An Investigation into the Migration of Segments in Crosslinked Fluorinated Polyimide Adhesive

Zhongyuan Huang a, Renguo Lu a, Ting Huang a, Hongyan Wang a & Tongsheng Li a

a Department of Macromolecular Science, State Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai, China

Accepted author version posted online: 22 Jan 2013. Published online: 29 Mar 2013.

To cite this article: Zhongyuan Huang, Renguo Lu, Ting Huang, Hongyan Wang & Tongsheng Li (2013): An Investigation into the Migration of Segments in Crosslinked Fluorinated Polyimide Adhesive, Journal of Macromolecular Science, Part B: Physics, 52:7, 937-949

To link to this article: http://dx.doi.org/10.1080/00222348.2013.764792

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.
An Investigation into the Migration of Segments in Crosslinked Fluorinated Polyimide Adhesive

ZHONGYUAN HUANG, RENGUO LU, TING HUANG, HONGYAN WANG, AND TONGSHENG LI

Department of Macromolecular Science, State Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai China

Crosslinked fluorinated polyimides (CFPI) were successfully synthesized to study and explore the effect of cross-linkage on the migration of fluorinated segments and on the adhesion strength. Characterization by dynamic thermomechanical analysis (DMA) and thermo gravimetric analysis (TGA) confirmed good thermal properties of CFPI. X-ray photoelectron spectroscopy (XPS) results showed that the ratio of fluorinated component (6FDA-ODA) concentration of the surface to the bulk decreased with the crosslink density. The water contact angle of CFPI was lower than that of non-crosslinked fluorinated polyimide, indicating that the migration of fluorinated groups to the surface was reduced by the presence of cross-linkage. Therefore, CFPI, with no fluorine segregation on the surface, exhibited excellent wetting of adherent surfaces and adhesion strength, which was proved by lap shear strength (LSS) measurements and scanning electron microscopy.

Keywords crosslink fluorinated polyimide, failure mode, fluorine segregation, lap shear strength, phenylethynyl termination agent.

Introduction

Fluorinated polyimide has been attracting considerable attention for many applications because of its excellent thermal stability and low dielectric constant and moisture absorption[1,2]. The fluorinated group, which has a strong electron-withdrawing ability, displays the characteristic of low surface energy. Many studies[3–6] have shown that the polymer component having the lower surface energy, such as fluorinated group segments, will migrate to a material’s surface, and as a result, minimize the surface energy. Thus, the lower surface energy component in polyimide will decrease the wetting of the adherent on the surfaces, which leads to poor adhesion.[7]

However, recent studies[8–13] have claimed that new types of fluorinated polyimides exhibited good adhesion properties. So, it is of significant interest to investigate the relationship between chemical structure of fluorinated polyimides and the adhesion properties because the surface chemical composition of a fluorinated polymer can be determined by
the changes in the crystallinity and morphology,[14,15] the molecular interactions[16–18] and the molecular weights of the polymer components.[16,19]

In the past few years, many studies have focused on phenylethynyl terminated polyimides.[11–13,20–24] The phenylethynyl group, typically placed at the ends of imide oligomers, were cured to final products with excellent properties, such as a broad processing window, good thermal oxidative stability and excellent mechanical properties. Harris et al.[11] and Hergenrother et al.[22] reported that the molecular weight of phenylethynyl terminated oligomer was a critical factor in lap shear tests of the cured polymer. Sun et al.[13] investigated the adhesion strength of phenylethynyl terminated oligoimides derived from 3,3’,4,4’-diphenylsulfoneteracarboxylic dianhydride (DSDA) at a temperature above the \( T_g \) and found that the strength maintained at a high level due to the formation of strong interchain bonds. Hence, with controllable molecular weight and strong interchain entanglements, phenylethynyl terminated polyimide was an ideal candidate for this study.

