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Factors Which Influence the High Temperature Adhesive Characteristics of Liquid Crystalline Copolyesters

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Liquid crystalline copolyesters of *p*-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid, with compositions 20/80 and 24/76, were studied in order to evaluate the effect of higher melting HBA/HNA copolyesters on the high temperature adhesive properties compared with data for the recently reported 73/27 system. A tetramer of HBA/HNA with a composition of 24/76 was synthesized to examine the effect on adhesion of wetting of the substrate at much lower temperatures. From the results of this study it is now possible to define approaches for achieving very good adhesion characteristics at temperatures well in excess of 250°C.

KEY WORDS high temperature adhesives; liquid crystalline copolyesters; interchain transesterification; chemically induced ordering; glass transition temperature; annealing; processability; lap shear strength; oligomer.

INTRODUCTION

Recently we reported that the 73/27 liquid crystalline copolyester of *p*-hydroxybenzoic acid (PHBA) and 2,6-hydroxynaphthoic acid (HNA) acted as a good adhesive at temperatures up to 180°C.¹ The unusually good adhesion characteristics were somewhat surprising^{2–4} in light of the rod-like nature of the liquid crystalline (LC) chains. Of more technological interest was the fact that this class of polyesters might be able to display good adhesion at even higher temperatures of 200–250°C.

In the present work a study has been made of two higher melting HBA/HNA copolyesters to evaluate the effect of degree of crystallinity and melting point on the high temperature adhesion properties. More specifically, the 20/80 and 24/76 HBA/HNA copolyesters were examined because of their much higher melting points and degrees of crystallinity as compared with the 73/27 copolyester. Other variables that were investigated included the effect of annealing to increase the

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transition enthalpy and the possibility to increase further the crystal to nematic transition temperature (T_{CN}) by 40–50°C, by chemical ordering.⁵ Also, the role of the glass transition temperature (T_g) on the high temperature properties was examined by determining the T_g of HBA/HNA copolyesters over the compositional range of 20/80 to 73/27. Because of the much higher melting points of these copolyesters compared with the 73/27 system, an oligomer of the 24/76 copolyester was prepared that could more effectively wet the adherend at much lower temperatures and then be further advanced.

EXPERIMENTAL

Materials and Methods

The 20/80 and 24/76 HBA/HNA copolyesters, with a weight average molecular weight of 20000, were supplied by Hoechst-Celanese while the 24/76 oligomer, with a degree of polymerization ~ 4 , was prepared in our laboratory according to the procedure outlined in the section "Preparation of the Oligomer."

The ASTM D 1002-83 test method, Strength Properties of Adhesives in Shear by Tension Loading (lap shear joint metal to metal), was followed for the evaluation of the adhesive bonding. This method was selected among others,⁶ as it is specified for adhesion on aluminum substrates.⁷

Characterization of Materials

The polymers used in this study were characterized by Thermal Analysis using a Du Pont 2000 Thermal Analyzer (heating rate 20°C/min). The copolyesters, after being applied on aluminum substrates, were given the following treatments:

- a) Annealing at 75°C below their melting points
- b) Heating of the annealed samples at 5°C above the melting points of the as received materials.

The annealing took place, under a pressure of 100 psi, in a heated plate hydraulic press, whereas heating was carried out in a Fischer Scientific Isotemp Vacuum Oven, Model 282, under nitrogen.

Preparation of the Oligomer

The 24/76 p-HBA/HNA oligomer was prepared using the acetoxy esters of p-hydroxybenzoic and 6-hydroxy-2-naphthoic acid as starting materials. The acetoxy ester of 6-hydroxy-2-naphthoic acid was prepared by direct acetylation of the sodium salt of the acid as described in detail elsewhere.^{8,9} Polymerization was carried out in a heat transfer fluid, Therminol 66 (Monsanto Co). The temperature was raised from 170° to 250°C over a period of 2 hours. The amount of acetic acid evolved was used to approximate the extent of reaction. A degree of polymerization

of 4 was assumed at the point that 75% of the total acetic acid was collected. No attempt was made to characterize the compositional distribution, but based on studies of reactivity ratios of the 50/50 HBA/HNA system,⁵ it would appear to approximate the composition of the starting material.

