

Addition Polyimides From Non-Mutagenic Diamines.

Peter Delvigs
Glenn Research Center
National Aeronautics and Space Administration
Cleveland, OH 44135

David L. Klopotek
St. Norbert College
DePere, WI 54115

DeNise Hardy-Green
University of Akron
Akron, OH 44325

Abstract. Studies were conducted to find an acceptable non-mutagenic diamine to replace 4,4'-methylenedianiline (MDA), a suspect carcinogen, which is currently being used in PMR-15 polyimide applications. Several diamines containing fluorine and trifluoromethyl substituent groups were synthesized. The diamines were polymerized with the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE), using the monomethyl ester of nadic acid (NE) as an endcap. The effect of diamine structure on rheological properties, glass transition temperature, and thermo-oxidative stability was investigated. Unidirectional laminates were fabricated from selected resins, using carbon fiber as the reinforcement. The results indicate that some of the diamines containing trifluoromethyl groups are non-mutagenic, and have potential to replace MDA in PMR polyimides for long-term applications at temperatures up to 300° C.

1. Introduction

During the last three decades, high-performance polymers and fiber-reinforced polymer composites have found increased application in aerospace structural components as replacement for metals, primarily because of weight saving [1]. Today one of the most widely used polymers, combining good processability, mechanical properties, and reasonable thermo-oxidative stability, are the PMR polyimides. Based on previous work by Lubowitz, [2] the PMR polyimides were first developed in this laboratory [3,4]. The commercially available PMR polyimide known as PMR-15 is prepared in two stages from three monomers: 2-carbomethoxy-3-carboxy-5-norbornene (nadice ester, NE), 4-4'-methylenedianiline (MDA), and the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE).

One of the monomers used in the PMR-15 resin, MDA, is a mutagen and suspected carcinogen. For this reason the Occupational Safety and Health Agency (OSHA) has established rigid regulations for the safe handling of materials containing MDA [5]. These regulations have resulted in significantly increased costs to suppliers and users of PMR-15 materials. Studies in this laboratory were performed to identify diamines as replacements for MDA without compromising the excellent processability and mechanical properties of PMR-15. Some recent efforts led to the synthesis of multi-aromatic ring diamines containing oxo and methylene connecting groups [6-8]. However, polyimides prepared from these flexibilized diamines exhibit lower glass transition temperatures, and in the case of AMB-21 (containing oxo linkages), also lowered thermo-oxidative stability compared to PMR-15 [6,9].

In a study of the mutagenicity of various diamines, Rao [10] observed that introduction of larger alkyl groups (such as isopropyl) on both phenyl rings of the diamine MDA significantly reduced or eliminated mutagenic activity. The approach used in this study was the synthesis of MDA-like diamines with bulky substituent groups, such as fluoro and trifluoromethyl groups, on the phenyl rings or the connecting methylene group. In view of the above study [10], the bulky substituents were expected to eliminate mutagenic activity without seriously compromising the other desirable properties of the MDA-like diamines.

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Six new aromatic diamines containing fluoro and trifluoromethyl substituent groups were synthesized and screened by the Ames test for mutagenicity. Neat PMR polyimide specimens were molded using NE, BTDE, and each of the new diamines. Differential scanning calorimetry (DSC) and rheological measurements were performed to establish molding cycles for each formulation. The effect of postcure on the glass transition temperature of the resins was studied. The weight loss characteristics of the resins were determined at two elevated temperatures. Unidirectional composites were fabricated from selected polyimides containing the new diamines, using T 650-35 graphite fiber as the reinforcement. Composite mechanical properties such as flexural properties and interlaminar shear strength were determined.

2. Experimental details

2.1. Monomers

The structures of all synthesized monomers were confirmed by ^1H and ^{13}C NMR spectroscopy, as well as IR spectroscopy. All new monomers were submitted for elemental analysis. The NMR spectra were obtained on a Bruker AM 300 Fourier transform spectrophotometer. Solutions were prepared in CDCl_3 using tetramethylsilane as the internal standard. IR spectra were performed on a Perkin-Elmer 1750 FTIR, using KBr pellets. Elemental analyses were performed by Spang Microanalytical Laboratory.

The structures of all monomers used in the synthesis of addition polymers are shown in Figure 1. The synthetic methods for the preparation of the diamines are outlined in Schemes 1 and 2.

