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Synthesis and properties of fluorinated thermoplastic polyurethane elastomer

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ABSTRACT

A series of fluorinated thermoplastic polyurethane elastomers (FTPU) based on self-synthesized fluorinate polyether diol (PFGE) were prepared by two-step polymerization. For the purpose of improving the molecular weight and mechanical property of FTPU, polybutylene adipate (PBA) was used to be compounded with PFGE as the soft-segment of FTPU. Effects of the mass ratio of PFGE/PBA and the mass fraction of hard-segment on the mechanical property of FTPU were investigated. The structure and morphology of FTPU were characterized by FTIR, GPC, DMA, surface tension and AFM analysis.

1. Introduction

By introducing fluorinated blocks into the molecular chains of thermoplastic polyurethane elastomer (TPU), the fluorinated thermoplastic polyurethane elastomers (FTPU) not only maintain most of the outstanding properties of TPU, such as high strength, high toughness and high damping properties, but also offer the basic advantages of improved solvent and chemical resistance, a lower surface tension, and low coefficient of friction, resulting in the wide applications in the areas of coating, leather decoration, textile and medicine [1–5].

There are however only few examples of commercially available fluorinated elastomers, such as the crosslinkable copolymers of vinylidenfluoride or tetrafluoroethylene with few suitable fluorinated comonomers like hexafluoropropene or perfluorovinylethers, the fluorinated thermoplastic elastomer recently developed by Daikin, where the soft phase is the vinylidene fluoride–hexafluoropropene copolymer. The use of short fluorinated chain extenders does not offer any advantage in terms of the surface properties and elastomeric properties. No more researches are found for other kinds of fluorinated thermoplastic elastomers. The main reason is perhaps the very limited availability of suitable fluorinated monomers or macromers [6–9].

At present, FTPUs are mainly applied as biomedicine materials. However, the low reaction activity of the fluorinated monomers led to the low molecular weight and poor mechanical properties of the resulting products, which restricted the wide applications of FTPUs. The aim of this work was to synthesize FTPUs with improved mechanical properties. The preparation and characteristic properties were studied.

2. Experimental

2.1. Materials

Diphenylmethylene diisocyanate (MDI) from Wanhua Polyurethane Co. Ltd. (Yantai, China) was used as received; 1,4-butanedilo (BDO), epichlorohydrin (ECH), and ethylene glycol (EG) all supplied by Bodi Chemical Co. Ltd. (Tianjin, China) were used after been purified; polybutylene adipate (PBA) ($\overline{Mn}$, 2000) was purchased from Huada Chemical Engineering Co. Ltd. (Yantai, China) and used after vacuum drying; tetrafluoropropanol (F–OH) from Jiachen Chemical Co. Ltd. (Shanghai, China) was used as received; boron trifluoride diethyl etherate ($BF_3{\cdot}Et_2O$) was purchased from Yangyuan Chemical Co. Ltd. (Changshu, China) and used after purified by vacuum distillation.

2.2. Synthesis of fluorinated polyether diol (PFGE)

Stoichiometric amounts of the ECH and NaOH were charged into the 3-necked round bottom flask equipped with a mechanical stirrer, and the temperature was raised to 50 °C under high speed

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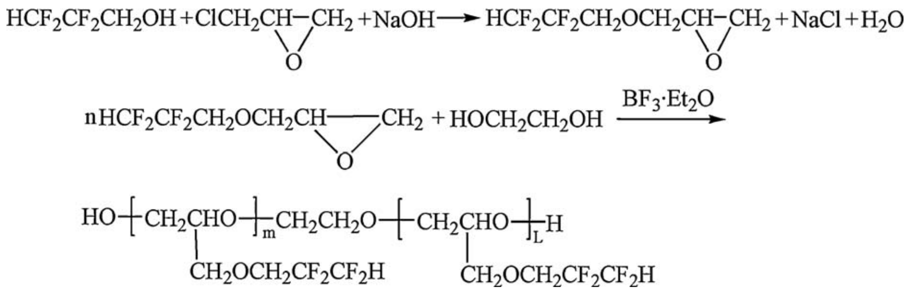


Scheme 1. The reaction formula of PFGE.

stirring. F–OH was slowly added to the reaction system, and followed by reacting at 50 °C for 2–3 h. Flurorinated glycidyl ether (FGE) was obtained after purified by vacuum distillation. Thereafter, stoichiometric amounts of $BF_3{\cdot}Et_2O$ and EG were charged into the 3-necked round bottom flask equipped with a mechanical stirrer in nitrogen gas and cooled to 0 °C. FGE was slowly added to the reaction system within 2–3 h, and maintained for 5 h. Then fluorinated polyether diol was obtained after washed and distilled. The reaction formula of synthesis of PFGE was shown in Scheme 1. The molecular weight of PFGE ($\overline{Mn}$) was 2089.

