Synthesis and Characterization of BDSDA/APB Polyimide

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Synopsis

A novel linear aromatic polyphenylene ethersulfideimide (BDSDA/APB) has been synthesized. Its physical, mechanical, thermal, and flow properties and its resistance to some of the more commonly used solvents were determined. The results of these property evaluations indicate this polymer system can be processed via conventional thermoplastic techniques. It has been molded, used as a resin, and cast into thin films and, accordingly, may have a wide variety of applications. Its molecular weight was varied by endcapping with phthalic anhydride. Over the $\overline{M}_n$ range 14,000–45,000 the apparent viscosities and G_{Ic} values varied only slightly. However, a change in $\overline{M}_n$ from 14,000 to 8700 resulted in a dramatic decrease in the apparent viscosity at both 250°C and 280°C. The G_{Ic} values for these same molecular weight materials decreased in a like manner as the $\overline{M}_n$ decreased, indicating tradeoffs can be made between process optimization and final mechanical properties when polymer systems are developed.

INTRODUCTION

Linear aromatic polyimides are a class of polymers which are generally not processable via conventional thermoplastic or hot-melt techniques. This class of polymers is, however, exceptionally thermally stable and has high glass transition temperatures.[1,2] These polyimides are also resistant to attack by common organic solvents.[3]

Linear aromatic polyphenylene oxides and sulfides are more easily processed than the polyimides,[1] generally exhibit lower glass transition temperatures, and still have relatively good thermal stability, although not equal to that of the polyimides.[4] These PPO and PPS systems do not possess the solvent resistance of the polyimides.[5]

A novel linear aromatic polyphenylene ethersulfideimide (BDSDA/APB) has been synthesized that has some of the favorable characteristics of each parent system. The polymer has been molded, used as a resin, and cast into thin films. A limited characterization indicates this system can be processed via conventional thermoplastic techniques and may have a wide variety of applications.

In an effort to maximize the use properties and processability of BDSDA/APB, its molecular weight was varied by endcapping with phthalic anhydride. This approach was taken because of the work previously reported by Fox and Flory.[6] They found that decreasing the molecular weight of polystyrene caused its melt viscosity to decrease. In the present study the effect of changing molecular weight was determined by measuring the melt vis-

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cosity and fracture energy (G_{Ic}) values for the different endcapped polymers whose chemical structure is shown by:
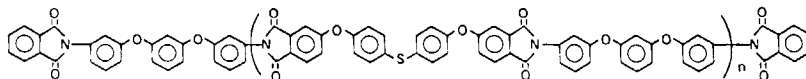
EXPERIMENTAL

Polymer Synthesis. To form the uncapped polymer, an equimolar ratio of 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride (BDSDA) and 1,3-bis(aminophenoxy)benzene (APB) were dissolved in bis(2-methoxyethyl)ether (also known as diglyme) at a 15% solids level in a flask equipped with magnetic stirring. This solution was allowed to stir for 1 h in order for molecular weight to build.

In the case of the endcapped systems the appropriate amount of APB was dissolved in the bis(2-methoxyethyl)ether and the endcapping agent, phthalic anhydride (PA), was added and the system was stirred for 15 min. Next the BDSDA was added and stirring continued for 1 h to again allow molecular weight to build. Table I shows the ratios of reactants that were used for the different endcapped systems. Note that since the BDSDA is difunctional, the decrease of 1% in this constituent must be offset with a concomitant increase of 2% in the PA which is monofunctional. This is done to maintain proper stoichiometry of amine to anhydride.

Molding Powder. The viscous 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 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 to effect conversion of the amide–acid to the imide.

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 160°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

TABLE I
Molar Ratios of Reactants for Endcapped Systems

Endcap system (%)	Mole ratio		
	APB	BDSDA	PA
1	1.000	0.995	0.010
2	1.000	0.990	0.020
4	1.000	0.980	0.040

to approximately 100°C and the molding was removed. This molding was light brown and transparent when prepared in discs up to 0.635 cm (0.250 in.) in thickness.

Adhesive Bonds. Two sets of adhesive bonds were prepared at different heat-up rates. Duplicate 2.54-cm-wide strips of 0.127 cm (0.050 in.) thick Ti-6Al-4V titanium alloy were grit blasted with 120-mesh aluminum oxide, washed with methanol, and treated with Pasa Jell 107.* These strips were washed with water and dried in a forced-air oven at 100°C for 15 min. Each strip was coated with the polyamide-acid solution. A piece of woven glass cloth (0.01 cm thickness) was laid into the wet polymer on one of the titanium panels. The coated panels were allowed to air dry for approximately 1 h and then placed in a forced-air oven and heated to 160–275°C in order to drive off solvent and to convert the polyamide–acid to the polyimide. Imidization occurs at temperatures above 160°C, and the degree of conversion is a function of time and temperature. An example of a cure is as follows:

> 1 h at 100°C
> 1 h at 200°C
> 1 h at 275°C

This treatment was repeated several times on the panel with the glass cloth in order to build up sufficient adhesive thickness for bonding.

The panels were then overlapped according to ASTM D1002-72 and bonded in a hydraulic press under 2.07 MPa (300 psi) pressure. This sample was heated to 316°C at 5°C/min and held at temperature for 15 min. The bonded specimen was allowed to cool to 100°C before removal from the press.

In order to achieve a higher heatup rate, another pair of adherends were placed into the press which had been previously heated to 343°C. The temperature rise on these panels was monitored, as in the previous case, using a thermocouple which was spot-welded at the edge of the bondline. This bonding procedure afforded an average 22°C/min heat rise to 316°C. A bonding pressure of 2.07 MPa was also used for this sample.

