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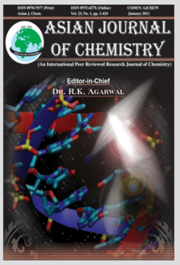

Synthesis and Characterization of Novel Fluorinated Polyurethane Elastomers†

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A series of fluorinated polyurethane elastomers were synthesized from 2-trifluoromethyl-4,4'-diaminodiphenyl ether, which was derived from 2-chlorobenzotrifluoride and *p*-nitrophenol. The structure and properties of fluorinated polyurethane elastomers were measured by fourier transform infrared spectroscopy, thermogravimetric analysis, microscale combustion colorimeter, water absorption and contact angle measurement. The results show the fluorinated polyurethane elastomers prepared from 2-trifluoromethyl-4,4'-diaminodiphenyl ether have lower surface tension, better hydrophobic property and thermal stability and good mechanical properties. Furthermore, the introduction of fluorine into fluorinated polyurethane elastomers improved the flame retardancy. With the content of fluorine increasing from 1.5 to 2.8 %, the peak heat release rate and total heat release decreased from 605.4 w/g and 23.7 kJ/g to 511.0 w/g and 22.4 kJ/g, indicating that the flame retardant property of polyurethane elastomer increased with the increase in the fluorine content.

Key Words: Fluorinated diamine, Fluorinated polyurethane elastomer, Surface property, Flame retardancy.

INTRODUCTION

Since the first patent about fluorinated polyurethane was published in England[1], it has attracted many scientists to do research in this area. There are mainly three major methods of synthesizing fluorinated polyurethane by the introduction of fluorinate diisocyanates[2], chain extenders[3-5] and soft segments[6-9]. For instance, Takakura[2] synthesized a series of fluorinated polyurethane elastomers (FPUEs) based on 2,2,3,3,4,4,5,5-octafluorohexamethylene diisocyanate. Yoon and Ratner[3] synthesized segmented fluorine-containing poly(ether urethanes) from 2,2,3,3-tetrafluoro-1,4-butanediol or 2,2,3,3,4,4-hexafluoro-1,5-pentanediol chain extender. Tan[5] synthesized poly(ether urethane)s and poly(carbonate urethane)s containing various amounts of chain extender: 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxy)propane-1,2-diol. Ho[8] synthesized fluorinated polyurethane based on 3-(trifluoromethyl)-3,4,4,5,5,6,6,7,7,8,8-undecafluoro-1,10-decanediol and 1,6-hexamethylene diisocyanate. The results of above studies show that FPUEs have good mechanical property and excellent surface property.

To the best of our knowledge, there are few reports in the literature on short-chain fluorinated aromatic diamine which acted as a chain extender to prepare FPUEs. There are few reports on the flame retardant properties of FPUEs. Although the combustion performance of FPUEs has attracted more and more attention with the expansion of their application.

In this paper, the synthesis and characterization of a novel fluorinated chain extender: 2-trifluoromethyl-4,4'-diaminodiphenyl ether (TDAP) and a series of fluorinated polyurethane elastomers (FPUEs) synthesized with various amounts of TDAP are reported. The surface tension, water absorption, flame retardant property and mechanical property of FPUEs are also studied.

EXPERIMENTAL

2-Chlorobenzotrifluoride (99 % purity, Huaian Yongchuang Chemical Co. Ltd.) *p*-nitrophenol (AR), potassium carbonate (AR), ethanol (AR) (all from Sinopharm Chemical Reagent Co., Ltd.), sulfuric acid (AR), hydrochloric acid (AR) and nitric acid (AR) (all from Guangdong Xilong Chemical Co., Ltd.) were used without further purification. N,N-Dimethylformamide (DMF) (AR) and methylglycol (AR) (both from Guangdong Xilong Chemical Co., Ltd.) were purified by distillation under reduced pressure over calcium hydride (Xilong Chemical Co., Ltd.). Toluene diisocyanate (TDI) was purchased from Mitsui Chemicals Co., Ltd. poly(tetramethylene ether glycol) (PTMEG, $\overline{Mn}$ = 1000, 2000) was purchased from Zhejiang Dongyue Chemical Co., Ltd.

