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16. Abstract

A polymer system has been prepared which has the excellent thermoplastic properties generally associated with polysulfones, and the solvent resistance and thermal stability of aromatic polyimides. This material, with improved processability over the base polyimide, can be processed in the 260-325°C range in such a manner as to yield high quality, tough unfilled moldings; strong, high-temperature-resistant adhesive bonds; and well consolidated, graphite-fiber-reinforced moldings (composites). The unfilled moldings have physical properties that are similar to aromatic polysulfones which demonstrates the potential as an engineering thermoplastic. The adhesive bonds exhibit excellent retention of initial strength levels even after thermal aging for 5000 hours at 232°C. The graphite-fiber-reinforced moldings have mechanical properties which makes this polymer attractive for the fabrication of structural composites.

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INTRODUCTION

Aromatic polysulfones, a class of polymers processable by thermoplastic means, have a major problem in their tendency to swell and dissolve in many common solvents. This dissolution causes structural components which are fabricated from these polymers to be susceptible to damage by these solvents and precludes use of polysulfones for many applications[1,2].

Aromatic polyimides, conversely, are a class of polymers which are known to be resistant to solvents, but they are generally not processable by thermoplastic means[3]. The polyimides are exceptional in their thermal stability and, like polysulfones, their use temperature is generally governed by the softening temperature of each system.

A polymer system which possesses the processability of the polysulfones and the solvent resistance of the polyimides offers a considerable advance to the state-of-the-art. The synthesis and characterization of such a system is the subject of this paper.

Although the subject polyimide has some unusual physical properties that make it interesting from an engineering standpoint, this is not the first polyimidesulfone to be prepared. Scroog, et al., have reported the preparation of polyimides from pyromellitic dianhydride and two isomeric sulfone-containing diamines[4]. Brode, et al., prepared several polyimides from sulfone arylether diamines[5], and Acle patented a copolyimide which contained sulfone units[6].

EXPERIMENTAL

Preparation of the Polymer. The monomers used in the preparation of the thermoplastic/solvent-resistant polyimidesulfone (PISO2) were 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 3,3'-diaminodiphenylsulfone (3,3' DDS). The BTDA was a polymer grade material used as received from Gulf Chemicals*, m.p. 215°. The 3,3'DDS was obtained from FIC Corporation and was used as received, m.p. 165-167°C.

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*Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

The polymerization of the two monomers in stoichiometric quantities was carried out in reagent grade bis(2-methoxyethyl-ether). This triether which is commonly called diglyme was obtained from at least four different commercial sources and used as the medium for polymerization. The reaction was conducted at 20-25°C at a concentration of 15-25% solids by weight in the reagent grade diglyme. A typical preparation was as follows: The BTDA (25.8 g) was added to a solution of 3,3' DDS (19.9 g) in diglyme (258.6 g). This mixture was allowed to stir at room temperature until all of the BTDA had dissolved. The solution was allowed to stir for an additional two hours to allow for molecular weight build up. At this stage the polymer in solution was the polyamide acid.

Characterization. The inherent viscosity of the polyamide acid solution was obtained at a concentration of 0.5 percent in N,N-dimethylacetamide at 35°C. Thermomechanical properties of the polymer were obtained by torsional braid analysis (TBA). Glass braids were coated with a 5 percent polymer solution and heated to 300°C in air before obtaining TBA spectra. Glass transition temperatures (T_g) of various films, composites, and moldings were measured by thermomechanical analysis (TMA) on a DuPont 943 Analyzer in static air at a temperature program of 5°C/min. Thermograms of the polymer were obtained by thermogravimetric analysis (TGA) by heating at a rate of 2.5°C/min in static air (dynamic TGA) or by holding the polymer at 316°C in static air (isothermal TGA). Melt flow properties were observed by use of a parallel plate plastometer accessory for the DuPont 943 Thermomechanical Analyzer. Mechanical properties of moldings, composites, and adhesive bonds were obtained on a Model TT Instron Testing Machine. Solvent resistance of films was deduced from their apparent glass transition depression as measured by TMA after solvent exposure as well as by their physical behavior in the solvents.