2.3. *Synthesis of fluorinated thermoplastic polyurethane elastomer (FTPU)*

Two-step procedure was adopted via bulk polymerization to prepare FTPU. The molar ratio of NCO/OH was 0.98. In the first step, the synthesis of the –NCO end-capped prepolymer was conducted by the bulk reaction of PFGE with MDI at 80 °C for 3 h. Then a certain amount of BDO was added, and mixed homogenously. Then the mixture was cast in a mold at 140 °C for 20 h.

2.4. *Measurements*

2.4.1. *FTIR analysis*

The composition of the synthesized FTPU was analyzed with Nicolet-560 Fourier-transform infrared spectrometer (FTIR) (USA). The specimen was prepared by casting the polymer solution film on KBr discs. The scanning rate is 20 min^{-1}, and the differentiate rate is 4 cm^{-1}.

2.4.2. *GPC analysis*

The number ($\overline{Mn}$) and weight ($\overline{Mw}$) average molecular weights, and the index of the molecular weight distribution $\overline{M_w}/\overline{M_n}$ of FTPU were measured by gel permeation chromatography (GPC) on a Waters 150-C instrument (USA) at 30 °C. Tetrahydrofuran (THF) was used as an eluent (flow rate = 1 ml/min).

2.4.3. *Tensile testing*

The tensile properties of samples were measured with a 4302 material testing machine from Instron Co. (USA) according to ISO527/1-1993 (E). The tensile speed and temperature were 200 mm/min and 23 °C, respectively.

2.4.4. *DMA analysis*

The dynamic mechanical analysis (DMA) was carried out using a TA Instrument Q800 DMA (USA). All the samples were measured with a single cantilever mode at a heating rate of 10 °C/min and a frequency of 30 Hz. The sample size was $35 \times 1 \times 0.2\ \text{mm}^3$.

2.4.5. *Contact angle*

The contact angles of water and glycerol as testing liquids on FTPU were measured by ErmaG-1 contact angle test apparatus (Japan) at room temperature by sessile drop method.

2.4.6. *AFM analysis*

The images of FTPU were visualized on a Digital Instruments Nanoscope IIIa AFM microscopy (USA) by tapping-mode. The sample was dissolved in THF and coated on the mica substrate, and then dried in vacuum at 60 °C for 12 h. It was measured in air at room temperature with a scanning area of 15 μm.

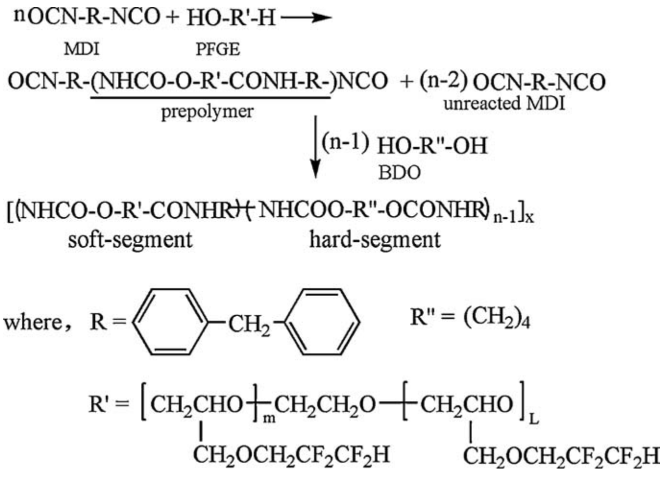
3. Results and discussion

The reaction formula of FTPU synthesized in this work was shown in Scheme 2. The composition of FTPU was analyzed by FTIR. As shown in Fig. 1, there was a strong N–H stretching vibration absorption peak at 3307.94 cm^{-1}; C═O stretching peak and N–H bending peak were observed at 1728.89 cm^{-1} and 1531.11 cm^{-1}, respectively; the peak at 1104.97 cm^{-1} was assigned to the stretching vibration of C–O–C; and the absorptions at 1226.72 cm^{-1} and 1299.76 cm^{-1} were attributed to the stretching vibration of C–F. The diisocyanate (–N═C═O) band at 2250–2275 cm^{-1} was absent in the spectra of the resulting FTPU, indicating that this group was completely consumed in the reaction [10].

