

# Siloxane-Modified Polyethersulfideimide

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## Synopsis

BSDA/APB, a novel linear polyethersulfideimide, was synthesized using siloxane units as flexible linkages in the backbone in an attempt to improve use properties and processability. The effect of these flexible linkages on molecular weight buildup ( $\bar{M}_n$  and  $\bar{M}_w$ ),  $G_{Ic}$ , flexural strength and modulus, glass transition temperature, and melt-flow properties was determined.

## INTRODUCTION

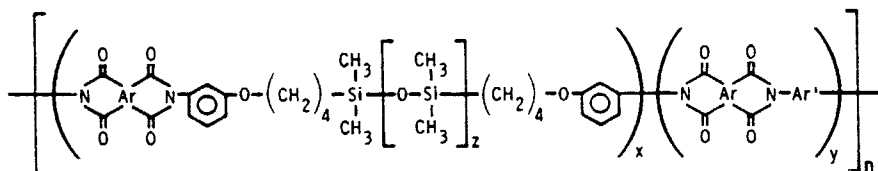
BSDA/APB, a novel polyethersulfideimide, has been shown to be desirable as an engineering thermoplastic due to its thermooxidative stability, high  $G_{Ic}$ , resistance to chemicals and moisture, and melt-flow properties.<sup>1</sup> In an attempt to maximize use properties and processability, molecular weight was varied over the  $\bar{M}_n$  range of 14,000–45,000 by endcapping with phthalic anhydride.<sup>2</sup> Work previously reported by Fox and Flory prompted this avenue of investigation.<sup>3</sup> They found that the melt viscosity of polystyrene could be decreased by decreasing its molecular weight. Processability could thus be improved.

This paper, a result of further effort to improve the use properties and processability of BSDA/APB, describes a variation of this linear polyimide synthesized using siloxane bonds as flexible linkages in the backbone. Previous work of this type was done by researchers on siloxane-modified polypyromellitimides.<sup>4</sup> Berger improved the solubility and adhesion of numerous polyimides by the inclusion of polysiloxane units.<sup>5</sup> Maudgal and St. Clair introduced a siloxane bond in the backbone of LARC-TPI, a linear polyimide that contains a meta-substituted diamine.<sup>6</sup> They investigated the effect of varying amounts of siloxane on processability, thermal, and thermooxidative stability and solvent resistance of this linear polyimide.

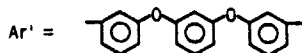
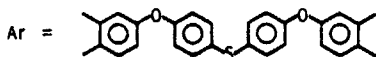
## EXPERIMENTAL

**Polymer Synthesis.** The synthesis of the BSDA/APB polymer has been reported<sup>1,2</sup> The siloxane-modified polyimide was prepared by M & T Chemical, Rahway, NJ and supplied in precipitated polyamide acid form. No endcapping was used for these materials. The general structure of the siloxane-containing polyimide is shown in Figure 1.

**Molding Powder.** The viscous polymer solution which did not contain siloxane units was poured into a mechanical blender containing distilled water. The contact with water caused polyamide acid to precipitate, and the rotating blender blades chopped this material into a fluffy consistency. Solid polymer was isolated by suction filtration and allowed to air dry overnight.



Where



Where on average  $z = 6$

Fig. 1. Chemical structure of siloxane-containing BDSDA/APB.

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 (diglyme). 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. 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 to approximately 100°C and the molding was removed. Discs, up to 0.406 cm (0.160 in.) in thickness, were dark brown and opaque.

**Flow Properties.** Melt flow properties for BDSDA/APB at 280 and 320°C were determined using a capillary rheometer (Instron Model 3211). The capillaries had length-to-diameter ratios of 33 and 66; therefore, no end corrections were required. Melt flow properties were not measured below 280°C because the pressure needed to force the polymer through the capillary was greater than the rheometer load cell was capable of measuring.