Preparation of Adhesive Scrim. The polyamide acid in diglyme solution was brush-coated onto 112 E-glass which had an amino-silane surface treatment (γ-aminopropylsilane). This glass cloth had a nominal thickness of 0.01 cm and was used as a carrier for the adhesive as well as for bondline thickness control. Coatings of the polyamide acid were applied to build up a scrim thickness of 0.020-0.025 cm. After each coating the scrim was air dried at room temperature until tack was lost and then placed in a forced air oven and subjected to the following cure schedules:

(1)	RT -> 100°C	hold 1/2 hour
(2)	100 -> 150°C	hold 1/2 hour
(3)	150 -> 200°C	hold 1/2 hour

This cure eliminated the diglyme as evidenced by TGA and also effected a conversion of the amide acid to the imide as evidenced by infrared spectroscopy. The water of imidization was lost primarily between 140-200°C and was carried out of the scrim along with the solvent.

Preparation of Molding Powder. The polyamide acid solution was poured very slowly into a mechanical blender containing distilled water. The contact with water caused the polyamide acid to precipitate and the blender blades chopped this material to a fluffy consistency. This solid polymer was washed with copious amounts of distilled water and was collected by suction filtration. The polymer was air-dried overnight. This solid was spread in a baking dish and placed in a forced air oven and heated to 100°C. The polymer was held at this temperature for one hour to drive off residual water and solvent. The temperature of the oven was then increased to 220°C and held for one hour to effect conversion of the amide acid to the imide.

Adhesive Bonding. The adhesive scrim cloth was used to bond titanium 6-4 adherends. The titanium adherends (Ti 6Al-4V) to be bonded were grit-blasted with 120 mesh aluminum oxide and treated with Pasa Jell 107* in order to form a stable oxide on the surface. A primer coating of the polyamide acid solution was applied to the adherends and they were thermally treated for one hour at 100°C and one hour at 200°C.

Single lap-shear specimens were prepared by sandwiching the scrim cloth between primed adherends using a 1.27 cm overlap. The specimens were bonded as follows:

(1) RT to 325°C at 7°C/min, apply 1.38 MPa (200 psi) at 280°C

(2) Hold 15 min. at 325°C

(3) Cool under pressure

Adhesively bonded specimens (4 per condition) were aged at various temperatures in forced air ovens and were tested according to ASTM D1002.

Preparation of Unfilled Moldings. Approximately 25 grams of molding powder was placed in a 5.72 cm diameter steel mold or 15 grams of the powder in a 19.0 cm x 2.5 cm rectangular steel mold and each cured according to the following cycle:

*Trade name for a titanium surface treatment available from Semco, Glendale, CA.

(1) Heat the charged mold to 200°C without the top

(2) Insert the top and apply 6.89 MPa (1000 psi)

(3) Heat to 280°C

(4) Cool under pressure

Fracture toughness testing of the 0.16 cm thick discs was performed at the Naval Research Laboratory, Washington, DC. Round compact tension test specimens were prepared from these discs and tested for G_{Ic} (the opening-mode strain energy release rate) according to ASTM E399-78A. Flexural strength and modulus were measured according to ASTM D-790. Tensile strength and modulus were measured according to ASTM D-638 on the dogbone shaped specimens that had been polished with #85 Barnesite. The tensile bars had longitudinal and latitudinal strain gages mounted on both sides.

Preparation of Graphite-Fiber-Reinforced Moldings. Graphite-Fiber-Reinforced moldings were prepared from the polyimidesulfone by initially applying the polyamide acid in diglyme at 5% solids onto drum-wound Celion® 6000 graphite fiber and subsequently coating with the same material at 15% solids. The initial coating at low solids content was employed to insure good wetting of the fibers. This prepreg was air dried on the rotary drum, cut into 7.6 cm by 17.8 cm pieces and stacked into 21-ply unidirectional preforms. The preform was next B-staged in a vacuum bag with release plies and bleeder plies on both sides. The vacuum bag assembly was heated under full vacuum to 200°C and held at that temperature for four hours.