Film. A 15% solution of BDSDA/APB in diglyme was used to cast a 381 μm 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

The cured film, approximately 40 μm thick, was removed from the glass for future testing.

CHARACTERIZATION METHODOLOGY

Flow Properties. Melt flow properties for BDSDA/APB in the range 250–350°C were determined using a capillary rheometer (Instron Model 3211).[7] The capillaries used had length-to-diameter ratios of 33 and 66;

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* Pasa Jell 107 is a commercial product of SEMCO. (Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.)

therefore, no end corrections were required. Melt flow properties were not measured below 250°C because the pressure needed to force the polymer through the capillary was greater than the rheometer load cell was capable of measuring. Above 350°C, the flow measurements became very erratic.

Physical Properties. Water absorption at ambient temperature was determined using four 0.635 cm × 0.635 cm × 3.493 cm bar samples 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 temperature 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, blotted dry, and again weighed.

Density determinations (g/cm³) were made on two molded discs 6.350 cm diameter × 0.318 cm thick and the average value reported.

Inherent viscosity measurements were made 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 five runs of this solution was reported.

The number-average molecular weight ($\overline{M}_n$) and weight-average molecular weight ($\overline{M}_w$) were determined at room temperature for the polyamide–acid dissolved in tetrahydrofuran.* A Knauer Membrane Osmometer was used for the $\overline{M}_n$ measurements and a Brice-Phoenix Light Scattering Photometer for the $\overline{M}_w$ measurements.

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

The flexural strength and modulus of three samples 0.635 cm × 0.254 cm × 3.175 cm, cut from a molded disc, were run in three-point bending using a span of 2.54 cm and a crosshead speed of 0.127 cm/min. Due to a lack of material, these samples had a span-to-depth ratio of 10 and not 16 as specified by ASTM Standard D 790-71. The average of three samples was reported.

The compressive strength was determined for four samples nominally 0.645 cm × 0.709 cm × 1.224 cm. They were run at 0.127 cm/min crosshead speed and the average value reported. ASTM Standard D 695-69 was used as a guide, but due to lack of material, sample size was decreased from the recommended ASTM standard size (1.27 × 1.27 × 2.54 cm).

The fracture energy value (G_{Ic}), the opening mode strain energy release rate, was determined from two compact tension samples. 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.

The lap shear tests were performed in accordance with ASTM Standard D 1002-72. Four samples bonded at a low heating rate (5°C/min) and four bonded at a high heating rate (22°C/min) were measured for lap shear strength and the average value reported.

Thermal Properties. The coefficient of thermal expansion was determined for the range 30–125°C using a DuPont Model 941 Thermomechanical Analyzer (TMA) operating in static air at a programed heating rate of 10°C/min. The glass transition temperature (T_g) was determined calorimetrically

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

with a DuPont Model 990 Thermal Analyzer/Differential Scanning Calorimeter in static air at a programed heating rate of 20°C/min. The apparent glass transition temperature was determined using a DuPont Model 943 Thermomechanical Analyzer in static air at 5°C/min, and also on a DuPont Model 1090 Dynamic Mechanical Analyzer under the same run conditions. Thermooxidative stability (weight loss vs. temperature) was determined using a Perkin-Elmer Model TGS-2 thermogravimetric system using a heating rate of 2.5°C/min and an air flow of 15 cc/min.

A thermomechanical spectrum of the polymer was obtained by torsional braid analysis (TBA). A glass braid was coated with a 10% diglyme solution of the polyamide–acid and precured to 300°C in air. This spectrum was obtained at a heating rate of 3°C/min in a nitrogen atmosphere.

Chemical Resistance. Six film samples approximately 40 μm thick were measured for T_g (apparent) using a DuPont Model 941 Thermomechanical Analyzer.[8] 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. When completely dry, they were again measured for T_g (apparent), and any change was noted.

RESULTS AND DISCUSSION

Synthesis

BDSDA/APB was synthesized according to the reaction scheme indicated in Figure 1. Reaction of the monomers in the ether solvent diglyme produced polyamide-acids which were characterized by inherent viscosity measurements. The thermal imidization of the polyamide–acid was carried out on the powder and resulted in linear high molecular weight polymers. The molecular weight buildup was controlled by the phthalic anhydride concentration. One sample of unendcapped polymer was prepared by M&T Chemicals (Rahway, N.J.) from their BDSDA and from APB that was supplied by NASA-Langley.

The polymers were thermally imidized at 200°C in air. The T_g varied only slightly as a function of molecular weight. The unendcapped NASA-prepared BDSDA/APB had a T_g of 161°C as shown by the TBA spectrum (Fig.
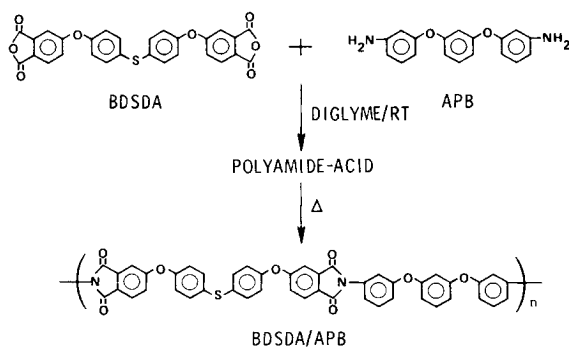

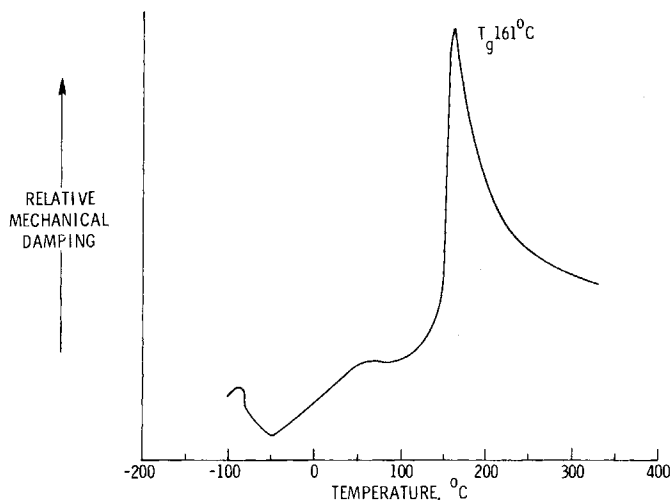Fig. 1. Polymer synthesis scheme for BDSDA/APB.

