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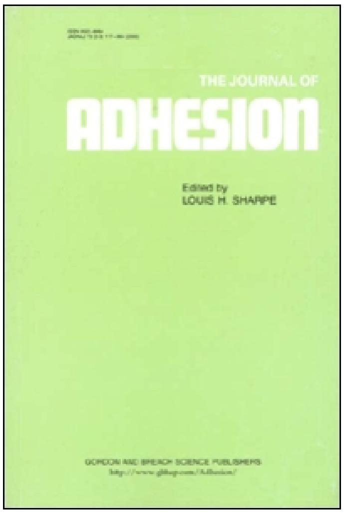

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James Economy[a]; Tania Gogeva[a]; Vijay Habbu[a]
[a] Department of Materials Science & Engineering, University of Illinois, Urbana, IL, U.S.A.

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Liquid Crystalline Copolyesters as High Temperature Adhesives for Aluminum

JAMES ECONOMY*, TANIA GOGEVA and VIJAY HABBU

Department of Materials Science & Engineering, University of Illinois, 1304 W. Green Street, Urbana, IL 61801, U.S.A.

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A liquid crystalline copolyester consisting of 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid, with a composition (73:27) was studied as a melt processible, high temperature adhesive. The polymer was used as received without any additional treatment and was applied on an aluminum substrate as a film. The adhesive joints were prepared using different processing conditions and good bonding between the two polymer surfaces was observed under most of these conditions. The reliability of the adhesive bond was estimated by measuring the lap shear strength (1.4–1.6 Ksi) and the crack propagation in the wedge test. Improved adhesion (2 times) over epoxy adhesives, applied on the same substrate, was observed when tested at room temperature and there was no significant decrease in the lap shear strength in the range RT–180°C. The post-failure surfaces were studied with SEM and it was observed that separation occurred within the adhesive.

KEY WORDS adhesive bonding; aluminum; copolyester; 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid; lap shear strength; SEM.

INTRODUCTION

Use of liquid crystalline (LC) aromatic copolyesters as structural adhesives has not been examined to date in any detail. On the other hand, these rod-like polymers are of considerable interest because of their excellent mechanical and thermal properties and high melt flow under shear.[1–6] One such system, a copolyester of p-hydroxybenzoic acid with biphenol terephthalate (Xydar®), has been shown to retain a significant percentage of its mechanical properties up to 350°C.[6] Thus, it would be highly desirable to design LC copolyesters for use as high temperature structural adhesives. Currently there are very few systems available commercially for extended use in the temperature range of 150°–340°C. For intermediate temperatures (up to 200°C) the adhesive systems that are available include unmodified epoxy, epoxy phenolic and nitrile phenolic. Typically their processing conditions are similar to conventional adhesives, *i.e.* curing at ~175°C and moderate pressures (up to 100 psi).[7] Adhesives for higher use temperatures of 200° to 340°C include

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*To whom all correspondence should be addressed.

polyimide, polyquinoxaline and polybenzimidazoles. These systems require significantly different processing; *e.g.* higher curing temperatures of 343°C, venting or permanent vacuum (to control volatiles) and they should be used with considerable caution.[7] These high temperature adhesives are applied after the substrate is pretreated (most often anodized)[8] and covered with an adhesive primer. They also require corrosion-inhibiting additives and a diluting solvent and display a limited shelf-life.[7]

One possible reason that the LC polyesters have not been evaluated as potential adhesives is the observation that good adhesion between stiff extended chain polymers such as polyimides can only be achieved if the polymer chains penetrate up to several hundred Å across the interface between the coatings.[9] Presumably the rod-like nature of the LC polyesters would further reduce the potential for chain entanglement. On the other hand, in some of our recent work we have shown that the rod-like aromatic copolyesters can undergo very rapid interchain transesterification reactions at elevated temperatures.[4] If such reactions were to occur at the interface between two LC polyester coatings, one would expect to produce a homogeneous composition across the interface between the two coatings. It was, in fact, these observations that led us to pursue the study of the LC polyesters as potential high temperature, structural adhesives.