Preparation and Testing of Specimens

Specimens were prepared according to ASTM D 1002-83, Strength Properties of Adhesives in Shear by Tension Loading. Sheets of aluminum, alloy 2024T-3, were cut into suitable sizes, *i.e.* 17.78 × 10.16 × 0.16 cm (7 × 4 × 0.064 inch) panels. 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), rinsed with distilled water 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, *i.e.* a steel plate with mounted pins as stoppers, forming a framework with the desired dimensions. Consolidation of the framework was carried out at room temperature. The amount of the adhesive used was about 0.016 g/cm² (0.1 g/in²). It was applied as a film on both substrate surfaces so that precoated aluminum sheets were produced. The deposition of the polymer film was carried out by heating above the melting point of the polymer used, at a pressure of about 100 psi, using Kapton polyimide films as a separating layer and as a spacer to keep the adhesive thickness constant. The precoated aluminum specimens were put together and compressed in a heated Carver Hydraulic Press. After trimming the edges, the panels were cut into individual specimens of 2.54 cm (1 in) width.

The lap shear strength measurements were carried out on a servohydraulic closed loop test system (MTS 880 Series) with a grip separation speed 1.3 mm (0.05 in) per min. The length of the specimens gripped in the jaws was constant at 50.8 mm (2 in). The measurements were carried out up to 220°C in an environmental chamber with control to within ±2°C. The specimens were kept at the testing temperature for 5 min in order to reach equilibrium.

Glass Transition Temperature Measurements

The Glass Transition Temperature (T_g) of the copolyesters used in this study was determined by DSC analysis. The samples were heated, in sealed pans, at temperatures above their melting points for about 15 min and then quenched in liquid nitrogen so that an amorphous product was formed.

DSC experiments were run at a heating rate of 20°C/min, from room temperature up to 400°C, in order to verify whether the samples were completely amorphous. The T_g was calculated from the change in slope shown in the plots of the DSC scans (see Fig. 5). The change in T_g with composition was determined by also characterizing the 30/70, 50/50, 60/40 and 73/27 HBA/HNA copolyesters.

RESULTS AND DISCUSSION

The DSC data for the 20/80 and 24/76 HBA/HNA copolyesters are shown in Table I and compared with the 73/27 system. These data were obtained from DSC curves similar to those presented in Figure 3. The observed differences between DSC's of the oligomer and the copolyesters are consistent with the much lower molecular weight of the oligomer. It is evident, from this Table, that these copolyesters display 40 to 60°C higher melting points compared with the 73/27 system. It therefore seemed reasonable that the above materials would display better high temperature adhesion as compared with the 73/27. On the other hand, the relatively low degree of crystallinity in these copolyesters (5–20%) would suggest that the glass transition temperature (more correctly nematic glass) might also play a significant role.

The data of Table I show that in all three cases the transition enthalpy can be increased by 3 to 4 times upon annealing at temperatures 75°C below the respective melting points. The double endotherm observed on annealing the as-received material can be interpreted either as a broad compositional distribution or a mixture of random and blocky copolymer. It was of interest to determine whether the higher degree of crystallinity would significantly increase the high temperature adhesion characteristics. Although it is difficult to quantify, we estimate from the transition enthalpies that the degree of crystallinity increases from well below 10% to about 25%.

Another variable that was examined in this study was the potential to increase the crystal-nematic transition temperature by 40–50°C by heating the material near its melting point for 20 hours. This kind of increase in the crystal-nematic transition temperature has been observed by various workers, although some confusion exists as to its origin; *i.e.* is it a physical or a chemical process.^{10–11} In some very recent studies⁹ we have concluded that it is chemical in nature and proceeds by carboxylic acid end group catalyzed interchain transesterification reactions that occur only within the existing crystalline regions.

It was found that the lap shear strengths at elevated temperatures for both the 20/80 and 24/76 systems showed significant improvement over the results reported with the 73/27 system. Thus, in Figure 1 the 20/80 HBA/HNA copolyester retains

TABLE I
DSC data for the 20/80 and 24/76 HBA/HNA copolyesters
compared with the 73/27 system

Composition	20/80	24/76	73/27
<i>Melting point</i> (°C)			
As received	342	325	281
Annealed ¹	312/349	304/334	243/277
Heated ²	378	370	332
<i>Endotherms</i> (J/g)			
As received	2.87	2.08	1.02
Annealed ¹	11.16	9.07	5.98
Heated ²	14.19	8.51	6.90

