

Processable Aromatic Polyimides

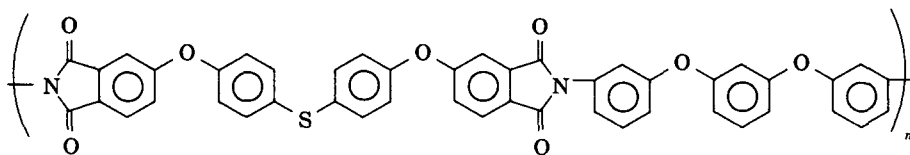
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Synopsis

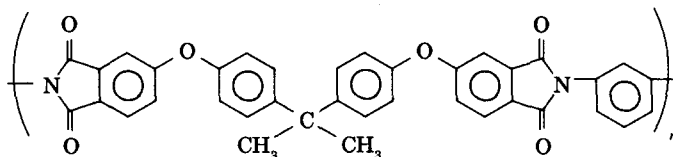
Two similar polyimide systems were synthesized and characterized. The only structural difference was a sulfide linkage in the anhydride-derived portion of the first system vs. a sulfone linkage in the second. Their physical, mechanical, melt-flow and thermal properties, and their resistance to some of the more common solvents were determined. The flow properties of these polyimides indicate a potential for melt processability.

INTRODUCTION

Two linear aromatic polyimides have been recently shown to have considerable potential for processing via hot-melt techniques.^{1,2} One is an experimental material developed at NASA-Langley and the other is the commercially available ULTEM* from General Electric. The chemical structures of these polyimide systems are shown below.



BSDSA/APB

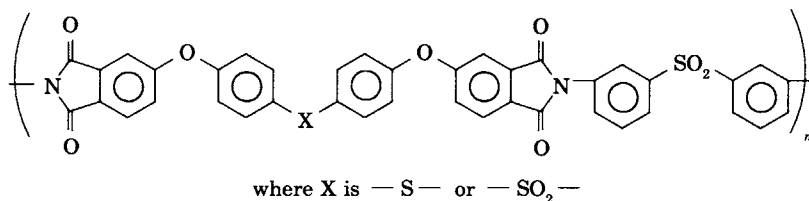


ULTEM*

There are two factors that appear to have produced this enhanced flow. The first and perhaps most important factor is the separation of the imide rings. In both structures the phthalimide moieties are separated by bisphenoxide units. This may have the effect of diluting the high associative forces that have classically imparted the high glass transition temperatures to linear aromatic polyimides.³ The second factor that is common to both systems is the incorporation of diamines with *meta* linkages. This technique has been proven to lower glass transition temperatures in polyimides.⁴ The articulation of both of these features gives the potential for some very

* ULTEM is the registered trademark of a General Electric Polyetherimide.

processable polyimides. The subjects of investigation for this report are the two polyimides of the following structure:



These two polymers were prepared and studied as part of a continuing program with the objective of developing hot-melt processable polyimides. The synthesis and characterization of these materials are discussed.

EXPERIMENTAL

Preparation

Polymer. To form the polymer, 0.1000 mol of 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride (BDSDA) and 0.1000 mol of 3,3'-diaminodiphenylsulfone (DDSO₂) were dissolved in bis(2-methoxyethyl)ether at 15% solids in a flask equipped with magnetic stirring. This solution was allowed to stir for one hour in order to build up molecular weight. The reaction is shown in Figure 1.

The same procedure was used for the polymer made from 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfone dianhydride (BDSO₂DA) and DDSO₂. However, no appreciable buildup in molecular weight occurred during this step. A buildup was noted when the precipitated polymer was heated as outlined in the next subsection on molding powder.

Molding Powder. The polymer solution was poured into a mechanical blender containing distilled water. The contact with water caused the polyamide-acid to precipitate and the rotating blender blades chopped this material into a fluffy consistency. The solid polymer was isolated by suction filtration and allowed to air dry overnight.