The objective of this research was to study and explore the effect of cross-linkage on the migration of fluorinated segments and on the adhesion strength. The research focused on a high thermal stability, crosslinked, fluorinated polyimide adhesive (CFPI), derived from 3,3’,4,4’-biphenyltetracarboxylic dianhydride (BPDA), 4,4’-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA), 4,4’-Oxydianiline (4,4’-ODA), and a phenylethynyl termination agent, 4-phenylethynylphthalic anhydride (4-PEPA), with CFPI calculated molecular weights of 2000, 5000, and 8000 \( \text{g mol}^{-1} \), respectively. For comparison, non-crosslinked fluorinated polyimide adhesives (FPI) with various 6FDA contents were also synthesized. X-ray photoelectron spectroscopy (XPS), which has gained importance in recent years in the characterization of polymer surfaces, was used to investigate the surface chemical composition of CFPI.[17,18] In addition, the adhesion properties of both series was investigated by lap shear strength (LSS) tests and scanning electron microscopy.

**Experimental**

**Materials**

3,3’,4,4’-biphenyltetracarboxylic dianhydride (BPDA) was obtained from Shanghai Research Institute of Synthetic Resins (China). 4,4’-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) was purchased from Hoechst (China). 4,4’-Oxydianiline (4,4’-ODA) and N,N’-dimethylacetamide (DMAc) were supplied by Sinopharm Group Chemical Reagent Co., Ltd. (China). 4-phenylethynylphthalic anhydride (4-PEPA) was provided by Changzhou Sunlight Pharmaceutical Co., Ltd. (China). 4,4’-ODA was recrystallized from ethanol/water (1:1) prior to use. Other reagents and materials were used directly as received.

**Sample Preparation**

Crosslinkable fluorinated polyimide (CFPIs) was obtained by the conventional amide acid route. The initial reaction is shown in Scheme 1. Poly (amic acid) (PAA) solutions were prepared by initially dissolving the diamines (4,4’-ODA) in DMAc in a nitrogen atmosphere. A mixture of BPDA, 6FDA and 4-PEPA slurry was added and the reaction was carried out at room temperature for 12 h. Then, the PAA solutions of FPI were cast into films (thickness 0.05 mm) on glass plates followed by a heat-induced imidization and cure procedure at 100,
Effect of Cross-Linkage on Fluorine Segregation

Scheme 1. Synthesis process of FPI and CFPI.

180, 250, and 350°C for 1 h, each successively. The monomer concentrations are shown in Table 1.

Non-crosslinked fluorinated polyimides (FPIs) with monomers 6FDA, BPDA, and 4,4'-ODA were synthesized using a similar procedure to the CFPIs as mentioned above.

Table 1
Molar ratios and calculated $M_n$ of CFPI

<table>
<thead>
<tr>
<th>Sample</th>
<th>6FDA</th>
<th>BPDA</th>
<th>4-PEPA</th>
<th>4,4'-ODA</th>
<th>Calculated (Mn)</th>
<th>$[\eta]$ (dL g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFPI-1</td>
<td>1</td>
<td>1</td>
<td>0.32</td>
<td>2.16</td>
<td>8000</td>
<td>0.36</td>
</tr>
<tr>
<td>CFPI-2</td>
<td>1</td>
<td>1</td>
<td>0.66</td>
<td>2.33</td>
<td>5000</td>
<td>0.27</td>
</tr>
<tr>
<td>CFPI-3</td>
<td>1</td>
<td>1</td>
<td>1.34</td>
<td>2.67</td>
<td>2000</td>
<td>0.16</td>
</tr>
</tbody>
</table>
The samples with various 6FDA/BPDA molar ratios of 0:1, 1:3, 1:1, 3:1, and 1:0 are designated as FPI-1, FPI-2, FPI-3, FPI-4, and FPI-5, respectively.

**Characterization**

FTIR spectra of thin polyimide films were recorded on a Fourier transform infrared spectroscope, Nexus-470 (Thermo Nicolet Co. Ltd., USA).

Dynamic thermomechanical analysis measurements were performed by a DMA-242 analyzer (Netzsch Co. Ltd., Germany). The films thickness was 0.05 mm and the tension-mode deformation was used at a frequency of 1 Hz, a dynamic force of 4 N and a heating rate of 5°C min⁻¹ in nitrogen. The tangents of loss angle (tan δ) were obtained as a function of scanning temperature.