¹Annealed at 75°C below the melting point, for 24 hours

²Heated at 5°C above the melting point, for 24 hours

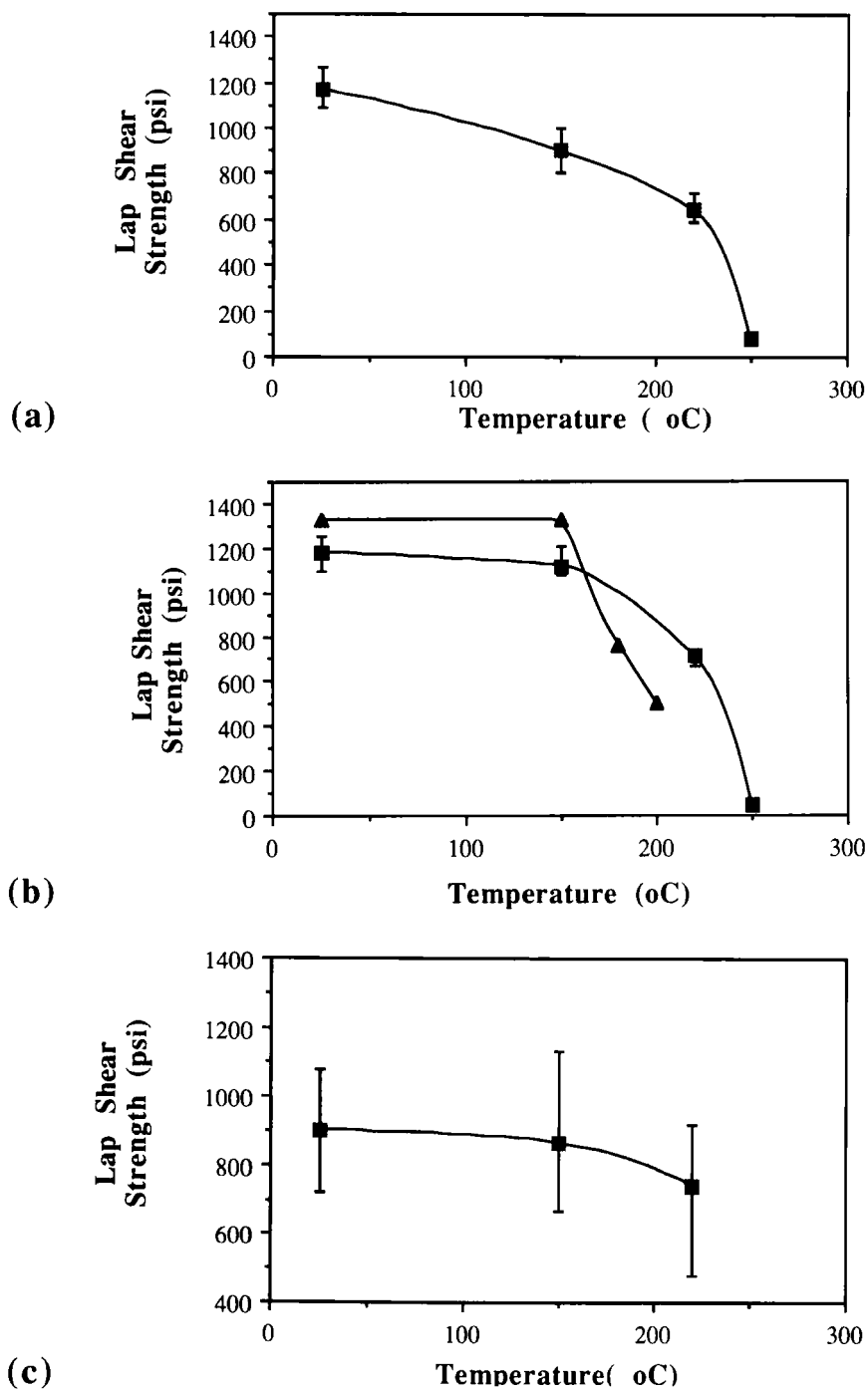


FIGURE 1 The lap shear strength for the 20/80 HBA/HNA copolyester: (a) As received, (b) Annealed at 270°C, (c) Heated at 350°C.