This B-staged panel with new release plies on both sides was then placed in a 7.6 cm by 17.8 cm matched metal mold with open ends. This unit was then vacuum-bagged and cured according to the following schedule:

(1) RT to 288°C at 5°C/min

(2) At 100°C, 1.38 MPa (200 psi) was applied

(3) AT 200°C the pressure was increased to 2.76 MPa (400 psi)

(4) These conditions were held for two hours

(5) The mold was allowed to cool to below 150°C prior to removal of the molding

(6) Postcure overnight at 250°C.

The resin content on each laminate was determined by sulfuric acid digestion of the polyimide resin. This technique leaves only the graphite fiber. The calculation of the percent resin or fiber is a simple gravimetric type as follows:

$$\% \text{ fiber} = \frac{\text{weight of dried fiber after digestion}}{\text{weight of sample prior to digestion}} \times 100$$

$$\% \text{ resin} = 100 - \% \text{ fiber}$$

Densities were determined from the weights of the laminate in air and in water. Flexural strengths and moduli of the laminates were determined using ASTM D-790. Short beam shear strengths were determined using a span-to-thickness ratio of four and crosshead speed of 0.127 cm/min on the Instron testing machine.

RESULTS AND DISCUSSION

Resin Chemistry and Properties. The subject polyimidesulfone was synthesized according to the reaction scheme in Figure 1. The synthesis was performed in diglyme because this solvent has been shown to yield polymers with high adhesive strengths[7]. Diglyme is also easily eliminated so that moldings or laminates can be prepared with essentially no voids[8].

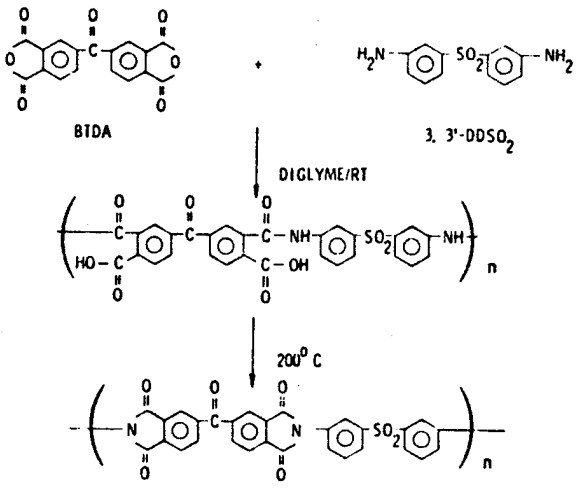

Figure 1. Polyimidesulfone preparation

The polyamide acid from the reaction scheme had inherent viscosities from several preparations that ranged from 0.4 to 0.8 dl/g. The thermal imidization of the polyamide acids resulted in linear, high molecular weight polyimides which had adequate flow to allow for thermoplastic processing. This ability to be processed as a thermoplastic relates to the flexibility of the polymer chain due to the meta linkages in the diphenylsulfone portion. This enhancement in thermoplastic processing due to the incorporation of meta linkages in linear, aromatic polyimides has been previously explained[9,10].

This polyimidesulfone exhibited good thermooxidative stability as evidenced by the isothermal and dynamic thermograms in Figures 2 and 3, respectively. After 350 hours at 316°C in air this polymer had lost only 3.5% of its initial weight. The dynamic thermogravimetric run at a heating rate of 2.5°C/min in air showed a temperature of 590°C for 50% weight loss.

