

## Synthesis and Characterization of Soluble Fluorine-containing Polyimides

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**ABSTRACT** *Synthesis and properties of a series of soluble fluorine-containing aromatic polyimides are described. Substituents of trifluoromethyl groups are placed on the aromatic rings of para-linked aromatic ether diamine so as to force the polymer chain prepared thereof into a noncoplanar conformation which ensure the polymer to enhance solubility. Another consequence of intruding trifluoromethyl groups in polyimide is to confer low moisture absorption and low dielectric constant which are desire features of materials for microelectronics applications.*

### Introduction

Aromatic polyimides have been widely used in aerospace and electrical and electronic applications due to their outstanding thermal stability, mechanical strength at elevated temperature and electrical properties.<sup>1-4</sup> However, polyimide materials are usually difficult to fabricate owing to the insolubility in most organic solvents and infusibility. One successful approach to overcome these shortcomings of aromatic polyimides without sacrificing thermal and mechanical properties is to introduce flexible functional groups in polymer backbone.<sup>5-6</sup> In addition, low moisture uptakes of polyimides were also major concern for microelectronics and optical applications such as buffer coatings in plastics packaging and interlayer dielectrics in multilayer structures.<sup>7-9</sup> Hence, research on synthesis of soluble polyimides have been interested in recent years.<sup>10-13</sup>

Polyimide derived from ether-bridged aromatic diamines with trifluoromethyl groups was found to show great solubility in organic solvents with low moisture uptakes and excellent hydrolytic resistance. The present article describes the synthesis and characterization of a series of soluble, low moisture uptake polyimides derived from 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene and various aromatic tetracarboxylic dianhydrides.

### Experimental

Pyromellitic dianhydride (PMDA) was purified by sublimation in vacuum at 200-215 °C. 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride/acetic acid and dried in vacuum oven 120 °C for 8 hours and then 180 °C for 10 hours. 4,4'-oxydiphthalic anhydride (ODPA, Shanghai Chemspec., Corp.) was recrystallized from acetic anhydride before use. 4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) (99%, Hoechst Celanese Corp.) was recrystallized from acetic anhydride and dried at 100 °C for 12 hours and then 160 °C for 10 hours. 1-Methyl-2-pyrrolidinone (NMP) was vacuum distilled over P<sub>2</sub>O<sub>5</sub>. Commercially obtained N,N-dimethylformamide (DMF), N, N-dimethyl -

acetamide (DMAc) were purified by distillation under reduced pressure over calcium hydride before use.

**Monomer Synthesis** 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (Diamine 4) has been synthesized by a three step synthetic route as shown in Scheme 1. Thus, 2-chloro-1-trifluoromethylbenzene (1) was converted to 2-chloro-5-nitro-1-trifluoromethylbenzene (2) by nitration with a mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. The product, purified by vacuum distillation, was coupled with 1,4-hydroquinone in the presence of strong base to yield 1,4-bis(4-nitro-2-trifluoromethylphenoxy)benzene(3) at high yield. After purification by recrystallization from 2-methoxyethanol, the dinitro-compound was reduced with Fe/HCl in ethanol/water to afford 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene.

**Synthesis of Polyimide.** 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (Diamine 4) (2.8998g, 6.77mmol) was dissolved into 40 mL of NMP. To this was added OPA (2.1002g, 6.77mmol) and additional 3.8 mL of NMP. The solution was stirred at room temperature under argon for 24 hours to yield a viscous polyamic acid (PAA) solution. Polyamic acid was converted into polyimide using thermal imidization or chemical imidization methods. For thermal imidization method, polyamic acid solution was casted onto a clean glass plate and heated (80 °C/1h, 120 °C/1h, 180 °C/1 h, 250 °C/4 h, and 300 °C/3 h) to produce a fully imidized polyimide film. Chemical imidization was carried out by adding an equimolar mixture of acetic anhydride and pyridine into the above-mentioned polyamic acid solution with mechanical stirring at ambient temperature for 2 h, and the heating at 60 °C for 4 h. The polyimide solution was poured into methanol. The precipitate was collected by filtration, washed thoroughly with methanol and dried at 80 °C in vacuum to give **Polyimide1**. IR (KBr) 1782, 1725, 1610, 1489, 1436, 1376, 1319, 1239, 1053, 962, 907, 825, 743 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.06(d, 2H), 7.85(s, 2H), 7.66(d, 2H), 7.63(d, 2H), 7.58(s, 2H), 7.25(s, 4H), 7.18(d, 2H) ppm; Anal. Calcd for C<sub>36</sub>H<sub>16</sub>F<sub>6</sub>N<sub>2</sub>O<sub>7</sub>: C, 61.53; H, 2.28; N, 3.99. Found: C, 61.22; H, 2.64; N, 4.05.