- 2.1.1. *3,3',4,4'-Benzophenonetetracarboxylic acid dianhydride (BTDA)*. BTDA was obtained from commercial sources. The dimethyl ester BTDE was prepared by refluxing the dianhydride BTDA in an amount of methanol calculated to yield a solution containing 50 wt% solids. The reflux was carried out for 2 h after the solid BTDA had dissolved. The resultant BTDE solution was used immediately for resin synthesis.
- 2.1.2. *The monomethyl ester of nadic acid (NE)*. NE (m.p. 102-103° C) was obtained from commercial sources and used as-received for resin synthesis.
- 2.1.3. *4,4'-Methylenedianiline (MDA)*. MDA (m.p. 90-92° C) was obtained from commercial sources and used as-received for resin synthesis.
- 2.1.4. *Bis(4-amino-2,3,5,6-tetrafluorophenyl)methane (1)*. 10.0 g (0.061 mol) of 2,3,5,6-tetrafluoroaniline was added to magnetically stirred trifluoroacetic acid (40 ml). After solution was complete, 40% formaldehyde solution (2.35 ml, 0.030 mol) was added, and the solution was heated under reflux for 1 h. The solution was poured over ice to give a precipitate. After filtration, the precipitate was dissolved in a saturated solution of KOH in 95% ethanol until the solution was basic to litmus paper. Distilled water (about 200 ml) was added to form a yellowish precipitate, which was filtered and washed with water. The crude product was recrystallized from ethanol and dried to yield 9.33 g (0.027 mol, 90%) of bis(4-amino-2,3,5,6-tetrafluorophenyl)methane, m.p. 144-145° C. Analysis: calc. for $\text{C}_{13}\text{H}_6\text{N}_2\text{F}_8$: C, 45.63%; H, 1.77%; N, 8.19%. Found: C, 45.51%; H, 1.90%; N, 8.33%.
- 2.1.5. *Bis(4-amino-2,5-difluorophenyl)methane (2)*. 50.0 g (0.388 mol) of 2,5-difluoroaniline was added to trifluoroacetic acid (150 ml) with stirring, followed by 40% formalin (16 ml, 0.193 mol). The solution was heated under reflux for 1 h, then poured over ca. 1 l of ice water. The mixture was made basic with a concentrated solution of KOH in water (4g per 10 ml), and allowed to stand overnight. The yellow crystals were filtered, washed with water and dried. The crude product was dissolved in hot 95% ethanol (15 ml per g) and filtered through celite. The solution was heated again, and water was added slowly until cloudiness, then cooled to form pale yellow crystals. The product was filtered and dried to yield 25.0 g (0.093 mol, 48%) of bis(4-amino-2,5-

difluorophenyl)methane, m.p. 131-132°C. Analysis: calc. for $C_{13}H_{10}N_2F_4$: C, 57.78%; H, 3.73%; N, 10.37%. Found: C, 57.90%; H, 3.59%; N, 10.24%.

2.1.6. *Bis(4-amino-3,5-difluorophenyl)methane (3)*. The same synthetic procedure was employed for this diamine as for its isomer 2 as outlined in the previous section, except that 2,6-difluoroaniline (50.0g, 0.388 mol) was the starting material. The crude product was recrystallized in the same manner as diamine 2 to yield 94.3g (0.349 mol, 90%) of bis(4-amino-3,5-difluorophenyl)methane, m.p. 135-136°C. Analysis: calc. for $C_{13}H_{10}N_2F_4$: C, 57.78%; H, 3.73%; N, 10.37%. Found: C, 57.65%; H, 3.61%; N, 10.48%.

2.1.7. *Bis[4-amino-3-fluoro-5-(trifluoromethyl)phenyl]methane (4)*. A mixture of 2-fluoro-6-(trifluoromethyl)aniline (50.0 g, 0.279 mol), 40% formalin (10.5 ml, 0.317 mol), and trifluoroacetic acid (150 ml) was stirred at room temperature for 45 min, then poured over ice to produce a white precipitate. Next 10% KOH/90% EtOH was added until the solution was basic to litmus paper (ca. 1.5 l). Water was added to double the volume, which yielded a precipitate. The product was filtered, washed with water, and dried to yield 49.6 g (0.134 mol, 96%) of bis[4-amino-3-fluoro-5-(trifluoromethyl)phenyl]methane, m.p. 119-120°C. No purification was necessary for polymer synthesis, but a small sample submitted for elemental analysis was recrystallized from 95% EtOH/water. Analysis: calc. for $C_{15}H_{10}N_2F_8$: C, 48.66%; H, 2.72%; N, 7.57%. Found: C, 48.81%; H, 2.61%; N, 7.39%.

2.1.8. *Bis[4-amino-3-(trifluoromethyl)phenyl]methane (5)*. A mixture of 2-(trifluoromethyl)aniline (10.0 g, 0.0621 mol), 40% formalin (4.8 ml, 0.145 mol), and trifluoroacetic acid (30 ml) was heated at reflux with stirring for 1 h. The solution was poured over ice to yield a red oil. Next 10% KOH/90% EtOH was added until the solution was basic to litmus paper. Water was added to double its volume, which produced a cloudy precipitate. On standing the precipitate turned to an oil. Repeated attempts to recrystallize the crude product from ethanol/water failed. It was purified by column chromatography, using acidic alumina, wet-packed with petroleum ether. The oil was added to the column by dissolving in the minimum amount of benzene. The column was then eluted successively with petroleum ether, 25% benzene, 50% benzene, 75% benzene, 100% benzene, followed by benzene containing 1% EtOH, 3% EtOH, and 5% EtOH. The desired product eluted with 100% benzene and 1% EtOH. A second purification was necessary to obtain a pure product. The yield of bis-[4-amino-3-(trifluoromethyl)phenyl]methane was 5.14 g (0.0154 mol, 48%), m.p. 88-89°C. Analysis: calc. for $C_{15}H_{12}N_2F_6$: C, 53.90%; H, 3.62%; N, 8.38%. Found: C, 54.09%; H, 3.53%; N, 8.18%.