Fig. 2. Torsional braid analyzer (TBA) spectrum of imidized unendcapped BDSDA/APB (braid precured to 300°C in air). Run conditions: heating rate 3°C/min in N_2.

2). Further imidization was accomplished by curing at successively higher temperatures. This further imidization was indicated by the increase in melt flow viscosity with increased cure temperature for this same unendcapped system (Fig. 3).

The polyamide acids that were prepared as previously described were characterized by inherent viscosity (η_{inh}) measurements at 35°C. There was a trend towards lower viscosity as the endgroup concentration increased, i.e., η_{inh} of 0.66, 0.35, 0.31, and 0.35 dL/g for the polymers containing 0%, 1%, 2%, and 4% phthalic endcaps, respectively. All of the polymers had similar appearances after precipitation and subsequent imidization. All of the powders had adequate flow at 160°C to effect consolidation. During the molding operation it was evident that flow was increasing with increasing endcaps. The number-average molecular weights ($\overline{M}_n$) for the series of po-

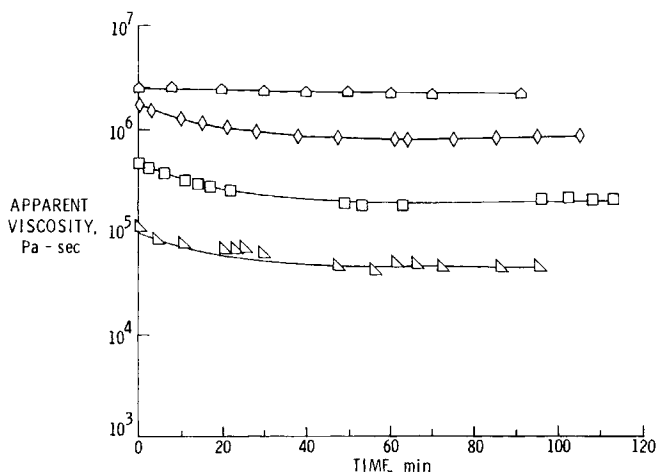
Fig. 3. Apparent viscosity of unendcapped BDSDA/APB as a function of time and cure temperature. Run conditions: 320°C; strain rate 0.406 s^{-1}. Cure conditions (°C in air): (△) 200; (□) 227; (◇) 255; (⬠) 325.
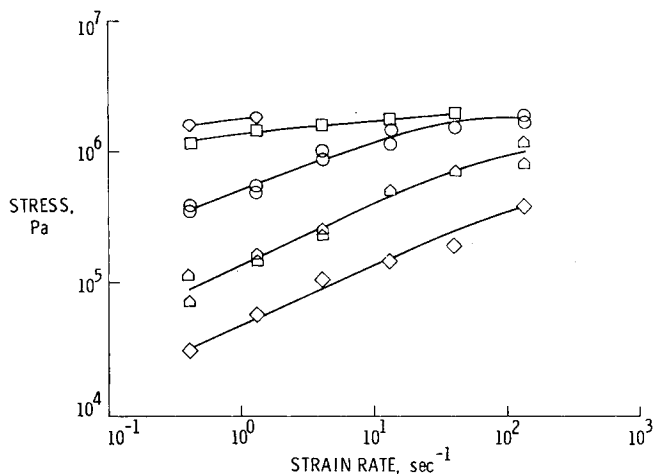
Fig. 4. Capillary Rheometer stress vs. strain rate data for unendcapped BDSDA/APB in the 250–350°C temperature range. (▽) 250; (□) 280; (○) 300; (◯) 320; (◇) 350.

lyamide acids were found to be lower with increasing endcapping, i.e., $\overline{M}_n$ of 13,900, 10,000, 8800, and 8700 for the polymers containing 0%, 1%, 2%, and 4% phthalic endcaps, respectively. Up to 2% endcapping this trend paralleled the inherent viscosity data. By contrast, the M&T Chemicals polymer which was unendcapped had an $\overline{M}_n$ of 45,000. The difference might be attributed to scaleup or a higher degree of monomer purity.

Characterization

Flow Properties. The melt flow properties of a polymer are important in determining how it should be processed. Compression molding, milling, calendering, extrusion, and injection molding are some of the more commonly used processing methods.[9] The melt flow properties of BDSDA/APB were determined for the shear strain rate region (10^{-1}–10^3 s^{-1}) that these processing methods cover.

The stress as a function of strain rate data (Fig. 4) obtained using the capillary rheometer indicates the polymer to be pseudoplastic, a non-Newtonian shear thinning flow 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 this polymer were within or exceeded this range. Consequently, high temperatures and low strain rates (i.e., long times) would be required for molding of BDSDA/APB.