**Polyimide 2**(6FDA/diamine 4) was synthesized from polymerization of 1 equiv of diamine 4 and 1 equiv of 6FDA at 10% solid content in NMP; **Polyimide 3** (BTDA/diamine 4) and **Polyimide 4** (PMDA/diamine 4) were prepared in the same method .

## Results and Discussion:

**Monomer Synthesis** Diamine 4 has been synthesized by a three step synthetic route. 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene was obtained at high yield. The structures of the compound was confirmed by elemental analysis, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS. The elemental analysis values of the dinitro and diamine compounds correspond to the calculated values of their structures. The trace of sodium and chloride and iron, determined by atom absorption spectrometer, were 0.45 ppm for Na<sup>+</sup> , 0.052 ppm for Cl<sup>-</sup> and 0.84 ppm for Fe<sup>++</sup>

**Polyimide Synthesis** Diamine 4 was polymerized with four different dianhydrides, OPDA, 6FDA, BTDA, and PMDA to produce polyimides: Polyimide 1, Polyimide 2, Polyimide 3 and Polyimide 4 (Scheme 2). In general , polyimide can be synthesized from condensation of a diamine and a dianhydride through either a two-

step condensation polymerization, that is, the formation of a polyamic acid followed by a thermal or chemical imidization to give polyimide, or a direct one-step solution polycondensation at high temperature. Both approaches were employed to synthesize polyimides in this study. In order to obtain polyimide with high molecular weights, the diamine should be purified carefully. Diamine 4 was purified by twice recrystallization from anhydrous alcohol and dried at 100 °C in oven in vacuum for 24 h. For two-step approach, polyamic acid was produced by the polymerization of diamine 4 with dianhydride in NMP with 10% (w/w) solid concentrations at ambient temperature for 24 h, then the formed polyamic acid was thermally imidized to polyimide by a schedule (80 °C/1h, 120 °C /1h, 180 °C /1 h, 250 °C /4 h, and 300 °C /1h), or chemically imidized by adding an equimolar mixture of acetic anhydride and pyridine into the polyamic acid solution at ambient temperature for 2 h followed by heating at 60 °C for 4 h. For one-step approach, polycondensation of diamine 4 and dianhydride was carried out in the presence of m-cresol and isoquinone at 160 °C for 4 h. Figure 1 was the <sup>1</sup>H NMR and <sup>13</sup>C NMR of Polyimide 1 in DMSO-*d*<sub>6</sub>. The assignments of the peaks were in good agreement with the proposed polyimide structure.

**Solution Properties** The intrinsic viscosities of the polyamic acids of Polyimide 1-4 ranged from 0.73-1.50 dL/g in NMP at 25 °C (Table 1). Polyimide derived from diamine 4 and ODPDA (Polyimide 1) exhibited the highest value in inherent viscosity while polyimide prepared with diamine 4 and BTDA (Polyimide 3) showed the lowest value. The polyimides prepared from the chemical imidization method or the direct one-step polymerization pathway showed great solubilities in NMP and DMAc. Polyimide 1 and Polyimide 2 prepared by chemical imidization of the polyamic acid showed excellent solubility in NMP. After the complete of chemical imidization, the polyimides can be isolated and purified by precipitation in methanol or ethanol, the solid polymers can be re-dissolved in NMP to form a homogeneous solution with solid content as high as 15-20%. The polyimide solution are very stable in room temperature, in which no precipitation, gelation or phase separation occurred in a storing period of more than 2 months. Elemental analysis results of the Polyimide 1 and polyimide 2 are consistent to the calculated data for the proposed polymer structures.