2.1.9. *1,1,1-trifluoro-2,2-bis(4-aminophenyl)ethane (6)*. A mixture of trifluoroacetaldehyde ethyl hemiacetal (12.0 g, 0.083 mol), aniline (65.1g, 0.70 mol), and aniline hydrochloride (16.2g, 0.125 mol) was heated under reflux for 24 h. The solution was made basic to litmus paper by adding solid KOH with stirring. This mixture was steam-distilled until all excess aniline had been removed. The organic layer was separated and allowed to dry. The crude product was dissolved in boiling ethanol (10 ml /1g), activated charcoal was added, and the hot solution was filtered through celite, and an equal volume of boiling water was added. The solution was placed into a separatory funnel. On cooling, the suspected ortho-ortho diamine impurity separated as an oil, and was drawn off. Overnight cooling of the remaining solution yielded colorless crystals, which were filtered, washed with water, and dried. A second recrystallization was required to obtain pure 1,1,1-trifluoro-2,2-bis(4-aminophenyl)ethane (9.71g, 0.0365 mol, 44%), m.p. 137-138°C. Analysis: calc. for $C_{14}H_{13}N_2F_3$: C, 63.15%; H, 4.92%; N, 10.52%. Found: C, 63.32%; H, 5.07%; N, 10.40%.

2.2. Mutagenicity assay of diamines

Diamines 1 through 6 were tested using the standard Ames mutagenicity test [10, 11]. The tester strains used were *Salmonella typhimurium* TA 98 and TA 100 which were obtained from Moltex™ (Boone, NC) and were grown in nutrient broth Oxoid No. 2. Aroclor 1254 S9, obtained from Moltex™, was used as a metabolic activator. 0.1 ml of the bacterial culture in 2 ml of top agar supplemented with a trace amount of histidine and biotin was combined with 0.1 ml of test compound dissolved in dimethylsulfoxide (DMSO), and 0.5 ml of a 10% S9 mix. The mixture was vortexed and poured over minimal Vogel-Bonner glucose agar plates. Plates at each concentration of test compound were done in duplicate, and three spontaneous revertant plates were included for each strain. Controls were performed with daunomycin for TA 98 and sodium azide for TA 100 to ensure the strains were reverting properly. 2-Aminoanthracene was used to ensure the S9 was activating correctly. Plates were incubated at 37°C for 48 h, and were visually counted using a Scienceware digital colony counter.

2.3. Resin fabrication and evaluation

Molding powders were prepared by the procedure described below. All resin formulations were prepared in the stoichiometric ratio of 2NE/2BTDE/3diamine.

The three monomers were dissolved in methanol at a solid content of 35-50 wt%. The solvent was evaporated to near dryness at 60-70°C. The mixture was heated for 1 h at 204 °C (400°F). The formulations containing diamines 1-3 were heated for an additional 0.5h at 232°C (450°F), then ground into a fine powder.

The general molding procedure for fabrication of resin specimens is the following: a cylindrical hardened steel die (2.54 cm diameter) equipped with a thermocouple was sprayed with a release agent (Frekote 44) and dried after each use. The base plate of the die was provided with a small slot close to the junction of the die wall to allow detection of resin flow during processing. A Wabash hydraulic press with electrically heated platens and a maximum capacity of 12 tons was used for application of pressure and temperature during cure.

All molding powders were examined by differential scanning calorimetry (DSC), using a Dupont 910 DSC and a high-pressure cell in nitrogen at a pressure of 1.38 MPa (200 psi) and a scan rate of 10° C min⁻¹. Thermogravimetric analyses (TGA) were performed in air in a Perkin-Elmer TGS-II at a rate of 10°C min⁻¹. Omnitherm thermal analysis system controllers and software were used for the DSC and TGA runs.

Mold cycle temperature/pressure parameters were based on the results of the above tests. During molding, the parameters were adjusted based on visual observation of resin flow at the base plate slot. In all cases press platens were preheated to a selected temperature, ranging from 232°C (450°F) to 280°C (536°F). A cold die, containing the molding powder (1.2 to 1.3g), was placed in the press. Stops were used to prevent the application of pressure on the material until the predetermined temperature was reached. The applied pressure ranged from 1.1 MPa (160 psi) to 5.51 MPa (800 psi). The final cure temperature was 316°C (600°F). The pressure and temperature were maintained for 2 h. The thickness of the molded discs ranged from 1.3 to 1.8 mm. The discs were cut into square pieces, 5 x 5 mm.

Post-cure and isothermal exposure of the resins was carried out in calibrated forced air ovens with an air change rate of 100 cm³ min⁻¹. The post-cure was carried out for 24 hr at 316°C (600°F). Isothermal exposure was performed in triplicate at two temperatures: 288°C (550°F) and 316°C (600°F). Sample weight was recorded at weekly intervals. Glass transition temperatures (T_g) were determined with a Dupont 943 thermomechanical analyzer at a heating rate of 10 °C min⁻¹, using a 5 g weight.

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2.4. Composite fabrication and evaluation

Composites were fabricated using T650-35 graphite fiber with UC 309 epoxy sizing and 8 harness satin weave. The fiber was drum-wound, brush-coated with the appropriate monomer solution in methanol at a solid content of 40-50 wt% and air-dried. The prepreg was removed and cut into 10.2 cm x 10.2 cm (4 in x 4 in) pieces. Ten unidirectional plies were stacked and heated in an air-circulating oven for 1 h at 204 °C (400 °F). The imidized preforms were placed in a matched hardened steel die, and placed in a press where the platens were preheated to a selected temperature ranging from 260 °C (500 °F) to 280 °C (536 °F). The applied pressure ranged from 3.45 to 5.52 MPa (500 to 800 psi). The final cure temperature was 316 °C (600 °F). The pressure and temperature were maintained for 1.5 h. All laminates were post-cured in a forced air oven by slowly increasing the temperature to 316 °C (600 °F), and holding for 16 h.