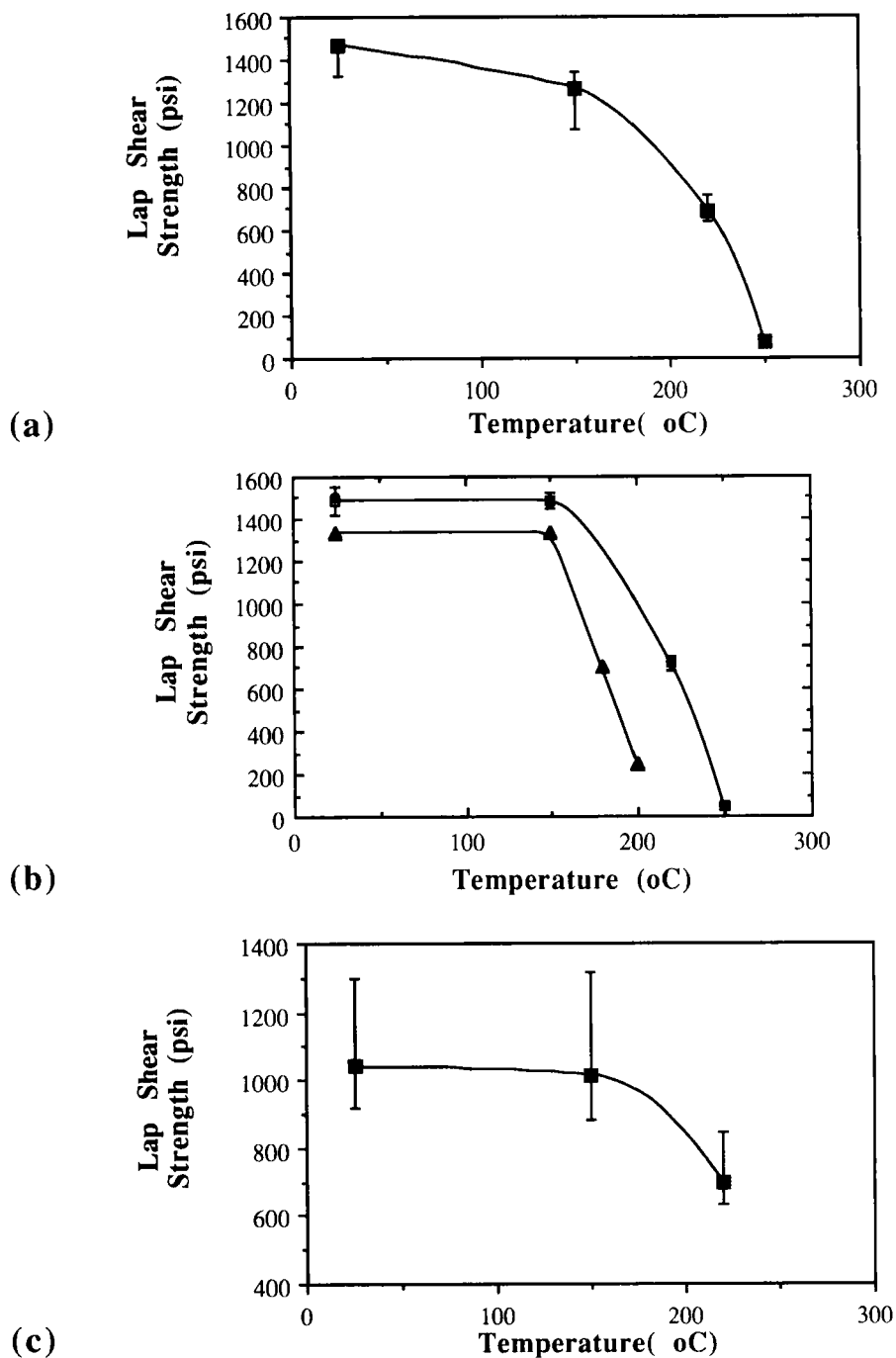


FIGURE 2 The lap shear strength for the 24/76 HBA/HNA copolyester: (a) As received, (b) Annealed at 250°C, (c) Heated at 330°C.

useful lap shear strength to 225°C as compared with the 73/27 which has lost most of its mechanical strength at 200°C. On the other hand, no additional improvement was observed in the 20/80 system either by annealing to increase the degree of crystallinity or by attempting to increase the crystal-nematic transition temperature by heating near the crystal-nematic transition point. The slightly lower lap shear strength at room temperature for the 20/80 *versus* 73/27 copolyester may be a result of having to use a much higher temperature for processing the 20/80 system. In the earlier work on the 73/27 system¹ it was reported that the adhesion dropped dramatically when the test samples were prepared at 340°C.

