SYNTHESIS AND CHARACTERIZATION OF COPOLYIMIDES WITH VARYING FLEXIBILIZING GROUPS

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INTRODUCTION

Aromatic polyimides are generally difficult to process because they exhibit only a limited degree of flow when subjected to high pressure even at high temperatures. These materials are, however, exceptionally thermally stable and resist attack by most solvents (1,2). In addition, they generally have very high glassy transition temperatures because of their aromatic character (3). Because of desirable properties such as resistance to solvents and high glassy transition temperatures, many attempts have been made to prepare aromatic polyimides which can be readily processed.

Some of these efforts include the synthesis of polymers incorporating sulfur linkages into a polyimide backbone (4), the use of particulated oligomeric polyetherimide-amide acids which may be converted to a high molecular weight polymer system by melt polymerization (5), and the use of varied proportions of different polyetherimide segments in an attempt to reach the optimum balance between processability and solvent resistance (6). Other efforts involve the incorporation of flexible moieties into the backbone to increase thermoplastic character (7) and the incorporation of phenylene ether units to improve melt-flow properties (8).
Although these efforts have contributed in various ways to improving the processability of linear aromatic polyimides, there is still a definite need for enhancing their melt-flow properties in order that they may be used for applications such as hot-melt adhesives or as matrix resins for fiber-reinforced composites. In an attempt to further improve the properties and processability of these materials, a series of polyimides and copolyimides with different flexibilizing groups (Table 1) were synthesized and a limited characterization was accomplished.

EXPERIMENTAL

Polymer Preparation. Copolyimide 413 was prepared according to the following procedure. 10.2096 g (0.02 moles) of 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride (BOSOA) (8), 1.0012 g (0.005 moles) of 4,4'-diaminodiphenyl ether (4,4'-ODA), and 1.6222 g (0.015 moles) of 1,3-diaminobenzene (m-POA) were allowed to react in 51.33 g of N,N-dimethylacetamide (OMAc) at room temperature for two hours. Molecular weight build up occurred during this time as evidenced by an increase in solution viscosity. Inherent viscosity of the solution as determined at 0.5% concentration in DMAC at 25°C was 0.378.

Copolyimide 422 was prepared by reacting 10.2096 g (0.02 moles) of BOSDA, 2.0024 g (0.01 moles) of 4,4'-ODA, and 1.08144 g (0.01 moles) of m-PDA in 53.172 g of DMAC at room temperature for two hours. The inherent viscosity was 0.441.

Copolyimide 431 was prepared by reacting 10.2096 g of BOSDA, 3.0036 g (0.015 moles) of 4,4'-ODA, and 0.54072 g (0.005 moles) of m-PDA in 55.016 g
of DMAC at room temperature for two hours. The inherent viscosity was 0.459.

The homopolymer of BDSDA and 3,3'-ODA was prepared by reacting 10.2096 g (0.02 moles) of BDSDA and 4.0048 g (0.02 moles) of 3,3'-diaminophenyl ether (3,3'-ODA) in 56.86 g of DMAC at room temperature for two hours. The inherent viscosity was 0.424. The homopolymer of BDSDA and 4,4'-ODA was prepared in the same way only substituting 4,4'-ODA for the 3,3'-ODA.

The BDSDA/m-PDA polymer was prepared by reacting 20.4192 g (0.04 moles) of BDSDA and 4.3258 g (0.04 moles) of m-PDA in 98.98 g of DMAC at room temperature for two hours. The inherent viscosity was 0.606.

Film. Films of the various polymers were prepared by casting each polymer solution onto a glass plate at a thickness of 0.05 cm and allowing the solvent to evaporate. The resulting polymer films were heated for 1 hour at 100°C then 1 hour at 200°C and finally 1 hour at 300°C. Removal of the films from the glass plate yielded very flexible, smooth yellow films.

