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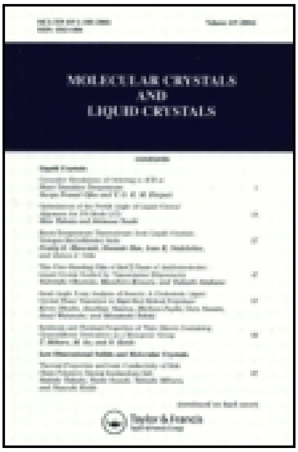

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Syntheses and Surface Characterization of Fluorinated Poly(imidesiloxane) Copolymers

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Syntheses and Surface Characterization of Fluorinated Poly(imidesiloxane) Copolymers

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The surface structure of fluorinated poly(imidesiloxane)s (FSIM) with different segment lengths and contents of siloxane was investigated by ATR-FTIR and X-ray photoelectron spectroscopy. Although fluorine and siloxane compounds have low surface energies, the surface composition of FSIM was strongly affected by their segment length. The longer segment length is, the higher surface segregation is. This indicates that the long segment has strong driving force to the surface.

Keywords Fluorinated poly(imidesiloxane)s; surface composition; surface energies

Introduction

The poly(imidesiloxane)s (PIS) have been used as adhesives and encapsulants due to their excellent adhesive properties, low electric constants, and good thermal and mechanical properties [1]. The introduction of the siloxane component allows for increased impact resistance, excellent adhesion, reduced water absorption, decreased dielectric constants, and gas permeability, while maintaining the thermal and mechanical stabilities. Fluorinated polyimide has also good properties such as low dielectric constant, low cohesive energy, high thermal and chemical stability, low water uptake, water and/or oil repellency, low permittivity, low refractive index, and resistance to wear and abrasion because of fluorine atom [2]. The polyimides have surface energies of 33–46 dynes/cm, while surface energies of carbon fluoride group and poly(dimethyl siloxane) (PDMS) are 15 and 20 dynes/cm, respectively [3]. In this study, we synthesized the combined polymers with fluorine and siloxane, fluorinated poly(imidesiloxane)s (FSIM). The introductions of fluorine atoms and siloxane into polyimides, therefore, are expected to produce polyimides which have much attractive surface property.

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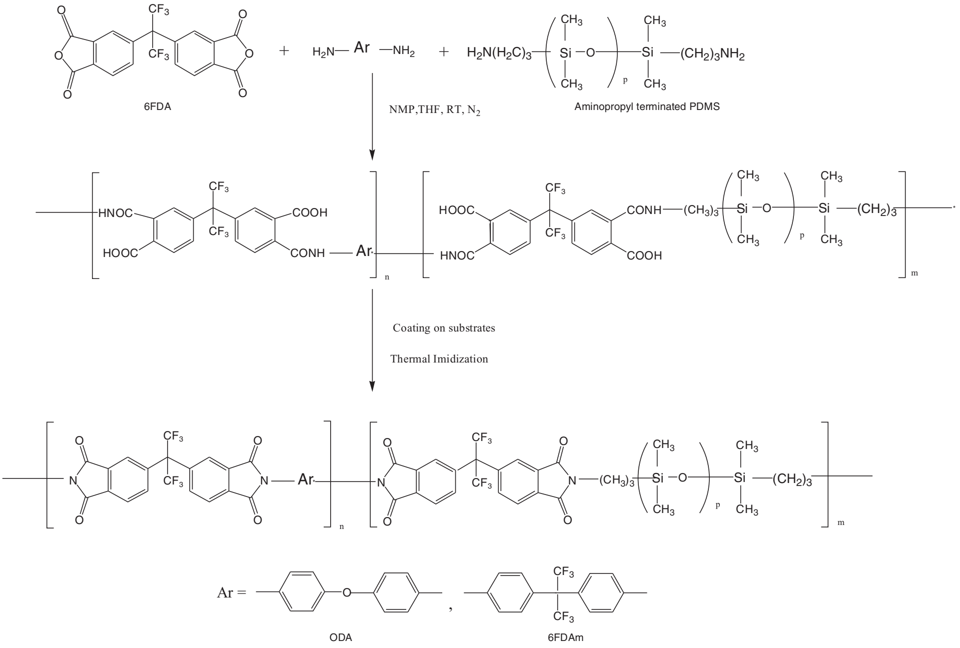
Experimental