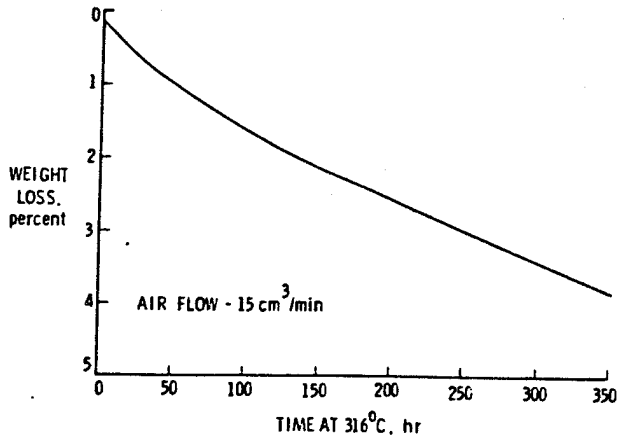

Figure 2. Polyimidesulfone weight loss at 316°C in air

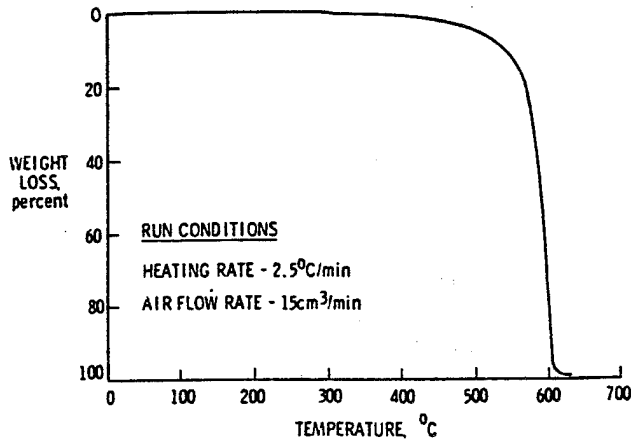

Figure 3. Polyimidesulfone weight loss in air with increasing temperature

The glass transition temperature (T_g) of the polyimidesulfone was determined by TMA on a film that had been cured in air for one hour at 100°C, one hour at 200°C, and one hour at 300°C. The T_g was found to be 273°C. The T_g as determined by TBA after the same pretreatment was 275°C as illustrated in Figure 4.

The effects of solvent exposure on the polymer are shown in Table 1. A 2 cm x 0.5 cm piece of 25μ thick film was immersed in each of the solvents listed in the table. After exposure for 24 hours they were removed and their T_g was determined using TMA by putting the solvent-laden samples under tension and subjecting them to a heat-up rate of 10°C/min[11]. The only solvent that caused a visible change in the polymer was N,N-dimethylformamide (DMF). This observation was verified by the TMA tests. The only film that showed a decrease in T_g was the sample that had been immersed in DMF. This T_g change was a depression from 273°C to 245°C.

Polymer softening characterization using the parallel plate plastometer showed the softening to begin about 250°C and reached

