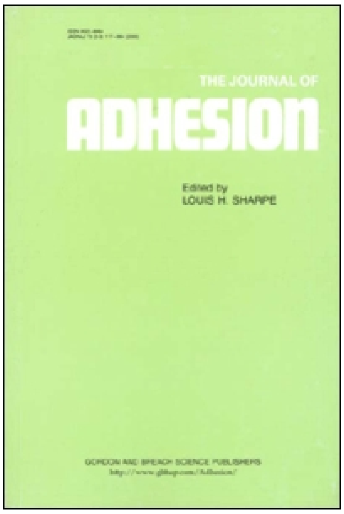

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Adhesion Behavior of Thermoplastic Polyimides and Poly(imide-siloxane) Segmented Copolymers: Influence of Test Temperatures

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Adhesion Behavior of Thermoplastic Polyimides and Poly(imide-siloxane) Segmented Copolymers: Influence of Test Temperatures

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Soluble and thermoplastically processable fully cyclized BTDA-DDS based polyimide homopolymers and multiphase poly(imide-siloxane) segmented copolymers with controlled molecular weight and non-reactive end groups were synthesized via solution imidization. Adhesive properties were investigated using melt-laminated, single-lap-shear samples prepared from surface-treated Ti-6Al-4V adherends and compression-molded adhesive films. Tests were conducted at room temperature, 100, 150, 200, and 250°C. The room-temperature adhesive bond strengths increased with poly(dimethylsiloxane) oligomer incorporation up to 30 weight percent and were optimum with the lowest controlled molecular weight range investigated (20,000 gm/mole). Lap shear values at 25°C as high as 50 MPA (7,000 psi) were obtained. The results suggest that melt flow and bond consolidation were critical parameters directly correlated with the lap shear strength. TMA penetration-temperature measurements were consistent with this view. As the test temperature was increased, the homopolymer and 10%-siloxane copolymer showed maximum bond strengths at 200 and 150°C, respectively, while 20% and 30% siloxane-modified copolymers demonstrated decreasing bond strength, relative to their room temperature values.

KEY WORDS polyimide; BTDA; DDS; segmented poly(imide-siloxane) copolymers; adhesion; melt lamination; lap shear; Ti-6Al-4V; molecular weight and end-group control.

INTRODUCTION

The applications of polyimides have been somewhat limited despite their attractive properties such as high glass transition temperatures and good thermal and mechanical properties. The reasons include poor processability and/or the production of water during the *in-situ* poly(amic-acid) to polyimide transformation. A number of approaches to enhance the processability, such as incorporation of flexible bridging units into the polyimide backbone[1-3] and bulky side groups,[4] utilization of diamines

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containing meta linkages[5] etc., have been somewhat successful in developing soluble and more processable high T_g polyimides. Recently, however, our laboratory has succeeded in synthesizing soluble and processable thermoplastic high T_g polyimides by newly-developed techniques such as solution imidization, siloxane incorporation, and molecular weight control with non-reactive end groups[6–9] without detracting from excellent properties.

Although polyimides are excellent candidates for structural adhesive applications, the major variables affecting their adhesive properties have still not been investigated in sufficient detail. Herein, we have investigated the role of several major factors on adhesive bond performance, such as molecular weight, molecular weight distribution and the incorporation of flexible units. Furthermore, an evaluation on the effect of scrim cloth, as well as trace amounts of residual solvent, on adhesive bond strength was also conducted since most studies have utilized precursor poly(amic-acid) supported on scrim cloth instead of fully-cyclized polyimide films. However, this investigation has focused on the effect of molecular weight, incorporation of flexible units such as siloxane oligomers and end-group control.

The major requirements for optimal adhesive performance are good bond consolidation and good mechanical properties. The molecular weight should be sufficiently high to produce chain entanglements which permit good mechanical properties, but low enough to provide adequate and stable melt flow under bonding conditions. Earlier studies[10,11] have shown that the adhesive bond strength as well as other mechanical properties certainly depend on the polyimide molecular weight. However, the range of molecular weights used in those studies were fairly narrow and melt stability issues were not addressed. Hence, in this study the effect of molecular weight variation on the adhesion behavior has been studied by using both nonreactive and melt-processable materials.