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Synthesis of 2-trifluoromethyl-4,4-diaminodiphenyl ether (TDAP): 2-Chlorobenzotrifluoride (80 mL) and sulfuric acid (60 mL) were introduced into a round-bottom 500 mL glass flask equipped with a thermometer, a condenser and a mechanical stirrer. After the reaction mixture was cooled to room temperature, a mixture of sulfuric acid (90 mL) and nitric acid (90 mL) was added dropwise over 2 h. The reaction mixture was maintained at 45 °C for another 2 h. The reaction mixture was poured into an excess amount of ice-water after the reaction ended. The formed precipitate was collected and washed with water several times to neutral. The resulting pure 2-chloro-5-nitro-trifluoromethylbenzene (CNFB) was purified by vacuum distillation (91.3 % yield).

80 g CNFB dissolved in 200 mL DMF, 28 g potassium carbonate and 50 g *p*-nitrophenol were introduced into a round-bottom glass flask. The reaction mixture was maintained at 120 °C for 24 h. The precipitate was removed by filtering. After vacuum distillation of the filtrate, 2-trifluoromethyl-4,4-dinitrodiphenyl ether (TDNP) was filtered and recrystallized from 2-mehoxyethanol, then dried in an 80 °C vacuum oven for 24 h (yield: 89.4%).

80 g reduced iron powder, 130 mL deionized water, 210 mL ethanol and 8 mL hydrochloric acid were introduced into a glass flask. The reaction mixture was heated to boiling for 0.5 h. After the reaction mixture was cooled to 30 °C, 80 g TDNP was added and then the mixture was maintained at 65 °C for 4h. The precipitate was removed by filtration. The filtrate thus obtained was poured into 1 L of stirring water, giving rise to a precipitate that was isolated by filtration and then TDAP was recrystallized from the ethanol/water mixture at a molar ratio of 2:8 with a yield of 87.5 %.

Synthesis of fluorinated polyurethane elastomers (FPUEs): PTMEG was introduced into a open round bottom 1 L glass reactor and then heated to 120 °C. It was stirred and vacuumed for 2 h to remove the trace water. Subsequently, the vacuuming was stopped and nitrogen gas was charged into the reactor. When the temperature was cooled to 70 °C, TDI was added and reacted for 2 h. The prepolymer was made after removing bubbles by vacuum.

The fixed molten TDAP or MOCA were added to stirring prepolymer and the mixture was cast onto a Teflon plate, heated at 75 °C for 2 h and 115 °C for another 4 h. The ratio of diisocyanates, chain extenders and soft segments were varied to yield polymers with different compositions. Table-1 gives a description of FPUEs and PUE.

Characterization: Infrared data were obtained with a Spectrum100 FTIR Spectrometer (Perkin-Elmer) between 4000 and 500 cm^{-1} at the resolution of 4 cm^{-1}. TDNP and TDAP for FTIR were prepared by pressing potassium bromide troche and FPUEs were recorded by attenuated total reflection (ATR). 32 Scans were averaged for each sample.

^{1}H NMR and ^{19}F NMR spectra were obtained with Bruker AV400. DMSO-d_6 was used as solvent and chemical shifts reported were internally referenced to Me_4Si (0 ppm) and $CFCl_3$ (0 ppm) for ^{1}H and ^{19}F, respectively.

The contact angles of water and ethylene glycol on FPUE were measured by JCZ 2000 contact angle goniometer at room temperature by the sessile drop method. Contact angles were measured on 1 pL of testing liquids and the images were caught immediately. 3 Testes were averaged for each sample.

TABLE-1
DESCRIPTION OF FPUEs AND POLYURETHANE

Sample	Molar ratio of TDI/soft segment (R)	Chain extension coefficient		F content (%)
		TDAP	MOCA	
FPUE-1	1.8:1	0.9	–	1.5
FPUE-2	2.0:1	0.9	–	1.9
FPUE-3	2.2:1	0.9	–	2.1
FPUE-4	2.4:1	0.9	–	2.6
FPUE-5	2.6:1	0.9	–	2.8
FPUE-6	2.0:1	0.9	–	3.2
PUE	2.0:1	–	0.9	0

a.All the soft segments used here are PTMEG ($\overline{Mn}$ = 2000) except FPUE-6 is PTMEG ($\overline{Mn}$ = 1000).
b.Chain extension coefficient is the molar ratio of NH_2 (chain extender) and NCO (prepolymer).