Molding Powder. Imidized powder forms of each polymer were prepared by pouring the amide-acid solution into water in a blender to precipitate the polymer. In each case the solid polymer was collected via suction filtration. Each polymer was air dried overnight and then subjected to a thermal profile in an air oven for 1 hour at 100°C, 1 hour at 200°C, and finally 1 hour at 300°C. The individual polymers were chopped to a granular consistency.

Adhesive Tape. Copolymer 422 was chosen as the material to study for its adhesive properties. Initial data indicated it to have the best overall properties of this series of materials. Adhesive tape was prepared by
brush-coating a 422 polyamic-acid, 20% solids solution in diglyme, \( \eta_{\text{inh}} \) of 0.789, on to 112 E-glass cloth with A-1100 finish (\( \gamma \)-aminopropylsilane). This solution was prepared as previously described except diglyme was used instead of DMAc. The flow properties of the 422 with 0.789 inherent viscosity are shown in Figure 1. This would indicate a lower degree of flow than the sample of 422 with a 0.441 inherent viscosity. Prior to coating, the glass cloth (tightly mounted in a metal frame) was initially oven-dried for 10 min at 100°C. The 0.01 cm thick glass cloth served as a carrier for the adhesive as well as for bondline thickness control and an escape channel for solvent. Coatings of the polymer solution were applied to the glass cloth until a thickness of 0.020 - 0.025 cm was obtained. After a primer coat (= 4% solids solution) was applied, each coat application thereafter was air-dried 0.5 hr, placed in a forced-air oven, and exposed to the following schedule:

1. Room temperature + 100°C, hold 1 hr
2. 100°C + 150°C, hold 2 hrs
3. 150°C + 175°C, hold 3 hrs

Some blistering of the polymer occurred due to the above treatment.

**Adhesive Bonding.** The prepared adhesive tape was used to bond titanium adherends (Ti 6Al-4V, per Mil-T-9046E, Type III Comp. C) with a nominal thickness of 0.13 cm. The four-fingered Ti(6Al-4V) panels were surface treated with a Pasa-Jell 107* treatment to form a stable oxide on the surface. The treated adherends were primed within one hour of the surface treatment by applying a thin coat, approximately \( 2.5 \times 10^{-2} \) mm of the 20% solution.

*Trade name for a titanium surface treatment available from Semco, Glendale, CA.
solids solution on the surface to be bonded. They were then air dried for 30 min in a forced-air oven for 15 min at 100°C and 15 min at 150°C. The primed adherends were stored in a polyethylene bag and placed in a desiccator until needed. Lap shear specimens were prepared by inserting the adhesive tape between the primed adherends using a 1.27 cm overlap (ASTM D-1002).

Several bonding cycles were investigated during this study to determine a bonding process which produced good strengths. The following processing cycles were used:

**Cycle 1**
(1) 2.1 MPa pressure, heating rate 8.2°C/min, RT + 316°C
(2) Hold 30 min at 316°C
(3) Cool under pressure to ~ 150°C and remove from bonding press

**Cycle 2**
Same as Cycle 1 except RT + 343°C

**Cycle 3**
Same as Cycle 1 except RT + 343°C, hold 1 hr

A bonding cycle was selected from the above cycles and used to determine the effects on lap shear strengths for thermal exposure for 1000 hours at 204°C. Thermal exposure was performed in a forced-air oven controlled within ±1% of exposure temperature. Lap shear tests were conducted at room temperature, 177°C, and 204°C before (controls) and after exposure.

A rather severe 72-hour water-boil test was conducted in laboratory glassware containing boiling distilled water. Lap shear specimens were immersed above the bonded area at all times during the 72-hour period. Lap shear strengths were determined at room temperature, 177°C, and 204°C.
CHARACTERIZATION METHODOLOGY

Flow Properties. Melt flow properties were determined at 350°C using a capillary rheometer (Instron Model 3211) (9). The capillary used had a length-to-diameter ratio of 33; therefore no end corrections were made. Melt flow properties were not measured below 350°C because the pressure needed to force some of the polymers 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 tensile strength and elastic modulus were determined for five polymers. Each polymer was extruded at six different strain rates and each of these six extrudates, approximately 0.17 cm diameter and 2.54 cm gage length, was measured for its tensile properties in the direction of extrusion at a crosshead speed of 0.51 cm/min. ASTM Standard D638-82A was used as a guide, but due to lack of material, sample size was decreased from recommended ASTM size.