Moderately improved lap shear strengths were obtained for the 24/76 copolyester compared with the 20/80 system, as shown in Figure 2. This may very well be the result of the use of lower processing temperatures. More pertinent to this study, both the 20/80 and 24/76 copolyesters showed far better retention of properties in the temperature range of 180°–225°C compared with the 73/27 copolyester.

Because of concerns with possible degradation at processing temperatures of 340° and higher, a low molecular weight 24/76 copolyester of HBA/HNA was prepared and evaluated. The DSC scans for the oligomer of about 4 units are shown in Figure 3. The changes in the DSC scans observed here are about the same as those for the 20/80 and 24/76 copolymers and the same interpretation should be applied here also.

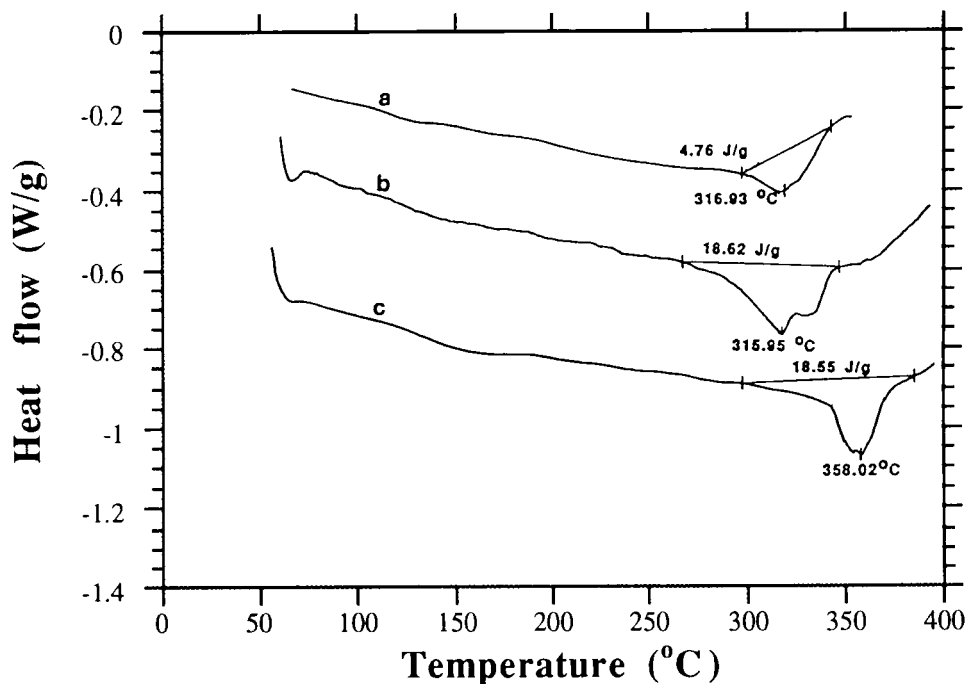


FIGURE 3 DSC scans for the processed 24/76 tetramer (heating rate 10°C/min): (a) As received, (b) Annealed at 240°C, (c) Heated at 310°C.

From the results shown in Figure 4, the 24/76 oligomer does not give higher lap shear strengths, even though better wetting was obtained because of the low viscosity. The oligomer was applied as a precoat at 280°C and then further advanced with elimination of acetic acid. It should be noted that aluminum may undergo undesirable changes during processing at temperatures in excess of 250°C. On the other hand, in all the lap shear tests shown in Figures 1, 2 and 4 failure took place within the adhesive layer, suggesting that the interfacial bonding to the aluminum surface is very strong. The morphology of the break surfaces was not examined in this work, although in Reference 1, Scanning Electron Microscopy (SEM) of specimens fractured at room and elevated temperatures did not reveal any transition from brittle to ductile fracture.

These results indicate that the high temperature adhesion characteristics of the HBA/HNA system can be improved by 40–50°C by using compositions with higher melting points. The fact that no additional improvements were observed by

