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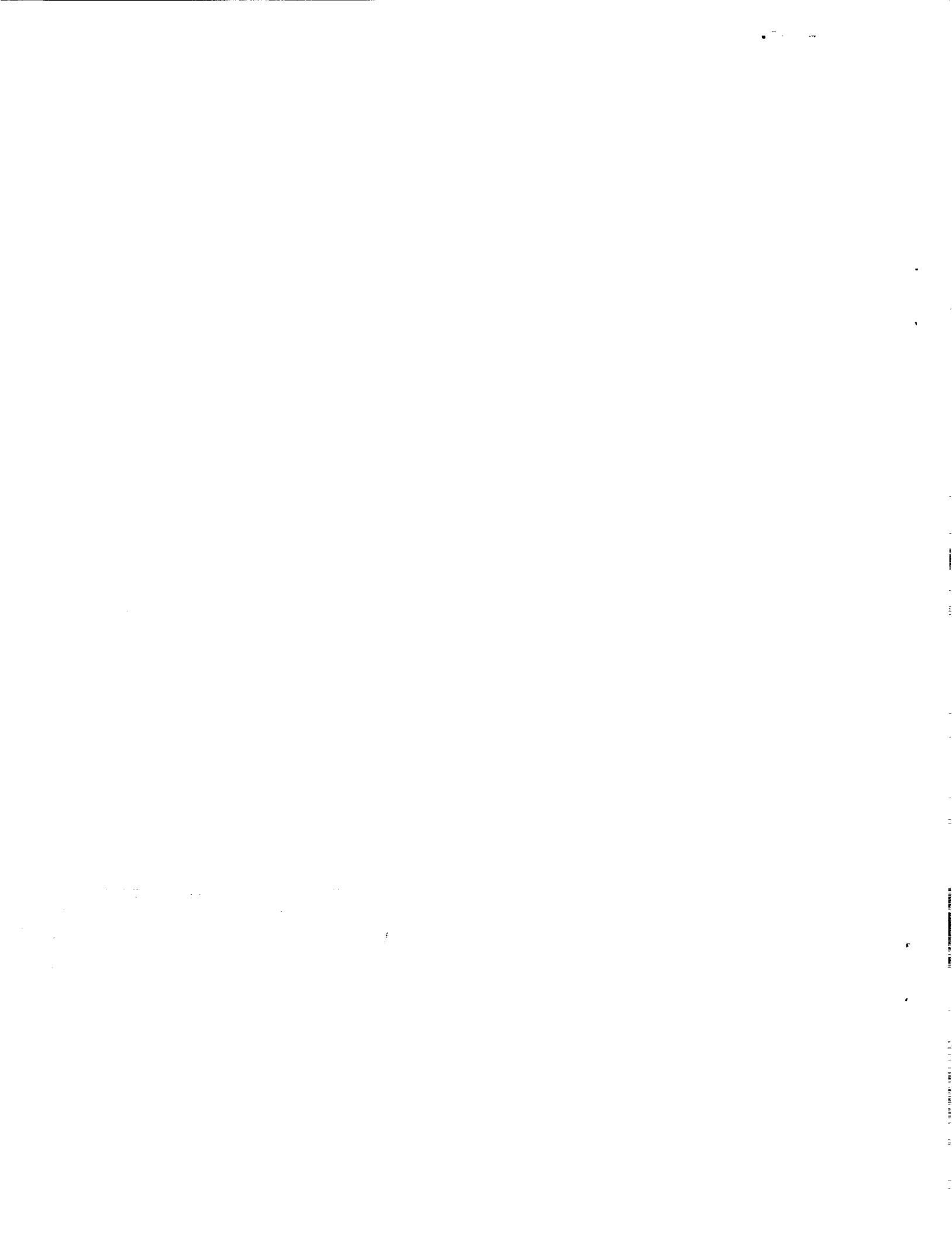
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SYNTHESIS OF IMIDE/ARYLENE ETHER COPOLYMERS FOR ADHESIVES AND COMPOSITE MATRICES

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INTRODUCTION

As part of an effort to develop high performance structural resins with an attractive combination of properties for aerospace applications, a series of block copolymers containing imide and arylene ether segments were synthesized. The copolymers reported herein represent an extension of previous work¹⁻⁴ on imide/arylene ether copolymers. The arylene ether block used in this study contains a bulky fluorene group in the polymer backbone while the imide block is semi-crystalline and contains an arylene ether ketone segment identical to that in the arylene ether block. One copolymer was selected for molecular weight control and end-capping studies to improve the compression moldability. This material was evaluated as an adhesive and composite matrix resin.

A few copolymers containing imide blocks and other blocks have been reported. The copolymers containing imide and siloxane blocks have received considerable attention.⁵⁻⁸ More recently, polyimide-polyformal block copolymers⁹ and triblock copolymers containing imide-aryl ether phenylquinoxaline blocks have been reported.¹⁰ Amide-

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terminated sulfones prepared by a method similar to that used herein has been used in polyimide formation.¹¹

EXPERIMENTAL

Synthesis

The amine-terminated poly(arylene ethers) (ATPAE) were synthesized as shown in Eq. 1 by aromatic nucleophilic substitution of 1,3-bis(4-fluorobenzoyl)benzene (FBB) with 9,9-bis(4-hydroxyphenyl)fluorene (BPF) and 4-aminophenol in N,N-dimethylacetamide (DMAc) using potassium carbonate. The oligomers were prepared at two different calculated number average molecular weights (\bar{M}_n) by adjusting the monomer ratio (BPF/FBB) to 0.816 and 0.908 to provide \bar{M}_n of 3110 and 6545 g/mole, respectively. The following procedure is representative of ATPAE synthesis. FBB (25.785 g, 80.0 mmol), BPF (22.867 g, 65.25 mmol), 4-aminophenol (3.218 g, 29.48 mmol) and potassium carbonate (24.0 g, 176 mmol) in DMAc (150 ml) and toluene (40 ml) were stirred under a nitrogen atmosphere. The toluene/water azeotropic mixture was removed using a Dean-Stark trap as the reaction was heated to and held at 155°C for 16 h. After filtering through sintered glass and neutralizing with acetic acid, the polymer was precipitated in water and subsequently washed with boiling water to provide ATPAE 3110 as an off-white solid in >95% yield.