**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 of each of five materials, each sample approximately  $0.638 \times 0.422 \times 3.175$  cm and 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 6 and not 16 as specified by ASTM Standard D 790-71. The average of three samples of each material was reported.

The fracture energy value ( $G_{Ic}$ ), the opening mode strain energy release rate, was determined from two compact tension samples of each of four materials. The samples were machined from discs approximately 5.715 cm diameter and nominally 0.422 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 of each material was reported.

**Molecular Weight.** Number-average molecular weight ( $\bar{M}_n$ ) and weight-average molecular weight ( $\bar{M}_w$ ) were determined at room temperature for the polyamide acid 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 weight determinations by ARRO Laboratory, Joliet, IL).

**Glass Transition Temperature.** The apparent glass transition temperature ( $T_g$ ) was determined in static air at 5°C/min using a DuPont Model 940 thermomechanical analyzer. Samples were cut from mold flashing removed from the  $G_{Ic}$  moldings.

## RESULTS AND DISCUSSION

**Polymer Synthesis.** The BDSDA/APB polyimide was prepared in diglyme at room temperature at 15% solids. The siloxane-containing polyimides were prepared in the same manner by M & T Chemical. The viscous solutions of the amide acids were stored at 0°C prior to use to assure stability of the polymer.

**Molding Powder.** The molding powders were prepared as previously described. During the thermal imidization of all of these polymers, there was a softening and coalescence of the powdery polyamide acid which resulted in a glassy flexible mass of polyimide. This glassy product was ground to a granular consistency before use as a molding powder or for rheological measurements.

**Unfilled Moldings.** The unfilled moldings were evaluated for fracture resistance using the compact tension specimen configuration as described in ASTM Standard E 399-78A. The highest  $G_{Ic}$  value was obtained for the highest molecular weight version ( $\bar{M}_n = 45,140$ ) of the BDSDA/APB which did not contain siloxane units (unmodified). The lower molecular weight ( $\bar{M}_n = 13,900$ ) unmodified system was comparable in fracture energy value to one of two samples of the siloxane-modified system with a 2.5% siloxane loading. Another 2.5% siloxane-containing sample yielded a lower value, and the 5.0% siloxane-containing sample was much lower (Table I). The fracture surfaces are described in Table I and representative fractured surfaces are shown in Figure 2. The unmodified samples which exhibited the highest  $G_{Ic}$  values exhibited relatively smooth fracture surfaces when compared to the modified materials. Generally failed samples with the rougher surface are expected to afford higher strengths, but, in this study, surface roughness may

TABLE I  
Effect of Siloxane Loading on the Molecular Weight and Fracture Energy ( $G_{Ic}$ ) of BDSDA/APB

Siloxane (%)	$\bar{M}_n$	$\bar{M}_w$	$G_{Ic}$ (J/m <sup>2</sup> )	Fracture surface
0	45,140	—	4775	Smooth
0	13,900	27,500	4100	Smooth
2.5	22,600	90,057	4232	Smooth
2.5	22,600	90,057	3419	Rough
5.0	20,644	79,501	2805	Rough