The T_g values of the laminates were determined in the same manner as those of the resin discs. The fiber content was determined by digestion with H_2SO_4/H_2O_2 . The laminates were inspected for defects using an ultrasonic C-scan technique. Flexural strength tests were performed in accordance with ASTM D-790, using a three-point loading fixture and a span ranging from 5.08 cm (2 in) to 6.35 cm (2.5 in). Interlaminar shear strength tests were performed in accordance with ASTM D-2344 at a constant span/depth ratio of 5. All mechanical tests were performed in triplicate.

3. Results and discussion

3.1. Monomer synthesis

The structures of the diamines used in this study are shown in Figure 1. Diamines 1 – 5 were obtained by reacting several substituted anilines with formaldehyde in trifluoroacetic acid, as outlined in scheme 1. With one exception, high yields of product were obtained. In the case of diamine 5 recrystallization attempts of the crude product were unsuccessful. Purification was accomplished by column chromatography, but the yield of pure diamine was only 48%. Since the starting material, 2-(trifluoromethyl)aniline, has an unsubstituted position *ortho* to the amino group, it apparently allows a significant extent of condensation at the *ortho* in addition to the preferred *para* position, leading to isomeric impurities which were difficult to remove from the desired product. Diamine 6 was obtained in 44% yield as shown in scheme 2. Again, the relatively low yield is apparently due to the presence of condensation products at the position *ortho* to the amino group.

The rationale for choosing the diamine structures for this study was to preserve the basic structure of MDA, while adding bulky substituents. Alston [12,13] postulated that benzylic-type diamines such as MDA provide enhanced thermo-oxidative stability (TOS) in end-capped PMR-type polyimides. Thus we endeavored to maintain this structural feature for maximum retention of TOS. The diamine MDA, however, is a known mutagen and suspected carcinogen. MDA is an intercalating agent and can assume a planar conformation that is able to mimic base pairs and slip in between the stacked nitrogen bases at the core of the DNA double helix. In this intercalated position MDA can cause single-nucleotide pair insertions or deletions. Intercalating agents can also stack between bases in single-stranded DNA, leading to a frameshift mutagenesis. Rao [10] has demonstrated that introduction of bulky alkyl groups such as isopropyl and isobutyl on both phenyl rings of MDA significantly reduces or eliminates mutagenic activity. Based on this observation, we postulated that introduction of bulky substituents such as fluoro or trifluoromethyl groups in the MDA skeleton would sterically prevent the diamines from assuming a planar conformation which leads to mutagenic activity. At the same time, these substituents were not expected to affect the TOS of polyimides prepared from the diamines to a significant extent.

In addition to the six above described diamines, we attempted to synthesize a diamine by the formaldehyde condensation of 3,5-bis(trifluoromethyl)aniline. In this case the desired condensation product was not

found. Instead, a heterocyclic ring compound was formed. This could be explained by the steric hindrance due to the presence of two trifluoromethyl groups *ortho* to the expected condensation site. These and similar synthesis studies are to be described elsewhere.

3.2. Mutagenicity assay of diamines

Since a very thorough mutagenicity determination for the six new diamines was beyond the scope of the present study, we limited the tests to an initial screening that would allow us to make a decision whether further evaluation studies were warranted. We used *Salmonella typhimurium* TA 98 strain for detection of frame-shift mutations and the TA 100 strain for detection of base-pair substitutions. The results indicate that diamines 4 – 6, all of which are substituted with at least one trifluoromethyl group, were nonmutagenic toward both bacterial strains. These results are consistent with the finding by Miller [14] that the introduction of the trifluoromethyl group in several aromatic amines renders them noncarcinogenic. It should be noted that diamines 1 – 3, which contain only fluoro substituent groups, were also found to be nonmutagenic in our study. The controls and spontaneous reversions were all within the appropriate ranges. Consequently all six diamines were evaluated as possible replacements for MDA in PMR-15 type addition polyimides.

3.3 Resin fabrication

The structures of the monomers used in the synthesis of polyimide resins are shown in figure 1. The control resin, PMR-15, is fabricated in several steps. The three monomers, (NE, MDA, and BTDE), are dissolved in methanol, and the solvent is evaporated at 60 – 70 °C. A low-molecular weight imide oligomer is formed by heating the monomer mixture at 120 – 232 °C. The oligomer is cured at 275 – 316 °C under pressure. Under these conditions the norbornenyl end-cap undergoes a retro Diels-Alder reaction and forms a crosslinked network structure via an addition mechanism. The monomer stoichiometry for the commercial PMR-15 resin is 2 NE/3.087 MDA/2.087 BTDE. This represents an average value of $n=2.087$ for the oligomer structure shown in figure 2. For the sake of simplicity, an average value of $n=2$ was used in this study for all resins, including the control, PMR-15. The slight difference in stoichiometry had virtually no effect on the glass transition temperature (T_g) of the PMR-15 resin.