The surface tension is calculated through the following equations[5]:

$$\gamma = \gamma^d + \gamma^p \tag{1}$$

$$(1+\cos\theta_{H_2O})\gamma_{H_2O} = \frac{4\gamma^d_{H_2O}\gamma^d}{\gamma^d_{H_2O}+\gamma^d} + \frac{4\gamma^p_{H_2O}\gamma^p}{\gamma^p_{H_2O}+\gamma^p} \tag{2}$$

$$(1+\cos\theta_{EG})\gamma_{EG} = \frac{4\gamma^d_{EG}\gamma^d}{\gamma^d_{EG}+\gamma^d} + \frac{4\gamma^p_{EG}\gamma^p}{\gamma^p_{EG}+\gamma^p} \tag{3}$$

in which γ is the elastomer surface tension. γ^d is the dispersion component and γ^p is the polar component. θ_{H_2O} and θ_{EG} are the contact angles of polymer with water and ethylene glycol. The numerical values used are $\gamma^d_{H_2O}$ = 21.8 mN/m, $\gamma^p_{H_2O}$ = 51 mN/m, γ^d_{EG} = 29.3 mN/m, γ^p_{EG} = 19.0 mN/m.

The thermogravimetric analyses of samples were carried out under N_2 atmosphere on a STA 409PC/PC by NETZSCH from 50 to 700 °C at a heating rate of 20 K/min. The mass of the sample was 8 to 9 mg.

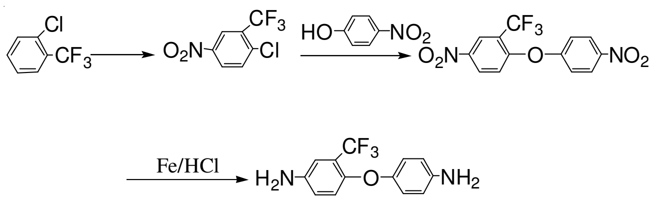
The water absorption of FPUE and PUE was performed according to the specifications of ASTM D570 and the test specimens were cut in a shape of 76.2 mm × 25.4 mm × 1.0 mm. The specimens were placed in a vacuum oven at 80 °C for 24 h and then cooled in a desiccator and immediately weighed to the nearest 0.001 g to get the initial weight (W_0). The conditioned specimens were entirely immersed in a container of deionized water maintained at 25 °C, after a specific time, the specimens were removed from the water, one at a time, surface water on specimens was removed with a dry cloth and the specimens were weighed immediately to get the weight, (W_1). The percentage of increase in weight of the samples was calculated to the nearest 0.01 % by using the formula (W_1 - W_0)/W_0. About 2-4 h once in the started 24 h, then 10 h once.

The microscale combustion colorimeter (MCC) tests were carried out on a Govmark MCC-2 microscale combustion colorimeter which was a pyrolysis combustion flow calorimeter. 4-6 mg samples were heated to 700 °C at a heating rate of 1 K/s in a stream of nitrogen flowing at 80 cm^3/min. The volatile, anaerobic thermal degradation products in the nitrogen gas stream were mixed with a 20 cm^3/min stream of pure oxygen prior to entering a 900 °C combustion furnace.

Tensile tests were carried out with a Reger 3010 Model Universal Testing machine at 25 °C and relative humidity of 50 %. The crosshead speed was 500 mm/min. Each sample was cut into dumbbells of 115 mm in length and 25 mm in width; the narrow section was 33 mm × 6 mm in area and 3 mm in thickness. The results reported are the mean values for five replicates.

RESULTS AND DISCUSSION

Characterization of TDAP: The synthesis route of TDAP is shown in **Scheme-I**. The chemical structures of TDNP and TDAP were identified by FTIR, ^1H NMR and ^{19}F NMR. Fig. 1 shows the FTIR of TDNP and TDAP. The nitro absorption peaks at 1590, 1348 cm^{-1} from -NO_2 asymmetric and symmetric stretching are found in TDNP and disappear in TDAP. The typical N-H stretching absorptions at 3410, 3321 and 3201 cm^{-1} and N-H bending absorption at 830 and 1648 cm^{-1} are found in TDAP. All the above results indicate that TDNP completely converts into TDAP[10]. The C-F multiple stretch bending absorptions from -CF_3 are observed[11] between 1300 and 1100 cm^{-1}.