In this paper, we report on the successful evaluation of an LC copolyester of 73/27 p-hydroxybenzoic acid, 2,6-hydroxynaphthoic acid (HBA/HNA) as a structural adhesive for aluminum.

EXPERIMENTAL

Materials

A copolyester of HBA:HNA = 73:27 (molar %), Vectra A-950®, with a melting temperature at about 280°C, was obtained from Hoechst-Celanese. The polymer was received in the form of granules and was ground before use. A commercial 5-minute curing epoxy adhesive, #10-114 (GC/Thorsen, Rockford, Illinois, U.S.A.), was used as a control. The material used as the adherend (the substrate) was an aluminum alloy 2024 T-3.

Sample Preparation

Specimens were prepared in accordance with ASTM D 1002–83, Strength Properties of Adhesives in Shear by Tension Loading (lap shear joint metal-to-metal) and ASTM D 3762–79, Adhesive-bonded Surface Durability of Aluminum (wedge test). Both types of specimens were made in multiples and then cut into individual test specimens. Sheets of the aluminum substrate were cut to suitable sizes—17.8 × 10.2 × 0.16 cm (7 × 4 × 0.064 in) panels (ASTM D 1002) and 15.2 × 15.2 × 0.32 cm (6 × 6 × 0.125 in) (ASTM D 3762). Prior to the application of the adhesive the surfaces in the overlapping area of each panel were cleaned by the Liquid Honing Process (Vapor Blast Mfg. Co.) using 200 mesh glass beads (soda lime glass) and then dried in a conventional oven (110°C).

The adhesive was applied to an area about 6 mm (0.25 in) longer than the overlap 12.7 mm (0.5 in) as recommended by the test method (ASTM D 1002). The length of the overlap was controlled within ±0.25 mm (0.01 in) using a special fixture—a steel plate with mounted pins (stoppers), forming a framework with the desired dimensions.

The amount of the adhesive used was about 0.016 g/cm^2 (0.1 g/sq. in). It was applied as a film on both substrate surfaces (precoating) or as a powder between the two adherends. The precoating was carried out by heating to 330°C at a pressure of about 100 psi, using polyimide (Kapton®) films as a separating layer and as a spacer to keep the adhesive thickness constant. Cooling was carried out under pressure and a cooling rate at 2°C/min.

With respect to the panels for the wedge test, after applying the adhesive and subsequent processing, a 19 × 152 × 0.025 mm (0.75 × 6 × 0.001 in) separation film was inserted along one of the 152 mm wide edges. The assembled panels were bonded at different temperatures, pressures and durations. All the processing experiments were carried out in an open lab hot press (Carver).

The panels were cut into 25.4 mm (1 in) wide specimens. A wedge was forced into the bondline of the ASTM D 3762–79 specimens and the adhesive system was dipped in water (71°C) for 1 hour. The wedge test was carried out because it is highly reliable in determining and predicting the environmental durability of adherend surface preparation. The method can be correlated with service performance in a manner more reliable than the usual lap shear and peel tests. The substrate was also cut into small pieces 10 × 20 mm and the surfaces were coated and assembled following the above described procedure and boiled in common water until debonding was observed. Cross-sections of the cleaned and precoated aluminum substrate were obtained by fracturing. Metal bars were notch cut, approaching the studied surface, and then separated by pulling apart. Also a plate was prepared for thermal analysis from the copolyester in a stainless steel mold at conditions comparable with those used for the precoating and assembling of the adhesive bond.

Sample Characterization

The thickness of each adhesive layer was measured before testing using a digimatic micrometer (Mitutoyo) with an accuracy ±0.001 mm (0.00005 in).