The anhydride-terminated poly(amic acids) were prepared by reacting 3,3',4,4'-benzophenonetetracarboxylic acid (BTDA) with 1,3-bis(4-aminophenoxy-4'-benzoyl) benzene (BABB) in DMAc,

N-methyl-2-pyrrolidinone (NMP) or *m*-cresol at two \bar{M}_n s as shown in Eq. 2 by adjusting the monomer ratio (BABB/BTDA) to 0.766 and 0.882 to provide \bar{M}_n s of 3110 and 6545 g/mole, respectively. The synthesis of BABB/BTDA 3110 is given as an example. BABB (1.3315 g, 2.660 mmol) was dissolved in DMAc (14 ml) followed by addition of BTDA (1.1278 g, 3.500 mmol) with stirring for 3 h at ambient temperature in a nitrogen atmosphere to form a clear yellow solution.

High molecular weight block copolymers were prepared as previously reported [3] by adding a solution of the ATPAE to the anhydride-terminated BABB/BTDA reaction mixture in the same solvent. Reactions at a stoichiometric ratio provided clear, viscous solutions. One block copolymer, ATPAE 3110//BABB/BTDA 3110, was prepared at controlled molecular weights by adjusting the oligomer ratio to 1:2 or 2:3 (ATPAE 3110 TO BABB/BTDA 3110) then adding the appropriate amount of aniline to provide phenyl-terminated block copolymers with \bar{M}_n s of 9,330 and 15,550 g/mole, respectively.

Characterization

Inherent viscosities (η_{inh}) were obtained on 0.5% solutions at 25°C. Differential scanning calorimetry (DSC) was performed at a heating rate of 20°C/min with the apparent T_g taken at the inflection point of the ΔT versus temperature curve. Torsional braid analysis (TBA) was performed at heating rate of 3°C/min with the T_g taken at the peak of the damping curve. The number average molecular weight was determined for the amine-terminated poly(arylene ethers) (ATPAE) by amine group titration

using a MCI Model GT-05 Autotitrator with 0.02 M HBr in glacial acetic acid as the titrant. The ATPAEs were dissolved in a 2:1 mixture of chlorobenzene and acetic acid.

Films

DMAc or NMP solutions (15% solids) of the polymers were centrifuged, the decantate doctored onto plate glass and dried at room temperature to a tack-free form in a dry air chamber. The films on glass were dried 1 h each at 100, 200 and 300°C. Mechanical tests were performed according to ASTM D882 on four specimens per test condition. Wide-angle x-ray scattering (WAXS) data was obtained on thin film specimens or solution imidized powders of the copolymers.

Moldings

The polymers were compression molded in a 1.25 in. square stainless steel mold. Polymer filled molds were heated to 400°C, a pressure of 500 psi was applied and maintained for 0.5 h, followed by cooling under pressure. Four compact tension specimens ~0.62 x 0.62 x 0.30 in. thick were cut from the 1.25 in. square molding and the critical stress intensity factor (K_{Ic}) was determined according to a known procedure.¹²

Adhesive Specimens

The as-synthesized poly(amic acid) solutions in NMP were used to brush coat 112 E-glass (A-1100 finish) secured on a frame. Each coat was dried in an air circulating oven for ~1 h each at 100 and 200°C which

converted most of the poly(amic acid) to polyimide. Several coats were required to provide a 12 mil thick boardy tape which contained <2% volatiles. Titanium (Ti-6Al-4V) to Ti tensile shear specimens with a Pasa-Jell 107 surface treatment were fabricated in a preheated hydraulic press, heating rapidly to temperature, applying pressure and holding 20 min. Four specimens were tested for each condition according to ASTM D1002.

Composites

Prepreg was prepared using a Research Tool Corporation Model 30 drum winder with the drum speed set at 3 rpm, the fiber tension at 0.1% and the transverse rate at 42%. Using a die with a 0.02 in. wide x 0.22 in. long gap and a guide roller of 0.22 in. (which determines the width of the tow as it is placed on the drum), NMP solutions (25% solids content) of the end-capped polymers were coated onto Hercules AS-4 graphite fiber (12K tow, unsized). Prepregs 76 in. long and up to 12 in. wide were prepared on this drum winder. The prepregs were air dried on the drum for 16 h followed by drying in an oven by slowly heating (4°C/min) to 200°C and holding for 1 h to produce prepreg with <2% volatiles. Unidirectional composites were prepared by stacking prepreg (10 layers for flexure specimen and 18 layers for short beam shear specimen) in a 3 in. x 3 in. stainless steel mold. The mold was then introduced into a hydraulic press with electrically heated platens preheated to 400°C. The mold was heated rapidly (during ~45 min.) to 380°C where a pressure of 300 psi was applied. The mold was

held at 380°C under 300 psi for 15 min. then allowed to cool to room temperature under pressure. The 10 ply panels were cut into flexural specimens (3 in. x 0.5 in.) and tested according to ASTM D790-86. The 18 ply panels were cut into short beam shear specimens (0.75 in. x 0.25 in.) and tested according to ASTM D2344-84.

RESULTS AND DISCUSSION

ATPAEs with calculated \bar{M}_n of 3110 and 6545 g/mole, prepared by offsetting monomer stoichiometry, had η_{inh} s of 0.18 and 0.30 dL/g and T_g s of 193 and 210°C, respectively. When the oligomers were reacted with a stoichiometric amount of BTDA, the η_{inh} and the T_g increased as expected indicating that the calculated \bar{M}_n s were essentially correct. Amine end-group analyses gave experimental \bar{M}_n s of 3500 and 6700 g/mole that correlated well with the calculated \bar{M}_n s of 3110 and 6545 g/mole, respectively.