Molding powders were prepared from NE, BTDE, and each of the diamines shown in figure 1. Differential scanning calorimetry (DSC) runs from all formulations exhibited an endotherm centered at 200 – 230 °C, indicating resin flow, and an exotherm centered at 340 – 360 °C, indicating reaction via the norbornenyl end-cap. Rheological measurements of the imidized oligomers were made to compare the flow properties. The complex shear viscosity (η^*) of glass-cloth composites impregnated with the resin formulation was measured. The specimens prepared from diamines 2 – 6 exhibited a complex shear viscosity very similar to that of PMR-15. Based on the DSC runs and rheological measurements, initial molding parameters identical to those for PMR-15 were selected for compression-molding of neat resin specimens. The molding parameters had to be slightly adjusted from visual observations during the initial molding trials to insure defect-free specimens. The formulation from diamine 1 (the octafluoro derivative of MDA) proved to be an exception. It exhibited a much lower shear viscosity compared to PMR-15. In addition, the DSC runs indicated a significant endotherm below 100 °C, suggesting incomplete reaction of the monomers. This was confirmed by FTIR analysis, which indicated absorption bands in the 3300 – 3400 cm^{-1} region due to aromatic amino groups. Attempts were made to increase the imidization temperature or time, but we were unsuccessful in eliminating the presence of some unreacted monomers in the molding powder. As a consequence, the molding powder exhibited excessive flow during compression-molding, and we were unable to fabricate resin discs from this formulation. Apparently the presence of eight fluorine atoms on the aryl portion of the diamine significantly deactivates the amino groups. This agrees with observations made by Hougham et al [15] for condensation polyimides prepared from highly fluorinated monomers. It

should be noted that diamines 2 and 3, containing four fluorine atoms, were apparently not sufficiently deactivated to prevent fabrication of defect-free discs from molding powders containing these diamines.

3.4 Resin Evaluation

Resin densities and glass transition temperatures (T_g) of the polyimides prepared from diamines 2 – 6 are shown in table 1. The densities are higher than that of PMR-15, reflecting the presence of fluoro or trifluoromethyl substituents. The T_g values of the as-cured resins (including PMR-15) are relatively low. It is therefore a common practice to subject PMR-type polyimides to a free-standing post-cure in air to complete curing of the resin, and to achieve further crosslinking. Typically a 24-hour postcure in air at 316 °C (600 °F) results in a T_g increase of 30-50 °C, compared to the as-cured resin. Table 1 shows that the T_g values of the resins from diamines 4 and 5 (containing trifluoromethyl groups on the phenyl rings) were higher than that of PMR-15. The T_g values of the other polyimides were slightly lower, but still sufficiently high to meet the general temperature requirements for PMR-15 applications.

The thermo-oxidative stability (TOS) of a matrix resin is also an important consideration for composite applications at elevated temperatures. Thermogravimetric analysis (TGA) in air is a common technique to assess the TOS of a matrix resin. However, it does not usually detect subtle differences in the TOS of structurally similar polymer formulations, which may not become apparent until a prolonged exposure at elevated temperatures. Consequently, the new resins were subjected to isothermal exposure in air at two different temperatures: 288 °C (550 °F) and 316 °C (600 °F). The weight loss results as a function of exposure time are presented in table 2, and are shown graphically in figures 3 and 4. The polyimides made from diamines 4 – 6 exhibit a trend toward a slightly higher weight loss compared to PMR-15. However, the differences were small, particularly at the lower exposure temperature. This is not unexpected for diamines 4 and 5, since both have the same benzylic diamine structure as MDA. Work by Alston [12, 13] has demonstrated that norbornenyl-capped PMR polyimides prepared from benzylic diamines containing methylene connecting groups consistently demonstrated a better TOS at 316 °C than resins from non-benzylic diamines at comparable monomer stoichiometry. In diamine 6 one of the methylene H atoms is replaced by a trifluoromethyl group. Despite that, the TOS of the resin from this diamine was closely comparable to that of PMR-15. Apparently the free radicals generated during exposure are capable of providing cross-linked structures similar to those in the PMR-15 polyimide. However, the weight loss values of the resins prepared from diamines 2 and 3 (both having the same benzylic skeleton as MDA) were significantly higher than those for PMR-15 at both exposure temperatures. A possible explanation is that the fluorine substituents deactivate the diamines during the imidization and initial cure, resulting in the presence of some unreacted monomers.

3.5 Composite fabrication and evaluation

Four of the six new diamines were selected for a preliminary composite evaluation. Since formulations from the octafluoro diamine 1 exhibited excessive resin flow during resin fabrication studies, it was eliminated from further studies. Diamine 5 was not selected at this time because of insufficient quantity due to the laborious purification procedure.

Since the viscosity and resin flow characteristics of PMR polyimide formulations from diamines 2, 3, 4, and 6 were closely comparable to those of PMR-15, essentially the same cure cycle as for PMR-15 could be employed. All resin formulations employed a monomer stoichiometry of 2 NE/ 2 BTDE/ 3 diamine. Compression-molded unidirectional laminates were fabricated, using T 650-35 graphite fiber as the reinforcement.

Some basic properties of the laminates are shown in table 3. The fiber content of the laminates was close to the target value of 60 volume percent. All laminates were subjected to a free-standing postcure in air at 316 °C, identical with that commonly used for PMR-15 composites. The T_g values did not differ significantly from those of the corresponding neat resins (see table 1). Mechanical properties were determined at room temperature, 288 °C (for composites from diamines 4 and 6 only), and 316 °C. The mechanical properties at room temperature were closely comparable to those of PMR-15 laminates [16].