Four different molecular weights of polyimide and poly(imide-siloxane) copolymers were prepared and investigated. The adhesion of these polyimides was studied as a function of the molecular weight of the polyimide, the poly(dimethylsiloxane) segment content and test temperatures. The study utilized Ti-6Al-4V adherends and compression-molded, fully-imidized thermoplastic polyimide films. Since the polyimide adhesives were fully cyclized prior to bonding, volatiles such as water were not produced during the formation of the bonded joints.

EXPERIMENTAL

Materials

The polyimide homopolymer studied herein was based upon 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), 3,3′-diaminodiphenyl sulfone (mDDS) and phthalic anhydride (PA) as an end capper.[9,10] The α,ω-aminopropyl poly(dimethyl-siloxane) oligomers (PDMS) were synthesized in our laboratory as previously described.[12] BTDA from Allco was used as received, and mDDS and PA (Aldrich) were purified by recrystallization and by sublimation techniques, respectively. All solvents were vacuum distilled after stirring overnight with phosphorous pentoxide as the drying agent.

Synthesis

Homopoly(amic-acids) were prepared from BTDA, mDDS and PA. The overall reaction was conducted at 15 wt% solids in N-methylpyrrolidinone (NMP) at room temperature under nitrogen flow for 8 to 12 hours (Figure 1). Small concentrations of phthalic anhydride were incorporated according to the Carrothers equation to obtain a polymer having number average molecular weights of 20,000, 30,000 and 40,000 g/mole which had non-reactive phthalimide end groups.

Poly(dimethyl siloxane) oligomers having a number average molecular weight of 1550 g/mole and aminopropyl end groups were incorporated into the polyimide backbone at concentrations of 10, 20 or 30 wt%. Due to the different solubilities of the siloxane oligomers and the aromatic diamine and dianhydride monomers, a cosolvent (tetrahydrofuran, THF) had to be utilized for the copolymer synthesis to provide a homogeneous solution mixture. Cyclization of the poly(amic-acid) was conducted via a solution imidization technique conducted at 15 wt% solids concentration in NMP (80%) with an azeotroping agent, cyclohexylpyrrolidinone (CHP) (20%), at 160°C for 24 hours under nitrogen flow. Full details have been provided previously.[6]

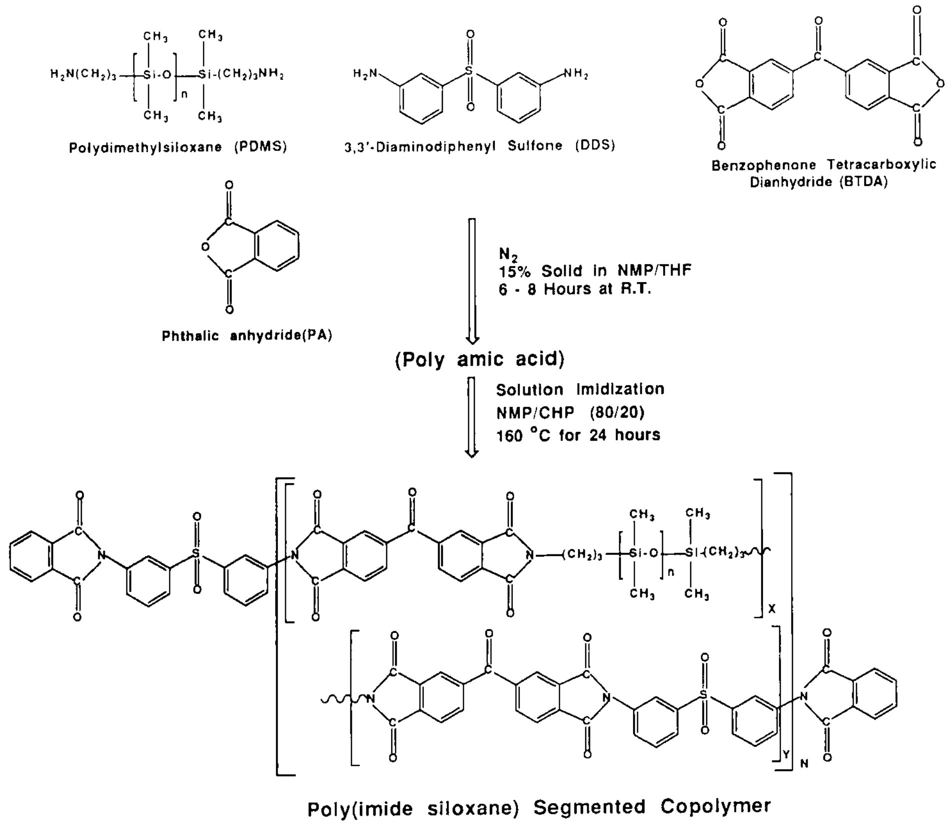

FIGURE 1 Synthetic scheme of poly(imide-siloxane) segmented copolymer.