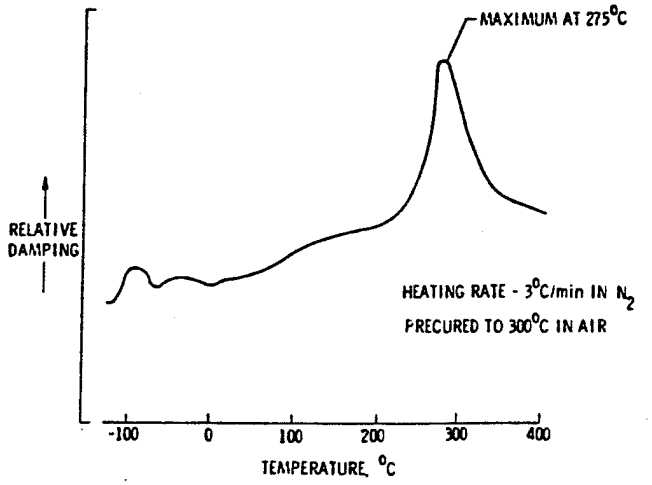

Figure 4. Torsional braid analysis of polyimidesulfone

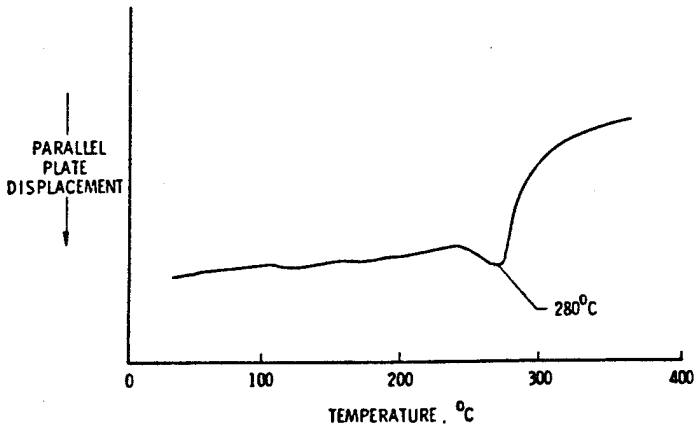

Figure 5. Softening profile of polyimidesulfone

Table I. Polyimidesulfone Solvent Resistance.

SOLVENT	IMMERSION EXPOSURE TIME, hours	VISUAL EFFECT	T_g AFTER EXPOSURE, C
NONE	—	—	273
CHLOROFORM	24	NONE	275
METHYLENE CHLORIDE	24	NONE	273
sym-TETRACHLOROETHANE	24	NONE	275
m-CRESOL	24	NONE	271
N, N-DIMETHYLFORMAMIDE	24	SHRINKAGE/SOFTENING	245
CYCLOHEXANONE	24	NONE	273
SKY JET IV	24	NONE	273

an apparent minimum at 280°C (Figure 5). Beyond 280°C there was an increase in parellel plate displacement which was due to a swelling or bulking of the sample. From processing experience it is apparent that the viscosity continues to decrease with increasing temperature beyond 280°C.

Adhesives. The titanium/titanium bonds were tested before and after aging. The data are shown in Table II and in Figures 6-8. The polyimidesulfone on the woven glass carrier was fully imidized prior to the bonding operation; therefore, the bonds were fabricated in a thermoplastic manner. The bondlines were examined after failure in the lap shear test and there was no evidence of voids in any bond. There was a decrease in lap shear strength with increasing test temperatue (4150 psi at ambient to 2620 psi at 232°C).

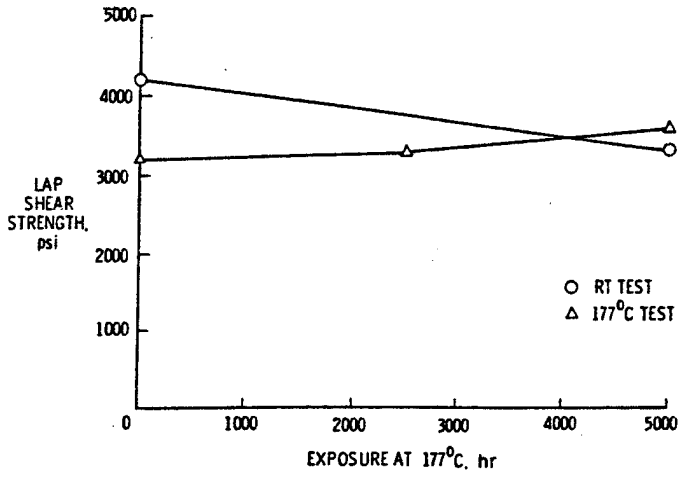

Figure 6. Adhesive strength of polyimidesulfone after 177°C exposure - titanium adherends

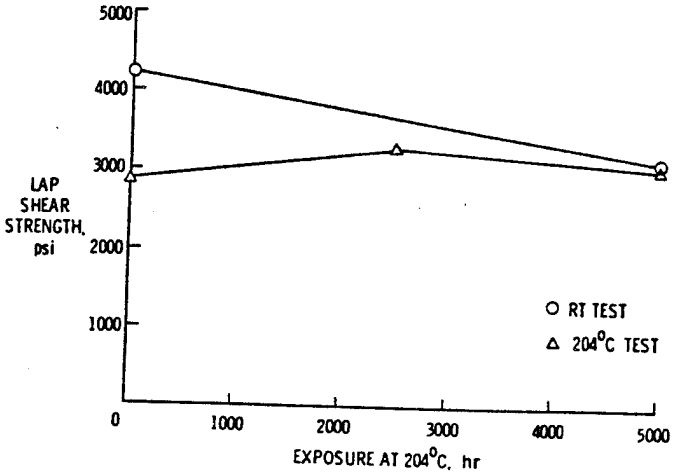

Figure 7. Adhesive strength of polyimidesulfone after 204°C exposure - titanium adherends