Some of the lap shear strength measurements were carried out using a screw driven tensile machine (MTS), but most of them were conducted on a servo hydraulic closed loop test system (MTS 880 Series), and with a crosshead speed 1.3 mm (0.05 in)/min in both cases. The length of the specimens gripped in the jaws was constant at 50.8 mm (2 in). The measurements were carried out in the range of room temperature (RT) to 200°C, using a flexible electric heating tape or in an environmental chamber (MTS 880 Series) with control to within 2°C. The specimens were kept at that temperature for 5 min before testing and the temperature was controlled with a thermocouple attached to the joint (in the first case). Other specimens were immersed in boiling water for a period of time and then tested. The crack propagation of the wedged specimens was measured using a magnifier (× 10).

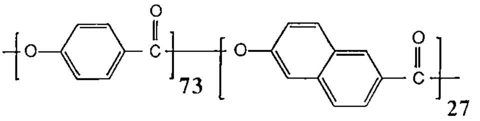
The calorimetric studies were performed on a differential scanning calorimeter (DSC) Shimadzu TA-50 at a scanning rate of 20°/min and a sample weight of about 5–9 mg.

Scanning electron microscopy (SEM) studies were carried out on a Hitachi S-800. Prior to viewing the adhesive surface, specimens were covered with a thin gold-palladium layer in a Polaron sputtering chamber.

RESULTS AND DISCUSSION

Nature of the Liquid Crystalline Copolyesters

The chemical structure of the liquid crystalline polymer used in the present work is given below:



The vendor indicates that this polymer has a Mw in excess of 20,000 and a melting temperature at about 280°C. Figure 1 presents a DSC trace of this material, and like some other authors[4] we observe that it is quite hard to reproduce accurately.