Characterization

Evidence for complete imidization was confirmed by infrared spectroscopy (Nicolet MX-1 FTIR). Intrinsic viscosity measurements were performed in NMP at 25°C using a Cannon-Ubbelohde viscometer to provide relative molecular weights. Differential Scanning Calorimetry (DSC) was utilized to determine the upper glass transition temperatures (T_g), corresponding to the polyimide-dominant phase, with a DuPont-912 at 10°C/min with a sensitivity of 10 mcal/second. The reported data were obtained from a second scan after heating and fast cooling. Thermal Gravimetric Analysis (TGA) was performed on a DuPont-915 in air at the flow rate of 10 cc/min. Thermal Mechanical Analysis (TMA) was carried out on a Perkin Elmer TMS-2 utilizing the penetration mode with a 10mg probe. TGA and TMA scans were run at 10°C/min in air.

Adhesion Study

Single lap shear specimens were prepared from Ti-6Al-4V coupons (2.54cm × 12.7cm), provided by NASA Langley Research Center, and compression molded polyimide film (about 0.254mm to 0.33mm thick). The adherend surface was sand blasted, treated with Pasa Jell 107®, ultrasonically cleaned and primed with a polymer solution to preserve the treated surface. The polymer used for primer preparation was the same polymer as the adhesive dissolved in NMP, 10% by weight. Compression molding of fully-cyclized polyimides was performed with a Tetrahedron hydraulic press. Pressure and holding time were fixed at 70 MPa and 10 min, respectively, but temperatures were varied from 330 to 380°C, depending on the nature of the polyimide. The compression molding temperature (CMT) reported was the lowest temperature at which good, flexible and bubble-free films were successfully obtained. The single lap shear samples (1.27cm overlap) were prepared by melt laminating the adhesive films between treated Ti-6Al-4V adherends. The bonding temperatures were optimized for the homopolymers and copolymers. The most general bonding procedure was to apply 1.38 MPa after reaching 280°C, then to heat to 360°C for thirty minutes, followed by cooling to room temperature under the same pressure. The single lap shear adhesive bond strengths were measured with an Instron Model 1123 at a crosshead speed of 1.27 mm/min at room temperature, 100, 150, 200 and 250°C according to ASTM D-1002. For elevated temperature tests, an environmental chamber (Instron-3116) was used. Fifteen minutes were allowed to equilibrate the temperature of the test specimens before each test. An average adhesive strength determined from at least four samples is reported.

RESULTS AND DISCUSSIONS

Characterization

The upper glass transition temperatures of the polyimide homo- and segmented copolymers increased with molecular weight and decreased with incorporated poly(dimethylsiloxane), $<M_n> = 1{,}550$ g/mole segment. The increased molecular weight promotes chain entanglements leading to physical integrity while incorporation of siloxane provides enhanced chain flexibility. The thermal stability varied slightly with siloxane incorporation but was independent of the molecular weight of the copolymer, as determined by dynamic thermogravimetric analysis (TGA) (Table I). Polyimide homopolymers were stable for short periods up to 500°C in air. Thermal stability decreased only slightly with minor amounts of siloxane incorporation (Figure 2). The increased char yield in air at high temperature obtained with greater siloxane incorporation is due to the conversion of siloxane to silicate-type materials. This is believed to enhance the flame retardation of the polyimide copolymers.[6]

Intrinsic viscosity measurements indicated that controlled molecular weights were obtained. As the target molecular weight increased (PA content decreased), higher intrinsic viscosities were obtained (Table I). The TMA results also support the intrinsic viscosity and DSC data. The TMA spectra of homopolymers in the penetration mode (Figure 3) indicated that penetration increased with temperature above T_g and that the rate of displacement in the melt was smaller for the higher molecular weight polyimides. The softening points correlated well with the DSC and TMA glass transitions. However, the compression molding temperatures were also a function of the molecular weight of polyimide homo- or copolymer and the siloxane content. The values increased with molecular weight and decreased with siloxane incorporation (Table I).