3.1. *Relationship between the chemical structure and mechanical property of FTPU*

The mechanical property of FTPU is related with the chemical bond, intermolecular force, and molecular weight of FTPU. It is finally determined by the chemical structure of soft-segment and hard-segment.

PBA was adopted to be combined with PFGE as the soft-segment of FTPU due to the low reaction activity of PFGE for the purpose of improving the molecular weight and mechanical property of FTPU. Effects of the mass ratio of PFGE/PBA and the mass fraction of hard-segment on the mechanical property of FTPU were investigated.



Scheme 2. The reaction formula of FTPU.

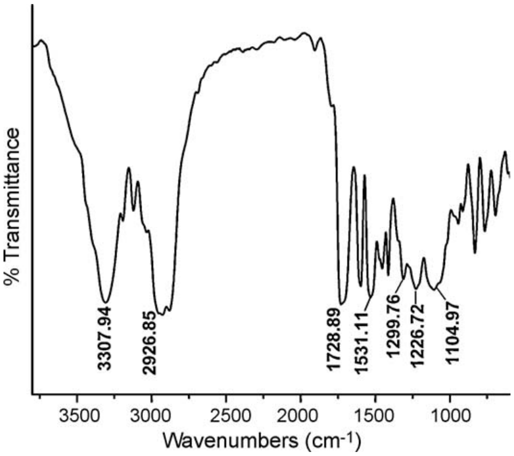


Fig. 1. FTIR spectrum of FTPU.

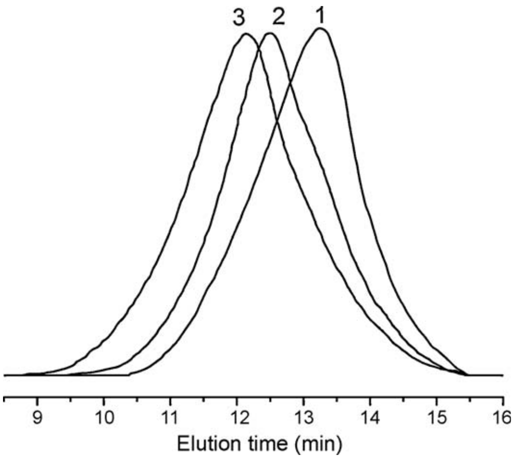


Fig. 2. GPC curves of FTPU.(1) PFGE/PBA (100/0); (2) PFGE/PBA (70/30); (3) PFGE/PBA (50/50)

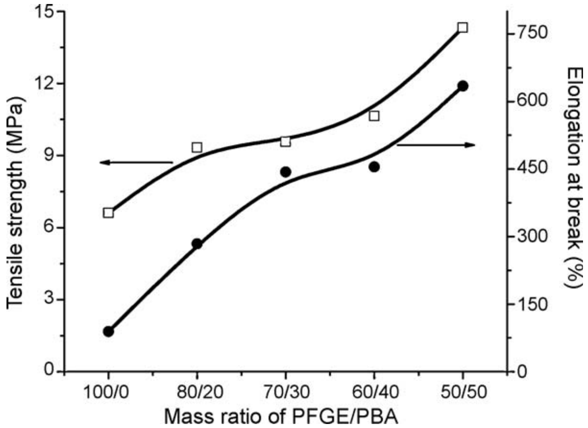


Fig. 3. Mechanical property of FTPU as a function of mass ratio of PFGE/PBA.

As can be seen from Fig. 2, the GPC curves of FTPU synthesized with varying mass ratio of PFGE/PBA were single bell-shaped without the distribution peak of small-molecular substance indicating that PFGE and PBA were all consumed to get the final product. The data of GPC results were listed in Table 1. With the decrease of the mass ratio of PFGE/PBA and fluorine content, the elution time of FTPU decreased and the molecular weight were improved without much influence on molecular weight distribution.