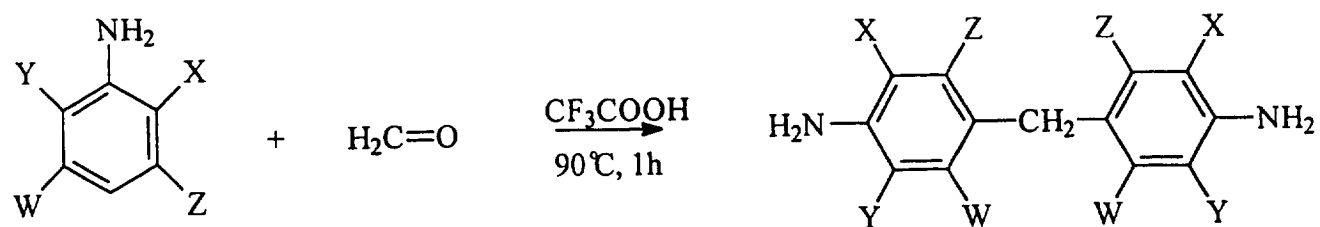
The interlaminar shear strength and flexural strength values at 316 °C are typical for laminates tested 30-50 °C below the T_g of the resin. The mechanical properties at 288 °C were slightly higher than the corresponding properties at 316 °C, and are also comparable to those of PMR-15 laminates at this temperature [16].

4. Conclusions

Based on the results of this study, several conclusions can be drawn. Six new diamines, containing fluoro or trifluoromethyl substituents, were synthesized and screened for mutagenicity by the Ames test. The preliminary test with two bacterial strains indicated that none of the diamines exhibited mutagenic activity by frame-shift mutations or base-pair substitutions. Replacement of 4,4'-methylenedianiline (MDA) with the new diamines in PMR-15 formulations did not have a significant effect on polymer processability (with the exception of the octafluoro-MDA). PMR-type polyimides prepared from the diamines exhibited comparable T_g values, but slightly higher isothermal weight loss than PMR-15. Graphite fiber-reinforced composites prepared from the four of the new diamines exhibited mechanical properties comparable to those of PMR-15 composites. These results indicate that the new derivatives of MDA, containing trifluoromethyl substituents, have a potential as non-mutagenic replacements for MDA in PMR-15 structural applications at elevated temperatures.

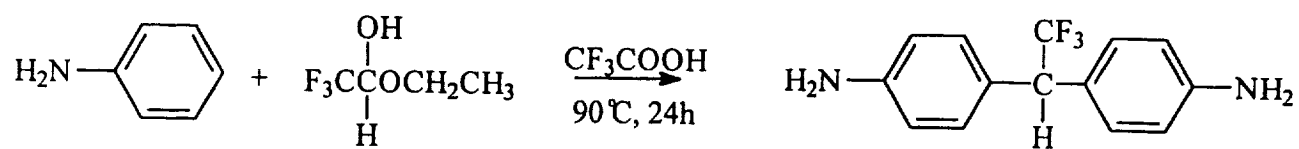
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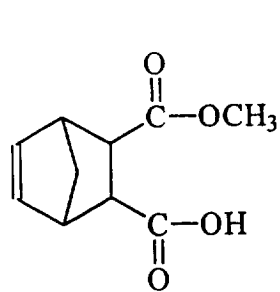


- 1 X,Y,Z,W=F
- 2 X,W=F; Y,Z=H
- 3 X,Y=F; Z,W=H
- 4 X=CF₃, Y=F, Z,W=H
- 5 X=CF₃, Y,Z,W=H

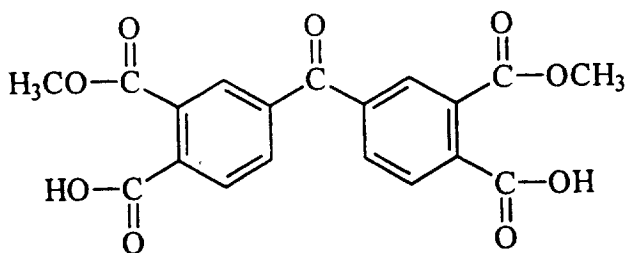
Scheme 1. Synthesis of diamines.



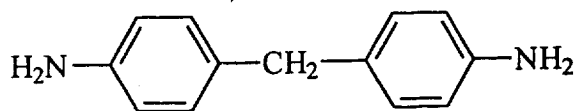
Scheme 2. Synthesis of 1,1,1-trifluoro-2,2-bis(4-aminophenyl)ethane.