Four different block copolymers were prepared as shown in Table I from the ATPAE and BABB/BTDA oligomers. The copolymers were prepared by reacting a stoichiometric ratio of oligomers. The last two polymers listed in the table were segmented copolymers of the same composition as the block copolymers with equal molecular weight blocks. They were prepared by adding the BTDA to a solution of the ATPAE and BABB in NMP, forming the copolymer and the imide block in the presence of the preformed arylene ether block. Copolymer η_{inh} ranged from 0.35 to 1.08 dL/g in DMAc, 0.75 to 1.04 dL/g in NMP and 0.61 to 0.72 dL/g in m-cresol. Several polymerizations as noted in the table, became very viscous and formed a gel within ~15 min which dissipated

upon heating to $\sim 70^{\circ}\text{C}$ overnight. This gelation occurred in each of the three solvents but not consistently in the preparation of the same copolymer in different solvents. The mechanism of gel formation is not fully understood.

Thermal characterization of the copolymers are shown in Table 2. As expected, the solvent does not have a large effect on resulting polymer T_g since high molecular weight copolymer is formed in each of the solvents used. Each copolymer displayed only one T_g since the T_g s of the homopolymers were essentially the same (222°C for the PI and 223°C for the PAE). However the T_g s occurred at a slightly higher temperature for the copolymers than for either homopolymer. All DSC samples were films that had been cured 1 h each at 100, 200 and 300°C . The last column under DSC shows T_g s and T_m s on powder samples obtained from solution imidization. This imidization technique produced copolymers with essentially the same T_g as the homopolymers.

Differences are obvious in the T_m s of the thermally imidized copolymers prepared in different solvents. Some copolymers display two melting endotherms while others show only one. However, all melting peaks were broad, some containing shoulders. The solution imidization technique produced only single T_m s and at temperatures higher than those from thermal imidization. The DSC trace of ATPAE 6545//BABB/BTDA 3110 did not exhibit an endotherm but there was an obvious change in slope in the 365 to 375°C range.

The last column in Table 2 gives T_g s as measured by TBA only on copolymers prepared in NMP. This mechanical measure gives different

results from DSC and a relatively wide range of temperatures (229-240°C). The lowest T_g was for the ATPAE 6545//BABB/BTDA 3110 in which the major component is the amorphous PAE. The next lowest T_g was for the copolymer containing both blocks of 3110 g/mole. The other two block copolymers, which contain the long PI block, had TBA T_g s 16-17°C above the T_g of the homopolymers. Apparently the crystalline regions in the polyimide blocks affects the TBA T_g for copolymers with shorter PI blocks. The TBA T_g of the ATPAE 3110 + [BABB +BTDA (3110)] segmented copolymer was 232°C, essentially equivalent to the T_g of the corresponding block copolymer. The TBA T_g of the ATPAE 6545 + [BABB + BTDA (6545)] segmented copolymer was 233°C or 7°C below the TBA T_g of the corresponding block copolymer, possible due to less crystallinity in the segmented version as a result of the different synthetic procedure.

Wide angle x-ray scattering analysis was performed on each of the copolymers. Judging by the peak intensities and sharpness, the copolymers with longer imide blocks were more crystalline than those with shorter imide blocks. Also, the segmented copolymers appeared to be less crystalline than the block copolymers of the same composition. This evidence supports the previous discussion in that the block copolymer had a higher T_g by TBA than the segmented copolymer of the same composition. DSC data indicates that the copolymers do not thermally recrystallize after heating above T_m . Wide angle x-ray diffraction was performed on copolymers that were molded at several different temperatures. Figure 1 shows the x-ray diffraction pattern for the solution imidized ATPAE 3110//BABB/BTDA 3110 copolymer powder

indicating a relatively high degree of crystallinity. Figures 2 and 3 are for the same copolymer molded 0.5 h at 320°C and 380°C, respectively. Molding at 320°C maintains crystallinity but does not produce well-consolidated moldings while molding at 380°C eliminates crystallinity but produces consolidated moldings. The crystallinity is not recoverable after annealing 2 h at 310°C.

Tensile properties of the clear yellow-orange films of the copolymers and homopolymers are shown in Table 3. The polyimide (BABB/BTDA) had higher strength and modulus than the poly(arylene ether) (FBB/BPF). The tensile strength and modulus of the copolymers are intermediate to those of the homopolymers and higher imide content produces higher strength and modulus. Fracture energy values [G_{1c} (critical strain energy release rate)] in Table 4 ranged from 5.7 to 8.8 in-lbs/in² with higher values corresponding to copolymers with longer blocks. These values are lower than a rule of mixtures analysis would predict for the copolymers.

In an effort to develop a more processable material, one copolymer was selected for molecular weight control and end-capping. Due to the excellent retention of tensile properties at 177°C, the ATPAE 3110//BABB/BTDA 3110 block copolymer was chosen. Since the imide block was crystalline and crystallinity acts as physical crosslinks, a copolymer with higher imide block content was prepared. The first controlled molecular weight copolymer studied was prepared by reacting a 2:1 ratio of BABB/BTDA 3110 with ATPAE 3110. This provided an anhydride-terminated copolymer with theoretical \bar{M}_n of 9330 g/mole which was end-capped with a stoichiometric amount of aniline. This

copolymer, designated ϕ -PI/PAE/PI- ϕ (3110), displayed excellent flow under low pressure but was too brittle for use as an adhesive. Therefore a higher molecular weight copolymer designated ϕ -PI/PAE/PI/PAE/PI- ϕ (3110) was prepared by reacting a 3:2 ratio of BABB/BTDA 3110 with ATPAE 3110 to provide an anhydride-terminated copolymer with theoretical \bar{M}_n of 15,550 g/mole which was end-capped with aniline. SI follows the copolymer designation for solution imidized versions.

Characterization of both the solution imidized and the thermally imidized copolymers is shown in Table 5. The powder from solution imidization was insoluble in DMAc, NMP and m-cresol. The η_{inh} of the poly(amic acid) copolymers ranged from 0.54 to 0.58 dL/g for several different batches. Copolymer T_g s by DSC are essentially the same while solution imidization produces a slightly higher T_m (377°C) than thermal imidization (370°C). The high molecular weight copolymers were crystalline as-prepared but once melted, the crystallinity was unrecoverable. However, the controlled molecular weight end-capped copolymers would readily recrystallize with the DSC crystallization peaks occurring at 305 and 320°C for the solution and thermally imidized copolymers, respectively. After curing 1 h at 300°C the copolymer exhibited a TBA damping peak maximum at 230°C, only slightly higher than the DSC T_g .