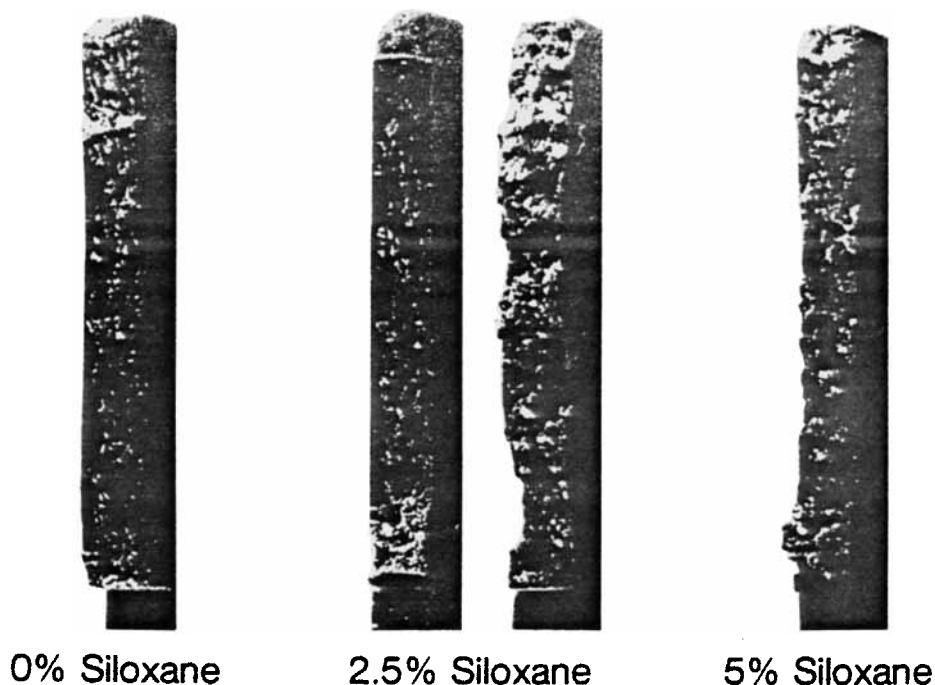


Fig. 2. Representative fracture surfaces of  $G_{Ic}$  compact tension specimen.

have been due to a separation of the siloxane moieties into domains which resulted in lower strength values. Other work in this laboratory has shown that higher loadings of siloxane into linear aromatic polyimides results in friable moldings.<sup>7</sup>

**Flow Properties.** The melt flow properties of a polymer have a major influence on how it can and should be processed. Since compression molding, calendaring, and extrusion are some of the more commonly used processing methods, the flow properties of siloxane containing BDSDA/APB polymers were determined for the strain rates ( $10^{-1}$ – $10^3$   $s^{-1}$ ) encountered using these processing methods.<sup>8</sup> The viscosity, calculated by dividing the flow stress by the strain rate, is an apparent viscosity rather than a true viscosity because the strain rate was calculated from the volumetric flow data and not corrected to obtain the wall rate.<sup>9</sup>

The apparent viscosity as a function of strain rate data at 280°C for 0, 2.5, and 5% concentrations of siloxane in BDSDA/APB is shown in Figure 3. As expected, the siloxane containing polymers had lower viscosity values than the BDSDA/APB that contained no siloxane. At the lowest strain rate ( $0.404$   $s^{-1}$ ) the 5% siloxane BDSDA/APB had an apparent viscosity of  $1.36 \times 10^6$  Pa s, a value one half that of the 0% siloxane-containing polymer with a viscosity of  $2.9 \times 10^6$  Pa s.

Figure 4 compares the apparent viscosity (at 320°C) of two 0% siloxane BDSDA/APB polymers with drastically different  $\bar{M}_n$  values. The higher molecular weight polymer ( $\bar{M}_n = 45,140$ ) exhibits a substantially higher viscosity than does the 13,900  $\bar{M}_n$  material (duplicate runs). This same molecular weight/apparent viscosity relationship for BDSDA/APB was