The dried polymer was spread in a baking dish, placed in a forced-air

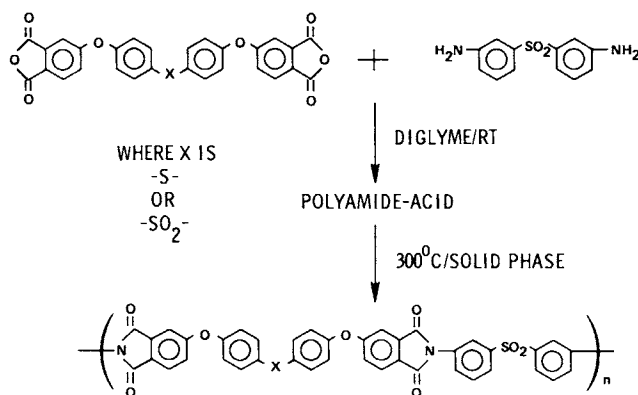


Fig. 1. Polymer synthesis scheme for BDSDA/DDSO₂ and BDSO₂DA/DDSO₂.

oven, and heated to 100°C. The polymer was held at this temperature for 1 h to drive off residual water and solvent. The temperature was increased to 200°C and held for 1 h to effect conversion of the amide-acid to the imide. Both systems fused into glassy solids at this stage. During this melt phase the BDSO₂DA/DDSO₂ system appeared to undergo further polymerization. These glassy polyimides were ground into powder form.

Unfilled Moldings. The polyimide powder was molded according to the following procedure. The imidized powder was placed in a matched-metal molding die which was preheated to 200°C. A pressure of 1.38–2.07 MPa (200–300 psi) was applied to effect consolidation. This temperature and pressure were held for 0.5 h. The mold and molding were allowed to cool to approximately 100°C, and the molding was removed. These moldings were light brown and transparent when prepared in discs up to 0.635 cm (0.250 ins.) in thickness.

Film. A 15% solution of BDSDA/DDSO₂ in diglyme was used to cast a 380- μ m thick wet film on plate glass using a doctor blade. The film was then cured in an air oven as follows: 1 h at 100°C; 1 h at 200°C; 1 h at 300°C. Since the BDSO₂DA/DDSO₂ did not build to high molecular weight during the solution polymerization, no films were prepared. The cured film of BDSDA/DDSO₂, approximately 40 μ m thick, was removed from the glass for future testing.

Characterization Methodology

Flow Properties. Melt flow properties for BDSDA/DDSO₂ and BDSO₂DA/DDSO₂ at 375°C were determined using a capillary rheometer (Instron Model 3211).⁵ The capillaries had length-to-diameter ratios of 33 and 66; therefore, no end corrections were required.

Physical Properties. Water absorption at ambient temperature was determined using three bar samples of each material, each sample nominally 0.254 \times 0.635 \times 2.337 cm cut from molded stock. The samples were weighed and oven-dried in air for 24 h at 100°C. They were then cooled to ambient in a desiccator and reweighed. They were immersed in distilled water for 24 h, removed and blotted dry, and reweighed. Samples were reimmersed for an additional 48 h, removed and blotted dry, and again weighed.

The density (g/cm³) was determined on a molded disc of BDSDA/DDSO₂ 5.715 cm diameter \times 0.254 cm thick. Density determinations for the BDSO₂DA/DDSO₂ were made on six-bar samples nominally 2.663 \times 0.639 \times 2.739 cm cut from molded stock and the average value reported.

Inherent viscosity measurements were made on the poly(amide-acid) form of BDSDA/DDSO₂ using a Cannon-Ubbelohde viscometer in a 35°C water bath. A 10-mL solution of 0.5% solids in DMAc was made and filtered. The average of four runs of this solution was reported.

The number-average molecular weight (\bar{M}_n) and weight-average molecular weight (\bar{M}_w) were determined at room temperature for the poly(amide-acid) form of BDSDA/DDSO₂ dissolved in tetrahydrofuran.* A Knauer Membrane Osmometer was used for the \bar{M}_n measurements and a Brice-Phoenix Light Scattering Photometer for the \bar{M}_w measurements.