Scheme-I: Synthesis route of TDAP

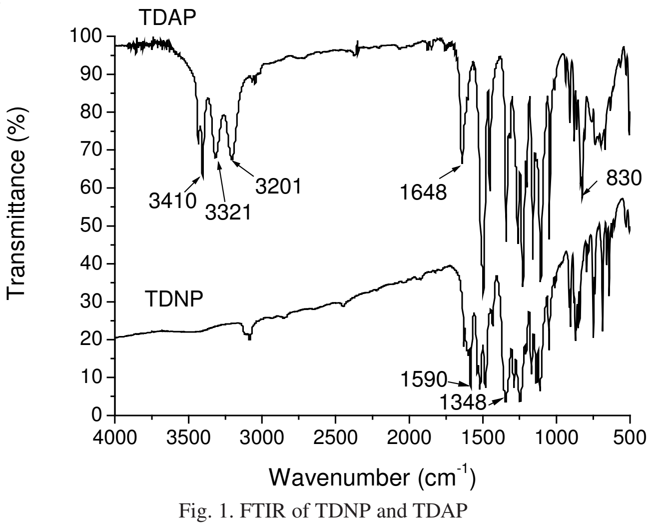


Fig. 1. FTIR of TDNP and TDAP

The ^1H NMR and ^{19}F NMR are shown in Figs. 2 and 3. In the ^1H NMR of TDAP, the electron-donating effect of amino/ether groups and proton-donating effect of trifluoromethyl groups in TDAP are demonstrated by the seven groups of peaks: 6.51-6.54 ppm (doublet, 2H, H_7), 6.63-6.76 ppm (triplet, 3H, H_5 and H_6), 6.86 ppm (doublet, 1H, H_3), 6.72-6.75 ppm (doublet, 1H, H_4), 5.23 ppm (singlet, 2H, H_1) and 4.85 ppm (singlet, 2H, H_2). The hydrogen peaks from H_5, H_6 and H_7 are in the high range due to the shielding effect of the electron-donating effect of amino/ether groups and H_7 is the highest with the strongest electron-donating effect of amino group. The hydrogen peaks from H_3 are the lowest for the shielding effect of the proton-donating effect of trifluoromethyl groups.

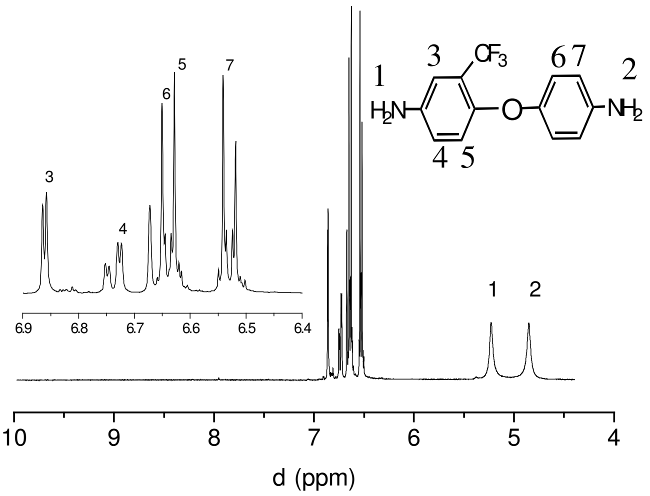


Fig. 2. ^1H NMR spectra of TDAP

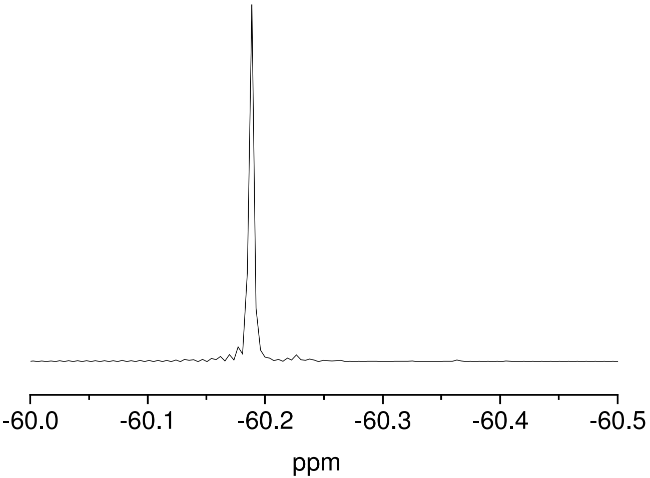


Fig. 3. ^{19}F NMR spectrum of TDAP

^{19}F NMR (Fig. 3) analysis provides a sharp single peak at -60.18 ppm, indicating that three F atoms of TDAP are in the same environment. The sharp single peak indicates high purity of monomers.