**Thermal Properties.** The thermal properties of these polyimides are investigated by means of TGA and DSC. TGA curves for these polymers, typical of which are shown in Figure 2, indicated that all of the polyimides did not lose weight until the temperature reaches to 450 °C in air. The decomposition temperature, 5% weight loss of decomposition temperature and 10% weight loss of decomposition temperature are summarized in Table 2. In air, the decomposition temperature was measured at 555 °C, and the 10% weight loss temperatures are 530-559 °C, which increased to 571-623 °C in nitrogen. The glass transition temperatures of the polymers ranged from 229-292 °C determined by DSC. Polyimide 2 derived from 6FDA and diamine 4 showed a lowest T<sub>g</sub> of 229 °C, while Polyimide 4 prepared from PMDA and diamine 4 give a higher T<sub>g</sub> of 292 °C. Clearly, the differences in T<sub>g</sub>s was attributed to the rigidity of the polymer chains. Figure 4 showed the thermo-oxidative stabilities of the polyimides.

The weight losses of the samples were increased linearly with the isothermal aging time at 371 °C in air flow. The thermo-oxidative stabilities of the polyimides were decreased in following order: Polyimide 1 > Polyimide 3 > Polyimide 2 > Polyimide 4. After isothermal aging at 371 °C for 100 hours, Polyimide 1 and Polyimide 3 loss less than 15-16 % of original weight, indicating that the polyimides possess great thermo-oxidative stabilities at high temperatures.

**Mechanical and Electrical Properties.** Table 3 showed the mechanical and electrical properties of the polyimides. Thin films ( 6.35 x 127 mm) were tested for tensile properties in Instron instrument at 25 °C. The films had tensile strength of 83-137 M Pa, elongation at break of 10-27%, and tensile modulus of 1.6-2.3 G Pa. The electric properties of polyimide films were also measured. The surface resistance and volume resistance were at a level of  $10^{14-15} \Omega$  and  $10^{15-16} \Omega/\text{cm}$ , respectively. The dielectric constants were at 2.8-2.9 at 1 kHz and the dissipation factor was  $3-5 \times 10^{-3}$ .

**Moisture uptakes and Hydrolytic resistance.** The polyimides exhibited low moisture uptakes. Two test methods were employed in this study. Method 1 is the immersion of the films in water at  $23 \pm 0.5$  °C for 24 h, then weighed immediately. Method 2 is boiling the films in water at 100 °C for 30 min, then weighed. It can be seen that the moisture uptake of polyimides was around 0.4-0.5 % except for Polyimide 3 which showed 0.71-0.82 % of moisture absorption. In order to ascertain the effect of high temperature hygrothermal environmental exposure upon the chemical and thermal properties, polyimide films are immersed in water at 120 °C and 2 atmosphere for 100 hours and was then investigated by SEM, DSC, TGA and FT-IR, etc. After thermal and accelerated hydrolytic exposures, the film surface did not loss its gloss and became degraded. The films did not show any brittle and are still flexible as fresh samples. SEM observation showed that there was no surface cracks, voids or other defects on surface of the aged specimens. The glass transition temperature did not shift up or down determined by DSC. The films showed no obvious change in TGA and IR spectrum compared with the unaged samples, indicating a good hydrolytic resistant to water vapors at high pressure and high temperature. This feature is very important for the microelectronics applications such as passivation or protection film, buffer coatings and interlayer dielectrics in MCM-D.

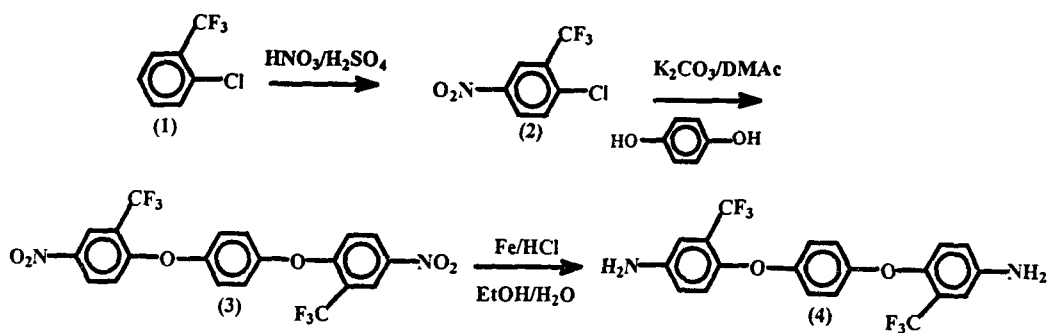
## Conclusion.