Thermal gravimetric analysis was investigated by using a TGA Pyris 1 (Perkin Elmer Co. Ltd., USA) in a nitrogen atmosphere with a heating rate of 20°C min⁻¹.

Contact angles were measured with a Contact Angles and Surface Free Energies Analyzer OCA-15 (Dataphysics Co. Ltd., Germany) at room temperature. The volume of the sessile drops was approximately 2 μl.

XPS spectra were obtained on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer Co. Ltd., USA) with Al Kα X-ray source. A detection angle of 54° was used. The pass energy was fixed at 23.5 eV to ensure sufficient resolution and sensitivity.

The morphology of the failure surfaces of the LSS samples, followed coating with Au, were examined with SEM, Tescan 5166 MM (Tescan Co. Ltd., Czech Republic).

**Adhesive Specimens and Measurement**

Stainless steel plates with the size of 100 mm × 25 mm × 1.6 mm were used as adherents. The bonded area was 25 × 12.7 mm². PAA solutions with a 30 wt.% concentration were directly coated on the adherent surface. These adherents were then placed in an oven and subjected to a staged-drying to a final temperature of 180°C. Standard LSS specimens were pressed at a pressure of 2 MPa and cured at 350°C for 2 h in an oven.

Lap shear strengths were determined according to ASTM D1002. The measurement was recorded on a universal testing machine (CMT4104, Shenzhen Sans Testing Machine Ltd., China) at a crosshead speed of 2 mm/min.

**Results and Discussion**

**Characterization**

The FTIR spectra of the FPIs are illustrated in Fig. 1; the appearance of some characteristic absorption peaks at 1780, 1720, and 1379 cm⁻¹, attributed to C=O stretching vibration of carboxyl groups and C–N–C stretching vibration of imide rings, confirmed that the imidization process had been finished. With the incorporation of 6FDA, the peak at 1240 cm⁻¹ strengthens and two new peaks at 1192 and 1209 cm⁻¹, assigned to C-F stretching vibrations of trifluoromethyl group, were observed, which indicates the successful synthesis of fluorinated polyimide. The PAA of CFPI exhibits the characteristic absorption around 2210 cm⁻¹ as shown in Fig. 2, which is related to the stretching vibrations of the ethynyl group. The result indicates the successful incorporation of 4-PEPA. In addition, the peak at 1610 cm⁻¹ shows the presence of the amide group of PAA. After thermal imidization
process those peaks disappeared, which confirms the CFPI had been completely imidized and cured.

The thermal data evaluated by DMA and TGA are listed in Table 2. The $T_g$ of CFPI shows that polyimides with higher molecular weight had a higher $T_g$. It is known that the terminal acetylenic groups undergo reactions, including cyclotrimORIZATION, crosslinking, and addition, simultaneously during the curing process.[25] The influence of a carbon chain on rigidity is smaller than that of 5 or 6-membered heteroaromatic imide rings in polyimide. As the crosslink density increased, the dominant structural unit of the polymer

![Figure 1. FTIR spectra of FPIs (Color figure available online).](image)

![Figure 2. FTIR spectra of poly (amic acid) and polyimide of CFPI-2.](image)
Table 2

Thermal properties of CFPI

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g , ^\circ\text{C}$</th>
<th>$T_{5\text{d}} , ^\circ\text{C}$</th>
<th>$T_{10\text{d}} , ^\circ\text{C}$</th>
<th>C% residue $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPI-3</td>
<td>298</td>
<td>563</td>
<td>589</td>
<td>61.4</td>
</tr>
<tr>
<td>CFPI-1</td>
<td>299</td>
<td>562</td>
<td>590</td>
<td>57.7</td>
</tr>
<tr>
<td>CFPI-2</td>
<td>291</td>
<td>559</td>
<td>589</td>
<td>62.0</td>
</tr>
<tr>
<td>CFPI-3</td>
<td>285</td>
<td>556</td>
<td>589</td>
<td>64.7</td>
</tr>
</tbody>
</table>

$^a$Determined by DMA at a frequency of 1 Hz and a heating rate of 5 $^\circ\text{C} \text{ min}^{-1}$.