The FSIM were synthesized from fluorinated aromatic dianhydride, hexafluoroisopropylidene dianhydride (6FDA, Aldrich reagent), the flexible aromatic diamine, oxydianline (ODA, Aldrich reagent), and α,ω'-aminopropyl PDMS (PCR Inc,) with different molecular weights. Scheme 1 showed the reaction process of FSIM of 252 ($p = 1$), 550 ($p = 5$), and 1207 ($p = 13$), where the p represents an average number of repeating unit of DMS in PDMS. First, the PDMS was added to a solution containing 6FDA in 1-methyl-2-pyrolidinone (NMP)/tetrahydrofuran (THF) mixture. The siloxane segments were incorporated into 6FDA-ODA backbone at a concentration of 5.4 wt% to form FSIM with different siloxane segment lengths. PDMS ($p = 1$) from 2.5 to 20 wt% were incorporated into the 6FDA-ODA backbone to form FSIM. A synthesized polymer in Table 1 was denoted as FPxxyy, where xx and yy represent the number of repeating unit and the wt% of PDMS, respectively.



Scheme 1. Preparation procedure of fluorinated poly(imidesiloxane)s.

The surface composition of synthesized FSIM was analyzed by attenuated total reflection fourier transform infrared (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) measurements. ATR-FTIR spectra (Perkin-Elmer FTIR 5500 spectrometer) with 45° Ge prisms were obtained using a thin film. The X-ray photoelectron spectroscopy (XPS) studies were performed on a PHI Quantera SXM X-ray photoelectron spectrometer with AlKα source(1486.6 eV) at 37.2 W. High-resolution scans of C1s(285 eV), N1s(402 eV), O1s(531 eV), Si2s(103 eV), and F1s (687 eV) were acquired at the takeoff angles of 15°, 30°, 45°, and 90°.

The surface composition of synthesized FSIM was analyzed by ATR-FTIR and XPS measurements. ATR-FTIR spectra with 45° Ge prisms were obtained using a thin film.

Table 1. Characteristics of the fluorinated poly(imidesiloxanes) synthesized in this study

Sample	PDMS		6FDA	Molecular weight		Refractive		Film
Code	No of unit	Weight %	weight %	Mn	PDI	index	Tg (°C)	formation
FP0102	1	2.72%	21.19%	384,000	3.18	1.521	228	yes
FP0105	1	5.43%	20.98%	281,000	2.85	1.520	226	yes
FP0110	1	10.91%	20.52%	180,000	2.37		149	yes
FP0116	1	16.22%	20.09%	163,000	2.61	1.551	120	yes
FP0120	1	19.53%	19.82%	129,000	3.00		80	yes
FP0505	5	5.43%	20.47%	395,000	2.64		229	yes
FP1305	13	5.43%	20.34%	319,000	2.60	1.520	228	yes

The XPS studies were performed on a PHI Quantera SXM X-ray photoelectron spectrometer with AlKα source(1486.6 eV) at 37.2 W. High-resolution scans of C1s(285 eV), N1s(402 eV), O1s(531 eV), Si2s(153 eV), and F1s (687 eV) were acquired at the takeoff angles of 15°, 30°, 45°, and 90°.

Results and Discussion

The DSC results in Table 1 showed that the Tg of FSIM copolymers with $p = 1$ decreased with increasing the content of PDMS from 2 wt% (228 ºC) to 20 wt% (80°C). However, the Tg of copolymers with long PDMS chain ($p = 13$) was slightly changed. These results indicate that at the same PDMS content, the short PDMS chains are more randomly dispersed in the copolymer. When the content of PDMS increases or the length of PDMS chain decreases, therefore, the sequence length of imide blocks became short and Tg decreases.

The surface depth sensitivity of ATR-FTIR is in the range of 0.5–3 μm. To obtain the information on the surface composition by ATR-FTIR, the PDMS calibration curve from various FSIM copolymers was obtained by using Lamber-Beer and internal standard methods.[4] C=O stretching peak at 1724 cm^{-1} from stable imide groups was used as