The apparent viscosity as a function of strain rate data at various temperatures (Fig. 5) 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.[10] The BDSDA/APB polymer should be processable via compression molding and calendering techniques. However, no conclusions can be drawn concerning the extrudability of the polymer above a strain rate of 135 s^{-1} due to the stress and strain rate limitations of the rheometer in its present configuration.
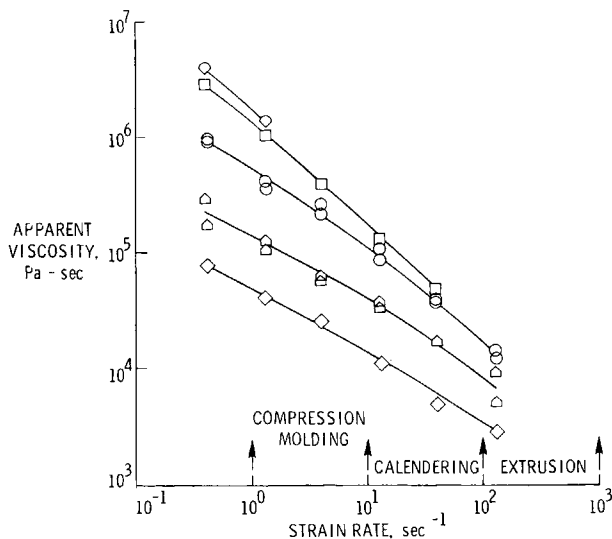
Fig. 5.   Apparent viscosity as a function of strain rate for unendcapped BDSDA/APB in the 250–350°C temperature range. Symbols same as Fig. 4.

Figure 6 compares the change in apparent viscosity with strain rate at the midrange processing temperature for this unendcapped polymer (BDSDA/APB), commercially available Torlon,* and a typical widely used ABS resin.[11] To our knowledge, no similar data have been generated on a linear aromatic polyimide system prior to this BDSDA/APB study. The BDSDA/APB exhibits a considerably lower melt viscosity (i.e., lower processing pressure) than Torlon or ABS resin throughout the range of strain rates investigated. This indicates BDSDA/APB to be a somewhat more easily processable material than the others shown in Figure 6.
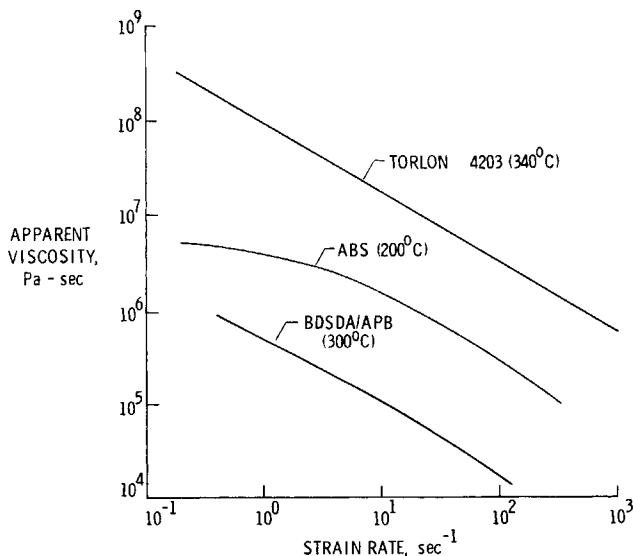

Fig. 6.   Comparison of apparent viscosity vs. strain rate curves for unendcapped BDSDA/ APB, ABS, and Torlon at their midrange processing temperatures.

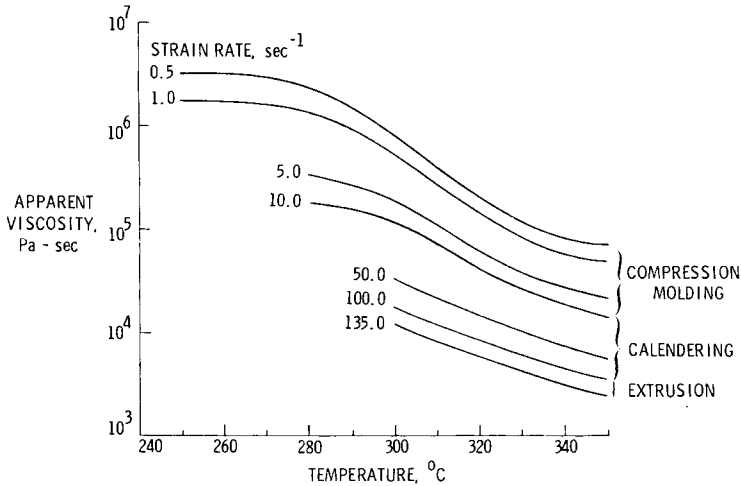* Torlon is the registered trademark of an Amoco poly(amide-imide).

Fig. 7. Apparent viscosity vs. temperature at various strain rates for unendcapped BDSDA/ APB for specific processing methods.

Curves of apparent viscosity as a function of temperature for selected strain rates corresponding to specific processing methods (Fig. 7) were constructed by cross-plotting the apparent viscosity–strain rate data. The curves show fairly uniform flow behavior with no apparent processing "windows." However, they do indicate a processing advantage, a well-defined decrease in viscosity with increased temperature for the different processing strain rates.