1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene has been synthesized from 1-trifluoromethyl-2-chlorobenzene and polymerized with dianhydrides to afford polyimides with high molecular weights. The introduction of trifluoromethyl groups in the ether-bridged diamine component of polyimides result in dramatic changes in their properties, especially in the improvement of solubilities and lowering of the moisture uptakes. The polyimides showed high thermal and thermo-oxidative stabilities at high temperatures, balanced mechanical properties, good electrical properties and excellent hygrothermal stabilities.

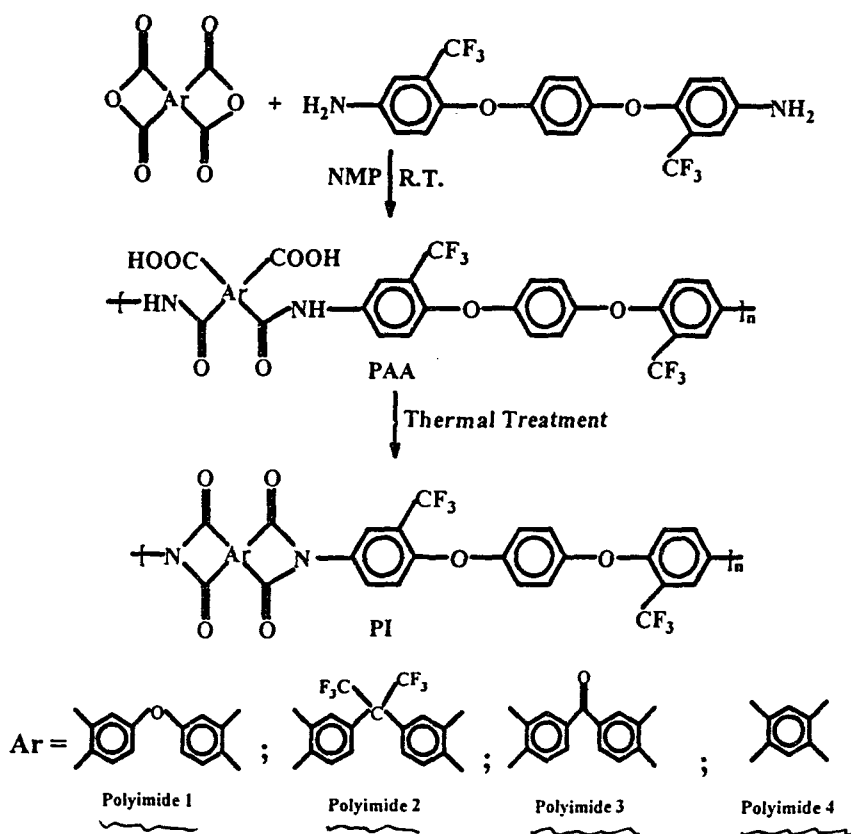
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Scheme 1. Synthesis of Monomer Diamine 4