FTIR result of FPUE: The FTIR spectrum of FPUE-6 is shown in Fig. 4. The absence of an NCO peak at 2270-2250 cm^{-1} indicates the reaction proceeds to essentially complete conversion[12]. The stretching vibration of N-H is red-shifted to 3260 cm^{-1} as the strong hydrogen bond in FPUEs. The 1220 and 1100 cm^{-1} are the absorptions of C-O-C of aromatic and PTMEG, respectively. The absorption at 1540 cm^{-1} is assigned to N-H and C-N stretching of urethane and ureido groups. The absorption at 1689 cm^{-1} is assigned to C-O stretching of urethane, the 2943 and 2850 cm^{-1} is due to CH_2 stretching of PTMEG and the C-F multiple stretching absorptions are also detected in the range of 1300-1100 cm^{-1}.

Surface property of FPUEs: Contact angle as a direct reflection of the surface energy of materials for practical application materials has important guiding significance. Table-2 shows the contact angle and surface tension of FPUEs and PUE. As listed in Table-2, the contact angle of water and ethylene glycol on the surface of FPUE increases with the

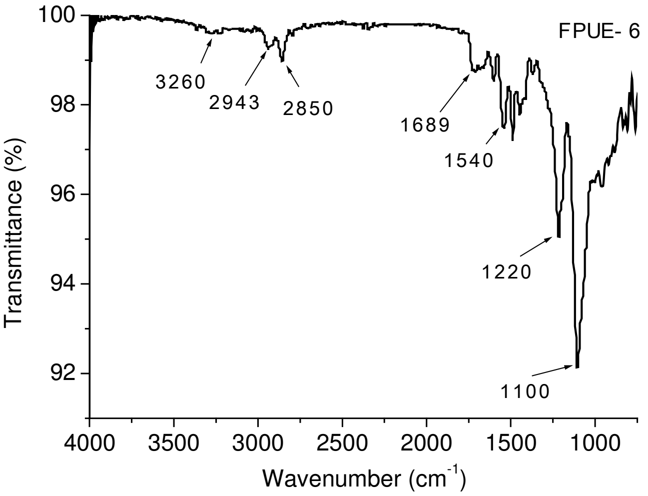


Fig. 4. FTIR of FPUE-6

TABLE-2
SURFACE PROPERTIES OF FPUEs AND POLYURETHANE

Sample	Contact angle (°)		Surface tension (mN/m)		
	Water	Ethylene glycol	γ^p	γ^d	γ
FPUE-1	82.1	57.4	15.6	15.1	30.7
FPUE-2	84.4	59.9	15.4	14.0	29.4
FPUE-3	86.4	64.9	13.1	14.3	27.4
FPUE-4	88.3	67.1	12.7	13.5	26.2
FPUE-5	90.0	69.6	12.0	13.2	25.2
FPUE-6	92.6	71.3	12.5	11.6	24.1
PUE	66.9	51.6	11.8	27.1	38.9

increase in the fluorine content. Compared to PUE, the contact angle of FPUE-1 which contains the lowest fluorine increases from 66.9°, 51.6° to 82.1°, 57.4° and the surface tension of FPUE-1 decreases from 38.9 mN/m to 30.7 mN/m. It indicates that the introduction of fluorine in the FPUEs decreases the surface tension greatly. The results of the six FPUEs show that with the increase in the chain extender (fluorine content), the surface tension decreases gradually and the lowest surface tension is just 24.1 mN/m. The main reason for this is that fluorocarbon groups bears relatively low surface energy, so they are easy to migrate to and enrich on the surface, which results in the higher concentration of CF_3 groups on the surface than in bulk, so the FPUEs show an excellent low surface energy[5,13].