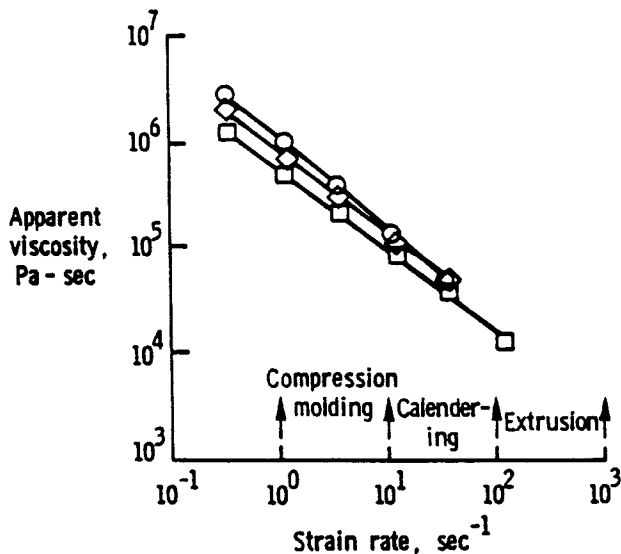


Fig. 3. Apparent viscosity as a function of strain rate at 280°C for different concentrations of siloxane-containing BDSDA/APB: (○) 13900  $\bar{M}_n$  (0% siloxane); (□) 20644  $\bar{M}_n$  (5.0% siloxane); (◇), 22600  $\bar{M}_n$  (2.5% siloxane).

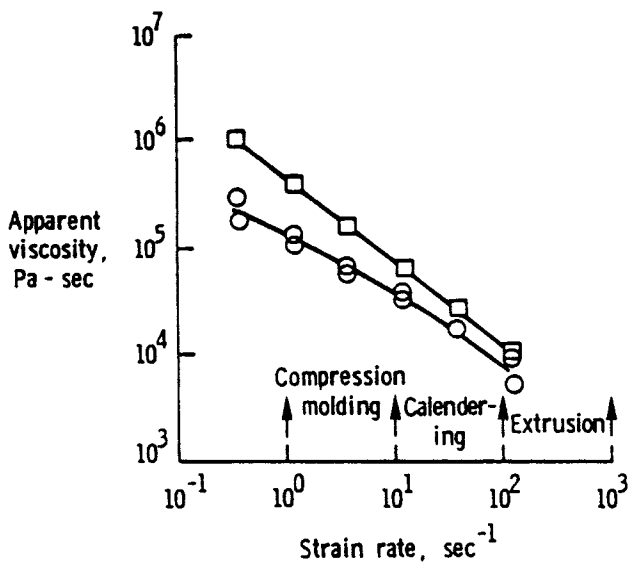


Fig. 4. Apparent viscosity as a function of strain rate at 320°C for two 0% siloxane BDSDA/APB polymers with drastically different molecular weights: (○) 13900  $\bar{M}_n$ ; (□) 45140  $\bar{M}_n$ .

discussed in a previously published report.<sup>2</sup> In that case molecular weight was controlled by endcapping with phthalic anhydride.

The siloxane content in the backbone seemed to negate the effect of higher  $\bar{M}_n$  values, which give rise to higher apparent viscosities, and ultimately lowers the apparent viscosity with increasing siloxane content.

**Mechanical Properties.** Flexural strength and modulus values were obtained on the extrudates of the unmodified and modified systems (Table II).

TABLE II  
Flexure Properties of Siloxane-Containing BDSDA/APB

Siloxane (%)	$\bar{M}_n$	Flexure	
		Strength (MPa)	Modulus (GPa)
0	45,140	105.9 (15.4 ksi)	2.91 (422.5 ksi)
0	13,900	75.1 (10.9 ksi)	3.48 (505.0 ksi)
2.5 <sup>a</sup>	22,600	102.2 (14.8 ksi)	2.54 (368.6 ksi)
2.5 <sup>b</sup>	22,600	63.2 (9.2 ksi)	2.79 (405.0 ksi)
5.0	20,644	59.3 (8.6 ksi)	2.83 (410.1 ksi)

<sup>a</sup> Material with smooth fracture surface area.

<sup>b</sup> Material with rough fracture surface area.

The strength results seemed to parallel the compact tension results. The highest value was for the high molecular weight unmodified BDSDA/APB, and the 2.5% siloxane-modified system was slightly lower for one sample and approximately 30% lower for the other sample. The 5.0% siloxane-modified sample had the lowest strength. No real trend was noted for the modulus values; however, a significant decrease in modulus was noted for the 2.5% sample which had the higher strength value. This difference in moduli is probably attributable to two distinctly different polymer morphologies.