Scheme 2. Synthesis of Polyimides Derived from Diamine 4 and Dianhydrides

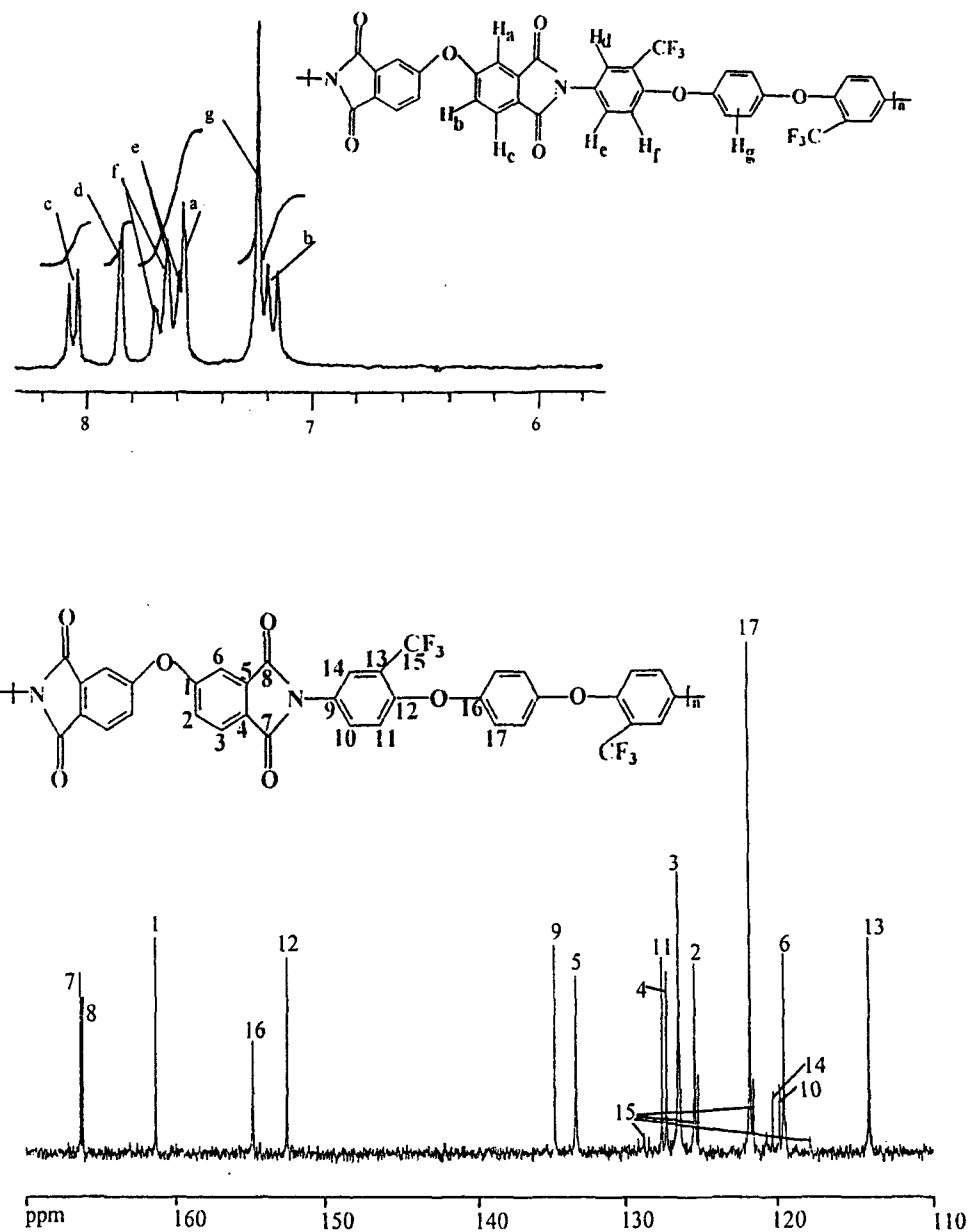


Figure 1.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  Spectra of Polyimide 1  
Derived from ODPa and Diamine 4

Table 1 Solubility of Polyimide

| Solvent    | Polyimide1 |       | Polyimide2 |       | Polyimide3 |       | Polyimide4 |       |
|------------|------------|-------|------------|-------|------------|-------|------------|-------|
|            | Cured at   |       | Cured at   |       | Cured at   |       | Cured at   |       |
|            | 250°C      | 300°C | 250°C      | 300°C | 250°C      | 300°C | 250°C      | 300°C |
| NMP        | ○          | ○     | ○          | ○     | ○          | ○     | ○          | ○     |
| DMAc       | ○          | ○     | ○          | ○     | ○          | ○     | ○          | ○     |
| DMF        | ○          | ○     | ○          | ○     | ○          | △     | ○          | △     |
| m-cresol   | ○          | △     | ○          | △     | △          | ×     | △          | ×     |
| THF        | △          | △     | △          | △     | △          | ×     | △          | ×     |
| Chloroform | △          | ×     | △          | ×     | △          | ×     | △          | ×     |
| Acetone    | △          | △     | △          | △     | ×          | ×     | △          | ×     |
| MeOH       | ×          | ×     | ×          | ×     | ×          | ×     | ×          | ×     |