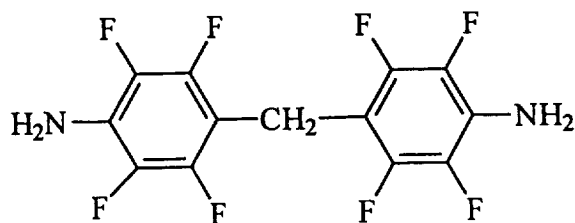
NE



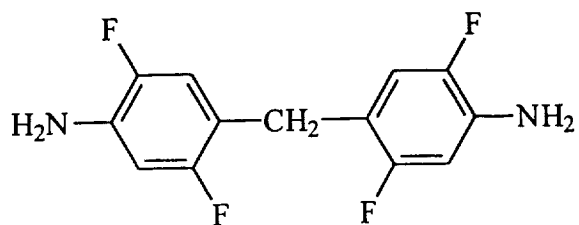
BTDE



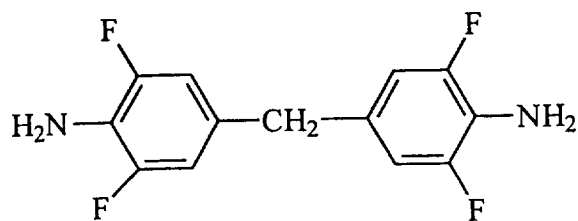
MDA



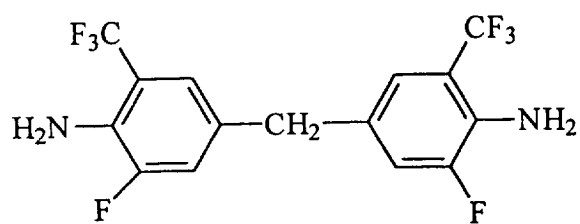
1



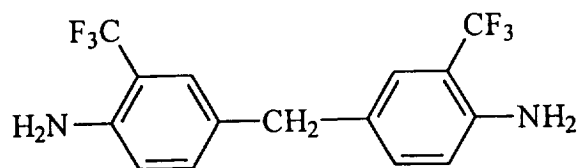
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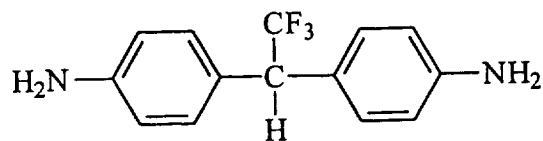
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4



5



6

Figure 1. Monomers used in addition polyimides.

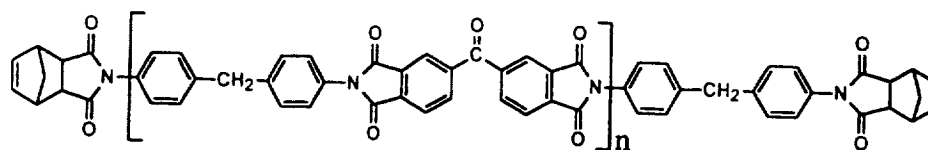


Figure 2. Idealized oligomer structure for PMR-15 polyimide ($n=2.087$).

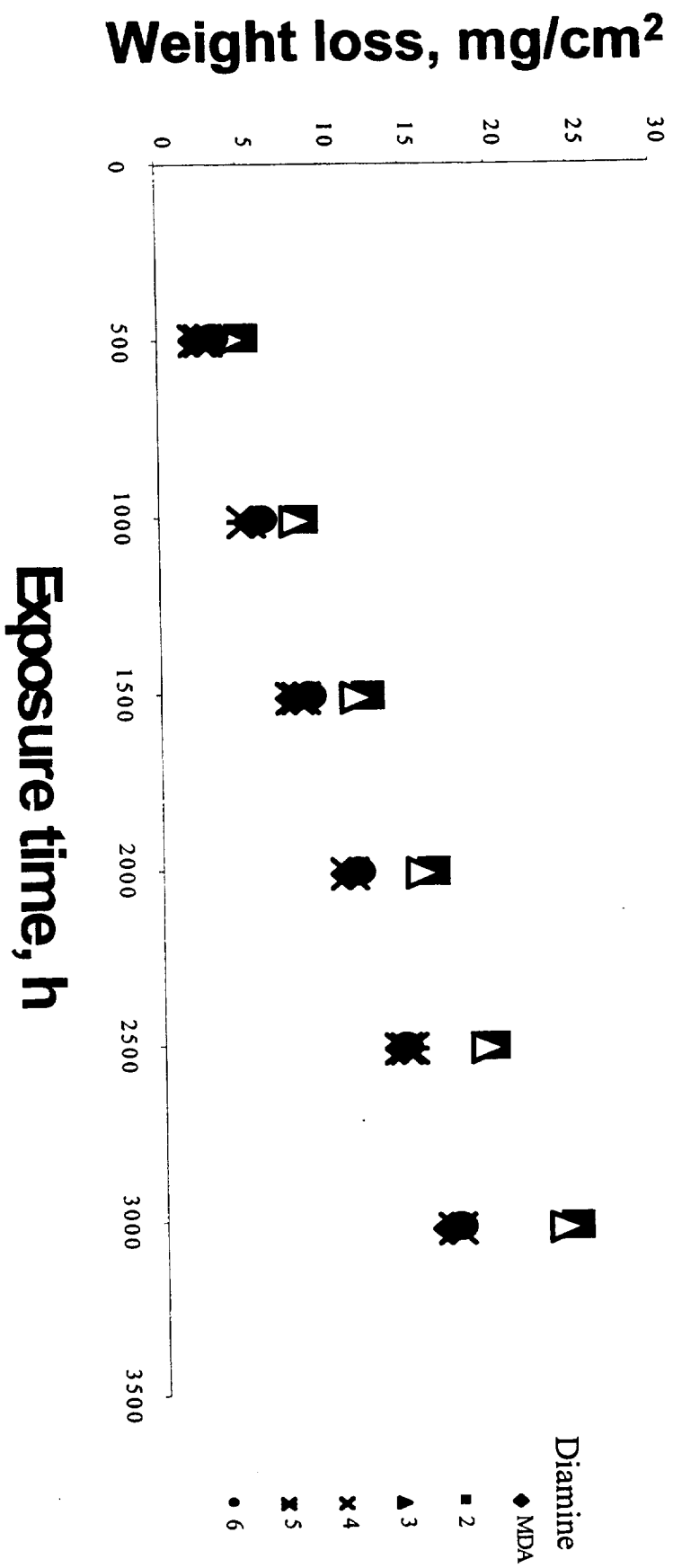


Figure 3. Weight loss of polyimides exposed in air at 288°C. Monomer stoichiometry: 2NE/2BTDE/3diamine.

