The results of several adhesive systems are presented in Table II. Here the "green strength" stands for the strength of the uncured system. Other values are for systems cured at their respective optimal temperature and duration, but without the addition of any curing agents.

The internal composition of the epoxy blend was found to be of major importance. The absence of any of the three components was noticeable through any of the following deleterious effects: poor wetting ability of the substrate and consequential delamination; very low green strength; excessively long curing times leading to marginal results; excessively long curing times before reasonable bond strength is developed. A graphical description of a typical epoxy blend system is presented in Figure 2. Here the bonds are lap shear joints and were effected with the epoxy blend alone. The cure was at 220°C and the bond strength testing was at room temperature. Each point in the figure is an average of not less than four closely spaced individual results.

The improvement in bond strength with curing was characteristic of all the successful adhesive systems. In several systems short cure times of 3–5 min were sufficient to develop lap shear joint strengths of over 1000 psi. The curing



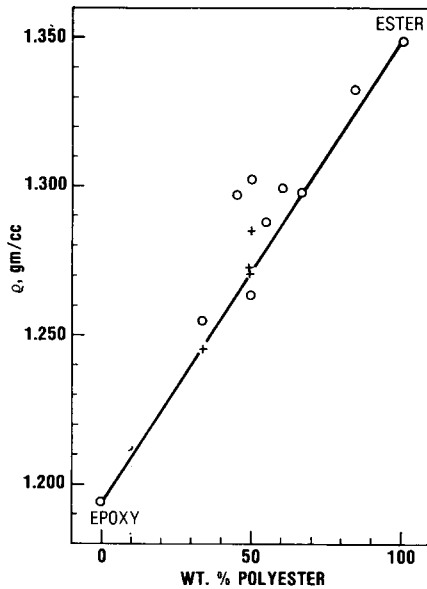


Fig. 7. Density as a function of composition for the copolyester B/epoxy blend system. + uncured; O cured.

process was found to be accompanied by some crosslinking. The amount of crosslinking was estimated from sol-gel fractionation in refluxing chloroform.

It was found that "excessive" crosslinking tended to lower the ultimate strength of the bond in the temperature interval of peak performance, while not affecting the strength significantly either below or above this temperature interval. The

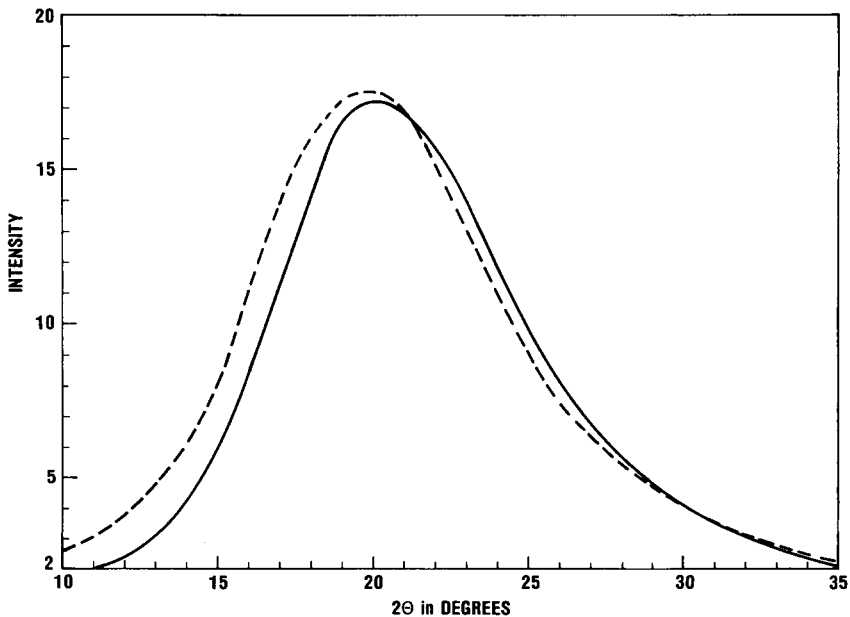


Fig. 8. X-Ray amorphous halo intensity for the system copolyester B/epoxy blend. ---, algebraic sum of the two ingredients in 1:1 proportion. —, experimental result for the solid solution having a 1:1 ratio of ingredients and dried at 140°C for 90 min.

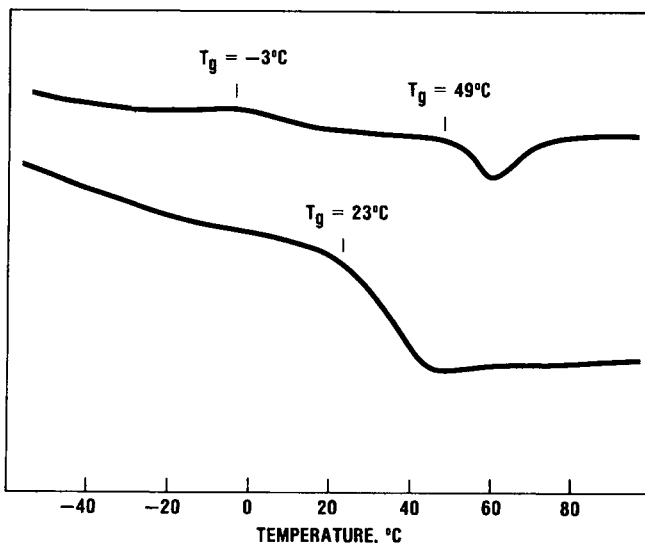


Fig. 9. Thermal scans of an epoxy blend/copolyester system. Top curve:  $T_g$  of copolyester is  $-3^\circ\text{C}$  and that of epoxy system is  $49^\circ\text{C}$ . Bottom curve: The above system after exposure to  $140^\circ\text{C}$  for 90 sec, only one  $T_g$ , at  $23^\circ\text{C}$  is discernible.