* Molecular weights determined by ARRO Laboratory, Joliet, IL.

Mechanical Properties. All mechanical properties were determined at room temperature using an Instron Testing Machine Model TT-C.

The flexural strength and modulus of BDSDA/DDSO₂ and BDSO₂DA/DDSO₂, each sample nominally 0.635 × 0.254 × 3.175 cm and cut from a molded disc, were determined in three-point bending in accordance with ASTM Standard D 790-71. Due to a lack of material, these samples had span-to-depth ratios of 10–12 and not 16 as specified by the ASTM Standard. The average of four samples was reported.

The fracture energy value (G_{Ic}), the opening mode strain energy release rate, was determined for two compact tension samples of the BDSDA/DDSO₂ system. G_{Ic} for the BDSO₂DA/DDSO₂ system was not determined due to a lack of material. The samples were machined from discs 5.715 cm diameter and nominally 0.127 cm thick, precracked, and run at a crosshead speed of 0.127 cm/min according to ASTM Standard E 399-78A. The average of two samples was reported.

Thermal Properties. The coefficient of thermal expansion was determined for the range 30–175°C using a DuPont Model 941 Thermomechanical Analyzer (TMA) operating in static air at a programmed heating rate of 10°C/min. The glass transition temperature (T_g) was determined calorimetrically with a DuPont Model 990 Thermal Analyzer/Differential Scanning Calorimeter (DSC) in static air at a programmed heating rate of 20°C/min. The apparent glass transition temperature was determined using a DuPont Model 943 Thermomechanical Analyzer (TMA) in static air at 5°C/min, and also on a DuPont Model 1090 Dynamic Mechanical Analyzer (DMA) under the same run conditions. The T_g (apparent) was also determined from a thermomechanical spectrum of BDSDA/DDSO₂ obtained by torsional braid analysis (TBA). A glass braid was coated with a 10% diglyme solution of the poly(amide-acid) and precured to 250°C in N₂. This spectrum was obtained at a heating rate of 3°C/min in an air atmosphere. Thermooxidative stability (weight loss vs. temperature) was determined using a Perkin-Elmer Model TGS-2 thermogravimetric analysis system (TGA) using a heating rate of 2.5°C/min and an air flow of 15 cc/min.

Infrared Analysis. Infrared spectra of BDSDA/DDSO₂ and BDSO₂DA/DDSO₂ in the 4000–400 cm⁻¹ wavenumber region were obtained using a Nicolet Model MX-1 FTIR Spectrometer. An attenuated total reflectance technique (ATR) using a KRS-5 crystal was employed because the polymer samples were too thick for standard transmission measurements. Each spectrum is the average of between 100 and 500 individual scans.

Chemical Resistance. Six film samples of BDSDA/DDSO₂ approximately 40 μm thick were measured for T_g (apparent) using a DuPont Model 941 Thermomechanical Analyzer.⁶ Each of the six samples was immersed in one of six commonly used solvents at room temperature for a period of 72 h. Their physical condition was noted, and they were removed and blotted dry. After blotting dry, T_g (apparent) data were again determined.

RESULTS AND DISCUSSION

Synthesis

BDSDA/DDSO₂ and BDSO₂DA/DDSO₂ were synthesized according to the reaction scheme shown in Figure 1. Reaction of the BDSDA/DDSO₂ mon-

omers in the ether solvent, diglyme, produced a viscous poly(amide-acid) with an inherent viscosity of 0.52 dL/g. As previously mentioned, the BDSO₂DA/DDSO₂ system did not build to a high molecular weight until the imidization step. The thermal imidization of both poly(amide-acids) were carried out on the powder, resulting in linear high molecular weight polymers which could be processed as hot-melt thermoplastics.