Water absorption is an important parameter of the hydrophilicity of materials. The results of water absorption are given in Fig. 5. It is evidence that both FPUEs and PUE are saturated in 22 h. From FPUE-1 to FPUE-6, the water absorption decreases gradually with the increase in the chain extender (fluorine content). The water absorptions of FPUEs are all lower than that of PUE. The water absorption of FPUE-6 which contains the most fluorine is only 2.88 % compared to 5.03 % of PUE. From Fig. 5, it can be concluded that the water absorption decreases gradually with the increasing of the chain extender (fluorine content), in other words, the hydrophobic property increases. The results of the water absorption test are in good agreement with the contact angle results.

Flame retardant property of FPUEs: The microscale combustion colorimeter (MCC) is a pyrolysis combustion flow calorimeter and the heat releasing rate recorded by MCC is calculated from the measured oxygen consumption rate, which is in accordance with that of cone calorimetry (CONE). Fig. 6 and Table-3 show the plots and data of FPUEs obtained from MCC. The total heat release (THR) and specific heat release rate (SHRR) are good predictors of flammability[14].

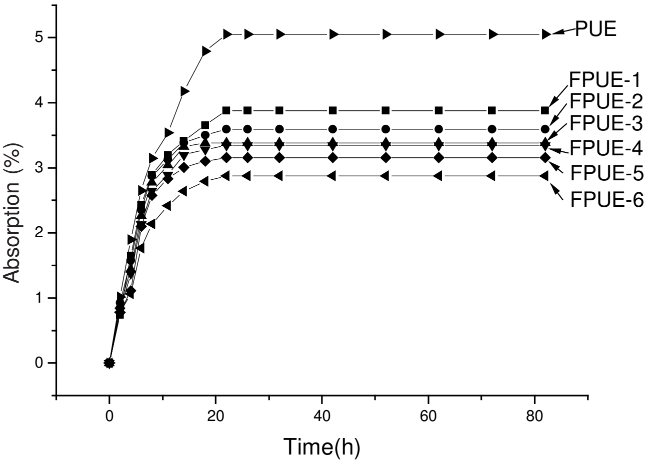


Fig. 5. Water absorption results of FPUEs and PUE

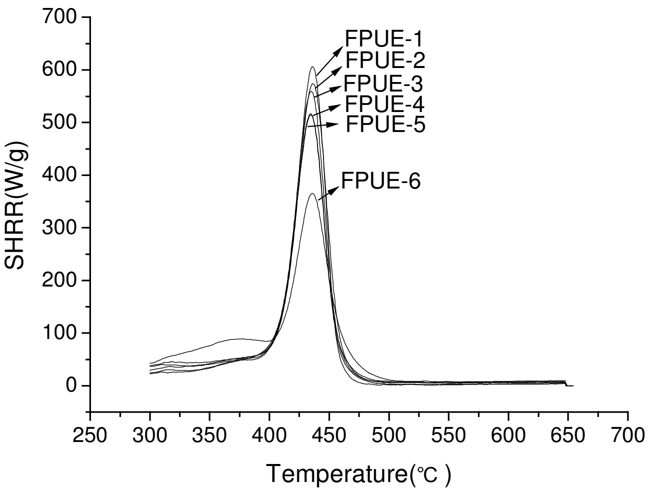


Fig. 6. Specific heat release rate curves of FPUEs

TABLE-3
MCC DATA OF FPUEs AND PUE

Sample	THR (KJ/g)	PHRR (W/g)	Ignition temperature (°C)
FPUE-1	23.7	605.4	436.2
FPUE-2	23.5	570.0	436.7
FPUE-3	23.2	554.9	436.1
FPUE-4	22.8	513.8	434.6
FPUE-5	22.4	511.0	435.6
FPUE-6	21.8	559.4	437.3

From the result of FPUE-1 to FPUE-5, the THR and peak heat release rate (PHRR) decrease from 23.7 KJ/g to 22.4 KJ/g and 605.4 W/g, to 511.0 W/g, respectively. With the increase in the chain extender (fluorine content), the THR and PHRR decrease. It shows that the flame retardation of FPUEs increases gradually with the increase in the fluorine content.

Thermal property of FPUEs: Fig. 7 shows the TGA of FPUEs and PUE while Table-4 gives the T_5, T_{50} and T_{max} from TGA. T_5, T_{50} and T_{max} are the temperature of the sample with a 5 %, 50 % and maximum mass loss.