The mechanical property of FTPU as a function of the mass ratio of PFGE/PBA was shown in Fig. 3. It can be seen that the tensile strength and elongation at break of FTPU increased with the decrease of the ratio of PFGE/PBA. When the mass ratio of PFGE/PBA was 50/50, the tensile strength of FTPU was improved from 6.61 MPa to 14.33 MPa, and the elongation at break of FTPU was improved from 89.1% to 634.3%.

Mechanical property of FTPU with different mass fraction of hard-segment was shown in Fig. 4. It can be seen that mass fraction of hard-segment had much influence on the mechanical property of FTPU. The sample with 30 wt% of hard-segment possessed relatively high elongation at break and low tensile strength. As the mass fraction of hard-segment increased, the tensile strength increased and the elongation at break declined.

3.2. *Dynamic mechanical property of FTPU*

Dynamical mechanical analysis provides information on glass transition and the damping property of a polymer. The

Table 1
GPC result of FTPU.

FTPU	Mass fraction of PFGE/PBA	Fluorine content (%)	Retention time (min)	$\overline{Mn}$ ($\times10^4$)	$\overline{Mw}$ ($\times10^4$)	$\overline{Mw}/\overline{Mn}$
1	100/0	23.9	13.27	0.62	1.53	2.5
2	70/30	16.6	12.60	1.07	2.87	2.7
3	50/50	11.9	12.14	1.48	4.17	2.8

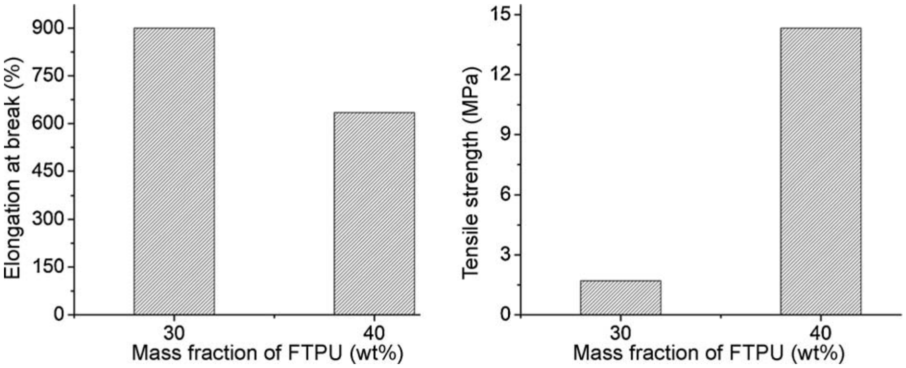


Fig. 4. Mechanical properties of FTPU as a function of mass fraction of hard-segment.

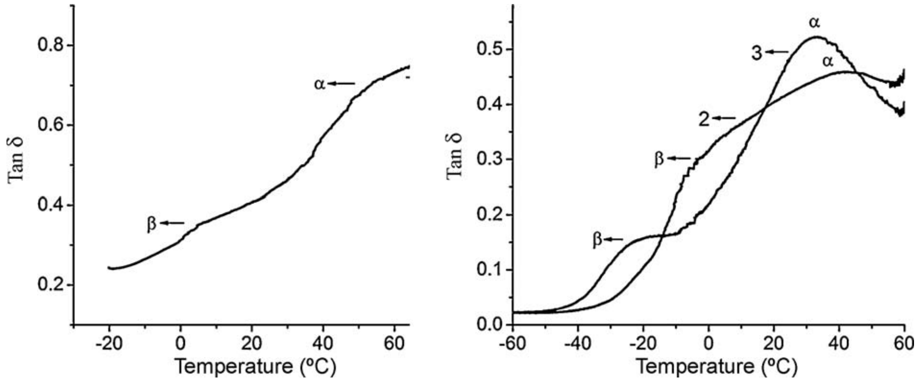


Fig. 5. Damping factors of FTPU. (1) PFGE/PBA (100/0); (2) PFGE/PBA (70/30); (3) PFGE/PBA (50/50)

Table 2
DMA parameters of FTPU.

$FTPU_2$	Mass fraction of PFGE/PBA	Fluorine content (%)	T_{gs} (°C)	T_{gh} (°C)	Tan δ_{max}	$T_{\tan\delta} > 0.3$ (°C)
1	100/0	23.9	5.31	57.06	0.72	>-1.7
2	70/30	16.6	−4.05	42.02	0.46	>-3.53
3	50/50	11.9	−22.86	33.47	0.52	>8.9

dynamical mechanical properties of FTPU were shown in Fig. 5. It can be seen that all the samples exhibited two loss peaks corresponding to the glass transition temperature of soft-segment and hard-segment, respectively, and the loss peak of FTPU shifted towards high temperature with the increase of fluorine content. Numerical DMA data of FTPU were listed in Table 2. It can be seen that the sample prepared completely with PFGE without PBA exhibited relatively high damping factor and wide damping range.