Moldings of the ϕ -PI/PAE/PI/PAE/PI- ϕ (3110) SI copolymer gave fracture toughness and fracture energy of $K_{1c} = 455 \text{ psi} \cdot \text{in}^{1/2}$ and $G_{1c} = 0.42 \text{ in-lbs/in}^2$. Higher values were expected since the theoretical \bar{M}_n is

15,550 g/mole, however good adhesive values were obtained so work continued on the copolymer at this molecular weight level.

Ti/Ti tensile shear specimens were fabricated under 200 psi at 380°C. The strengths (Table 6) from RT to 177°C were excellent for the as-prepared samples but very poor at 232°C. Since the T_g of the copolymer is 223°C, poor values at 232°C were expected. In an effort to improve this value, samples were annealed 16 h at 310°C to induce crystallinity. As shown in the second column in Table 6, a slight decrease in strength at RT and 93°C but significant improvement at 177°C and 232°C was observed. Aging samples for 100 h at 316°C, much higher than the anticipated use temperature, resulted in decreased RT and 177°C strength but an increase in strength at 232°C, suggesting a higher degree of crystallinity.

Examination of the bonds revealed excessive resin flow indicating that lower pressure may produce good strengths. Therefore, bonding pressure of 100 psi was studied with the results shown in Table 7. Bonding at 100 psi and 380°C produced bond strengths equivalent to 200 psi bonding pressure. These samples were tested at 200°C instead of 232°C and strengths were good but failure modes were primarily adhesive. After soaking for 24 h in hydraulic fluid, the adhesive strengths had decreased to 72% and 60% of original strength when tested at RT and 177°C, respectively. Lap shear specimens were aged 1000 h at 204°C (400°F) and strengths are shown in Table 7. This aging process caused a significant decrease in strength at RT but only a slight decrease (~10%) in strength at 177°C. Adhesive strength at 200°C actually increased 65% after aging at 204°C. Finally, the adhesive was processed

at only 50 psi and 380°C to explore lower pressure limits on adhesive strengths. Surprisingly, lap shear strengths were 75-80% of the strength using 100 psi bonding pressure for RT, 93°C and 177°C.

Unidirectional composites using Hercules unsized 12K AS-4 graphite fiber and ϕ -PI/PAE/PI/PAE/PI- ϕ (3110) were prepared. Prepreg was prepared by coating the fiber with 25% solids copolymer solution in NMP resulting in prepreg with 36.3% and 37.7% resin on consecutive runs. Unidirectional composites were prepared in a 3 in. x 3 in. stainless steel mold by heating to 380°C under 300 psi and holding at temperature and pressure for 15 min. Ten ply composite panels were prepared for flexural specimen (~0.075 in. thick) and 18 ply composite panels were prepared for short beam shear specimen (~0.125 in. thick). Results from flexural and short beam shear tests are shown in Table 8. The flexural properties were measured at RT, 93°C and 177°C while short beam shear strength was also tested at 232°C. The flexural strength of 216 ksi is good for a thermoplastic matrix composite and retention of flexural strength at 177°C is excellent (> 77% strength retention at 177°C). The flexural modulus is also good at RT and retention of modulus at 177°C is excellent. The short beam shear strengths were measured on the as prepared composite and on composite which had been annealed for 16 h at 310°C. The properties from the as-prepared composite are good at RT and 93°C but decrease extensively at 177°C and higher. Samples annealed to induce crystallinity had similar properties to the unannealed samples at RT and 93°C, but much better short beam shear strengths at 177°C and 232°C than the as-prepared sample.

CONCLUSIONS

A series of novel imide/arylene ether copolymers were prepared from the reaction of arylene ether and semi-crystalline imide oligomers. One block copolymer was end-capped and the molecular weight was controlled to improve compression moldability. The compression moldability of the end-capped controlled molecular weight copolymer showed a significant improvement over the imide homopolymer and provided attractive adhesive and composite properties.

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Table 1. Inherent Viscosity of ATPAE//BABB/BTDA Copolymers

| Copolymer | Polyamic Acid η_{inh} , dL/g ^a | | |
|--|--|-------------------|-------------------|
| | DMAC | NMP | m-Cresol |
| ATPAE 3110//BABB/BTDA 3110 | 1.02 | 0.82 | 0.61 |
| ATPAE 3110//BABB/BTDA 6545 | 1.08 | 0.75 | 0.64 |
| ATPAE 6545//BABB/BTDA 3110 | 0.47 ^b | 1.04 | 0.61 ^b |
| ATPAE 6545//BABB/BTDA 6545 | 0.35 ^b | 0.96 | 0.72 |
| ATPAE 3110 + [BABB + BTDA (3110)] Segmented | ---- | 1.00 ^b | ---- |
| ATPAE 6545 + [BABB + BTDA (6545)] Segmented | ---- | 0.89 ^b | ---- |

^aMeasured at 25°C and 0.5% concentration

^bFormed a gel which dissipated upon heating to ~70°C

Table 2. Thermal Characterization of ATPAE//BABB/BTDA Copolymers

| Copolymer | DSC T _g (T _m), °C ^a | | | DMAc ^c | TBA T _g , °C ^b |
|--|---|------------------|------------------|-------------------|--------------------------------------|
| | DMAc | NMP | m-Cresol | | |
| ATPAE 3110//BABB/BTDA 3110 | 228 (335,352) | 227 (331,350) | 228 (332,360) | 223 (365) | 233 |
| ATPAE 3110//BABB/BTDA 6545 | 228 (337,352) | 227 (332,352) | 225 (330,350) | 225 (372) | 239 |
| ATPAE 6545//BABB/BTDA 3110 | 227 (345) | 228 (340,352) | 228 (338) | 227 (----) | 229 |
| ATPAE 6545//BABB/BTDA 6545 | 228 (353) | 228 (347,357) | 232 (355) | 223 (372) | 240 |
| ATPAE 3110 + [BABB + BTDA (6545)] Segmented | ---- | 227 (332,350) | ---- | ---- | 232 |
| ATPAE 6545 + [BABB + BTDA (6545)] Segmented | ---- | 231 (350) | ---- | ---- | 233 |