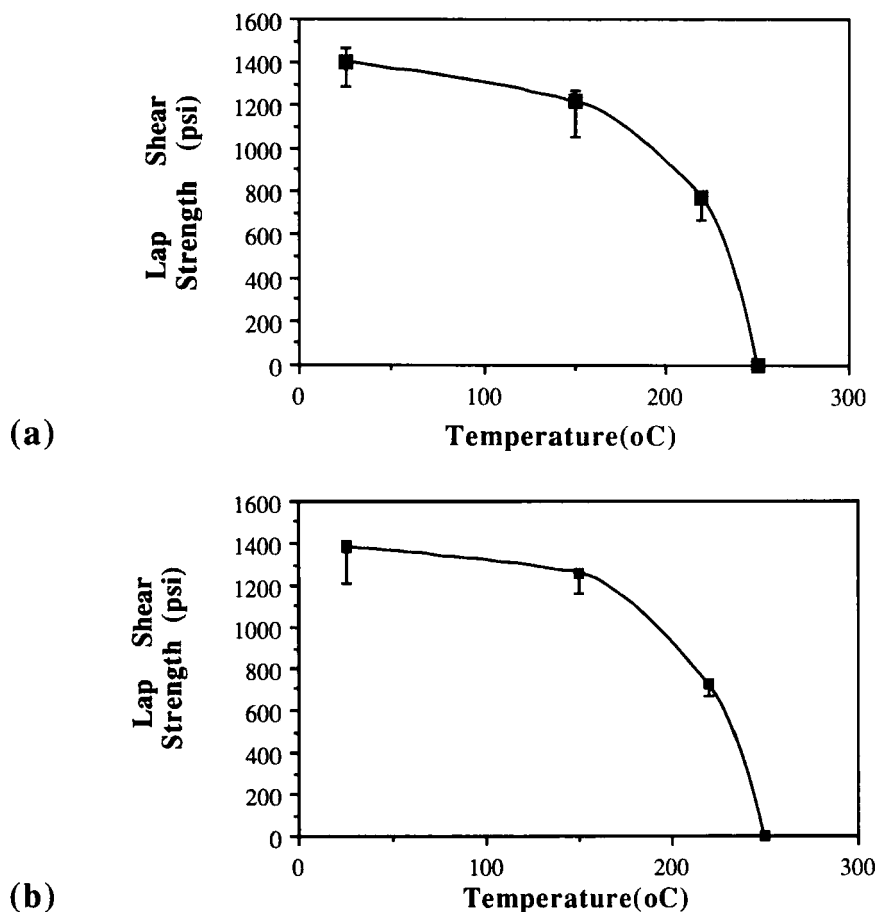


FIGURE 4 The lap shear strength for the 24/76 HBA/HNA tetramer: (a) As processed, (b) Annealed at 250°C.

annealing at 75°C below the crystal-nematic transition, or by heating near the crystal-nematic transition point to increase the melting point further by 40–50°C, was surprising. It is certainly possible that within the contained geometries of the aluminum adherends the potential for further crystallization and/or ordering were greatly reduced. Also, the carboxylic acid end groups in the copolyester may have interacted with the aluminum surface, reducing the concentration necessary to catalyze the chemical ordering process. Since the coatings were very thin it was not possible to scrape off the polymers to measure their thermal characteristics.

The glass transition temperature (T_g) was determined for the copolyesters used in this study as well as for the 30/70, 50/50, 60/40 and 73/27 HBA/HNA. The fact that all of these copolyesters display a degree of crystallinity of only 5–20% would suggest that retention of properties at elevated temperatures would be strongly influenced by the T_g . Typical DSC curves for these compositions are shown in Figure 5. The T_g 's were calculated based on the changes in deflection of the curves. T_g 's are plotted *versus* composition of the copolyesters in Figure 6. It is clear from the curves of Figure 6* that T_g passes through a minimum corresponding to an approximate composition of 45/55 HBA/HNA. Hence, the very modest increase in T_g cannot be used to interpret the 50°C improvement in lap shear strength of the 20/80 and 24/76 systems.