3.3. Surface property of FTPU

The surface tension of solid (γ_s) contains both polarity component (γ_s^p) and dispersion component (γ_s^d) [11,12].

(1)$\gamma_s = \gamma_s^p + \gamma_s^d$It can be calculated with geometric-mean equation: [13]

(2)$\gamma_{lV}(1 + \cos\theta) = 2(\gamma_l^d \gamma_s^d)^{1/2} + 2(\gamma_l^p \gamma_s^p)^{1/2}$

In the equation, θ is contact angle; γ_{lV} is surface tension of liquid; γ_l^d, γ_l^p are polarity component and dispersion component of liquid, respectively; γ_s^d, γ_s^p are polarity component and dispersion component of solid, respectively.

Water and glycerin were selected as the test liquids and the surface tension of FTPU can be obtained along with geometric-mean equation. As listed in Table 3, with the increase of fluorine content, the contact angle of water and glycerin on the surface of FTPU increased, and the surface tension of FTPU decreased from 42.4 mN/m to 36.3 mN/m.

The –CF_2H unit with a relatively low surface energy moved onto the surface of FTPU, which led to the decrease of the surface energy of FTPU, as shown in Fig. 6.

3.4. Aggregation morphology of FTPU

The molecular chains of FTPU are composed of the soft-segment originating from polyol, the hard-segment originating from diisocyanate and the chain extender. Ideally, the two segments are immiscible and phase separation occurred during the formation of morphology.

Table 3
Surface properties of FTPU with varying fluorine content.

Mass fraction of PFGE/PBA	Fluorine content (%)	Contact angle (°)		γ_s^d (mN/m)	γ_s^p (mN/m)	γ (mN/m)
		Water	Glycerin			
100/0	23.9	72.4	80.6	1.2	35.1	36.3
80/20	19.0	71.6	80.0	1.1	36.0	37.1
70/30	16.6	69.2	77.0	1.7	36.7	38.4
60/40	14.3	67.0	74.4	2.1	37.3	39.4
50/50	11.9	64.0	72.0	2.2	40.2	42.4

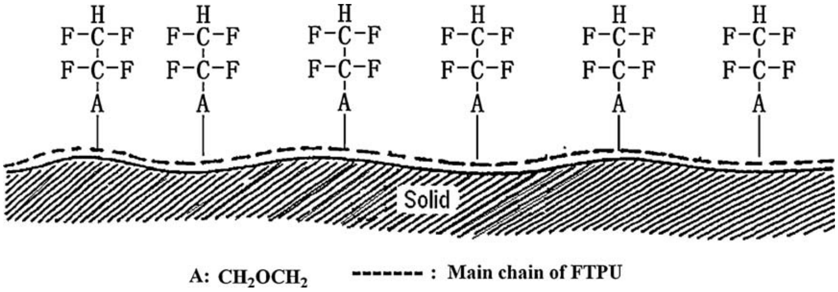


Fig. 6. Schematic illustration of fluorinated group of FTPU enriching at air–polymer interface.