The polymers, after thermal imidization at 200°C in air, exhibited T_g 's of 209 and 205°C, respectively, for the BDSDA and BDSO₂DA systems. Further molecular weight buildup was accomplished for the BDSO₂DA system by curing at 200°C as evidenced by an increased resistance of the polymer to being powdered by mechanical means.

Characterization

Flow Properties. The melt flow properties of a polymer are important in determining how it should be processed. Compression molding, milling, calendaring, extrusion, and injection molding are some of the more commonly used processing methods.⁷ The melt flow properties of BDSDA/DDSO₂ and BDSO₂DA/DDSO₂ were determined for the shear strain rate region (10^{-1} – 10^3 s⁻¹) that these processing methods cover.

Capillary Rheometry was used to determine stress vs strain rate for BDSDA/DDSO₂ and BDSO₂DA/DDSO₂ at 375°C (Fig. 2). These polymers were shown to be pseudoplastic, a non-Newtonian shear thinning property typical of molten polymers. The pressures associated with commercial molding presses correlate, generally, with stresses in the 10^4 – 10^5 Pa range. Most of the measured stresses for these polymers exceeded this range. They also exceeded the stresses required for BDSDA/APB as previously reported.¹ Consequently, higher temperatures and low strain rates (i.e., longer times) would be required for molding of BDSDA/DDSO₂ and BDSO₂DA/DDSO₂ as compared to BDSDA/APB.

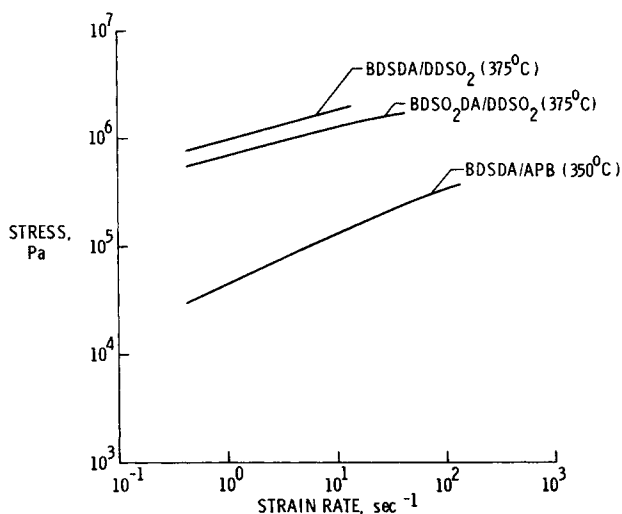


Fig. 2. Capillary rheometer stress vs. strain rate for BDSDA/DDSO₂, BDSO₂DA/DDSO₂, and BDSDA/APB.

The apparent viscosity as a function of strain rate at 375°C (Fig. 3) is shown for the strain rates encountered in different industrial processes. The apparent viscosity was calculated by dividing the flow stress by the strain rate. As the strain rate was calculated from the volumetric flow data and was not corrected to obtain the wall rate, the viscosity is an apparent rather than a true viscosity.⁸ The BDSDA/DDSO₂ and BDSO₂DA/DDSO₂ polymers should be processable via compression molding and calendering techniques. However, no conclusions can be drawn concerning the extrudability of the polymers above a strain rate of 40 s⁻¹ due to the stress and strain rate limitations of the rheometer in its present configuration.

Figure 3 also compares the change in apparent viscosity with strain rate of BDSDA/DDSO₂ and BDSO₂DA/DDSO₂ at 375°C with BDSDA/APB at 350°C.¹ At low strain rates BDSDA/DDSO₂ and BDSO₂DA/DDSO₂ exhibit higher melt viscosities (thus requiring higher processing pressures) than BDSDA/APB and maintain this relationship even at the higher strain rates. This would indicate that they are somewhat less easily processable than BDSDA/APB.