TABLE I
Physical characteristics of adhesives

Samples	<Mn>[1]	[η][2]	T_g(°C)[3]	DT(°C)[4]	CMT(°C)[5]
Homopolymer	20K	0.21	259	550	340
	30K	0.26	265	545	350
	40K	0.39	263	560	380
	UEC[6]	0.95	266	565	N/A
10%PDMS Copolymer	20K	0.27	248	550	340
	30K	0.29	248	550	340
	40K	0.40	249	555	350
	UEC	0.56	250	550	370
20%PDMS Copolymer	20K	0.20	231	530	320
	30K	0.39	228	530	330
	40K	0.43	236	530	330
	UEC	0.92	236	525	350
30%PDMS Copolymer	20K	0.21	209	510	300
	30K	0.24	218	505	310

[1] Theoretical molecular weight
[2] NMP at 25°C
[3] Measured by DSC, 10°C/min., in 2nd scan
[4] Degradation Temperature (10% weight loss in air)
[5] Compression Molding Temperature (at 10klb, for 10 min)
[6] Unendcapped (1:1 stoichiometric reaction)

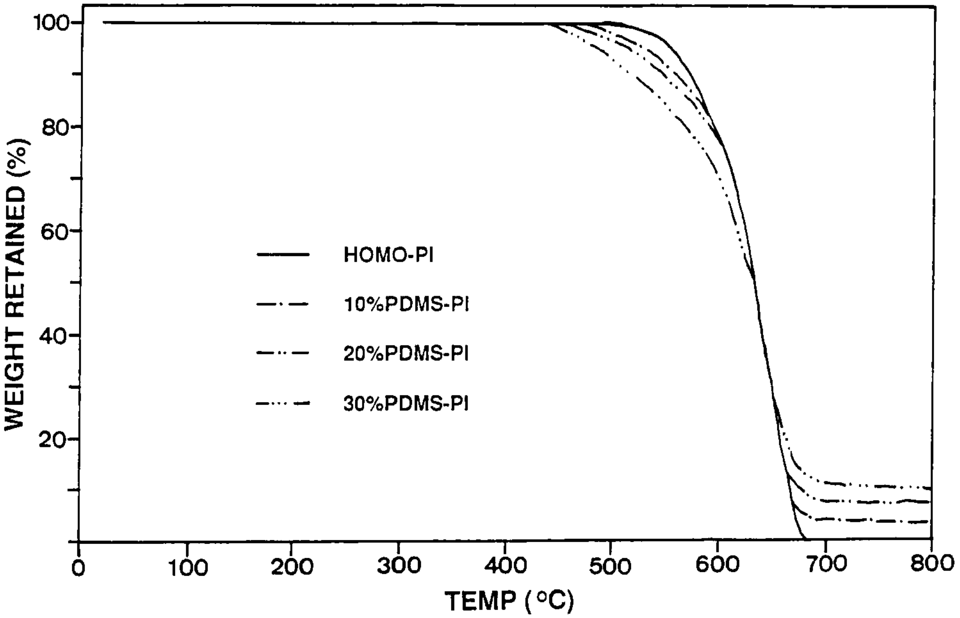

FIGURE 2 TGA spectrum of polyimide homopolymer and copolymers (molecular weight of 20,000 g/mole).