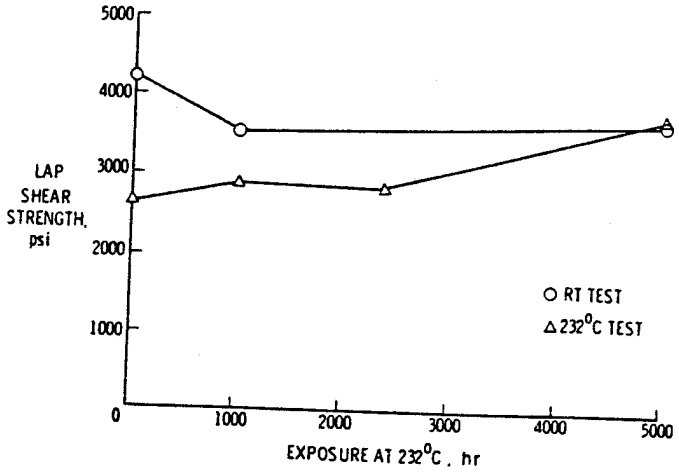

Figure 8. Adhesive strength of polyimidesulfone after 232°C exposure - titanium adherends

Table II. Polyimidesulfone Adhesive Properties.

TEST TEMPERATURE, ^{o}C (^{o}F)	AGING TEMPERATURE, ^{o}C	AGING TIME, hours	LAP SHEAR STRENGTH, psi *
AMBIENT	—	0	4650
	177	5000	3250
	204	5000	2980
	232	1000	3500
	232	5000	3640
177 (350)	—	0	3210
	232	1000	3230
	177	2500	3320
	177	5000	3670
204 (400)	—	0	2920
	204	2500	3180
	204	5000	2980
232 (450)	—	0	2620
	232	1000	2920
	232	2500	2790
	232	5000	3560

* PER ASTM D1002, TITANIUM ADHERENDS

The data in Table II shows this adhesive has exceptional thermal aging characteristics at temperatures to 232°C. After 5000 hours aging at 177°C, 204°C, and 232°C the ambient-temperature-tested lap shear samples exhibited pronounced decreases in strength; however, the elevated temperature samples (tested at the aging temperature) all exhibited strength increases. This behavior is indicative of a completion of cure or an annealing effect.

The ambient temperature strength of lap shear specimens (4 per condition) that had been aged for 5000 hours at 232°C was 3640 psi and the 232°C strength of specimens aged under these same conditions was 3560 psi. These data show this adhesive to have considerable potential for aerospace structural applications.

Unfilled Moldings. Four rectangular moldings of the polyimidesulfone were machined into tensile specimens according to ASTM D638. These moldings were amber in color and transparent. Latitudinal and longitudinal strain gages were mounted on both sides of these specimens and they were tested, according to the same ASTM standard, with strain gage readouts recorded.

The tensile data is summarized in Table III. Of particular interest is the tangent modulus of this polymer. The average initial modulus was 719 ksi; 661 ksi average at 0.005 strain level; and 603 ksi average at 0.01 strain level. The tensile modulus reported for an unfilled polysulfone is 360 ksi[12]. The high modulus exhibited by this polymer makes it attractive as a matrix resin for the fabrication of graphite-reinforced structures for aerospace applications. The failures on all four samples were of a flaw-initiated, brittle type. The average failure strain was 0.0133. The average Poisson's ratio was 0.38. The average tensile strength for the four samples was 9.1 ksi with a range of 8.6 to 9.7 ksi.