Adhesive Properties. Lap shear strength was obtained according to ASTM D-1002 using a Model TT-C Instron Universal Testing Machine. The average lap shear strengths reported represent at least four lap shear specimens tested for any one condition. The range of the lap shear strength is indicated by dashed lines in the figures. Bondline thickness was determined as the difference between the total bonded thickness and the titanium adherend thicknesses. The average bondline thickness was 0.20 mm with a range of 0.12 mm to 0.24 mm. Specimens were heated in a clam-shell, quartz-lamp oven and were held at temperature for 10 minutes prior to
testing. Temperatures were controlled to within ±3°C for all tests. Glass transition temperatures (Tg) for the adhesive of fractured lap shear specimens were determined by thermomechanical analysis (TMA) on a DuPont 943 Analyzer in static air at a heating rate of 5°C/min using a hemispherical probe with a 15 g load.

**Thermal Properties.** The glass transition temperature (Tg) was determined calorimetrically using a DuPont Model 990 Thermal Analyzer/Differential Scanning Calorimeter in static air at a programmed heating rate of 50°C/minute.

Thermooxidative stability (weight loss vs. temperature) was determined using a Perkin-Elmer Model TGS-2 thermogravimetric system at a heating rate of 2.5°C/minute and an air flow of 15 cc/minute.

**RESULTS AND DISCUSSION**

**SYNTHESIS**

The polymers in Table 1 were prepared via the reaction of BDSDA with the corresponding diamines in DMAc to produce the polyamide-acids. These materials were characterized by inherent viscosity measurements in DMAc at 25°C. The polyamide-acids were precipitated into water and allowed to air-dry overnight and were subsequently cyclized to the imide form by heating in an air-oven to 300°C and maintaining that temperature for one hour. Since these polymers were unendcapped and were well above their glass transition temperatures (196 - 220°C), the potential for chain extension existed.
In the synthesis of the copolymers the two diamines were added simultaneously. The reaction was carried out in this manner in order to prepare random copolymers. However, when this method is employed, the possibility for block growth always exists due to unforeseen kinetic and/or thermodynamic factors. Differential scanning calorimetry characterization showed only one glassy transition for each copolymer. More discussion on this subject is made in the Thermal Properties section.

CHARACTERIZATION

Flow Properties. The melt flow properties of polymers are important in determining how they should be processed. Compression molding, milling, calendering, extrusion, and injection molding are some of the more commonly used processing methods (10). The melt-flow properties of BDSDA/3,3'-ODA, 413, 422, 431, and BDSDA/m-PDA were determined for the shear strain rate region ($10^{-1}$-$10^{3} \text{ sec}^{-1}$) these processing methods cover.

The stress as a function of strain rate data at 350°C (Figure 2) obtained using the capillary rheometer indicate the polymers 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 $10^{4}$-$10^{5} \text{ Pa}$ range. Most of the measured stresses for these polymers were within or exceeded this range. Consequently, high temperatures and low strain rates (i.e., long times) would be required to mold them.

The apparent viscosity as a function of strain rate data at 350°C (Figure 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 (11). The apparent viscosity of ULTEM®, a commercially available polyetherimide resin, was determined and shown for comparison as a typical state-of-the-art engineering thermoplastic. Although polymers under study exhibited higher viscosities than ULTEM, they should be processable via compression molding and calendering techniques. However, no conclusions can be drawn concerning their extrudability above a strain rate of 135 sec⁻¹ due to the stress and strain rate limitations of the rheometer in its present configuration.