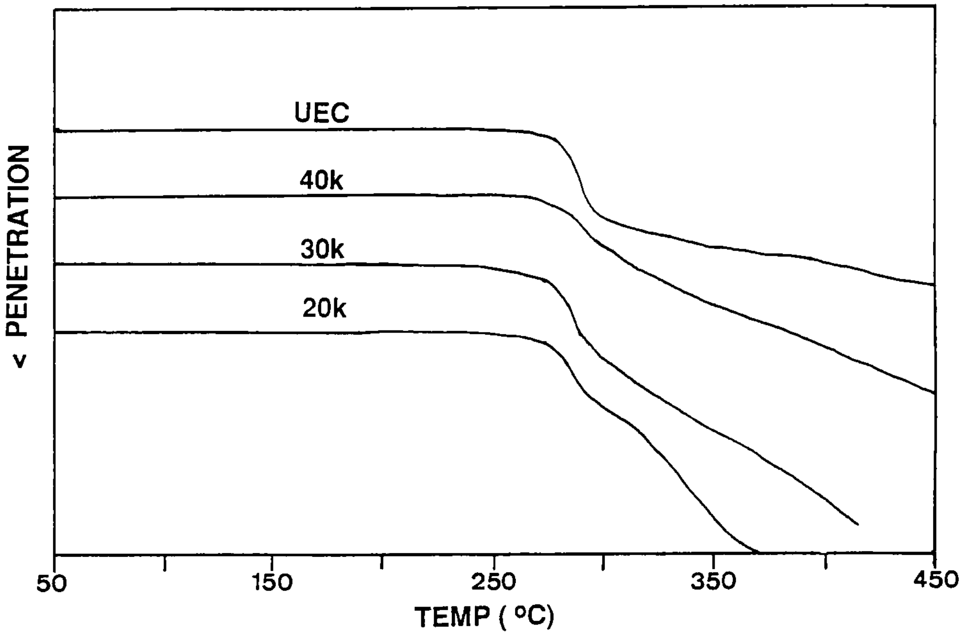

FIGURE 3 TMA spectrum of polyimide homopolymers (in air, 10°C/min).

Effect of Molecular Weight

In general, the adhesive bond strengths decreased with increasing molecular weight of polyimides as indicated in Figure 4. Compared with the lowest molecular weight homopolyimide specimen (20,000 g/mole), homopolyimides of 30,000 and 40,000 g/mole showed very low bond strengths at room temperature and at 200°C, probably due to poor flow, which led to poor bond consolidation. The dependence of bond strength on molecular weight was insignificant as siloxane incorporation increased (Figure 4). As the test temperature increased, the dependence of the adhesive bond strength on molecular weight diminished; e.g., at 200°C, the 10% and 20% siloxane-modified copolymers exhibited only an apparent slight dependence on molecular weight. Note that even the lowest molecular weight (20,000 g/mole) polyimide used in this investigation was clearly above the critical entanglement required for achieving good mechanical properties.

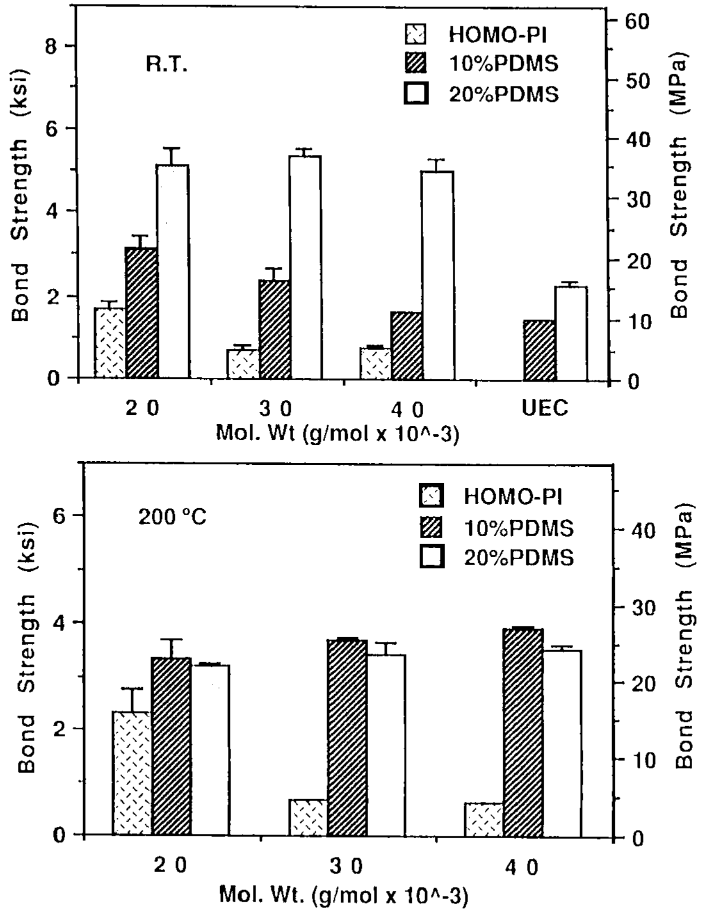

FIGURE 4 Effect of molecular weight on the adhesive bond strength at 25°C and 200°C.