Melt Fracture. As was the case with the previously reported BDSDA/APB,¹ both BDSDA/DDSO₂ and BDSO₂DA/DDSO₂ exhibited pronounced distortion when extruded at 375°C at shear stresses in the 2×10^5 Pascal region. This distortion, referred to as "melt fracture,"^{9,10} increased with increasing stress during the extrusion process. BDSDA/DDSO₂ and BDSO₂DA/DDSO₂ at 375°C exhibited comparable melt fracture, and exceeded the melt fracture exhibited by BDSDA/APB at 350°C. Therefore, BDSDA/DDSO₂ and BDSO₂DA/DDSO₂ might be more difficult to extrude.

Physical Properties. Physical properties for BDSDA/DDSO₂ and BDSO₂DA/DDSO₂ are listed in Table I, which shows the polymers to be essentially identical in these properties. Ambient equilibrium moisture contents of 0.69% and 0.67%, respectively, by weight were determined by oven drying the samples in air for 24 h at 100°C. A 72-h water soak restored the

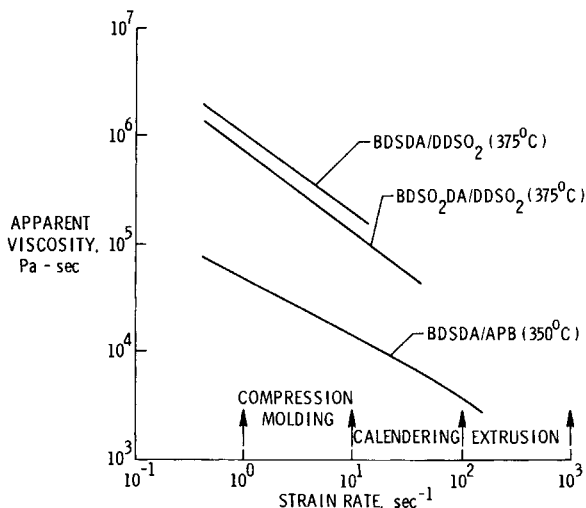


Fig. 3. Apparent viscosity as a function of strain rate for BDSDA/DDSO₂, BDSO₂DA/DDSO₂, and BDSDA/APB.

TABLE I
Physical Properties of Polymers

	BSDA/DDSO ₂	BDSO ₂ DA/DDSO ₂
Water absorption ^a		
24 h soak	0.25%	0.25%
72 h soak	0.43%	0.42%
Equilibrium ^b	0.69%	0.67%
Density ^c	1.38 g/cm ³	1.37 g/cm ³
Inherent Viscosity ^d	0.52 l/g	—
Molecular weight ^e		
Number average (\bar{M}_n)	8500	—
Weight average (\bar{M}_w)	12,100	—

^a Bar samples nominally 0.254 × 0.635 × 2.337 cm cut from molded stock.

^b Equilibrium water absorption in air.

^c BSDA/DDSO₂-molded disk 5.715 cm diameter × 0.254 cm thick; BDSO₂DA/DDSO₂-bar samples nominally 2.663 × 0.639 × 2.739 cm cut from molded stock.

^d Polyamide-acid solution with 0.5% solids in DMAc at 35°C.

^e Values determined on the amide acid by Arro Labs.

samples to approximately two-thirds of their original weight. An interim check at 24 h showed the samples had regained approximately one-third of their original ambient moisture content. These values are an average of three samples of each polymer taken at room temperature. The densities were determined to be 1.38 g/cm³ and 1.37 g/cm³, typical for amorphous, linear aromatic polymers. The inherent viscosity of 0.52 dL/g for the poly(amide-acid) form of BSDA/DDSO₂ reflects the molecular weight of the poly(amide-acid). Because the polymer melts during subsequent processing to the imide form, there is a possibility for either an increase or decrease in its molecular weight, as occurred in the BDSO₂DA/DDSO₂ system where an increase was evident. The number-average molecular weight (\bar{M}_n) for the poly(amide-acid) form of BSDA/DDSO₂ was 8500. This was the average of nine determinations (three measurements for each of three solution concentrations). The weight-average molecular weight (\bar{M}_w) was 12,100 (two measurements for each of four solution concentrations). Inherent viscosity and molecular weight were not determined for the BDSO₂DA/DDSO₂. In its poly(amide-acid) form it was soluble, but very low in molecular weight. In the imide form the molecular weight increased, but it was now insoluble, thus precluding the determination of its inherent viscosity and molecular weight.