Note: ○-----soluble  
 △-----partially soluble or swells  
 ×-----insoluble

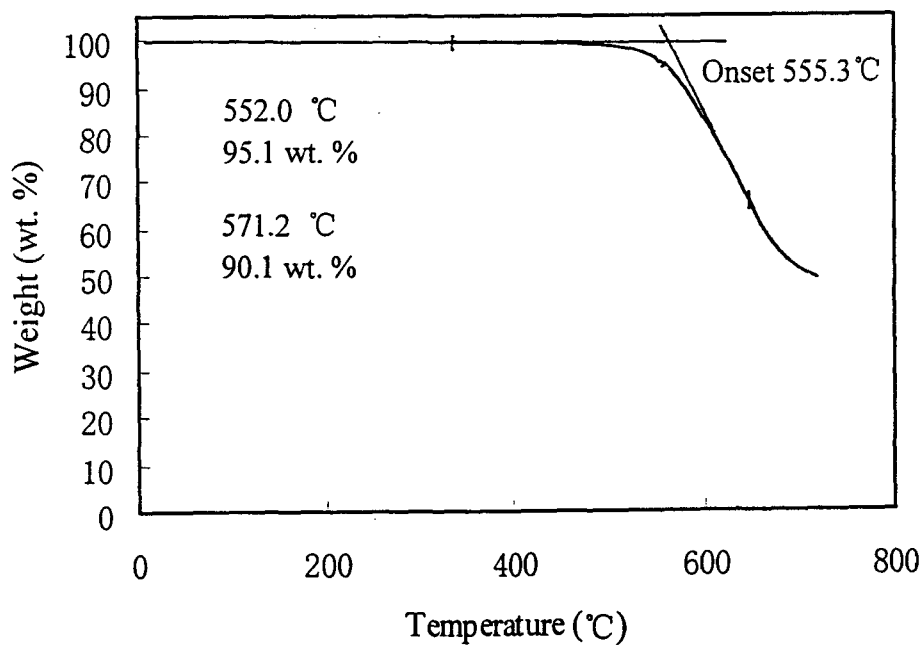


Figure 2. TGA Curve of Polyimide 1 Derived from ODPA and Diamine 4 in Air



Table 2 Thermal Properties of Polyimides

|   | Polyimide1 |                   | Polyimide2 |                   | Polyimide3 |                   | Polyimide4 |                   |
|---|------------|-------------------|------------|-------------------|------------|-------------------|------------|-------------------|
|   | in air     | in N <sub>2</sub> | in air     | in N <sub>2</sub> | in air     | in N <sub>2</sub> | in air     | in N <sub>2</sub> |
| Decomposition Temperature (°C)          | 520        | 555               | 525        | 607               | 540        | 609               | 548        | 599               |
| Temperature at 5% of Weight loss (°C)   | 491        | 552               | 485        | 599               | 477        | 603               | 435        | 541               |
| Temperature at 10% of weight Loss (°C)  | 530        | 571               | 539        | 623               | 552        | 628               | 559        | 598               |
| Glass Transition Temperature (DSC) (°C) | 254.6      |                   | 229.2      |                   | 243.8      |                   | 292.4      |                   |

Table 3 Mechanical and Electrical Properties of Polyimides

|                             | Polyimide1             | Polyimide2             | Polyimide3             | Polyimide4             |
|-----------------------------|------------------------|------------------------|------------------------|------------------------|
| Elongation at Break (%)     | 10                     | 27                     | 12                     | 22                     |
| Tensile Strength (M Pa)     | 92.1                   | 127.4                  | 137.2                  | 83.6                   |
| Young's Modulus (G Pa)      | 1.76                   | 1.97                   | 2.31                   | 1.61                   |
| Volume Resistance, (Ω · cm) | 4.2 x 10 <sup>15</sup> | 1.2 x 10 <sup>15</sup> | 5.7 x 10 <sup>15</sup> | 2.4 x 10 <sup>15</sup> |
| Surface Resistance (Ω)      | 5.6 x 10 <sup>14</sup> | 5.6 x 10 <sup>15</sup> | 5.6 x 10 <sup>14</sup> | 1.9 x 10 <sup>15</sup> |