^aMeasured at a heating rate of 20°C/min after curing 1 h at 300°C

^bMeasured at a heating rate of 3°C/min after curing 1 h at 300°C

^cSolution imidized, toluene azeotrope at 155°C for 16 h

Table 3. Film Properties of ATPAE//BABB/BTDA Copolymers

| Polymer | Tensile Strength, ksi (Modulus, ksi) [Elongation, %] | | |
|--|--|------------------|-----------------|
| | RT | 93°C | 177°C |
| ATPAE 3110//BABB/BTDA 3110 | 13.0 (489) [3.3] | 13.0 (452) [3.6] | 7.6 (442) [2.5] |
| ATPAE 3110//BABB/BTDA 6545 | 15.0 (480) [4.1] | 13.3 (428) [4.5] | 8.6 (435) [5.9] |
| ATPAE 6545//BABB/BTDA 3110 | 14.7 (425) [5.0] | 12.8 (415) [4.6] | 8.2 (379) [3.2] |
| ATPAE 6545//BABB/BTDA 6545 | 15.9 (408) [6.0] | 11.6 (354) [4.8] | 7.3 (331) [3.0] |
| ATPAE 3110 + [BABB + BTDA (3110)] Segmented | 13.2 (427) [3.7] | 11.5 (406) [9.2] | 6.2 (367) [7.1] |
| ATPAE 6545 + [BABB + BTDA (6545)] Segmented | 12.8 (409) [4.8] | 11.5 (355) [8.1] | 7.5 (357) [2.9] |
| FBB/BPF | 13.5 (378) [4.6] | 10.0 (349) [3.5] | 5.5 (304) [2.5] |
| BABB/BTDA | 22.0 (630) [8.3] | ---- | 15.2 (540) [21] |

Table 4. Fracture Toughness and Energy of ATPAE//BABB/BTDA Copolymers

| Polymer | Fracture Toughness (K _{Ic}) psi • in. ^{1/2} | Fracture Energy G _{Ic} , in.-lbs/in. ² |
|----------------------------|---|---|
| ATPAE 3110//BABB/BTDA 3110 | 1670 | 5.7 |
| ATPAE 3110//BABB/BTDA 6545 | 1950 | 7.9 |
| ATPAE 6545//BABB/BTDA 3110 | 1940 | 8.8 |
| ATPAE 6545//BABB/BTDA 6545 | 1860 | 8.5 |

Table 5. Characterization of ϕ -PI/PAE/PI/PAE/PI- ϕ (3110) Copolymers

| Copolymer | η_{inh} , dL/g ^a | DSC T _g (T _m), °C | DSC Recrystallization Peak, °C |
|---|----------------------------------|--|--------------------------------|
| ϕ -PI/PAE/PI/PAE/PI- ϕ (3110) SI | ----- | 225 (377) | 305 |
| ϕ -PI/PAE/PI/PAE/PI- ϕ (3110) | 0.54-0.58 | 223 (370) ^b | 320 ^b |

^aPoly(amic acid) measured in NMP at 25°C and 0.5% concentration

^bFilm cured 1 h each at 100, 200 and 300°C

Table 6. Adhesive Properties^a of ϕ -PI/PAE/PI/PAE/PI- ϕ (3110) Copolymer

| Test Temperature | Ti/Ti Tensile Shear Strength After Exposure, psi | | |
|------------------|--|------------------------|---------------------|
| | None | Annealed 16 h at 310°C | Aged 100 h at 316°C |
| RT | 5050 (Coh) ^b | 4950 (Coh) | 4200 (Coh) |
| 93°C | 4950 (Coh) | 4850 (Coh) | ----- |
| 177°C | 3350 (Coh) | 4250 (Coh) | 3700 (Coh) |
| 232°C | 300 (Ad) | 110 (Ad) | 1250 (Ad) |