The two polymers, BDSDA/m-PDA and BDSDA/4,4'-ODA, were run as extremes in comparison for the three copolymers, 413, 422, and 431. The BDSDA/3,3'-ODA was prepared as an example of a similar polymer with two types of flexibility in the diamine unit. Attempts to extrude the BDSDA/4,4'-ODA through the capillary were unsuccessful. Its apparent viscosity exceeded the upper limit capability of the rheometer (≈ 5 x 10⁶ Pa-sec) and, consequently, its flow properties could not be measured.

Rheological data was obtained for the other polymers. The smaller the apparent viscosity value the greater is the ease of flow. From Tables 2 and 3 it is clear that the 422 system measured at 350°C has the lowest

*ULTEM® is a registered trademark of the General Electric Company for their polyetherimide resin. (Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.)
viscosity for the six strain rates measured. It was quite surprising that in each case the BDSDA/3,3'-ODA exhibited the highest viscosity since this system has flexibility due to the oxygen bridging group as well as the added flexibility introduced through the meta-linkages (7). However, in each case, this polymer was extrudable where the corresponding BDSDA/4,4'-ODA with only one flexibilizer (oxygen bridge) was not.

The key feature in Tables 2 and 3 is that the 422 copolymer always exhibited the lowest viscosity and all of the copolymers (413, 422 and 431) flow through the capillary whereas the BDSDA/4,4'-ODA does not. In addition the 422 copolymer exhibits a lower viscosity in each case than do the other copolymers or BDSDA/m-PDA. This attribute is an unexpected result which makes this copolymer very attractive for fabrication procedures.

Curves of apparent viscosity as a function of fractional copolymer composition for selected strain rates corresponding to specific processing methods are shown in Figure 4. They were constructed by cross-plotting the apparent viscosity-strain rate data. The three lower strain rates (0.404, 1.346, 4.037 sec⁻¹) correspond to those encountered in compression molding. Since compression molding is the major processing method used in laminating composites, it was deemed extremely important to determine the flow properties, at these lower strain rates, for this series of copolymides.

It is obvious that copolymer 422 (molar ratio 2:2 of 4,4-ODA to m-PDA) at the lowest strain rate exhibits the lowest apparent viscosity, a decided advantage in compression molding. Its viscosity is 43% below that for copolymer 431 (3:1) and 29% below that for BDSDA/m-PDA (0:4). This advantage is minimized at the higher strain rates associated with
calendering (13.456 sec\(^{-1}\)) and extrusion (134.560 sec\(^{-1}\)).

BDSDA/4,4'-ODA (4:0) could not be compared with copolymer 422 because, as previously noted, its flow properties could not be measured.

**Mechanical Properties.** The mechanical properties of these polymers are listed in Table 4. The tensile tests were performed on the extrudate from various capillary rheometer runs. Of particular note is that the 422 copolymer and the BDSDA/m-PDA polymer exhibit nearly identical tensile strengths and moduli and the variability in strength is slightly lower for the 422 copolymer. This indicates that no sacrifice in mechanical properties results due to copolymerization. Also of importance is the degree of melt fracture (undesirable) is only moderate for the 422 copolymer and the BDSDA/m-PDA. In all other cases the degree of melt fracture was more severe.

Thus, copolymers of polyimides with both flexible bridging groups and meta-linkages in the diamine-derived portion of the polymer have improved flow properties over either of the corresponding homopolymers. This technique and these compositions have resulted in polyimides with unusual and unexpected improved flow properties.

**Adhesive Evaluation.** Since the particular copolymer which contained equimolar amounts of m-PDA and 4,4'-ODA (422) exhibited the highest degree of flow, it was evaluated as an adhesive using titanium adherends. This evaluation, based on lap shear strengths, involved the determination of a bonding cycle along with thermal and boiling water exposure.

Selection of a bonding cycle for the 422 polyimide adhesive from those presented in Figure 5 was based on lap shear strength as well as Tg. For
the three bonding cycles investigated, no significant effects on the lap shear strengths were observed for tests performed at either room temperature or 177°C. Only complete cohesive failure was observed for those tests. However, there is an obvious improvement in strength at 204°C for those bonded at 343°C for 30 minutes (Cycle 2) and 60 minutes (Cycle 3). Samples bonded for 60 minutes at 343°C had a slightly higher average lap shear strength (15.6 MPa) than those bonded for 30 minutes at 343°C (12.9 MPa). Failure modes were primarily cohesive.