A sample of unendcapped BDSDA/APB was cured to a temperature of 200°C in air and allowed to cool to ambient. This procedure was repeated for three additional samples at 227°C, 255°C, and 325°C. Figure 3 shows the apparent viscosity for these four samples at 320°C as a function of elapsed time at that temperature. The viscosity increase with increasing cure temperature may be due to either a continuing buildup of molecular weight of
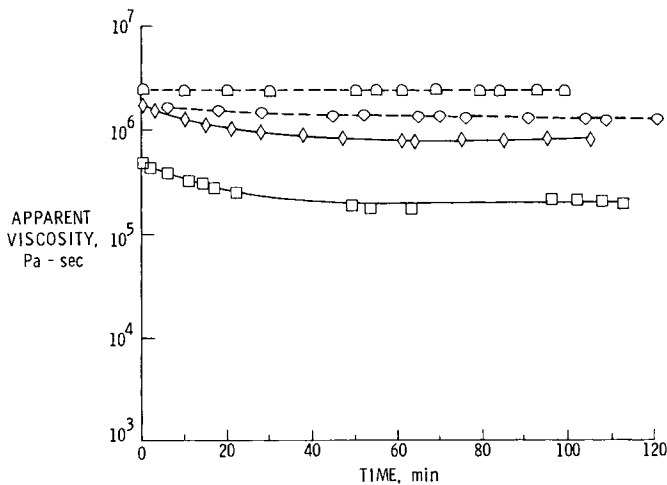

Fig. 8. Comparison of apparent viscosity vs. time for air and nitrogen cured unendcapped BDSDA/APB. Run conditions: 320°C; strain rate 0.406 s^{-1}. Cure conditions (°C) in air: (□) 227; (◇) 255; in N$_2$: (▽) 227; (△) 255.

the polymer in the melt form or crosslinking taking place. The viscosity at the three lower cure temperatures does not assume a constant value until the polymer has been at its run temperature of 320°C for 40–55 min. The viscosity of the sample cured at 325°C did not change with time. Samples of the same polymer were then cured at 227°C and 255°C in nitrogen and the viscosities compared with the air cured value (Fig. 8). The viscosity for the 227°C nitrogen-cured sample was 1.50 MPa s, which is 1.31 MPa s higher than that for the air-cured. The viscosity stabilized after approximately 30 min at the 320°C run temperature. The viscosity for the 255°C nitrogen-cured sample was 2.40 MPa s, which is 1.6 MPa s higher than that for the air-cured. The viscosity of that sample was constant from the beginning of the 320°C run. Further studies would be required to determine the specific mechanisms that cause this effect.

Rubbery type flow of molten polymers during extrusion, especially in the 2×10^5 Pascal shear stress region, can cause distortion or "melt fracture" in the extrudate.[12,13] The unendcapped BDSDA/APB polymer exhibited this characteristic during melt flow determinations. Three samples of the polymer extruded at 300°C and generated at increasingly higher stresses were compared (Fig. 9). Extrudate (a) was formed at the lowest stress (3.57×10^5 Pa) and exhibited a relatively smooth uniform surface, indicative of a low degree of melt fracture. Extrudates (b) and (c) were generated at successively higher rates of 10.71×10^5 Pa and 17.01×10^5 Pa, respectively, and the melt fracture characteristics, as expected, became more pronounced. Although higher extrusion temperatures did not materially alter the melt fracture, lower molecular weight polymer might exhibit less melt fracture.[12]

(a) 3.57×10^5 Pa

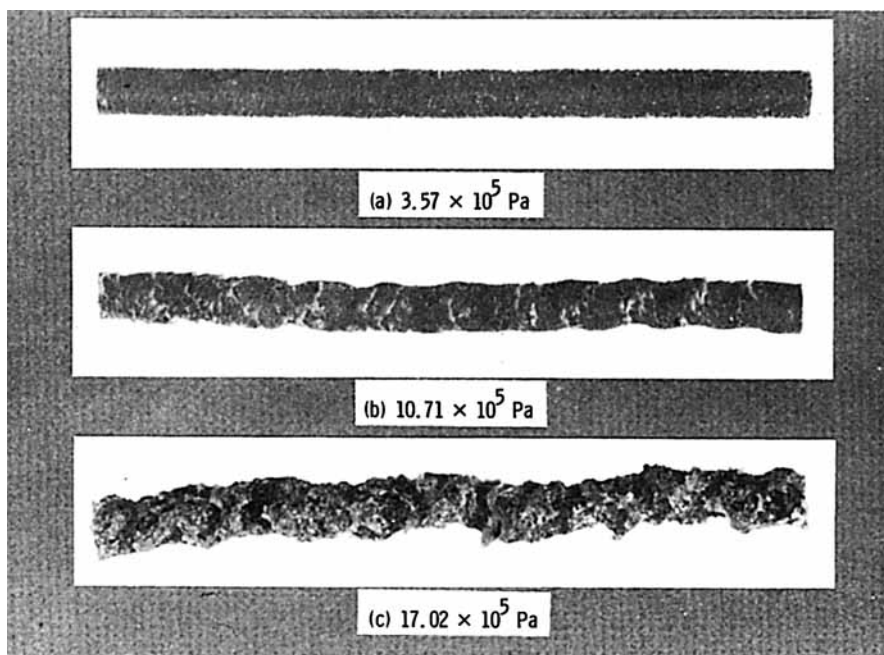(b) 10.71×10^5 Pa

(c) 17.02×10^5 Pa

Fig. 9.　Effect of increasing stresses on the "melt fracture" of unendcapped BDSDA/APB extrudate at 300°C.
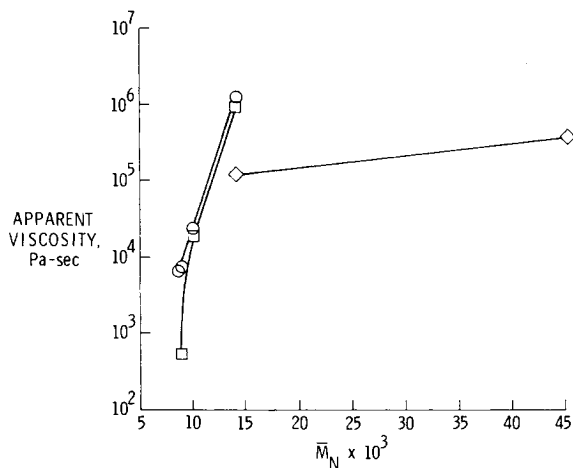
Fig. 10. Effect of molecular weight and temperature on the apparent viscosity of BDSDA/APB. °C: (○) 250; (□) 280; (◇) 320. Strain rate 1.346 s^{-1}.