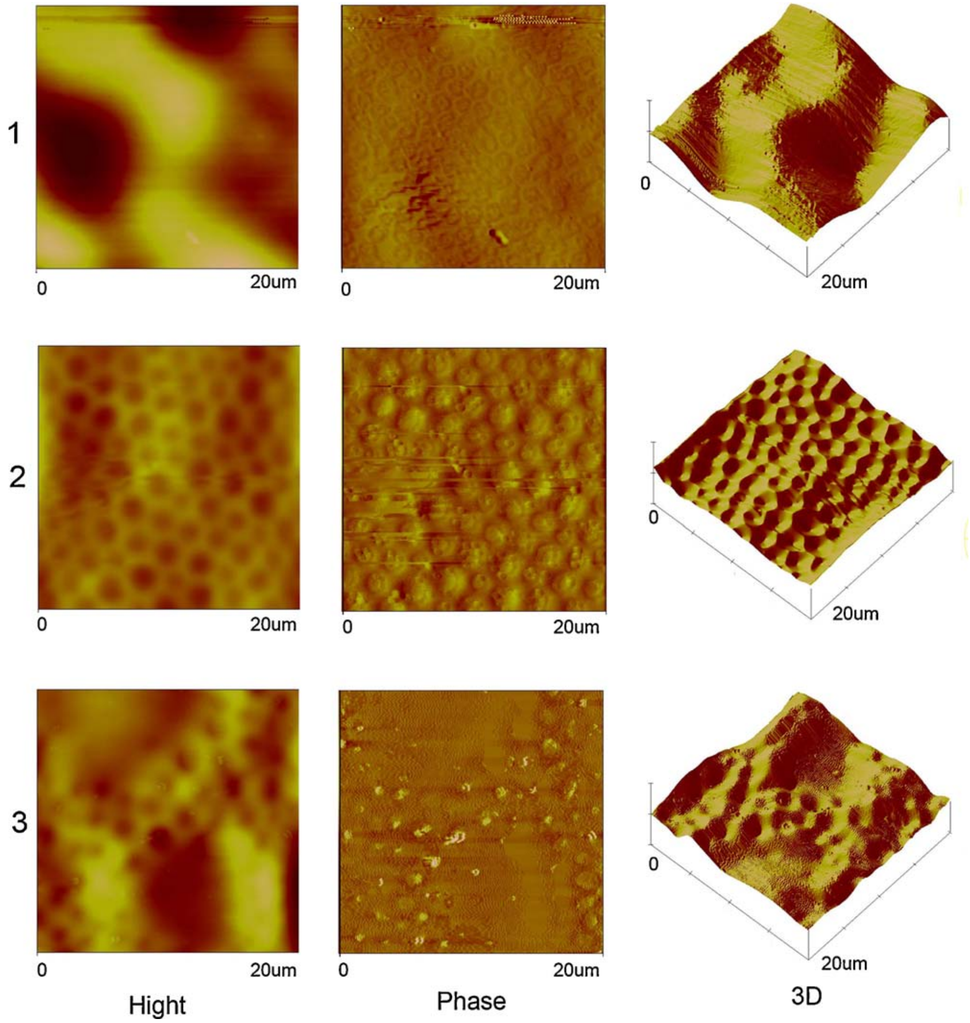


Fig. 7. AFM images of micro-phase separation of FTPU (the observation domain: 20 μm). (1) PFGE/PBA (100/0); (2) PFGE/PBA (70/30); (3) PFGE/PBA (50/50)

The multi-phase nature of FTPU has been strongly implied from AFM analysis [14,15]. Fig. 7 presented the height image, phase image and 3D image of FTPU. The scope of observation was 20 μm. A typical two-phase structure can be observed. The comparatively bright part corresponded to the hard-segment of FTPU, and the grey part corresponded to the soft-segment of FTPU. In the 3D image, lots of parts of "wave trough" corresponding to the soft-segment and parts of "wave crest" corresponding to the hard-segment can be observed, which indicated that there was a micro-phase separation in the molecules of FTPU. Furthermore, it can also be seen that with the increase of fluorine content, the degree of the phase separation increased, and the soft and hard-segment exhibited continuous phase morphology, respectively, for the sample of FTPU with PFGE/PBA (100/0).

4. Conclusions

Two-step procedure was adopted via bulk polymerization to prepare FTPU. The composition of FTPU was analyzed by FTIR. PBA was adopted to be combined with PFGE as the soft-segment of FTPU due to the low reaction activity of PFGE. With the increase of PBA content, the molecular weight of FTPU was improved, the tensile strength and elongation at break of FTPU increased. For the sample with PFGE/PBA (50/50), the tensile strength and the elongation at break of FTPU can reach 14.33 MPa, and 634.3%, respectively. All the samples of FTPU exhibited two loss peaks, corresponding to the glass transition temperature of soft-segment and hard-segment, respectively, and the loss peak of FTPU shifted towards high temperature with the increase of fluorine content. It can be seen that the sample prepared completely with 100% PFGE exhibited relatively high damping factor and wide damping range. With the increase of fluorine content, the surface tension of FTPU decreased, while the extent of the phase separation increased, and the soft and hard-segment exhibited continuous phase morphology for the sample of FTPU with PFGE/PBA (100/0).

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