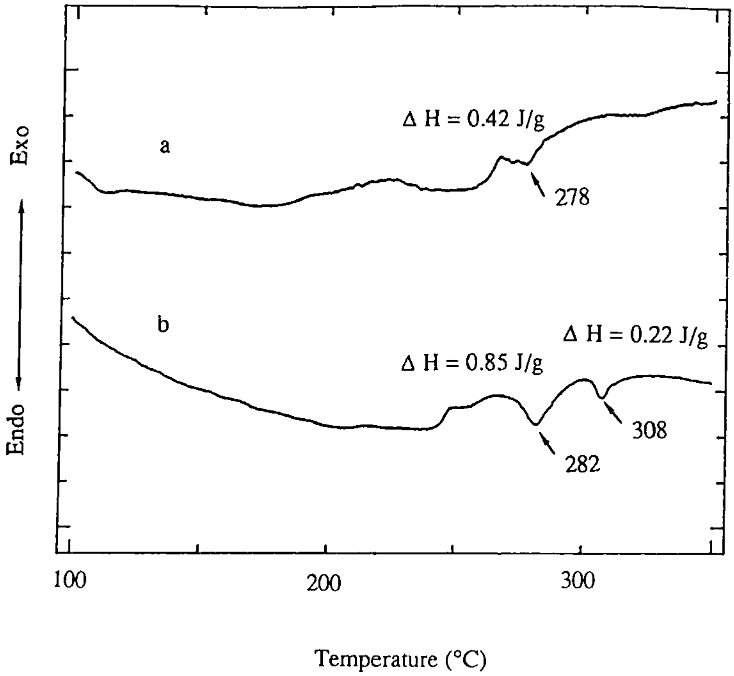


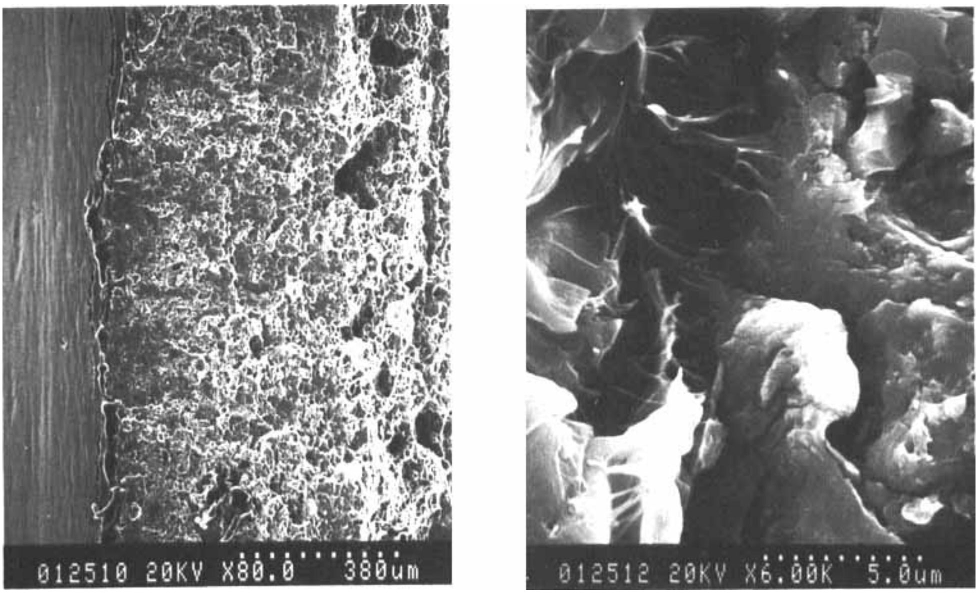
FIGURE 1 DCS scans of (a) the 73/27 composition as received and (b) processed at 300°C, 30 min and 700 psi.

The thermal behavior of the as received (curve a) and as processed (curve b) materials shows that the enthalpy values are low and the degree of crystallinity is correspondingly low. This should not be surprising considering that the microstructure of the copolyester is random.

The 73/27 copolyester on melting at its transition temperature at about 280°C converts into a nematic structure. Studies on the rheological behavior of this copolymer showed that samples, when kept at temperatures close to the melting point, displayed a significant increase in the complex modulus[5] which appears related to formation of higher melting crystals. Heating at 320°C resulted in a reversion of the more ordered state back to the original system with a m.p. ~278°C. This unusual behavior has recently been interpreted to arise from interchain transesterification reactions.[3] Thus on heating near the crystal nematic transition an ordering of the microstructure within the existing crystallites occurs. On the other hand, heating well above these temperatures results in randomization back to the original microstructure.[4]

Adhesion Studies

The copolyester was applied onto the aluminum surface and heated to a temperature of 330°C (precoating of the substrate). During this step pressure was applied to enhance the flow of the melt. SEM examination of the non-coated and adhesive precoated surfaces (pressure about 100 psi, 330°C) shows that the polymer melt has effectively wet the aluminum surface and formed an even film (Fig. 2).



(a) (b)

FIGURE 2 SEM micrographs of the coated aluminum plates: (a) 80×, (b) 6000×.