A major objective of this research was to determine the effect of $\overline{M}_n$ on melt-flow properties of this polymer (BDSDA/APB). Based on the work of Fox and Flory,[6] it was expected that, as the $\overline{M}_n$ decreased, the melt flow would increase. However, the degree of change must be determined for each individual polymer system. In the endcapped polyimide study there was a direct relationship between $\overline{M}_n$ and apparent viscosity as shown in Figure 10. At 250°C there was no deviation from linearity, but at the higher extrusion temperature of 280°C the viscosity dropped precipitiously for the systems with an $\overline{M}_n$ below 10,000. The apparent viscosity of the 4% endcapped material was too low at 280°C for the capillary rheometer to measure. Particularly noteworthy was the drop of 2 orders in magnitude for the apparent viscosity at 250°C when the $\overline{M}_n$ changed from approximately 14,000 to 8700.

The effect of blending different molecular weights of the polymer (BDSDA/APB) on its apparent viscosity at 280°C is shown in Figure 11. The resultant polymer mixtures with effective $\overline{M}_n$ values of 11,900 and 10,300
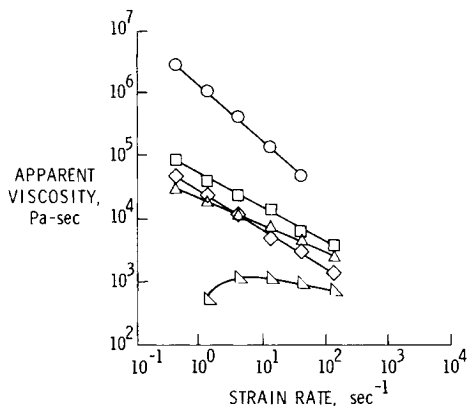

Fig. 11. Effect of molecular weight $(\overline{M}_n)$ variation on the apparent viscosity/strain rate relationship of BDSDA/APB at 280°C. $\overline{M}_n$: (○) 13,900; (□) 11,900 (blend of 13,900 and 10,000); (◇) 11,300 (blend of 13,900 and 8,800); (△) 10,000; (▷) 8,800.

TABLE II
Physical Properties of Unendcapped BDSDA/APB

Water absorption[a]	
24 h soak	0.07%
72 h soak	0.15%
Density[b]	1.34 g/cm³
Inherent viscosity[c]	0.66 dL/g
Molecular weight[d]	
Number average ($\overline{M}_n$)	13,900
Weight average ($\overline{M}_w$)	27,500

[a] Bar samples nominally 0.635 × 0.635 × 3.493 cm cut from molded stock.
[b] Molded disks 6.350 diam × 0.318 cm thick.
[c] Solution of 0.50% solids in DMAc at 35°C.
[d] Values determined on the amide acid by Arro Labs.

exhibited flow properties consistant with those of the nonblended endcapped polymer. This information should be valuable in optimizing processability.

Physical Properties. Some physical properties for the unendcapped BDSDA/APB are listed in Table II. The ambient moisture content of 0.15% by weight was determined by oven drying the sample in air for 24 h at 100°C. A 72-h water soak restored the sample to its original weight. An interim check at 24 h showed the sample had regained approximately one-half of its ambient moisture content. These values are an average of four samples taken at room temperature. The density was determined to be 1.34 g/cm³, reasonable for an amorphous, linear aromatic polymer. Because this polymer melts during subsequent processing to the imide form, there is a possibility for either an increase or decrease in its molecular weight. The imide form of the polymer is insoluble, thus precluding the determination of its inherent viscosity. The number-average molecular weight ($\overline{M}_n$) for each of the polyamide–acids was the average of nine determinations (three measurements for each of three solution concentrations). The weight-average molecular weight ($\overline{M}_w$) was four measurements for each of two solution concentrations.

Table III compares the number-average molecular weight ($\overline{M}_n$) to glass transition temperature (T_g) and inherent viscosity (η_{inh}) for all of the various BDSDA/APB systems that were investigated. The number-average molec-

TABLE III
Polymer Characterization

Endcap (%)	$\overline{M}_n$	T_g (°C)[b]	T_G (°C)[c]	Inherent viscosity
0	45,000	167	—	—
0	13,900	168	152	0.660
0/1 (blend)	11,900[a]	165	—	0.505[a]
0/2 (blend)	11,300[a]	166	—	0.483[a]
1	10,000	171	147	0.350
2	8800	156	140	0.306
4	8700	158	143	0.352

[a] Calculated values.
[b] Film tested in tension mode.
[c] Molding tested in penetration mode.

TABLE IV
Mechanical Properties of Unendcapped BDSDA/APB

	$\overline{M}_n$	
	13,900	45,000
Flexural strength	75.1 MPa (10.9 ksi)	100.0 MPa (14.5 ksi)
Flexural modulus	3.48 GPa (505 ksi)	3.34 GPa (485 ksi)
Compressive strength	153 MPa (22.2 ksi)	—
Critical rate of release of strain energy,		
G_{Ic}	4100 J/m²	4700 J/m²
Lap shear strength (Ti/Ti)[a]		
Low heating rate (5°C/min)	40.3 MPa (5.85 ksi)	—
High heating rate (22°C/min)	43.4 MPa (6.30 ksi)	—

[a] Bonded and tested according to ASTM Standard D 1002-72.

ular weights and inherent viscosities for the blends are calculated values. No significant trends are evident except for the viscosity–molecular weight relationship.