A significant difference in Tg was obtained for samples bonded at 316°C (Tg of 192°C) compared to those bonded at 343°C for 30 minutes (Tg of 201°C) and 60 minutes (Tg of 203°C). The low Tg for those samples bonded at 316°C probably contributes to the lower lap shear strength at 204°C.

The high lap shear strength (15.6 MPa) at 204°C and high Tg (203°C) were taken into consideration for selecting Cycle 3 as the bonding cycle to use for the thermal and water-boil exposure tests.

The effects on lap shear specimens of thermal exposure in a forced-air oven at 204°C for 1000 hours is shown in Figure 6. Lap shear strengths were determined at room temperature, 177°C, and 204°C. The control samples and the thermally exposed samples had essentially the same lap shear strengths when tested at either room temperature or 177°C. A 22 percent increase in average lap shear strength at 204°C was obtained for the samples thermally exposed at 204°C compared to the controls. Tested specimens failed 100 percent cohesively except for the 204°C control specimens which failed primarily cohesively with some adhesive type failure.
A significant increase in Tg (18°C) was determined for the thermally exposed specimens which is a common occurrence due to further polymer cure, polymer oxidation, and/or elimination of trapped volatiles. This possibly could account for the increase in lap shear strength seen for the thermally exposed specimens tested at 204°C.

Subjecting lap shear specimens to a 72-hour water-boil is a rather severe test to determine an adhesive's resistance to water (or humidity). Results of the water-boil test for 422 adhesive bonded titanium are shown in Figure 7. Obviously, the test produced decreased strengths at all test temperatures indicating a common lack of resistance to the effects of water on the adhesive system, i.e. the adhesive and treated titanium surface. The lap shear strength values decreased by 20 percent at room temperature, 41 percent at 177°C, and 70 percent at 204°C. A more realistic test would be to expose the lap shear specimens to a controlled cyclic humidity condition more representative of what an adhesive system would experience during the intended application.

A bonding cycle was chosen from those cycles studied which provided good lap shear strengths from room temperature to 204°C. This cycle also afforded a reasonable strength retention level after exposures to 204°C for 1000 hours and decreased retention after the 72-hour water boil.

**Thermal Properties.** The thermooxidative stability (weight loss vs. temperature) of BDSDA/4,4'-ODA, copolymer 422, BDSDA/m-PDA, and BDSDA/3,3'-ODA in powder form are compared in Table 5. This data was taken from dynamic TGA curves obtained at a heating rate of 2.5°C/min and an air flow rate of 15 cc/min. The thermooxidative onset (1% weight loss) temperature
exhibited by copolymer 422 was 450°C, a significant 22°C above that for BDSDA/m-PDA. Likewise, it underwent total degradation (100% weight loss) at 650°C, a substantial 45°C above that for BDSDA/m-PDA. The data for both BDSDA/4,4'-ODA and BDSDA/3,3'-ODA indicated that they are even less thermooxidatively stable than BDSDA/m-PDA.

The differential scanning calorimetry (DSC) study of the polyimides afforded glass transition temperatures for each polymer. The transitions are graphically illustrated in Figure 8. The T_g for the BDSDA/3,3'-ODA polymer was the lowest at 196°C. The T_g's for all of the polymers are in Table 1 for comparison. The most well defined transitions (those occurring over the narrowest range) were for the polymers with one anhydride and one diamine. The copolymers exhibited transitions over wider temperature ranges, but only one glassy transition was noted for each copolymer. However, with the glassy transitions for the BDSDA/4,4'-ODA and BDSDA/m-PDA being so close, 217 and 224°C, respectively, no double transition would be expected even if the copolymers were block rather than random in structure. A phenomenon that should be noted was that each of these more regular systems (BDSDA/4,4'-ODA and BDSDA/m-PDA) exhibited "ordered" glassy transitions on the first heat-up (12). These DSC traces are shown in Figure 9. After these samples were cooled to ambient temperature, they were rerun and exhibited more familiar glassy transition patterns.