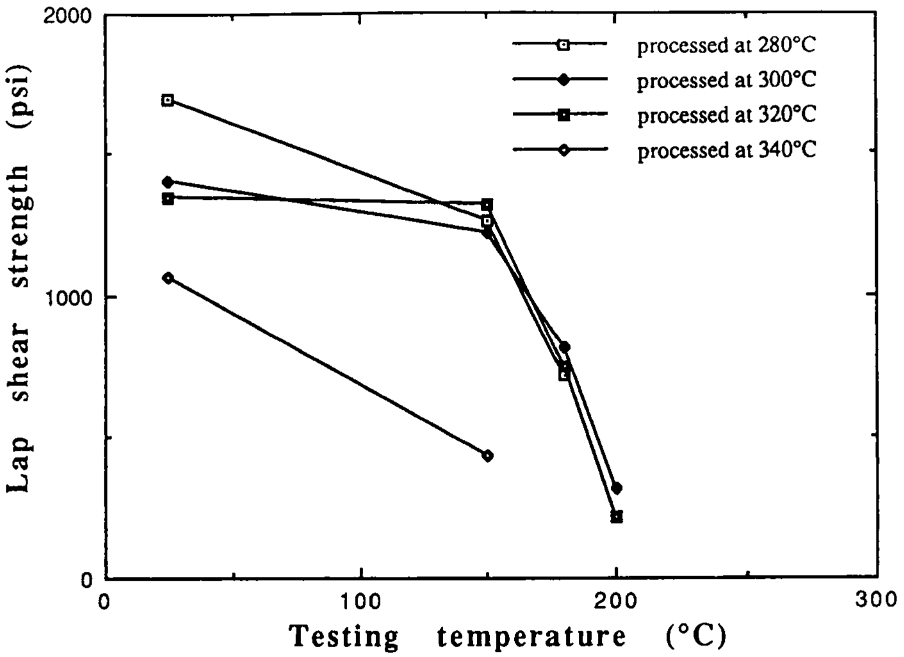


FIGURE 3 Effect of the processing temperature on the lap shear strength for specimens tested at different temperatures.

The precoated adherend panels (cooled to RT) were overlapped and processed in a hot press over a temperature range of 250° to 340°C, at pressures of 100, 700 and 1400 psi and durations of 30, 45 and 60 min. Also, samples were prepared from nonprecoated specimens (the polymer was applied as a powder between the adherends). In this latter approach lower mechanical property data was observed, most probably because of the poorer alignment during processing as well as changes in the processing conditions. In this latter case, the adhesive (between the two aluminum plates) was heated to 330°C, kept there for 5 min and then cooled to the processing temperature and kept at this temperature for the designated time (usually 30 min). The lap shear data for samples prepared at different times showed relatively poor bonding after 15 min, very good results for 30 or 45 min and a decrease in the values for 60 min. The latter may be due to decomposition.

The lap shear strength *vs* processing temperature is given in Figure 3, while in Table I these results are summarized along with the wedge test data. Micrographs of representative fracture surfaces are shown in Figure 4 a and b. In Figure 5 the lap shear strength *vs* the processing pressure is illustrated at room temperature and 180°C. The excellent resistance of these adhesive joints to boiling water is shown in Figure 6.

The excellent adhesion of the Vectra A-950® liquid crystalline polymer to aluminum may in part be due to the fact that the polymer at the metal polymer interphase tends to orient on cooling from the melt in such a way as to minimize the mismatch in the coefficient of thermal expension (CTE). Presumably, while cooling in the melt the LC polymer responds to the contraction of the substrate to minimize the stress and thus approximate the CTE of the substrate. This process

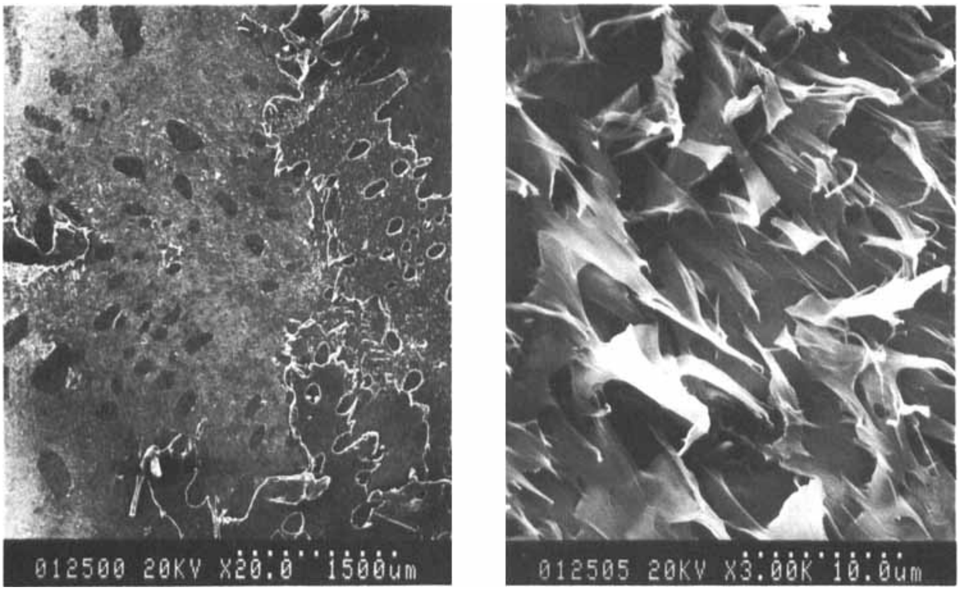
TABLE I
Lap shear strength and wedge test data for specimens processed at different temperatures