$^b$The temperatures for 5 and 10 wt.% of weight loss was determined by TGA at a heating rate of 20 $^\circ\text{C} \text{ min}^{-1}$.

$^c$The residual weight retention was determined by TGA at 800 $^\circ\text{C}$.

Chains changed from imide groups to long –C=C–C=C– chains, thus resulting in the slight reduction in $T_g$.

According to Table 2, the temperatures of $T_g$ and 5 and 10 wt.% weight loss of the CFPIs remained in the same range, 285–299 $^\circ\text{C}$, 556–563 $^\circ\text{C}$, and 589–590 $^\circ\text{C}$, respectively, as that of FPI-3, exhibiting excellent thermal properties. Figure 3 illustrates the thermal degradation rate of FPI-3 and the CFPIs. As the crosslink density increased, the curves showed the same pattern and no extra peaks were observed. The results suggested the crosslinked structure maintained high thermal stability during thermal degradation. The whole degradation process may depend on two stages, trifluoromethyl groups degrade at 580 $^\circ\text{C}$ [26] and ether groups degrade at 650 $^\circ\text{C}$.[27]

Surface Properties

The relationship between the static water contact angles on the surface of the polyimide films and the (6FDA-ODA) content is plotted in Fig. 4. The contact angle was sensitive to the (6FDA-ODA) content in the polyimide. The curve, related to the low cohesive
and surface energies of the trifluoromethyl groups, confirms the hydrophobic nature of the (6FDA-ODA) group as mentioned in the literature.[28] In the case of CFPI, the water contact angles showed a similar tendency with the (6FDA–ODA) content as the FPIs. However, comparing the data of FPI and CFPI, an unexpected result was noted; all the points of the CFPIs were below the FPI curve, showing that the surfaces of the CFPIs were more hydrophilic.

The XPS results of the polyimide films showed the presence of four elements: carbon, oxygen, nitrogen, and fluorine. No signal from other contaminants was detected. The C1s spectrum of CFPI-2 is illustrated in Fig. 5. The C1s spectrum was fitted with 5 component peaks centered at 285.0 eV (carbon of phenyl rings), 287.6 eV (C–O bonds), 289.0 eV (O–C–N bonds), 290.5 eV (–C(CF3)2 bonds), and 292.5 eV (–CF3 bonds).[29,30]
Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molecular weight</th>
<th>Φ_{surf} (6FDA–ODA)</th>
<th>Φ_{bulk} (6FDA–ODA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPI-3</td>
<td>–</td>
<td>50.0</td>
<td>57.3</td>
</tr>
<tr>
<td>CFPI-1</td>
<td>8000</td>
<td>46.3</td>
<td>48.7</td>
</tr>
<tr>
<td>CFPI-2</td>
<td>5000</td>
<td>42.9</td>
<td>42.7</td>
</tr>
<tr>
<td>CFPI-3</td>
<td>2000</td>
<td>37.4</td>
<td>35.6</td>
</tr>
</tbody>
</table>

The surface and bulk compositions of the FPIs and CFPIs were determined using the following equations:

\[
\Phi_{surf} (6FDA–ODA) = R_{F/N}/3
\]

(1)

\[
\Phi_{bulk} (6FDA–ODA) = m_{6FDA}/m_{4,4'}-ODA
\]

(2)

In those equations, \( \Phi_{surf} (6FDA–ODA) \) and \( \Phi_{bulk} (6FDA–ODA) \) represent the surface and bulk composition of (6FDA–ODA), \( R_{F/N} \) is the atomic ratio of fluorine to nitrogen calculated from the XPS data and \( m_{6FDA} \) and \( m_{4,4'}-ODA \) represent the moles of 6FDA and 4,4’-ODA as used in the polymer preparation. Since the \( Mn \) from the measured intrinsic viscosity\(^{22} \) was equal to the predicted value. It was assumed there was no loss of 6FDA to the surface.