The G_{Ic} value determined on this polymer system was 1400 J/M^2 (average of two tests). This result indicates the polyimidesulfone is quite tough when compared to crosslinked systems such as addition-curing polyimides or epoxies[13].

Graphite-Fiber-Reinforced Moldings. The graphite-reinforced laminates that were prepared from the polyimidesulfone were screened by monitoring the short-beam-shear strengths of the unidirectional fabricated panels. Approximately 40 test panels with nominal dimensions of 7.5 cm x 15 cm x 0.5 cm were prepared from the solvent-impregnated prepreg. The variables studied included prepreg resin content, B-stage conditions, molding conditions and postcures. The physical and mechanical properties from the

Table III. Polyimidesulfone Tensile Properties.

SPECIMEN	TENSILE STRENGTH, ksi	INITIAL TANGENT MODULUS, ksi	TANGENT MODULUS, ksi		FAILURE STRAIN, cm/cm	POISSON'S RATIO
			AT 0.005 STRAIN	AT 0.01 STRAIN		
1	8.6	722	644	600	0.0123	0.38
2	9.3	733	689	622	0.0133	0.37
3	9.7	702	667	611	0.0141	0.38
4	8.9	720	644	578	0.0135	0.37
AVERAGE	9.1	719	661	603	0.0133	0.38

resulting laminates that were monitored were thickness, resin content, glass transition temperature, density, short-beam-shear strength at room temperature and elevated temperature, and overall weight loss during processing. These panels had considerable variability in properties initially, but this variability lessened as better cure cycles were developed. Representative data on laminates prepared according to the procedure described in the experimental section are in Table IV.

Table IV.- Properties of Graphite-Fiber-Reinforced Polyimidesulfone Composite Panels

Short-beam shear strength, psi	
ambient - 11,000 to 12,000	
121°C - 7,500 to 8,500	
172°C - 6,500 to 7,500	
Flexural strength, ksi	190
Flexural modulus, ksi	21,000
Resin content, percent by weight	35 to 38
Density, g/cm^3	1.50 to 1.56
Laminate thickness, cm	0.25 (nominal)
Weight loss during cure, percent by weight	12.8 to 18.3

CONCLUSIONS

A novel polyimidesulfone which shows considerable potential as an engineering thermoplastic has been synthesized and characterized. It is a high molecular weight linear aromatic system which is flexible, tough, and thermooxidatively stable. Imidized molding powder of this polymer was fabricated into void-free neat moldings which exhibited a tensile strength in excess of 9 ksi and a modulus of 719 ksi. This tensile strength is average for engineering thermoplastics. However, the modulus is approximately double the value reported for such thermoplastics. The G_{Ic} value for this polyimidesulfone is 1400 J/M^2.

Adhesive bonds prepared with the subject polymer and titanium alloy adherends had high initial lap shear strength values at room temperature (>4500 psi) and good adhesive strength was retained at test temperatures up to 232°C (>2600 psi). After aging at temperatures up to 232°C for 5000 hours the lap shear strengths were still high at room temperature (>3600 psi) and had increased when tested at 232°C (>3500 psi).

Graphite-reinforced composites were successfully prepared from the polymer system using solvent-impregnated prepreg. The short-beam-shear properties of unidirectional laminates were 11 to 12 ksi when tested at room temperature and 6.5 to 7.5 ksi for 177°C tests.

The solvent resistance of this polymer system also sets it apart from the more commonly used thermoplastics. There was no change in the polymer when immersed in chlorinated hydrocarbons, cresol, cyclohexanone, and aircraft hydraulic fluid (tricresylphosphate-base). There was slight swelling in dimethylformamide and it is expected that other amide solvents will effect the polymer in a similar fashion; however, these solvents are not likely to be encountered in most service applications.

The combination of properties that this polyimidesulfone exhibits makes it a very attractive candidate for aircraft structural applications such as adhesives and composites. Also, because of the ready availability of raw materials necessary for its preparation, the polymer has considerable commerical potential.

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