	Process conditions**		Lap shear strength, psi		Wedge test	
Nu	T°C	(psi)	RT	180°C	σ (mm)	Δσ (mm)
7*	RT	700	887			
2	280	700	1426	764		
3	300	700	1404	812	70.4	8.9
4	320	700	1346	750		
5	280	100	2025	597	61.7	6.7
6	300	100	2105	578	65.7	9.8
7	320	100	1800	593	60.9	11.3
8***	300	700	1330	750	56.5	23.1

*Epoxy
**30 minutes
***Not precoated

could continue well below the crystal-nematic transition. In addition, the bonding between the aluminum and polymer would be greatly enhanced through the dipolar interactions of the carboxylate ester with the oxide coating on the aluminum.

The good polymer-polymer adhesion observed in this study appears to be primarily a result of rapid ester-ester interchange reactions at the surface with perhaps a minor contribution from chain diffusion processes. The earlier cited work[9] demonstrates convincingly the problem of developing good adhesion between coat-



(a) (b)

FIGURE 4 SEM micrographs of fracture surfaces: (a) 20×, (b) 3000×.

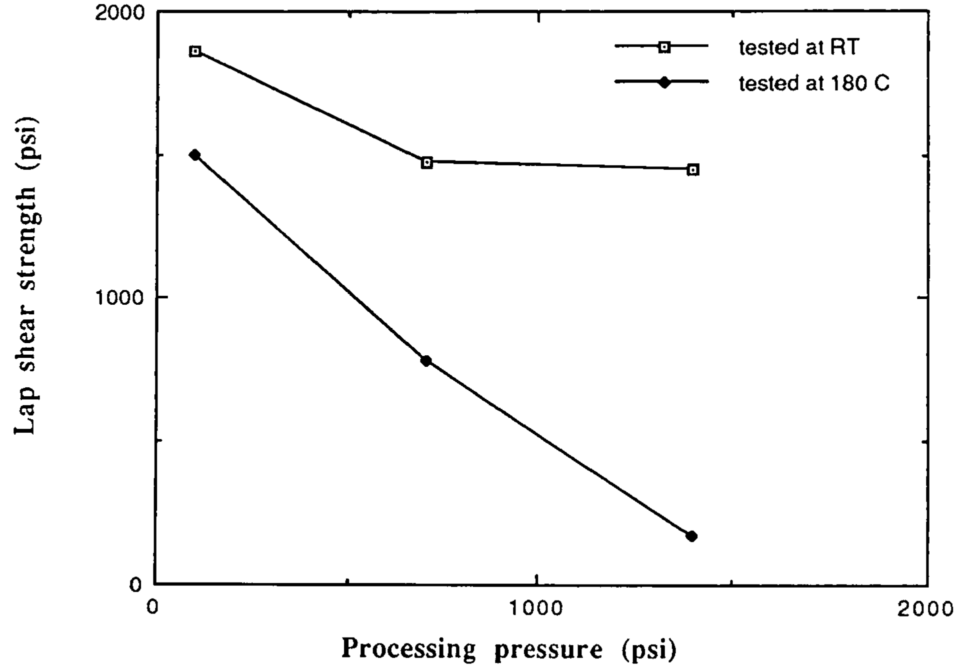


FIGURE 5 Effect of the processing pressure *vs* shear strength for specimens heated at room temperature and 180°C.

ings of stiff chain polymers such as polyimide. Additional evidence for interchain transesterification is available from the literature where a mixture of deuterated and undeuterated polyethylene terephthalate was completely randomized on heating at 300°C for one hour.[10] On the other hand, at processing temperatures of 250°C the rate of the ester interchange reaction would be much slower (assuming an Arrhenius process). To summarize, the possibility of rapid interchain transesterification reactions[3] provides a mechanism for forming a good adhesive bond across an interface. The interchain transesterification is most likely catalyzed by the carboxylic acid end group. This kind of reaction is temperature dependent and would appear to require only seconds at 425°–450°C, minutes at 350°–375°C, and hours at 250° to 275°C. Presumably, such a mechanism cannot occur with polyimides.