^aBonded 20 min. at 380°C under 200 psi

^b(Coh) = cohesive failure, (Ad) = adhesive failure

Table 7. Adhesive Properties^a of ϕ -PI/PAE/PI/PAE/PI- ϕ (3110) Copolymer

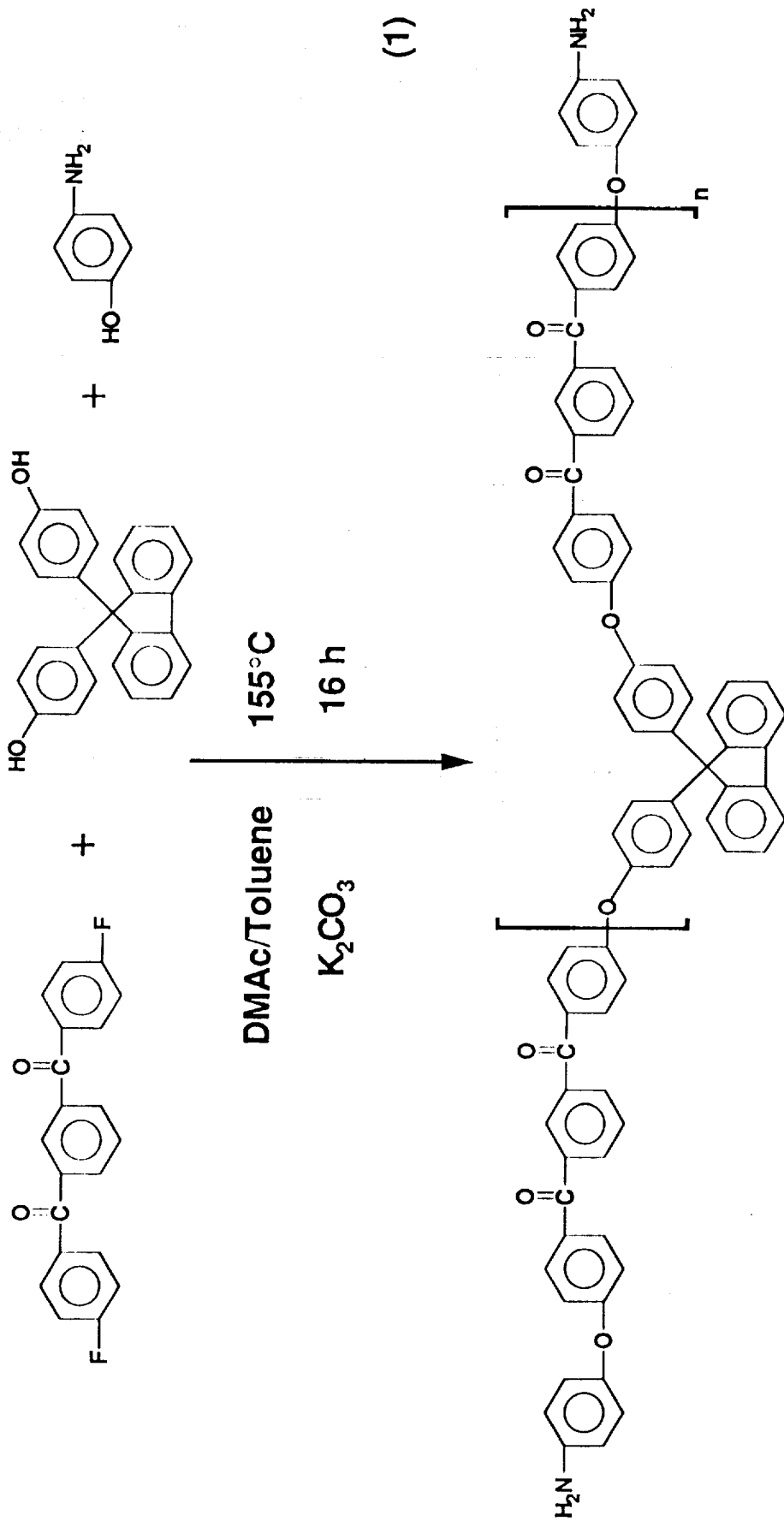
| Test Temperature | Ti/Ti Tensile Shear Strength After Exposure, psi | | |
|------------------|--|-------------------------|----------------------|
| | None | Soak in Hydraulic Fluid | Aged 1000 h at 204°C |
| RT | 5050 (Coh) ^b | 3650 (Coh) | 3300 (Coh) |
| 93°C | 4850 (Coh) | ----- | ----- |
| 177°C | 3350 (Coh) | 2000 (Coh) | 3000 (Coh) |
| 200°C | 1150 (Ad) | ----- | 1900 (Ad) |

^aBonded 20 min. at 380°C under 100 psi

^b(Coh) = cohesive failure (Ad) = adhesive failure

Table 8. Unidirectional Unsized AS-4 12K Laminate Properties of ϕ -PI/PAE/PI/PAE/PI- ϕ (3110) Copolymer

| Test Temperature | Flexural Strength, ksi | Flexural Modulus, msi | Short Beam Shear Strength, ksi | |
|------------------|------------------------|-----------------------|--------------------------------|------------------------|
| | | | As Prepared | Annealed 16 h at 310°C |
| RT | 216, | 17.0 | 10.7 | 10.1 |
| 93°C | 198, | 16.4 | 9.4 | 9.3 |
| 177°C | 167, | 16.5 | 6.7 | 8.3 |
| 232°C | --- | --- | 1.4 | 5.6 |