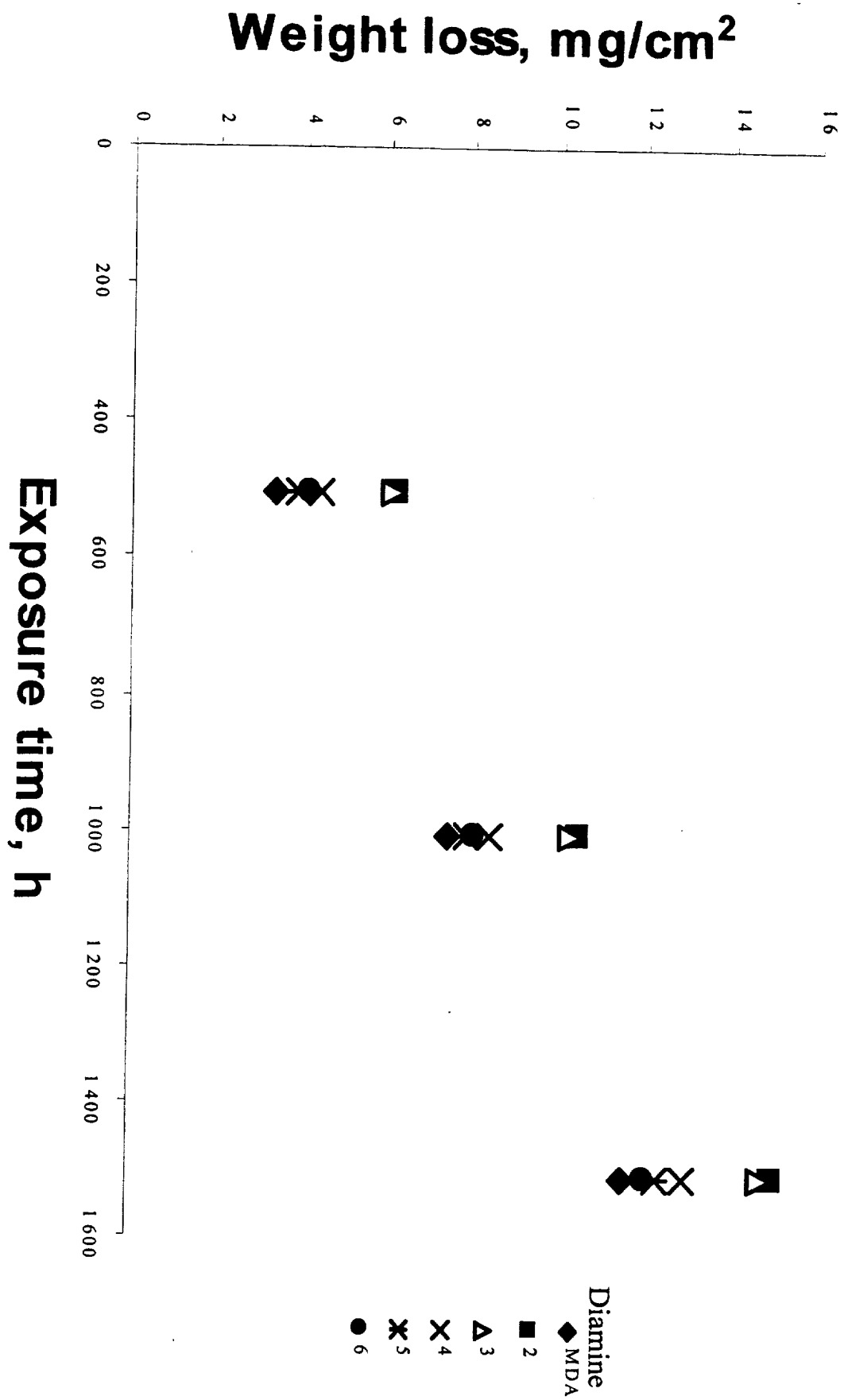


Figure 4. Weight loss of polyimides exposed in air at 316°C. Monomer stoichiometry: 2NE/2BTDE/3diamine.

Table 1. Properties of polyimide resins^a

Diamine	Density g/cm ²	T _g , °C	
		Before post cure	After post cure
MDA	1.30	299	339
2	1.32	265	327
3	1.32	267	334
4	1.37	268	342
5	1.38	280	352
6	1.34	264	329

a. Monomer stoichiometry: 2NE/2BTDE/3Diamine

Table 2. Weight loss of polyimide resins after exposure in air^a

Diamine	Resin weight loss, mg/cm ²	
	After 3024 h at 288°C	After 1512 h at 316°C
MDA	17.2	11.7
2	23.4	14.8
3	23.3	14.7
4	17.8	13.1
5	17.8	12.4
6	17.5	12.0

a. Monomer stoichiometry: 2NE/2BTDE/3diamine

Table 3. Properties of T650-35/polyimide composites^a

Diamine	Fiber volume %	T _g , °C ^b				Flexural strength, MPa			Flexural modulus, GPa		
			25°C	288°C	316°C	25°C	288°C	316°C	25°C	288°C	316°C
2	60.4	329	114	-	47.6	2050	-	862	137	-	114
3	59.8	335	121	-	49.0	2130	-	889	139	-	116
4	60.3	340	122	53.8	49.6	2030	1120	1020	137	119	117
6	59.2	332	118	53.1	48.3	2020	945	827	133	115	110

a. Monomer stoichiometry: 2NE/2BTDE/3diamine

b. Postcured 16 hours in air at 316°C