Mechanical Properties. The mechanical properties determined for BSDA/DDSO₂ and BDSO₂DA/DDSO₂ at room temperature are listed in Table II. The flexural strength and flexural modulus for the BSDA/DDSO₂ of 27.1 MPa and 3.74 GPa, respectively, represent the average of three samples. The flexural strength and flexural modulus for the BDSO₂DA/DDSO₂ of 74.1 MPa and 3.36 GPa, respectively, also represent the average of three samples. The critical rate of release of strain energy (G_{Ic}) for BSDA/DDSO₂ was determined to be 268 J/m². The low values for flexural strength and G_{Ic} for the BSDA/DDSO₂ polymer are attributed to its low molecular weight.¹¹

TABLE II
 Mechanical Properties of Unfilled Polymers

	BSDA/DDSO ₂	BDSO ₂ DA/DDSO ₂
Flexural strength	27.1 MPa (3.93 ksi)	74.1 MPa (10.7 ksi)
Flexural modulus	3.74 GPa (542 ksi)	3.36 GPa (487 ksi)
Critical rate of release of strain energy, G_c	268 J/m ²	—

Thermal Properties. Some of the more common thermal properties were determined for BSDA/DDSO₂ and BDSO₂DA/DDSO₂ and are listed in Table III. The coefficients of thermal expansion $4.99 \times 10^{-5} \text{C}^{-1}$ and $4.96 \times 10^{-5} \text{C}^{-1}$, respectively, are typical for state-of-the-art polyimides. The glass transition temperatures (T_g), measured calorimetrically, were determined to be 209 and 205°C, respectively. The T_g (apparent) values, determined using TMA, were 211°C for both polymers. The DMA method established a T_g (apparent) of 192°C for BSDA/DDSO₂ and 200°C for BDSO₂DA/DDSO₂. BSDA/DDSO₂ exhibited a T_g (apparent) of 208°C when measured by TBA (Fig. 4).

The thermooxidative stabilities of BSDA/DDSO₂ and BDSO₂DA/DDSO₂ film are basically the same, as shown in the thermograms Figure 5. The dynamic TGA curves obtained at a heating rate of 2.5°C/min, and an air flow rate of 15 cc/min indicate that the films undergo essentially no weight loss below 380°C. They exhibit a 50% weight loss temperature of approximately 590°C and experience complete degradation at approximately 650°C.

Infrared Analysis. The spectra between 4000 and 400 cm⁻¹ were run on a BSDA/DDSO₂ film cured in a nitrogen atmosphere, a molding of the air-cured BSDA/DDSO₂, and a molding of the air-cured BDSO₂DA/DDSO₂. The spectra between 2000 and 400 cm⁻¹ of the N₂-cured BSDA/DDSO₂ film and the air-cured BDSO₂DA/DDSO₂ molding are shown in Figure 6. It is evident in this comparison that the two spectra are virtually identical. In Figure 7 the moldings from each system are compared. Again both systems appear identical. The logical explanation seems to be an oxidation of the sulfide group to the sulfone. The similarity of other physical properties which were previously discussed might be attributed to this conversion.

 TABLE III
 Thermal Properties of Unfilled Polymers

	BSDA/DDSO ₂	BDSO ₂ DA/DDSO ₂
Coefficient of thermal expansion (30–175°C)	$4.99 \times 10^{-5} \text{C}^{-1}$	$4.96 \times 10^{-5} \text{C}^{-1}$
Glass transition temp (T_g), calorimetric	209°C	205°C
Thermomechanical T_g (apparent)		
TMA	211°C	211°C
DMA	192°C	200°C
TBA	208°C	—
Decomposition temp ^a	588°C	575°C

^a 2.5°C/min heating rate, 15 cc/min air flow, 50% wt loss.