CONCLUSIONS

A series of polyimides was prepared and characterized in order to evaluate the effect of copolymerization on their rheological behavior. The
approach involved the use of one very flexible dianhydride (BDSDA) to prepare polyimides containing varying amounts of m-phenylene diamine (m-PDA) and 4,4'-oxydianiline (4,4'-ODA). The polyimide with only BDSDA and 4,4'-ODA exhibited a viscosity greater than could be measured (X 10^6 Pa-sec) on the capillary rheometer. The polyimide with only BDSDA and m-PDA exhibited excellent flow. An unusual phenomenon was observed: random copolymers of these systems did not exhibit rheological properties that would be expected from a "rule-of-mixtures". The particular copolymer with equimolar amounts of m-PDA and 4,4'-ODA exhibited the lowest viscosity at all strain rates studied. Since this particular polymer, designated 422, exhibited the best flow properties, it was also evaluated as an adhesive and was found to have exceptional characteristics for this application.
REFERENCES


TABLE 1. EFFECT OF VARYING COPOLYIMIDE FLEXIBILIZING GROUPS ON THEIR GLASS TRANSITION TEMPERATURES.

![Diagram]

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>COPOLYMER MOLAR RATIO</th>
<th>GLASS TRANSITION TEMPERATURE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y:X</td>
<td>( T_G, ^\circ C )</td>
</tr>
<tr>
<td>BDSDA/( m )-PDA</td>
<td>0:4</td>
<td>224*</td>
</tr>
<tr>
<td>413</td>
<td>1:3</td>
<td>220</td>
</tr>
<tr>
<td>422</td>
<td>2:2</td>
<td>216</td>
</tr>
<tr>
<td>431</td>
<td>3:1</td>
<td>217</td>
</tr>
<tr>
<td>BDSDA/4,4'-ODA</td>
<td>4:0</td>
<td>217</td>
</tr>
<tr>
<td>BDSDA/3,3'-ODA</td>
<td>--</td>
<td>196</td>
</tr>
</tbody>
</table>

*ORDERED TRANSITION
TABLE 2. APPARENT VISCOSITY AS A FUNCTION OF STRAIN RATE FOR COPOLYIMIDES 413, 422, AND 431.

<table>
<thead>
<tr>
<th>STRAIN RATE (sec(^{-1}))</th>
<th>APPARENT VISCOSITY (Pa·sec), (\times 10^5)</th>
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<tbody>
<tr>
<td></td>
<td>413</td>
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<tr>
<td>0.404</td>
<td>3.040</td>
</tr>
<tr>
<td>1.346</td>
<td>1.330</td>
</tr>
<tr>
<td>4.037</td>
<td>0.647</td>
</tr>
<tr>
<td>13.456</td>
<td>0.346</td>
</tr>
<tr>
<td>40.368</td>
<td>0.191</td>
</tr>
<tr>
<td>134.560</td>
<td>0.107</td>
</tr>
</tbody>
</table>

*MEASUREMENTS MADE AT 350°C
TABLE 3. APPARENT VISCOSITY AS A FUNCTION OF STRAIN RATE FOR POLYIMIDES BDSDA/3,3'-ODA AND BDSDA/M-PDA.