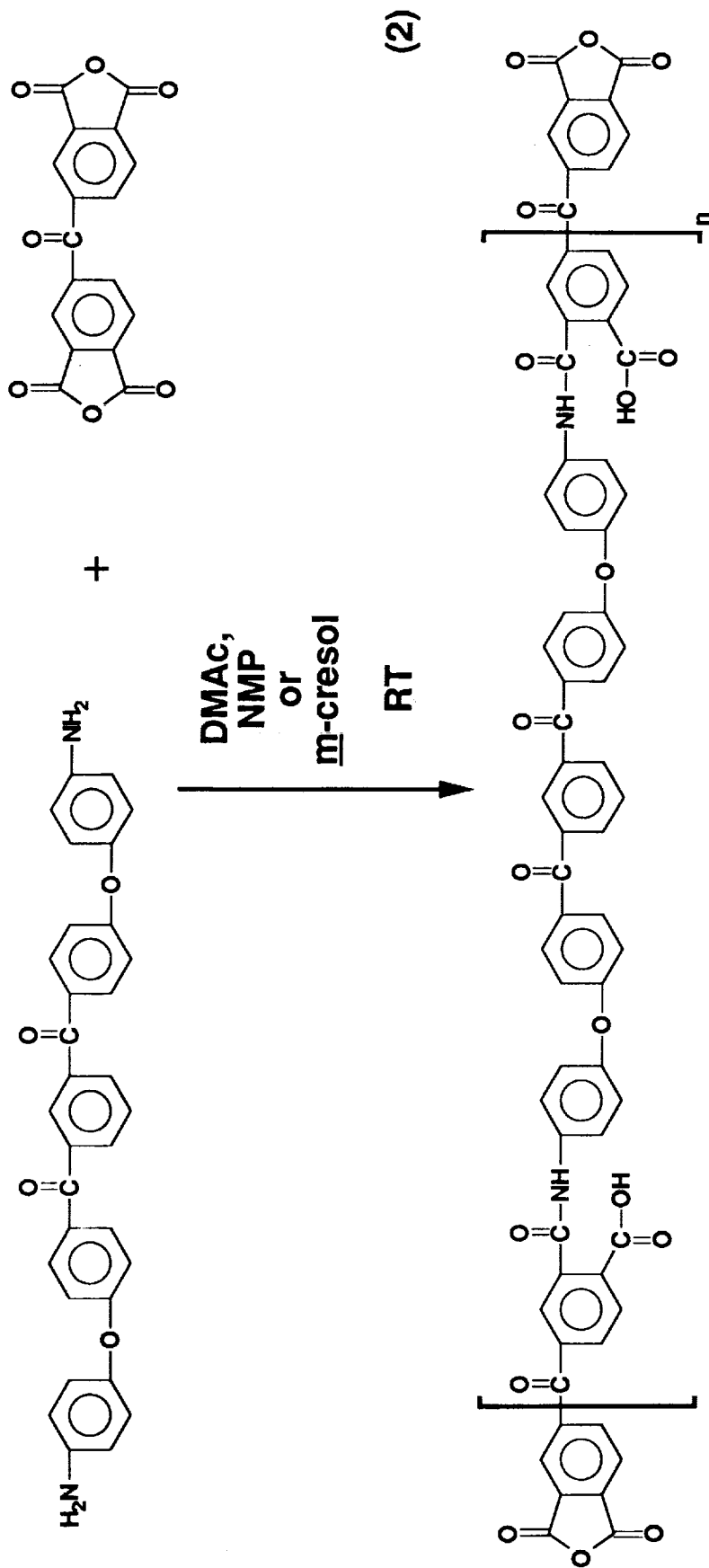
ATPAE

$\bar{M}_n = 3110\text{ g/mole}$ and $\bar{M}_n = 6545\text{ g/mole}$

$r = 0.816$

$r = 0.908$

$r = \text{ratio of BPA to FBB}$



BABBB/BTDA AA

$\bar{M}_n = 3110 \text{ g/mole}$ and $\bar{M}_n = 6545 \text{ g/mole}$

$r = 0.766$

$r = 0.882$

$r = \text{ratio of BABBB to BTDA}$

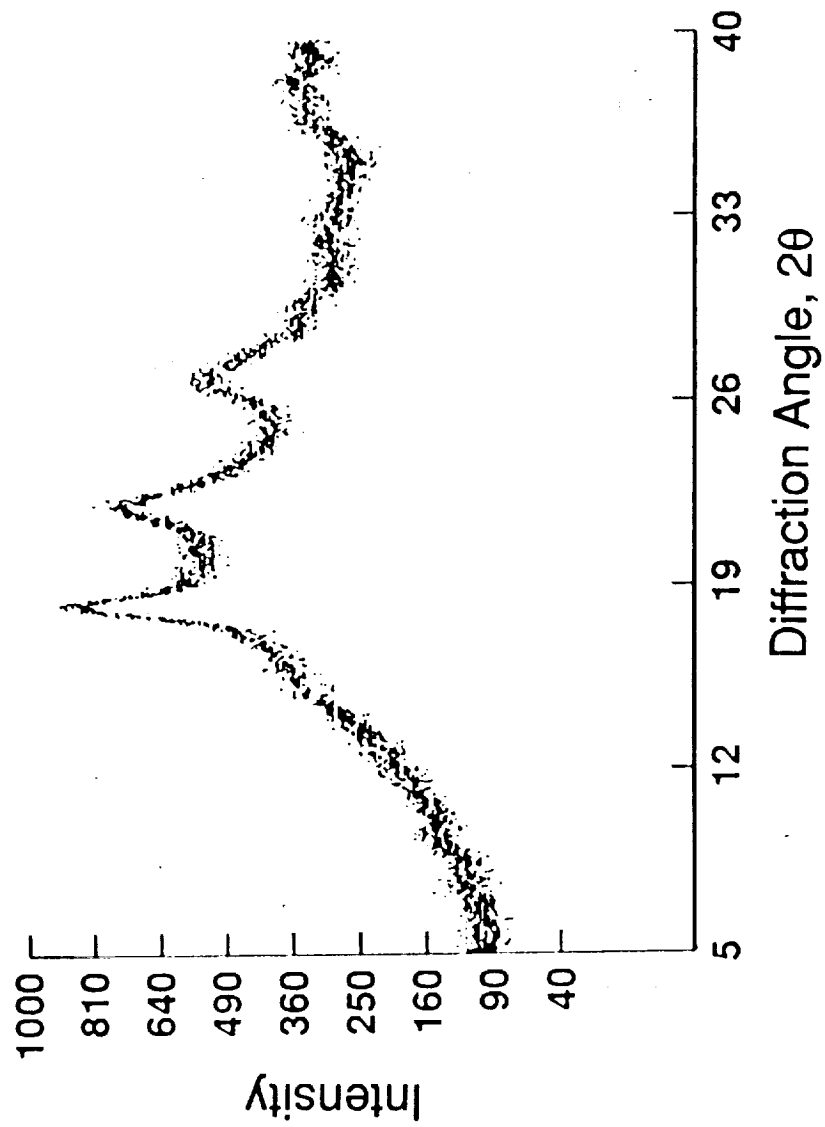


Figure 1. X-ray diffraction pattern for solution imidized ATPAE 3110//BABB/BTDA 3110 copolymer powder.