Effect of Siloxane Incorporation

The inherent flexibility of the poly(dimethylsiloxane) oligomers resulted in the development of a low T_g phase at about −120°C and also reduced upper glass transition temperatures of the segmented copolymers. Siloxane incorporation also provides several advantages, such as UV and oxygen stability, reduced water adsorption, increased impact resistance and surface modification.[6–8] Enhanced bond consolidation and ductility from siloxane incorporation led to higher adhesive bond strengths at room temperature (Figure 5). These strengths increased linearly with siloxane incorporation from 11.6 MPa for the homopolyimide (20K) to a remarkably high value of 50.5 MPa (7,000 psi) for the 30% siloxane-polyimide copolymer (20K). However, higher siloxane incorporation decreased the adhesive bond strength at elevated temperature, no doubt due to the elastomeric nature of the siloxane[9] and the semi-continuous nature of the morphology.

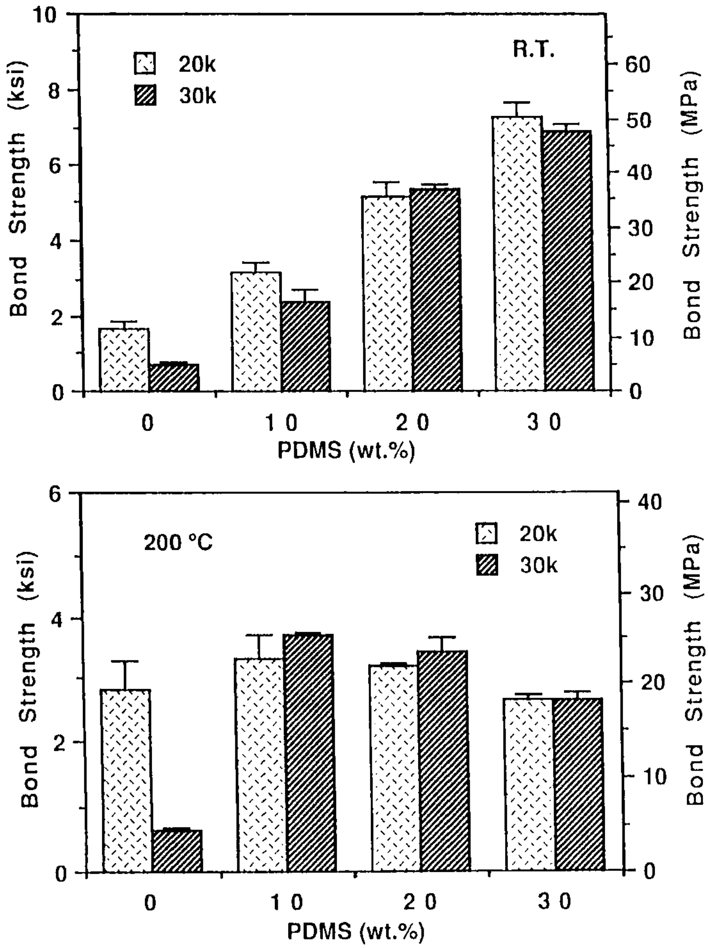

FIGURE 5 Effect of siloxane incorporation on the bond strength at R.T. and 200°C.

In the literature, two important studies on the adhesive properties of acetylene-terminated and thermoplastic polyimides have been reported.[13,14] Acetylene-terminated polyimides[13] were reported to show increased bond strengths with siloxane incorporation, while thermoplastic polyimide[14] resulted in decreased bond strengths. However, the former system is a network polyimide having low ductility. Thus, it could be argued that the siloxane incorporation enhanced the ductility and bond consolidation and that this feature resulted in increased bond strength. In the latter study, scrim cloth adhesives were employed and were dried at 100°C for 30 minutes, which may not have been sufficient to remove all of the solvent.[15] These studies demonstrated that ductility and residual solvent are also important factors for adhesive bond strength. The effect of residual solvent on the bond strength has been studied.[16] The study indicated that small amount of residual solvent may be desirable for good bond consolidation but it may decrease the high temperature adhesive bond strength.