Mechanical Properties. The mechanical properties determined for BDSDA/APB at room temperature are listed in Table IV. The flexural strength and flexural modulus of 75.1 MPa and 3.48 GPa, respectively, represent the average of three samples for the unendcapped material. A compressive strength of 153 MPa was the average for four samples.

The M&T Chemicals polymer which had a $\overline{M}_n$ of 45,000 exhibited a flexural strength of 100.0 MPa and a flexural modulus of 3.34 GPa. The higher flexural strength was expected for the higher molecular weight system. Likewise the lower molecular weight polymers should exhibit lower flexural strengths. These were not tested because of lack of material.

When moldings were prepared from the different molecular weight polymers, it was obvious that the higher $\overline{M}_n$ systems resisted cracking more than the lower $\overline{M}_n$ systems. The G_{Ic} data proved that a considerable loss in fracture resistance does occur as the molecular weight decreases. This relationship is shown in Figure 12. Fracture surfaces are shown in Figure
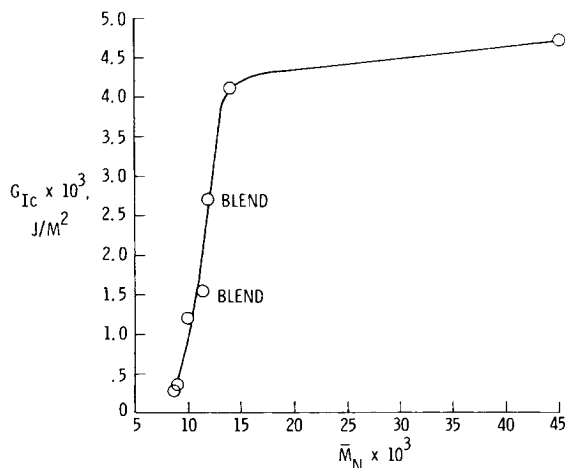

Fig. 12. Effect of molecular weight on the fracture energy (G_{Ic}) of BDSDA/APB.

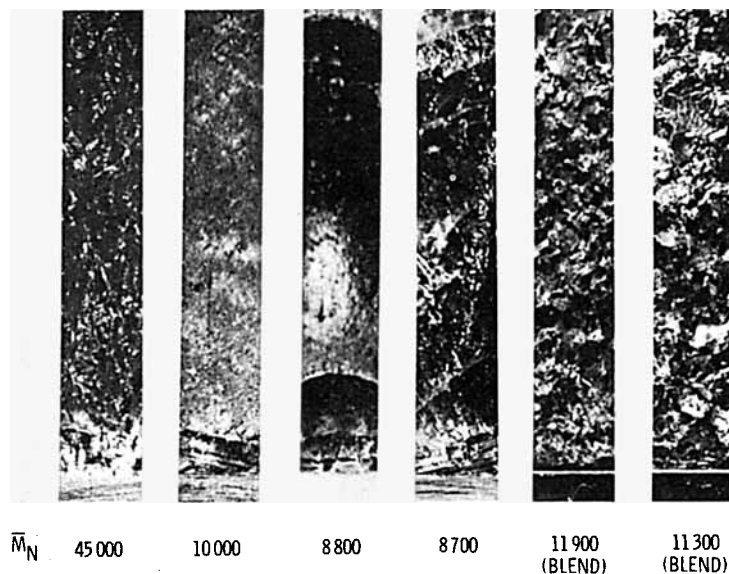| $\overline{M}_N$ | 45 000 | 10 000 | 8 800 | 8 700 | 11 900 (BLEND) | 11 300 (BLEND) |

Fig. 13. Fracture surfaces of G_{Ic} test specimens.

13. The blends of high–low molecular weights exhibited fracture behavior similar to the high molecular weight component. Of particular interest was that over the $\overline{M}_n$ range of 13,900 to 8700 the G_{Ic} values were linearly related to the number-average molecular weight. The steep slope of this relationship was quite surprising. The change in $\overline{M}_n$ from 13,900 to 10,000 resulted in nearly a 3000 J/m^2 loss in G_{Ic}. The higher $\overline{M}_n$ polymer (45,000) had a G_{Ic} value similar to that of the 13,900 $\overline{M}_n$ polymer.

In summary, the change in $\overline{M}_n$ from 13,900 to 8700 resulted in a dramatic decrease in the apparent viscosity at both 250°C and 280°C when the rheological properties of the polymer system were studied. The G_{Ic} values for these same molecular weight materials decreased in a like manner as the $\overline{M}_n$ decreased. From this $\overline{M}_n$ vs. viscosity and G_{Ic} data it is obvious that tradeoffs can be made between process optimization and final mechanical properties when polymer systems such as those in this investigation are developed.

Adhesive bonds were fabricated at heating rates of 5°C/min and 22°C/min using 6Al–4V titanium adherends. In both cases the room temperature lap shear values of 40.3 MPa and 43.4 MPa, respectively, were quite high compared to conventional polyimide adhesives.[14]

Thermal Properties. Some of the more common thermal properties were determined for the unendcapped BDSDA/APB and are listed in Table V. The coefficient of thermal expansion, 5.14×10^{-5} °C^{-1}, is typical for state-of-the-art polyimides. The glass transition temperature (T_g), measured calorimetrically, was determined to be 160°C. The T_g (apparent) values for a dry-molded sample and for one water soaked for 72 h at room temperature were measured thermomechanically. The T_g of the water soaked sample, run wet, was 145°C, 7°C below that for the dry sample (152°C).