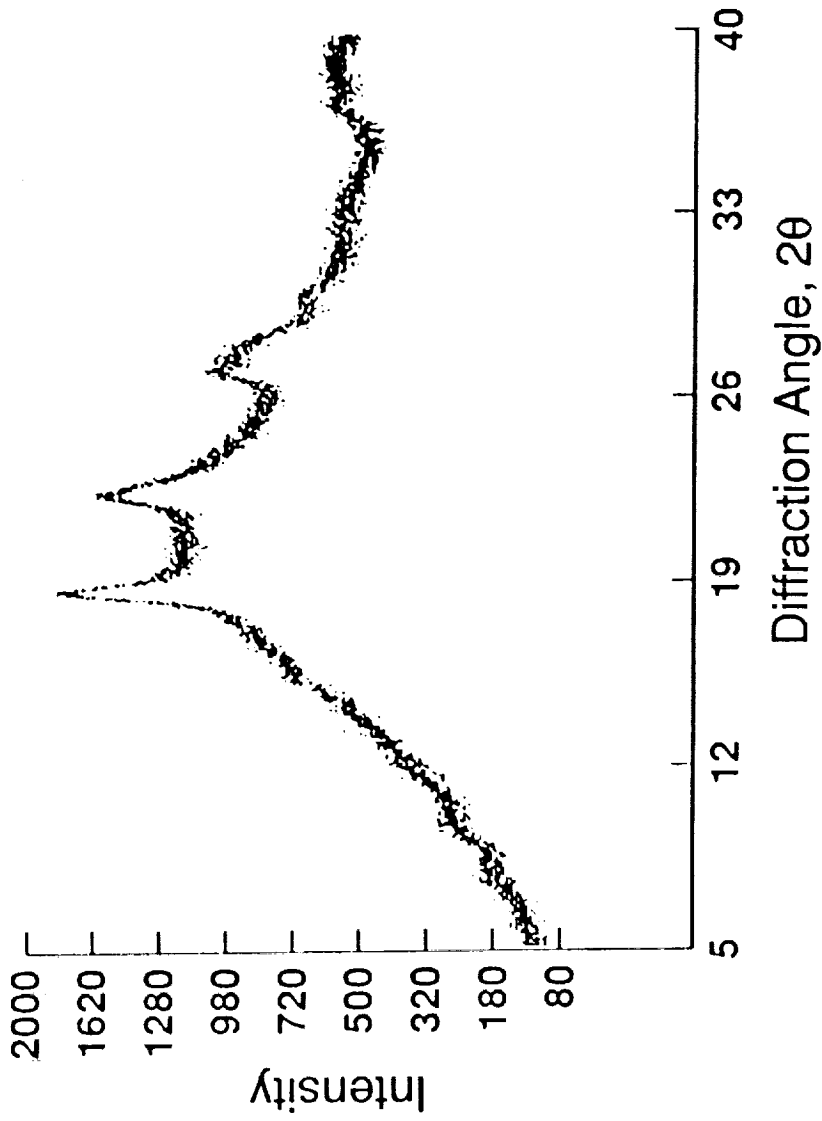


Figure 2. X-ray diffraction pattern for solution imidized ATPAE 3110//BABB/BTDA 3110 copolymer molded 0.5 h at 320°C.

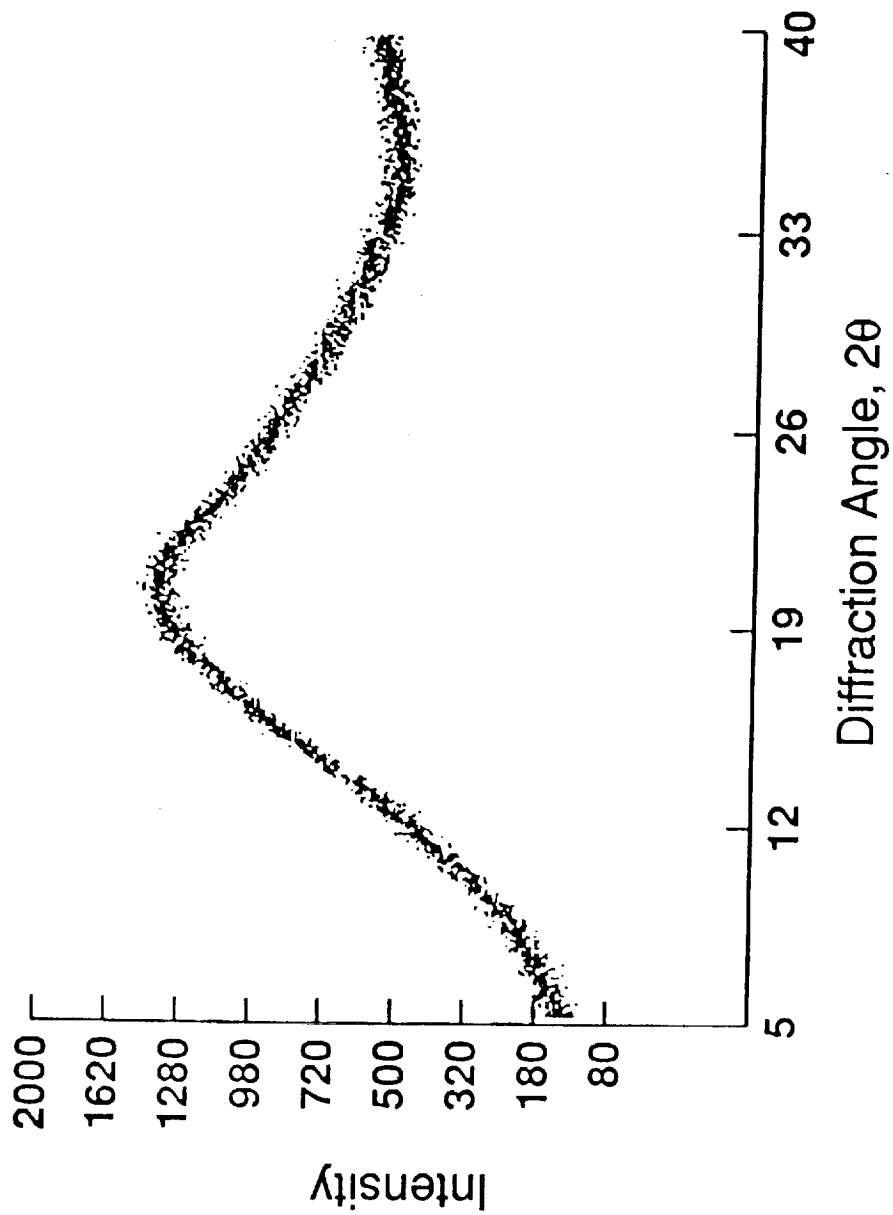


Figure 3. X-ray diffraction pattern for solution imidized ATPAE 3110//BABB/BTDA 3110 copolymer molded 0.5 h at 380°C.



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| 16. Abstract <p>A series of novel imide/arylene ether copolymers were prepared from the reaction of an amorphous arylene ether oligomer and a semi-crystalline imide oligomer. These copolymers were thermally characterized and mechanical properties were measured. One block copolymer was end-capped and the molecular weight was controlled to provide a material that displayed good compression moldability and attractive adhesive and composite properties.</p> | | | | | |
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