Effect of Test Temperature

With increasing test temperature, the adhesive bond strength of the polyimide homo- and copolymers showed distinctive features depending on the siloxane content (Figure 6a). The adhesive bond strength of the homopolymer (20K) increased from 11.6 MPa at room temperature to 19.5 MPa at 200°C, then decreased to 13.0 MPa at 250°C, as the T_g was approached. The 10% siloxane copolymers exhibited maximum bond strengths at 150°C (21.7 at R.T. to 29 MPa at 150°C), which is a quite different trend from that reported in the literature.[17-19] However, the 20% and 30% siloxane copolymers showed decreasing adhesive bond strength, which is a similar trend to that previously reported.[17-19]

Further analysis of the 10% siloxane copolymers showed an interesting trend as shown in Figure 6b. The maximum bond strength was obtained at 150°C from the lower molecular weight adhesives (20,30K) and at 200°C from the higher molecular weight adhesive (40K). Such a difference may be explained by not only the melt viscosity, but also by the brittle-ductile behavior of the polyimide, which is a function of both the siloxane content and the test temperature.

Proposed Model

The adhesive bond strengths are certainly a function of tensile and shear strength, as well as ductility. However, high strength and high ductility are normally mutually exclusive. Polyimides can be somewhat brittle material systems that display high chain rigidity. However, as the temperature rises, the strength of the polymer decreases while ductility is enhanced. Conceivably, an optimum combination of strength and ductility may be obtained for a given test temperature, siloxane content and/or molecular weight, which provides the maximum adhesive bond strength (Figure 7a).

Siloxane incorporation enhances not only bond consolidation but also ductility, which could explain the improved adhesive bond strength at room temperature. The maximum adhesive bond strength at room temperature was obtained at 30%

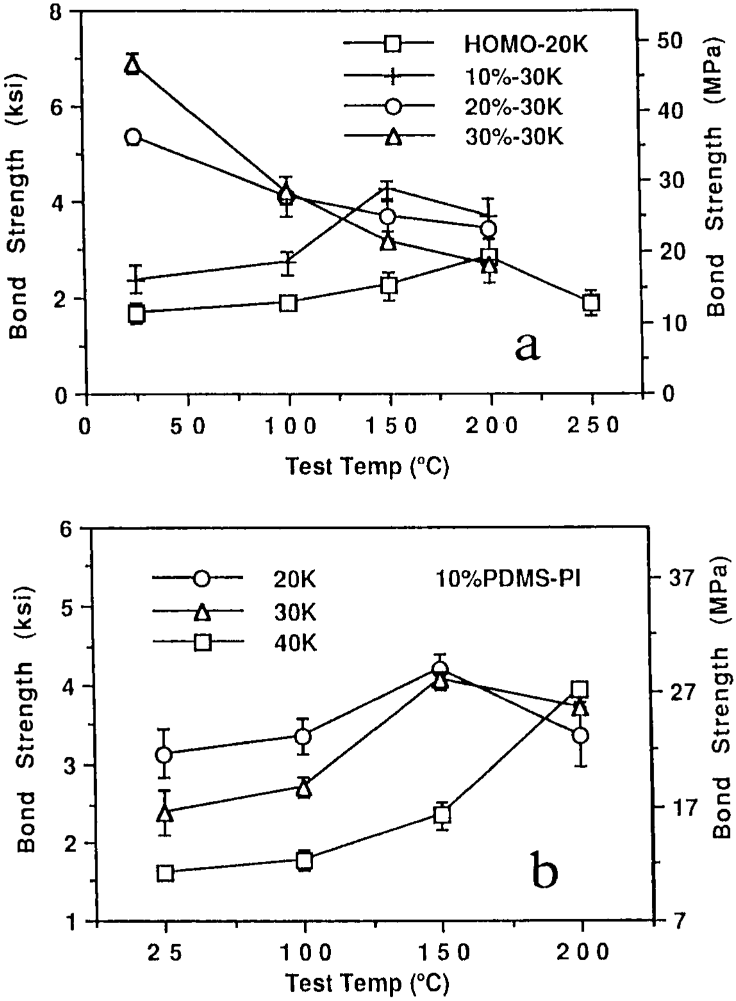

FIGURE 6 Effect of test temperatures on adhesive bond strength: a) selected polyimide homo and copolymers, b) 10% siloxane copolymers.

siloxane content in this study. However, a high soft segment content allows the siloxane to become the continuous phase which then affords elastomeric properties.[9] Thus, low adhesive bond strengths would likely be observed, in spite of high ductility. As the temperature increased, the enhanced ductility but reduced strength resulted in a shift of the maximum bond strengths to lower siloxane contents. Thus, the maximum adhesive bond strength at 200°C was obtained with 10% siloxane incorporation. Moreover, the maximum adhesive bond strength moved to lower test temperatures as the siloxane content increased as shown in Figure 7b. One may conclude that a good combination of the polymer mechanical properties and the bond consolidation (processing) is essential for maximum bond strength.