amount of crosslinking yielding the best adhesive joint results corresponds to about 25% insolubles and 75% solubles in sol/gel fractionation. It is of interest to note that the ratio of polyester to epoxy in the soluble fraction was not much higher than the ratio in the insoluble part. Ultimate tensile strengths of the cured adhesive films were determined as a function of temperature for each of the materials. In Figure 3 one observes that at  $T_g$  the ultimate tensile strength of the adhesive material with 25% insolubles drops precipitously while the bond strength passes through a major peak. When the amount of insolubles increases to 60%, in Figure 4, the bond strength at peak performance dropped markedly, from about 3600 psi to about 2400 psi, while the ultimate tensile strength of the adhesive material below  $T_g$  increased slightly. A different system, with higher  $T_g$ , was cured to yield 95% insolubles. The results of its mechanical testing are presented in Figure 5. Here the peak in lap shear bond strength disappeared completely, yielding an essentially uniform performance in the temperature range below  $T_g$ . This is typical of crosslinked systems.<sup>7</sup> Concomitantly, the ultimate tensile strength of the material in the  $T < T_g$  increased significantly over the comparable values of the less crosslinked systems.

From the facts that optimally cured systems perform better than in the "green" state, and that when excessive crosslinking takes place the performance is poorer than for the optimal systems, one may conclude that a relatively low degree of crosslinking, one that allows large scale chain mobility at  $T_g$ , is necessary for maximum performance of the adhesive joints.

All of the above mechanical data were obtained at a strain rate of 0.05 in./min. Tests of the strain rate dependence of the ultimate bond strength and work done to break the bond were conducted on several systems at room temperature. The results in Figure 6 are typical. Here one notes that the ultimate bond strength of the cured epoxy blend is strain rate independent, while the work to break such a bond is mildly dependent on the strain rate. In the case of a cured "solid solution" copolyester/epoxy blend, at its peak performance, a mild dependence



Fig. 10. Transmission electron microscope scan of the epoxy blend/copolyester system described in Figure 9, prior to heating.

on strain rate of the bond strength but a strong dependence of the work to break are manifested. It is apparent that in the "solid solution" copolyester/epoxy system, it is the polyester component that distributes the stress efficiently throughout the bulk of the polymer, and imparts to it its excellent load-bearing capacity.

### STRUCTURAL CHARACTERISTICS

Several techniques were used in order to determine whether the adhesive systems reached or were approaching the state of "solid solution." These were density measurements, wide-angle x-ray scans, thermal scans, and electron microscopy.