**Molecular Weight.** Number average molecular weights for polymers under investigation ranged from 13,900 to 45,140 for unmodified BDSDA/APB and from 20,644 to 22,600 for siloxane modified versions of the same system (Table II). The weight average molecular weight of the higher molecular weight unmodified polymer could not be determined because of partial insolubility. The lower molecular weight unmodified polymer exhibited an  $\bar{M}_w/\bar{M}_n$  value of approximately 2. The  $\bar{M}_w/\bar{M}_n$  values for the two siloxane-containing versions was approximately 4.

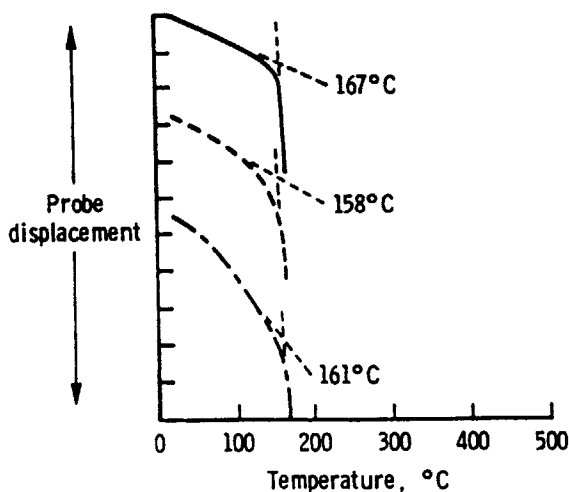


Fig. 5. Glass transition temperatures ( $T_g$ ) of 0, 2.5, and 5% siloxane-containing BDSDA/APB: (—) 45140  $\bar{M}_n$  (0% siloxane); (---) 22600  $\bar{M}_n$  (2.5% siloxane); (-·-) 20644  $\bar{M}_n$  (5.0% siloxane).

**Glass Transition Temperature.** The mechanically determined  $T_g$  for three of the polymers studied is shown in Figure 5. The high molecular weight BDSDA/APB exhibited the highest  $T_g$  value of 167°C. The specimens which contained 2.5 and 5.0% siloxane exhibited  $T_g$  values of 158 and 161°C, respectively. The incorporation of siloxane did lower the glass transition as expected because of enhanced flexibility of the polymer backbone.

## CONCLUSIONS

BDSDA/APB, a linear polyimide, exhibits physical properties and a degree of processability characteristic of engineering thermoplastics. In an attempt to further improve these characteristics, a variation of this polyimide was synthesized using siloxane bonds as flexible linkages in the backbone.

As expected, the siloxane-containing polymers had lower viscosity values than the BDSDA/APB that was siloxane free. At the lowest strain rate (0.404 s<sup>-1</sup>) the 5.0% siloxane BDSDA/APB had an apparent viscosity of  $1.36 \times 10^6$  Pa s, a value one half that of the 0% siloxane-containing polymer ( $2.9 \times 10^6$  Pa s).

The highest molecular weight version ( $\bar{M}_n = 45,140$ ) of the unmodified BDSDA/APB (0% siloxane) exhibited the highest  $G_{Ic}$  value (4775 J/m<sup>2</sup>) and the 5.0% siloxane-containing sample had the lowest  $G_{Ic}$  value (2805 J/m<sup>2</sup>). The unmodified sample (highest  $G_{Ic}$ ) exhibited a relatively smooth fracture surface when compared to the 5.0% siloxane sample surface. The rougher fracture surface may have been due to a separation of the siloxane moieties into domains which could give rise to lower strength values.

Flexural strength trends paralleled the compact tension ( $G_{Ic}$ ) trends, while the flexural modulus values remained basically unchanged. The incorporation of siloxane in the polymer backbone lowered the glass transition temperature because of the increase in backbone flexibility.

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