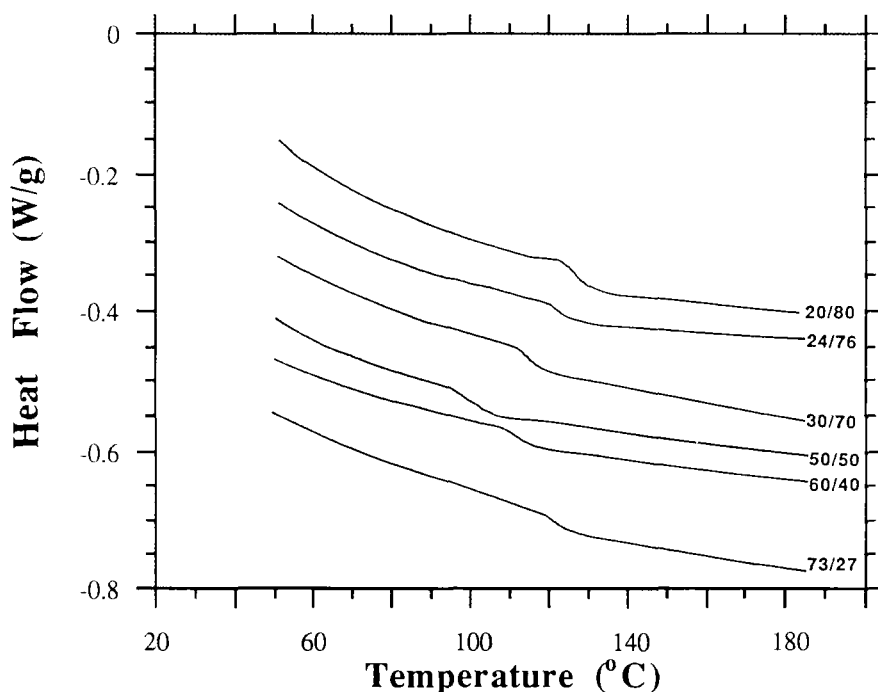


FIGURE 5 Typical DSC curves for quenched HBA/HNA copolyester systems (heating rate 10°C).

*A similar curve for the same series of copolyesters was established by other researchers¹² who determined a minimum in T_g values for an HBA content of 50%.

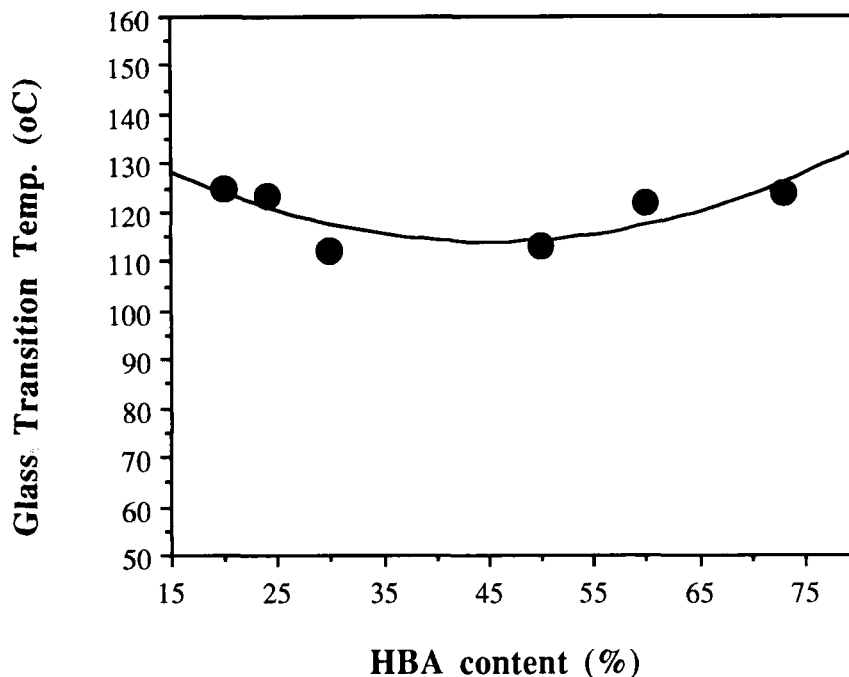


FIGURE 6 The glass transition temperature as a function of composition of HBA/HNA copolyesters.

Some subtle changes in lap shear strength could be detected with specimens annealed at 75°C below T_{CN} . In both the 24/76 and 20/80 systems the lap shear strength remained constant from room temperature to 150°C. In the case where the specimens were annealed slightly above T_{CN} the room temperature lap shear strength was reduced by ~25% suggesting the possibility of high temperature degradation.

CONCLUSIONS

This study shows that:

1. The high temperature adhesive characteristics of the HBA/HNA copolyester system can be significantly improved by using compositions with higher melting points.
2. Attempts to increase the high temperature properties further through annealing and/or chemical ordering were unsuccessful, probably because of interactions of the substrate with the polymer.
3. With all systems studied so far, excellent bonding to the aluminum surface is observed, which suggests potential for further optimization of the cohesive character using fillers.

4. Use of more easily processable oligomeric polyesters has been demonstrated. This permits a far simpler approach to coating and processing of the substrates and also opens the door to processing of even higher melting polyesters.

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