It is interesting to note that the LC 73/27 copolyester retains good adhesive characteristics well above the polymer glass transition temperature of the LC copolyester ($T_g \sim 110°C$) but well below the crystal nematic transition ($T_m = 278°C$). Presumably, the small amount of crystalline order present in these copolyesters enhances the retention of mechanical properties well above T_g. It should be noted that the potential exists to increase the high temperature mechanical properties further by first annealing at 50–70°C below the T_m and then by heating near the crystalline nematic transition for several hours. The annealing increases the transition enthalpy by a factor of 3–4 while heating near the crystal-nematic transition raises the melting point by 40–60°C.[3] Also by using HBA/HNA compositions with much higher

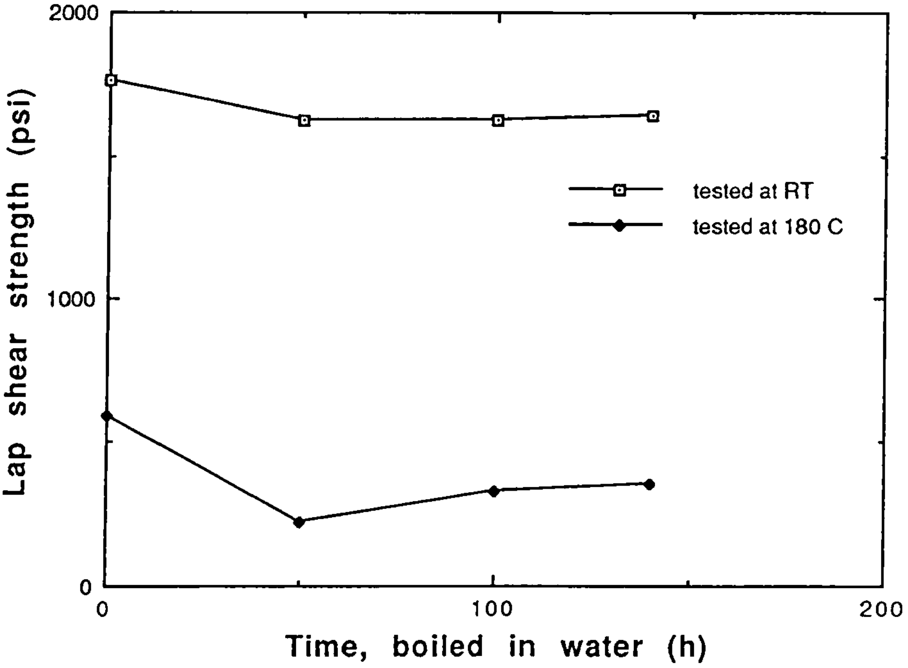


FIGURE 6 Data which demonstrate the outstanding resistance of these adhesive joints to boiling water.

melting points (*e.g.* 350°C), one could obtain an additional enhancement in retention of properties at high temperatures. All these possibilities are now being examined.

CONCLUSIONS

1. The melt processible LC aromatic copolyesters have been shown to function as excellent high temperature adhesives with very good resistance to a corrosive environment.
2. The excellent adhesion to the aluminum substrate appears to be the result of good wetting, and likely the tendency for the polymer to orient at the surface to produce a stress-free interface.
3. Adhesive behavior between the polymer coatings applied to the aluminum arises primarily from chemical processes at the interface of the polymers, *i.e.* interchain transesterification.

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