TABLE V
Thermal Properties of Unendcapped BDSDA/APB

Coefficient of thermal expansion (30–125°C)	5.14×10^{-5} °C^{-1}
Glass transition temp (T_g), calorimetric	160°C
Thermomechanical T_g (apparent)	
TMA—dry	152°C
TNA—wet	145°C[a]
DMA	159°C
Decomposition temp	561°C[b]

[a] 72 h water soak, tested wet.

[b] 2.5°C/min heating rate, 15 cc/min air flow, 50% wt loss.

Unendcapped BDSDA/APB film exhibits thermooxidative stability similar to Kapton* film as shown in the thermogram Figure 14. 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 both films undergo essentially no weight loss below 400°C. The 40 μm film of BDSDA/APB exhibits a 50% weight loss temperature of 561°C, only 19°C below that for the thinner Kapton (25 μm), while both films undergo complete degradation at approximately 610°C.

The thermooxidative stabilities of endcapped BDSDA/APB films with $\overline{M}_n$ values of 10,000, 8800, and 8700 are compared in Figure 15. It is apparent that the higher molecular weight materials begin to lose weight at a lower temperature in this test, while the 50% weight loss temperature is not considered significantly different for the three molecular weight materials shown. As in the case of the unendcapped BDSDA/APB, the three endcapped polymers also undergo complete degradation at approximately 610°C.

Chemical Resistance. The chemical resistance of unendcapped BDSDA/APB thin film (40 μm thick) to six common solvents was determined and the results listed in Table VI. Methyl ethyl ketone, cyclohexanone, xylene,
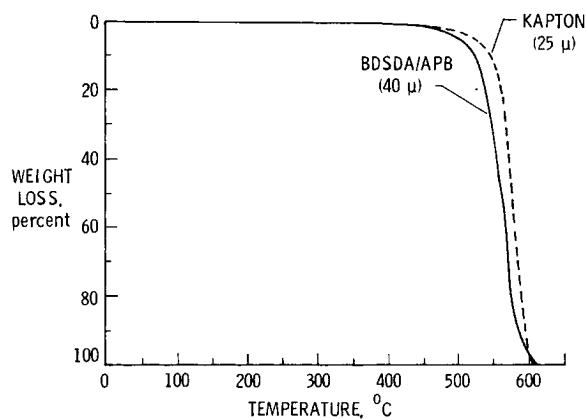

Fig. 14. Comparison of thermooxidative stability of unendcapped BDSDA/APB and Kapton polyimide film. Run conditions: heating rate 2.5°C/min; air flow rate 15 cc/min.

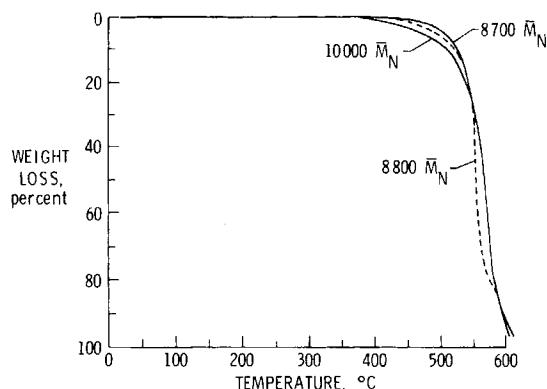§ Kapton is a registered trademark of the E. I. DuPont Co. for its polyimide film.

Fig. 15.   Effect of molecular weight ($\overline{M}_n$) on the thermooxidative stability of BDSDA/APB. Run conditions: heating rate 2.5°C/min; air flow rate 15 cc/min.

and tricresyl phosphate had no visible effect on the film, and there was no change in T_g (apparent). Methylene chloride and cresol caused severe swelling and T_g measurements were not possible, although the methylene chloride-soaked film did maintain sufficient integrity as a film to allow mounting in the T_g fixture.

CONCLUSIONS

A novel linear aromatic polyimide (BDSDA/APB), which has some of the favorable characteristics of polyimides and linear aromatic polyphenylene oxides and sulfides, was synthesized and characterized. Thermal imidization of the polyamide-acid at 200°C resulted in a linear, high molecular weight polymer with a T_g of 161°C that could be processed as a hot-melt thermoplastic. This polymer had mechanical properties comparable to engineering thermoplastics. The polymer exhibited a considerably lower melt viscosity at its midrange processing temperature (300°C) than did either commercially available Torlon or a widely used ABS resin, both measured at their midrange temperatures, 340°C and 200°C, respectively. It also exhibited a major well-defined decrease in viscosity with increased temperature, a definite processing advantage.

TABLE VI
Chemical Resistance of BDSDA/APB Film[a]

Solvent	Effect	Change in T_g, (apparent) (°C)[b]
Methyl ethyl ketone	None	None
Cyclohexanone	None	None
Xylene	None	None
Tricresyl phosphate	None	None
Methylene chloride	Swelled	Not determined
Cresol	Swelled	Not determined

[a] 40 μm thick film.

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

In an effort to maximize the use properties and processability, the molecular weight was varied by endcapping with phthalic anhydride. Over the $\overline{M}_n$ range of 14,000–45,000 the apparent viscosities and G_{Ic} values varied only slightly. However, a change in $\overline{M}_n$ from 14,000 to 8700 resulted in a dramatic decrease in the apparent viscosity at both 250°C and 280°C when the rheological properties of the polymer system were studied. The G_{Ic} values for these same molecular weight materials decreased in a like manner as the $\overline{M}_n$ decreased. From this $\overline{M}_n$ vs. viscosity and G_{Ic} data it is obvious that tradeoffs can be made between process optimization and final mechanical properties when polymer systems are developed.

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