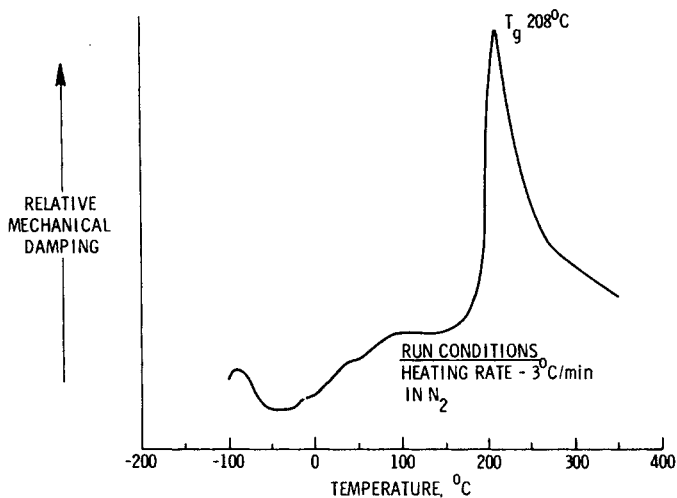


Fig. 4. Torsional braid analyzer (TBA) spectrum of imidized BDSDA/DDS₂ (braid precured to 300°C in air).

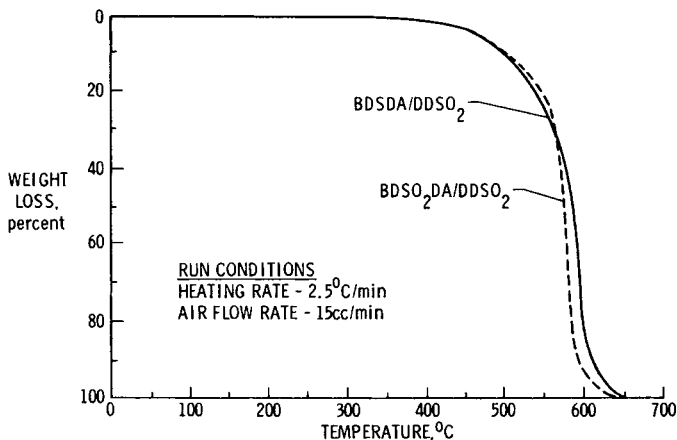


Fig. 5. Comparison of thermooxidative stability of BDSDA/DDS₂ and BDSO₂DA/DDS₂ polymer film.

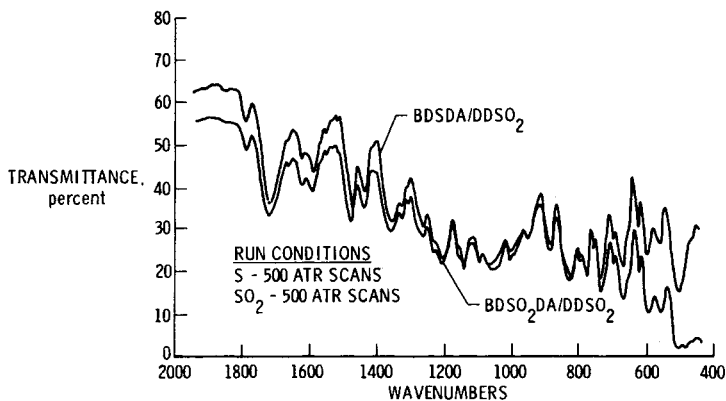


Fig. 6. Comparison of polymer moldings by infrared analysis.