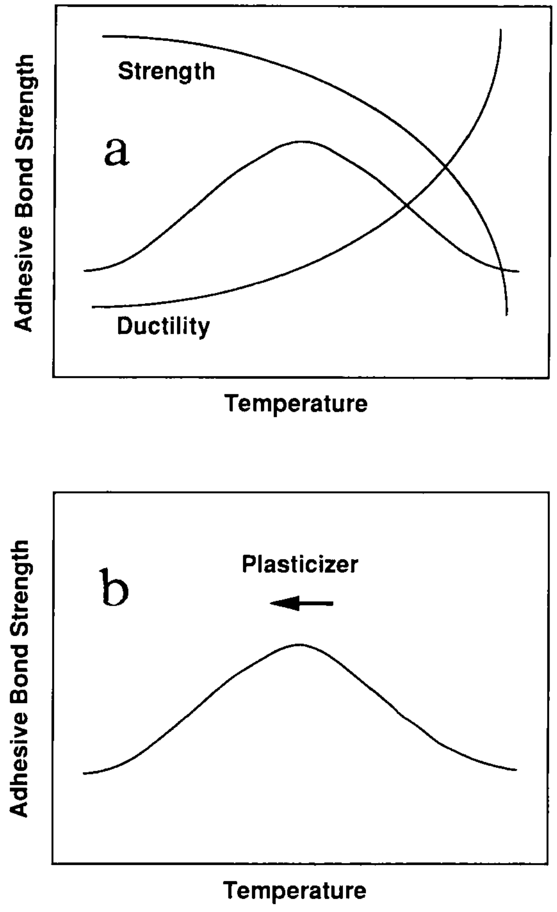

FIGURE 7a Relationship among strength, ductility and bond strength; 7b. Proposed model.

Most of the previously-reported studies[17-19] have not shown that it was possible to increase adhesive bond strength with test temperature. This may be explained by considering the nature of the polymer and residual solvent. If the polymer has enough toughness at room temperature, (e.g., as for 20% or 30% siloxane copolymers), the additional ductility provided by the higher test temperature would decrease the mechanical strength and single lap shear adhesive strength. Recall also that, in the previous studies, scrim cloth was utilized as a carrier of the poly(amic-acid). In our experiments, even scrim-cloth adhesive dried at 175°C still contained significant amounts of residual solvent, as was confirmed by Dezern and Young[15] as well as our own work.[16] The residual solvent could certainly act as a plasticizer with similar effects on the adhesive bond strengths as siloxane incorporation. Therefore, the residual solvent is envisioned as enhancing both the adhesive bond consolidation and ductility, increasing adhesive bond strengths at room temperature but lowering the same properties at elevated temperatures. In addition, aging at high temperatures increases adhesive bond strengths at high temperature, but decreases bond strength at room temperature.[15,17] A possible explanation is that high temperature aging removes residual solvent, resulting in decreased ductility and thus increased bond strength at elevated temperature and decreased bond strength at room temperature. Alternatively, the process of physical aging could occur, which is well known to enhance modulus and reduce ductility.

CONCLUSIONS

Soluble and processable polyimide homopolymers and siloxane-containing segmented copolymers were successfully synthesized. Stoichiometry was successfully adjusted to permit molecular weight control with non-reactive phthalimide endgroups. This was indicated by TMA results, intrinsic viscosity measurements and compression molding temperatures. Adhesive bond strengths were measured at room temperature, 100, 150, 200 or 250°C as a function of molecular weight and siloxane incorporation. Several conclusions were drawn from these data.

1. Decreasing molecular weight to 20,000 gm/mole increased bond strength for homopolymers tested at room temperature, probably due to enhanced flow.
2. As the siloxane incorporation increased, adhesive bond strength first increased at room temperature due to enhanced bond consolidation and ductility.
3. As the test temperature was raised, the homopolyimides and the 10% siloxane copolymers showed maximum bond strengths at 200 and 150°C, respectively, while 20% and 30% siloxane copolymers showed decreased bond strengths.
4. A model was proposed which could successfully explain the adhesion behavior of the polyimide homopolymers and copolymers on the basis that a balance is required between strength and ductility.

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