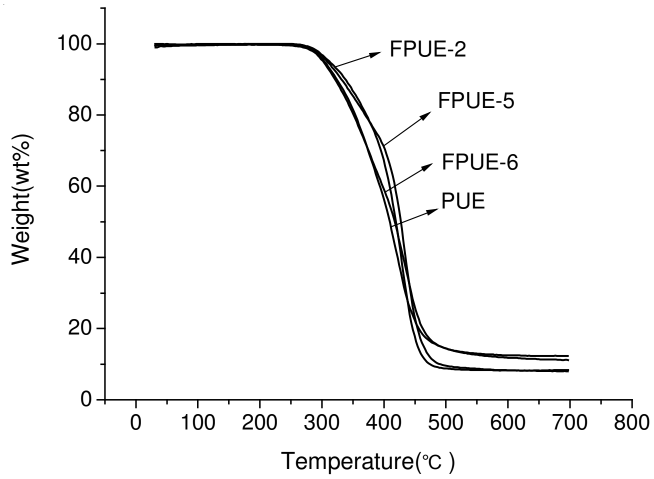


Fig. 7. TGA curves of FPUEs and PUE

TABLE-4
TGA DATA OF FPUEs AND PUE

Sample	T_5 (ºC)	T_{50} (ºC)	T_{max} (ºC)
FPUE-2	308	419	430
FPUE-5	308	427	433
FPUE-6	301	417	436
PUE	303	409	428

Both T_5 and T_{50} of FPUE-2 are higher than those of PUE and reach 308 and 419 °C. In the fluorinated polyurethane elastomers, the strongly polar -CF_3 leads to strong hydrogen bonding between the soft and hard blocks, which results in the increasing of the degree of microphase separation and much more heat is needed to destroy the hydrogen bond and furthermore, the CF_3 holds better thermal stability, so the thermal stability of FPUEs improves.

Compared to FPUE-2, T_5 and T_{50} of FPUE-6 decrease from 308, 419 ºC to 301, 417 °C, respectively. It indicates that the thermal stability decreases with the increase in the hard segment content, resulting in the formation of biuret and allophanate which have poor stability.

T_{max} of all FPUEs are above 430 °C. FPUEs exhibit good thermal stability.

Mechanical property: Table-5 shows the mechanical properties of FPUEs. From FPUE1 to FPUE6, the modulus increases from 14.97 to 24.95 MPa and the elongation decreases from 847 to 492 %. The general trend is that the tensile modulus increases and the elongation decreases with the hard segment content increasing. From FPUE-1 to FPUE-6, on the one hand, the crosslink and crosslink density increase with the increase in the content of NCO in FPUEs. On the other hand, the hard segments contain polyurethane and polyurea which have strong polarity, hydrogen bonding and dipole interaction of hard segment results in the physical crosslink increase. So the modulus increases and the elongation decreases with the increasing of the hard segment content.

TABLE-5
MECHANICAL PROPERTIES OF FPUEs

Sample	Tensile strength (MPa)	Elongation (%)
FPUE-1	14.97	847
FPUE-2	16.15	768
FPUE-3	17.89	680
FPUE-4	19.83	596
FPUE-5	21.91	524
FPUE-6	24.95	492

Conclusion

TDAP was synthesized from 2-chlorobenzotrifluoride and its structure was confirmed by FTIR, ^{1}H NMR and ^{19}F NMR. Fluorine containing polyurethane elastomers were obtained with two-step bulk polymerization based on TDAP.

FPUEs have a low surface tension from 24.1 mN/m to 30.7 mN/m and a low water absorption from 2.9 to 3.8 %. All of them decrease notably in comparison with those of PUE.

The TGA results reveal that FPUEs have better thermal stability than PUE and the thermal stability decreases with the increase in the hard segment content, which results in the formation of biuret and allophanate with poor stability.

With the content of F increasing from 1.5 to 2.8 % (FPUE-1 to FPUE-5), PHRR and THR decrease from 605.4 w/g and 23.7 kJ/g to 511.0 w/g and 22.4 kJ/g, indicating that the fluorine content increase contributes to improved flame retardant properties.

These properties should make these FPUEs attractive for practical applications.

ACKNOWLEDGEMENTS

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