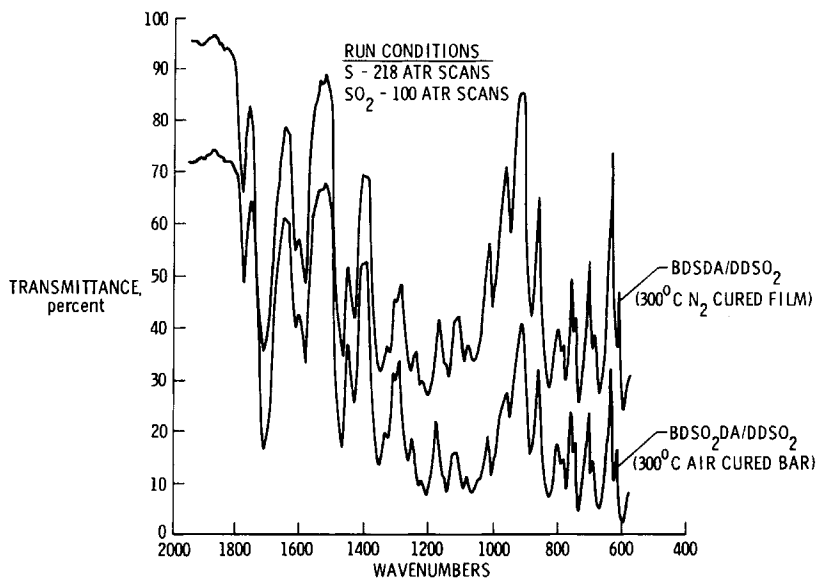


Fig. 7. Infrared analysis of 300°C air cured samples.

However, in another study of polyimides where a methylene bridge was converted to a carbonyl during cure, a crosslinking phenomena occurred which resulted in a higher T_g than was found for the corresponding carbonyl-containing polymer that had been unequivocally synthesized.¹² In the present study there seems to be little evidence for crosslinking since the T_g 's are so similar.

Chemical Resistance. The chemical resistance of BDSDA/DDSO₂ thin film (40 μm thick) to six common solvents was determined and the results listed in Table IV. Methyleneethyl ketone, xylene, and tricresylphosphate had no visible effect on the film and there was no change in T_g (apparent). Cyclohexanone had only a slight visible effect on the film with no change in T_g . Methylene chloride and cresol caused only minor swelling. The T_g for the methylene chloride soaked film was not measured because the film softened at approximately 110°C, preventing a T_g determination. The cresol-soaked film exhibited severe shrinkage above 50°C, and no T_g was detectable.

TABLE IV
Chemical Resistance of BDSDA/DDSO₂ FILM^a

Solvent	Effect	T_g (apparent) (°C) ^b
Methylethyl ketone	None	211 (no change)
Cyclohexanone	Slight swelling	213 (no change)
Xylene	None	213 (no change)
Tricresylphosphate	None	214 (no change)
Methylene chloride	Minor swelling	Not determined ^c
Cresol	Minor swelling	Not determined ^d

^a 40 μm thick film.

^b Thermomechanical analysis of solvent-laden films soaked 72 h at room temperature and blotted dry.

^c Film softened at $\sim 110^\circ\text{C}$ and T_g (apparent) could not be measured.

^d Film underwent severe shrinkage above 50°C and T_g (apparent) could not be measured.

CONCLUSIONS

As part of a continuing research program to investigate concepts which will lead to development of high temperature polymers with enhanced hot-melt processability, two similar polyimide systems were synthesized and characterized. The polyimides differed in that the anhydride-derived portion contained a sulfide linkage in one and a sulfone linkage in the other. During cure, the sulfide linkage in the first material appeared to oxidize to the sulfone, as indicated by infrared analyses. Thus, the slight differences observed in the physical properties of the two materials are probably due to differences in molecular weights.

Both materials exhibited melt-flow. Apparent viscosities were determined using capillary rheology; flow characteristics of both polyimide materials were similar. While both appear to have potential for melt processability with good thermal stability and chemical resistance, they are not as processable as a previous polyimide material (BDSDA/APB) developed earlier in this program.

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