



Direct fluorination of para-aramid fibers 1: Fluorination reaction process of PPTA fiber



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ABSTRACT

Fluorination reaction process of PPTA fiber is studied in detail by means of X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) spectra. We prove that the reaction of F_2 with the amide groups is easier than that with benzene rings at the low partial pressure of F_2 ($F_p \leq 10$ kPa) due to higher charge density of N atom. With the further increase of F_p , the increase of reaction degree of F_2 with the amide group gradually decreases, which may be due to the decrease of the concentration of amide groups. On the contrary, the reaction of F_2 with benzene rings gradually becomes more favorable when F_p is higher than 10 kPa resulting from the saving high concentration of benzene rings. The results of FTIR prove that the reaction of F_2 with benzene rings is mainly an addition reaction, rather than a substitution reaction. As the value of F_p is lower than 10 kPa, fiber surface morphology is smooth with few grooves. However, more and more lengthwise furrows and grooves are observed on the surface of fluorinated fiber with the further increase of F_p . Moreover, the mechanical properties of fluorinated PPTA fibers almost keep constant at the low F_p ($F_p \leq 10$ kPa). However, when the F_p is higher than 10 kPa, the tensile strength of fluorinated PPTA fibers gradually decreases while the initial modulus and crystallinity have a little change.

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1. Introduction

Fluorinated polymers have a set of unique properties such as chemical stability, thermostability, fire resistance and good barrier properties, etc. [1–6]. However, practical use of specially synthesized fluorine-containing polymers is restricted by their high cost and complexity of synthesis. Direct fluorination is an effective way to obtain fluoropolymers on the surface of polymers. It is a simpler, cheaper and more convenient way to apply a surface treatment of polymers [4,5]. Direct fluorination of polymers is a heterogeneous, exothermic and spontaneous reaction of gaseous F_2 and its mixtures with a polymer surface [6,7]. It is well known that the direct fluorination of hydrogen–carbon based polymers leads to disruption of C–H and C–OH bonds and saturation of conjugated bonds followed by a formation of CF, CF_2 and CF_3 groups [8,9]. These features of the direct fluorination initiate its wide industrial utilization for enhancement of the barrier properties of polymers and gas separation properties of polymer membranes [4,5]. What's

more, adhesion properties of polymers can be significantly improved after direct fluorination.

Para-aramid fibers, including Kevlar, Armos, and Twaron, have been widely used as reinforcement in the fields of space engineering, aviation and military application due to their high strength and modulus [7,10,11]. However, the adhesion between para-aramid fiber and most matrices is poor as a result of the high crystallinity, the inert chemical structure and smooth surface [7,12–15]. In recent years, direct fluorination has been paid more and more attention to resolve the problem of the interfacial adhesion between para-aramid fibers and polymeric matrices [7,12–14,16,17]. Singh and co-workers [15] studied the effect of surface fluorination of poly(*p*-phenylene terephthalamide) fiber. Their results indicated that the polar content of the surface significantly increased after fluorination and the modified fiber become rougher compared to the untreated fiber. Lee et al. [17] investigated the surface modification of aramid fibers by direct fluorination at different temperatures, and the results indicated the phenol resin wettability and the impregnation of the fluorinated aramid fabric improved as the fluorination temperature increased. In our previous paper [7], poly-*p*-phenylene-benzimidazole-terephthalamide fiber was surface modified by direct fluorination under different routes. The results showed

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that the highest interlaminar shear strength (ILSS) value of fluorinated fiber reinforced epoxy resin was 51.0 MPa, which was improved 32.5% compared with that of the virgin fiber (38.5 MPa).

It is well known that fluorine gases show high reactivity and the reactions of polymers with F_2 are difficult to control. In those previous papers, the investigation on direct fluorination of para-aramid fibers was mainly focused on surface chemical elements [7,17], including $-CF$, $-CF_2$, $-CF_3$ and $-COOH$, wettability [12,13,17] and interfacial adhesion between the fabric and the polymer matrix [5,7,12,14,16]. Thus, the fluorination reaction process is still unclear, for example: is F_2 preferentially reacted with the benzene ring or amide group? Is the reaction of F_2 with benzene rings an addition reaction or a substitution reaction?

Poly (*p*-phenylene terephthalamide) is the simplest macromolecular structure of para-aramid, which is composed of benzene rings and amide groups. In this paper, PPTA fiber was chose to study the fluorination reaction process. The PPTA fiber was fluorinated with different F_2/N_2 pressure. With the increase of partial pressure of F_2 (F_p), competing fluorination reaction between benzene rings and amide groups of PPTA is studied in detail. Substitution and addition reaction with F_2 is also discussed. In the end, preliminary fluorination reaction process is proposed. The results can provide theoretical guidance for surface modified of aramid fiber by direct fluorination.

2. Experimental

2.1. Materials

Poly(*p*-phenylene terephthalamide) fibers (Kevlar 29) were supplied by DuPont. The F_2/N_2 (10 vol% for F_2) with purity up to 99.99% was obtained from Chendu Kemeite Fluorine Industry Plastic Co., Ltd.