<table>
<thead>
<tr>
<th>STRAIN RATE (sec(^{-1}))</th>
<th>APPARENT VISCOSITY (Pa·sec),(^*) X 10(^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BDSDA/3,3'-ODA</td>
</tr>
<tr>
<td>0.404</td>
<td>7.950</td>
</tr>
<tr>
<td>1.346</td>
<td>3.560</td>
</tr>
<tr>
<td>4.037</td>
<td>1.600</td>
</tr>
<tr>
<td>13.456</td>
<td>0.669</td>
</tr>
<tr>
<td>40.368</td>
<td>0.337</td>
</tr>
<tr>
<td>134.560</td>
<td>0.134</td>
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\(^*\)MEASUREMENTS MADE AT 350°C
TABLE 4. MECHANICAL PROPERTIES.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>TENSILE PROPERTIES*</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>STRENGTH, AVG. MPa</td>
<td>STRENGTH, RANGE MPa</td>
<td>MODULUS, AVG. GPA</td>
<td>DEGREE OF MELT FRACTURE**</td>
<td></td>
</tr>
<tr>
<td>BDSDA/4,4'-ODA</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>NO FLOW</td>
</tr>
<tr>
<td>413</td>
<td>60.0 (8.71 KSI)</td>
<td>39.1 - 87.9</td>
<td>1.26 (182 KSI)</td>
<td>HIGH</td>
<td></td>
</tr>
<tr>
<td>422</td>
<td>82.7 (12.0 KSI)</td>
<td>72.1 - 92.1</td>
<td>1.48 (215 KSI)</td>
<td>MODERATE</td>
<td></td>
</tr>
<tr>
<td>431</td>
<td>66.7 (9.68 KSI)</td>
<td>43.8 - 91.7</td>
<td>1.40 (204 KSI)</td>
<td>HIGH</td>
<td></td>
</tr>
<tr>
<td>BDSDA/1-PDA</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>BDSDA/3,3'-ODA</td>
<td>85.1 (12.3 KSI)</td>
<td>58.0 - 100.2</td>
<td>1.47 (214 KSI)</td>
<td>MODERATE</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30.4 (4.40 KSI)</td>
<td>17.7 - 39.9</td>
<td>0.99 (143 KSI)</td>
<td>VERY HIGH</td>
<td></td>
</tr>
</tbody>
</table>

*Each value is the average of one polymer extruded at six different strain rates in the range 0.404 - 134.560 sec\(^{-1}\)

**Melt fracture at highest strain rate (134.560 sec\(^{-1}\))
### Table 5. Thermooxidative Stability.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>TEMPERATURE, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ONSET</td>
</tr>
<tr>
<td>BDSDA/4,4'-ODA 422</td>
<td>420</td>
</tr>
<tr>
<td>BDSDA/11-PDA</td>
<td>428</td>
</tr>
<tr>
<td>BDSDA/3,3'-ODA</td>
<td>413</td>
</tr>
</tbody>
</table>
Figure 1. Effect of inherent viscosity on the apparent viscosity at 350°C.
Stress as a function of strain rate at 350°C.

Figure 2. Stress as a function of strain rate at 350°C.
Figure 3. Apparent viscosity as a function of strain rate at 350°C.
Figure 4. Apparent viscosity as a function of fractional copolymer composition for selected strain rates at 350°C.
Figure 5. Lap shear strength of polymer 422 adhesive vs. bonding cycle measured at room temperature, 177°C, and 204°C.
Figure 6. Effect of thermal exposure on the lap shear strength of polymer 422 adhesive measured at room temperature, 177°C, and 204°C.
Figure 7. Effect of moisture on the lap shear strength of polymer 422 adhesive measured at room temperature, 177°C, and 204°C.
Figure 8. DSC thermograms of (a) BDSDA/3,3'-ODA, (b) 413, (c) 422, (d) 431, (e) BDSDA/4,4'-ODA, and (f) BDSDA/m-PDA.
Figure 9. DSC thermograms of (a) BDSDA/4,4'-ODA, (b) BDSDA/4,4'-ODA rerun, (c) BDSDA/m-PDA, and (d) BDSDA/m-PDA rerun.
A series of polyimides and copolyimides with varying flexibilizing groups in their backbone were prepared. They were characterized in order to evaluate the effect of these groups on their rheological, mechanical, adhesive, and thermal properties.

A copolymer with equimolar amounts of m-PDA and 4,4'-ODA exhibited the lowest viscosity at all strain rates studied. Since this particular polymer exhibited the best flow properties, it was also evaluated as an adhesive and was found to have exceptional characteristics for this application.
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