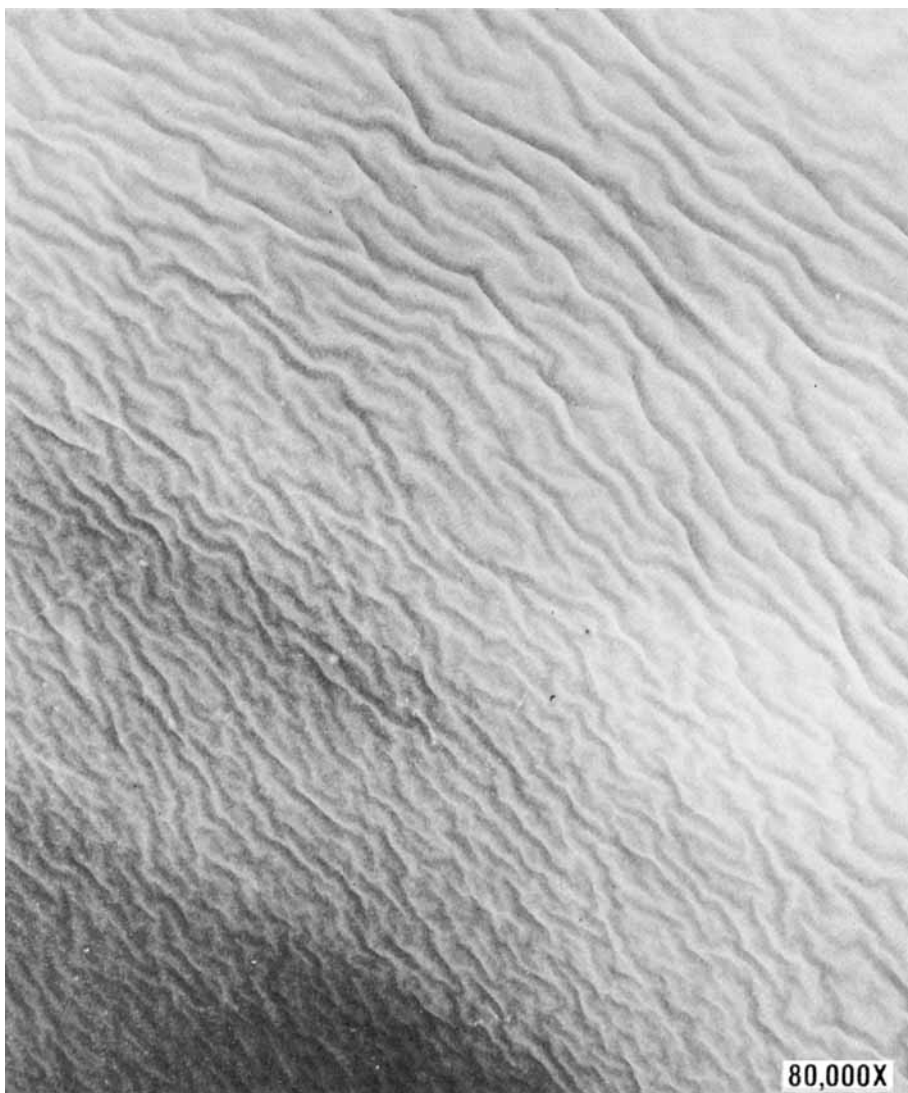


Fig. 11. Transmission electron microscope scan of the epoxy blend/copolyester system described in Figure 9, after heating at 140°C for 90 sec.

In the density measurements, the densities of the carefully dried systems and their components were measured in density gradient columns. For each system a single column was used. From the knowledge of the proportions of the polyester and epoxy blend, and the densities of these ingredients, a density for each system was calculated on the assumption of linear additivity of densities. These were compared with the experimentally determined ones. It was found that in case of compatibility, the experimental densities were higher than the calculated ones, while in case of incompatibility and phase separation the experimental and calculated values were about the same. In Figure 7, a typical example is presented. It is apparent that the range of best compatibility is in the close neighborhood of 1:1 copolyester to epoxy blend. Whenever a system was compatible, it was found that the range of compatibility straddled the 1:1 ratio.

Compatibility by means of wide-angle x-ray scans was determined in the following manner: scans of both components were obtained. Unless a minor amount of crystallinity in the copolyester manifested itself by minor humps on the scattered intensity curve, the curves were of the smooth appearance commonly encountered in amorphous polymers. Normalizing according to the ratio of copolyester to epoxy blend, an algebraic sum of the scattering curves of the individual components was synthesized. This algebraic sum curve was compared with the experimentally obtained intensity curve for the particular composition in mind. When the components were incompatible and phase separation occurred, the algebraic and experimental curves superimposed one on the other. When the components were compatible and formed a solid solution, the peak of the experimental curve appeared at higher angle than the peak of the algebraic curve. This indicates a smaller average intersegmental distance than is expected from simple mathematical averaging. The width of the scattering curve at half-height, also, was narrower for the experimental curve of each solid solution than the half-height width of the algebraic curve. The relative narrowness of the experimental peak indicates too that there is less variability in the intersegmental distances. A typical experimental-algebraic pair of curves is shown in Figure 8. From the smaller average size of intersegmental distance and from the narrower distribution of these distances, one gathers that indeed the polymers are mixed on a molecular level in the solid solutions. The interpolymer interaction, on the molecular level, is stronger than the intrapolymer interaction.

Another method to determine the formation of amorphous polymer-polymer solid solution is by means of thermal scans. Here one observes a single  $T_g$  point for the solid solution instead of two  $T_g$  points for a phase separated bicomponent system. Figure 9 is typical of such a system. The scans were performed on a duPont 990 DSC instrument at  $20^\circ/\text{min}$  heating rate. One deals here with a copolyester whose  $T_g = -3^\circ\text{C}$  and an epoxy blend whose  $T_g$  in the cured form is  $49^\circ\text{C}$ . The top curve reflects the fact that at this point the system is phase separated. Transmission electron microscopy (Fig. 10) of microtomed sections indicated that at this point particles, ranging in size from  $1.5\ \mu\text{m}$  down to  $0.3\ \mu\text{m}$  of the denser polyester were present in the lighter epoxy blend. These are similar to the particles observed in interpenetrating polymer networks.<sup>6</sup> Upon exposure of the system to  $140^\circ\text{C}$  for 90 sec, during the film molding operation, the system exhibited only one  $T_g$  point, at  $23^\circ\text{C}$  (lower curve in Fig. 9), and the microscopy scans revealed that the two-phase system became homogeneous down to a scale of  $100\ \text{\AA}$  (Fig. 11).

Several of the above-mentioned techniques, i.e., density measurements, thermal scans and electron microscopy, are considered as helpful in the determination of whether the system is a solid solution or not.<sup>8</sup> From the observations above one may conclude that in quite a few of the polyester/epoxy systems a state of solid solution does exist. Correlation with the mechanical tests of the adhesive bonds indicates that the systems exhibiting the best performance are those which exist in a state of solid solution.

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