2.2. Direct fluorination treatment

The PPTA fiber was dried in the drying oven under vacuum to remove physisorbed water (about 6 wt%) trapped in the fiber. 10 g PPTA fibers were fluorinated in closed stainless steel vessels at room temperature for 60 min every time. The fluorinated F_2 gases partial pressure in the fluorination ambience was 2 kPa, 5 kPa, 10 kPa, 20 kPa and 32 kPa, respectively. The fluorinated samples are denoted as Df-2, Df-5, Df-10, Df-20 and Df-32, respectively. The untreated PPTA fiber is denoted as Df-0.

2.3. Characterization

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos ASAM 800 spectrometer (Kratos Analytical Ltd., U.K.), making use of nonmonochromatic Al $K\alpha$ (1486.6 eV) X-ray source (a voltage of 15 kV, a wattage of 250 W) radiation. The vacuum chamber pressure was controlled at a range of 10^{-6} – 10^{-7} Pa. Mechanical properties including the initial modulus, tensile strength and elongation at break of the PPTA fibers were measured on KOL KDIII-5000 with a strain rate of 25 mm/min. The fixture span was 215 mm. Wide angle X-ray diffraction (WAXD) measurements were performed at room temperature in both reflection and transmission goniometry, using a Rigaku vertical diffractometer (Model Ultima IV) with a rotating anode X-ray generator. The Cu $K\alpha$ radiation operated at 40 kV \times 40 mA. The crystallinity (X_c) was calculated with Eq. (2-1) following the peak-fitting [18,19].

$$X_c = \frac{A_c}{A_c + A_a} \times 100\% \quad (2-1)$$

A_c is crystallization peak area; A_a is the amorphous peak area. Attenuated total reflection/Fourier transform infrared spectroscopy (ATR-FTIR) spectra of PPTA fibers were measured at a Nicolet Magna 650 spectroscope in the range 4000–400 cm^{-1} . The frequency scale was internally calibrated with a reference helium–neon laser to an accuracy of 0.2 cm^{-1} . Molecular simulation was determined with Dmol3 software embedded in Material Studio 4.0 (Accelrys, USA) package on the basis of density function theory (DFT).

3. Results and discussion

3.1. Chemical composition analysis

The surface chemical composition of the untreated and fluorinated PPTA fibers was characterized using XPS analysis. The resulting elemental analysis results are shown in Table 1. With the increase of partial pressure of F_2 (F_p), the content of F and F/C atomic ratio gradually increases from 0% to 26.06% and from 0 to 44%, respectively.

The chemical bonds of the untreated and five fluorinated PPTA fibers were investigated via C1s and N1s deconvolution. The results are shown in Fig. 1(a) and (b), respectively. The C1s spectra of untreated PPTA fiber are fitted to four peaks with binding energy near about 284.6 eV, 285.7 eV, 286.7 eV, 288.8 eV, which contribute to C–C, C–N, C=O of amide groups and $-COOH$, respectively [7,20]. The presence of the $-COOH$ groups in the C1s spectrum indicates that a part of the amide groups in the original PPTA fibers has already been hydrolyzed before fluorination treatment. A new peak with binding energy at 289.7 eV is found for Df-2 and Df-5. This peak is corresponded to C–F [7], including C=CF– and $-HCF-$. With the increase of F_p , the fluorinated PPTA fibers show a large decrease in the C–C groups while a large increase in the $-COOH$ and C–F groups. It is well known that the amide bonds of the PPTA would be partially broken and formed $-COF$. And then $-COF$ groups are hydrolyzed to carboxylic acid groups ($-COOH$) during the re-exposure to air atmosphere [21]. Fluorination at a higher F_p introduces more F_2 and C- F_2 groups with binding energy at 291.5 eV is found for Df-10. C- F_3 groups with binding energy at 293.5 eV are observed for Df-32 only. The results of previous paper indicated that benzene rings would be broken, leading to the formation of C- F_3 [22]. Thus, benzene rings of Df-32 have been broken. Moreover, as shown in Table 1, O/C atomic ratio gradually increases from 16.6% to 18.3% and then keeps constant. The formation of carboxylic acid groups ($-COOH$) leads to the increase of O/C atomic ratio. As the F_p is higher than 10 kPa, the broken of amide group and benzene ring may lead to the formation of hyperfluorination, such as CF_4 , C_2F_6 and oxygenated compounds gas, resulting in the unchanged of O/C atomic ratio.

The N1s spectra of the untreated and five fluorinated PPTA fibers are shown in Fig. 1(b). Only one peak at 399.5 eV, corresponding to C–N, is observed for untreated PPTA fiber. A new peak at about 401.4 eV is observed for Df-2 and Df-5, which

Table 1
The XPS surface elemental analysis parameters of the PPTA fibers.

Samples	Atomic percent			Atomic ratio	
	C1s (%)	O1s (%)	F1s (%)	F/C (%)	O/C (%)
Df-0	83.7	13.9	0	0	16.6
Df-2	80.9	14.2	2.70	3.3	17.6
Df-5	79.4	14.2	4.3	5.4	17.7
Df-10	73.5	13.4	10.5	14.3	18.3
Df-20	67.4	12.3	16.9	25.1	18.3
Df-32	59.3	10.9	26.1	44.0	18.3

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