Table 3 compares the surface and bulk compositions of FPI-3 and CFPIs. The surface (6FDA–ODA) concentration of FPI-3 was higher than the bulk, showing fluorine segregation to the polyimide surface, which is due to the migration to the surface of low free energy (6FDA-ODA) mers, as expected. However, as the crosslink density in CFPI was increased, the surface chemical composition became more or less identical to the bulk. It is of interest to find that the surface composition (6FDA–ODA) of CFPI-2, 3 do not become larger than the bulk. Figure 6 shows the relationship between the degree of surface segregation and crosslink density. The tendency clearly reveals that, as the crosslink density became higher, leading to a serious interchain entanglement, the migration of fluorinated groups

![Figure 6](https://example.com/image)

**Figure 6.** Ratio of (6FDA-ODA) concentrations of the surface to the bulk.
(6FDA–ODA) to the surface was severely restricted. It means that the possible decrease in surface energy induced by the migration of the fluorinated groups was offset by the presence of cross-linkages, thus leading to the decrease in water contact angle.\textsuperscript{[17,31]}

**Adhesion Properties**

The adhesive strength of the FPI and CFPI series, evaluated by the LSS test are illustrated in Fig. 7. The LSS of FPI-2 at room temperature was measured to be 21.7 MPa, as shown in Fig. 7(a). The LSS gradually decreased and finally reached a value of 15.6 MPa when the (6FDA–ODA) content was increased to 100%. However, compared with FPI-3, the LSSs of CFPI-1 and CFPI-2 with the same ratio of 6FDA to BPDA, as presented in Fig. 7(b), were enhanced by 19.1% and 25.4%, respectively. This result indicates that appropriate crosslinks will enhance the adhesive strength of fluorinated polyimides. It is suggested that

![Figure 7](image-url)

**Figure 7.** Lap shear strength of (a) FPIs and (b) CFPIs.
the CFPI-3 sample had a low LSS. Since, having a low initial Mn before fabrication, a thinner adherent bond layer was produced.

The fracture surfaces of the adhesive joints prepared with FPIs were analyzed using SEM; the micrographs are shown in Fig. 8. The surface of the joint prepared with FPI-1 shows a uniformly distributed pattern, indicating good wetting and spreading of the adhesive. After the incorporation of 6FDA, poor adhesion of the adhesive layer to the base can be observed, showing that the adhesive joints underwent a “cohesive/adhesive” failure. As mentioned above, the fluorinated groups of the FPIs migrated to the surfaces and reduced the surface energy, which led to a decrease in wetting of the adhesive on the surfaces, thus resulting in a reduction in LSS.

Figure 9 illustrates the SEM micrographs of fracture surfaces of the adhesive joints prepared with CFPIs. It is clear that all CFPI resulted in a rough and deformed fracture surface, indicating the failure mode was “cohesive”. Note that this kind of rough fractured surface was not present on the surfaces of the FPIs. As the XPS results showed, no obvious fluorine segregation of CFPI was observed. The increasing cross-linkage restricted the migration of (6FDA–ODA) segments. This result led to an improvement of the wetting of the adherent surfaces and resulted in a better metal-adhesive interface bonding strength than the non-crosslinked fluorinated polyimide.
The above results show the incorporation of phenylethyl termination agents into fluorinated polyimide improved the adhesion properties. The failure mode moves toward an “adhesive” mode with the increasing of fluorinated group content and back to a “cohesive” mode by the presence of cross-linkages.

Conclusions

In this study CFPI with excellent thermal stability were successfully synthesized. The CFPI showed low water contact angles induced by the increasing of the crosslink density which prevented migration of fluorinated segments to the surface. XPS data confirmed that the crosslinks restricted the migration of (6FDA–ODA) from the bulk to the surface. Therefore, the ratio of (6FDA–ODA) concentration of the surface to the bulk decreased obviously with increasing crosslinking, leading to an enhancement in wetting of the adherent surfaces and an improvement in adhesion strength.

References