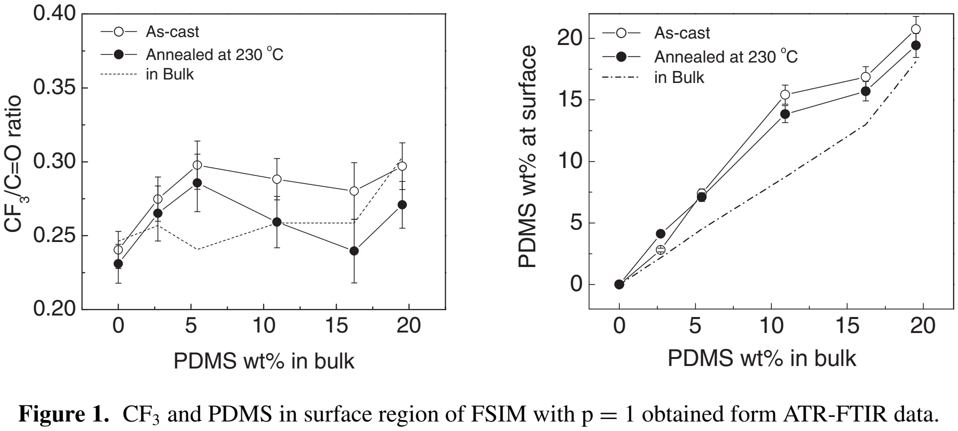


Figure 1. CF_3 and PDMS in surface region of FSIM with $p = 1$ obtained form ATR-FTIR data.

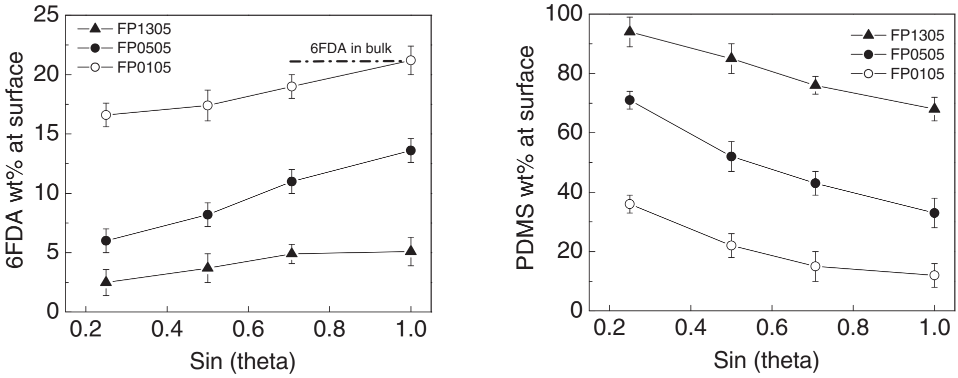


Figure 2. Surface wt% of 6FDA and PDMS of FSIM copolymers with different PDMS segment lengths, calculated by atomic% of XPS data. The PDMS content in FSIM was fixed at 5 wt%.

a internal standard peak. For the surface information of CF_3 groups, the area ratio of $CF_3/C{=}O$ was used. Figure 1 shows the $CF_3/C{=}O$ ratio of FSIM ($p = 1$) with different PDMS wt% measured by ATR-FTIR. The results indicate that the $CF_3/C{=}O$ ratios are similar to those of bulk within error whereas PDMS wt% at surface region shows higher than that of bulk (10–50%).

The depth resolution of XPS is a few nm and the obtained XPS results are expected to be significantly different from the ATR-FTIR one. XPS data can provide quantitative analysis of surface composition from atomic%. Figure 2 shows 6FDA and PDMS surface compositions of FSIMs (5 wt% PDMS) with different segment lengths of PDMS, calculated by atomic% of high-resolution XPS. The surface composition of 6FDA is lower than that of bulk while FSIMs show the surface segregation of PDMS (35–95 wt%), regardless of PDMS segment length. Also, the surface composition of PDMS increases progressively with decreasing a photoelectron take-off angle and increasing PDMS segment length while that of fluorocarbon increases. This suggests that the PDMS chains are segregation at the topmost surface. Although both groups have low surface energies, the driving force to surface is mainly affected by the length of each group. Therefore, the surface property of FSIM could be controlled by change of the segment length of a component with low surface energy.

Conclusion

The surface structure of various fluorinated PIS was investigated by ATR-FTIR and XPS measurements of which analyzing depths are around μm and nm orders, respectively. There is the competition on surface segregation between CF_3 and PDMS which have low surface energies. The results showed that the PDMS composition at the top-most surface by XPS was gradually increased with the length of PDMS block while a short chain CF_3 showed lower surface composition than bulk one. Thus, the surface segregation of long PDMS chains prevents short fluorine compounds moving to surface.

Acknowledgments

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