Defence Science Journal, Vol. 64, No. 3, May 2014, pp. 230-235, DOI : 10.14429/dsj.64.7321

Effect of Surface Fluorination of Poly (*p*-Phenylene Terephthalamide) Fiber

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ABSTRACT

Direct fluorination is one of the most important and effective method to modify the polymer surface. It is a simple and fast method that allows the simultaneous treatment of outer and inner surfaces of complex shaped polymeric materials. Poly-p-phenylene terephthalamide fibers which are a very important class of material was surface modified by direct fluorinaton. An extensive characterization of both the virgin and the fluorinated materials were performed by various techniques (XRD, FT-IR, Surface energy and DSC, TGA). From these data, possible effects of fluorination are discussed.

Keywords: Direct fluorination, fiber, FTIR, surface energy

1. INTRODUCTION

Aromatic polyamides were first introduced in a commercial application in the early 1960s, with the meta-aramid fiber, Nomex, by DuPont. This fiber is a highly heat resistant material still used in thermal and electrical insulation and also produced by Teijin under the trade name, Teijinconex, and in Europe by Kermel under the trade name Kermel since the early 1970s. Based on earlier research by Monsanto and Bayer, a fiber with much higher tenacity and elastic modulus was developed also in the 1960s-1970s by DuPont and AKZO Nobel, both profiting from their knowledge of rayon, polyester and nylon processing. Much work was done by Stephanie Kwolek in 1961 while working at DuPont and that company was the first to introduce a para-aramid called Kevlar in 1973. A similar fiber called Twaron with roughly the same chemical structure was introduced by AKZO in 1978. Twaron is currently owned by the Teijin company. Aramids share a high degree of orientation with other fibers such as ultra high molecular weight polyethylene (UHMWPE) fiber. Para-aramid fibers such as Kevlar and Twaron, provide outstanding properties such as high Young's modulus, low creep etc. They are used in many high technology applications[1,2], such as aerospace and military applications, for bullet-proof body armor fabric, ropes, cables, composite material[2-4], sporting goods and as an asbestos substitute. According to the Federal Trade Commission, the definition of aramid fiber is: 'A manufactured fiber in which the fiber-forming substance is a long-chain synthetic polyamide in which at least 85% of the amide linkages, (-CONH-) are attached directly to two aromatic rings'. Poly-p-phenylene terephthalamide is a product of *p*-phenylene diamine and terephtaloyl dichloride. World capacity of para-aramid production was estimated at about 41,000 tons/yr in 2002 and increasing each year by 5-10%[3-4].

Why surface modification is required for poly-*p*-phenylene terephthalamide fiber?

Poly-p-phenylene terephthalamide is a lightweight, super strong synthetic fiber made from aramid polymers. Aramid molecules are characterized by relatively rigid polymer chains, linked by strong hydrogen bonds, which transfer mechanical stress back and forth, rather like a zipper. This permits the use of chains of relatively low molecular weight. Poly-p-phenylene terephthalamide's unique characteristics derive from the ability of the aramid molecules to orient themselves along the line of flow during the spinning process producing the fiber, forming straight strands that resemble uncooked spaghetti. By comparison, the much weaker fibers made from polymers such as nylon and polyester resembles the tangled mass that cooked spaghetti becomes. Poly-p-phenylene terephthalamide fiber exhibits an excellent thermal stability, as well as superior tensile strength and modulus[5]. And owing to its high tenacity, this fiber is widely used in manufacture of advanced composites. It is well known that the mechanical properties of fiber reinforced composites depend on the effectiveness of the interactions between the fiber and the matrix; however, the adhesion between poly-*p*-phenylene terephthalamide fiber and most matrices is poor as a result of the high crystallinity resulting in a chemical inertness and smooth surface of the fiber[6]. Therefore, to use poly-*p*-phenylene terephthalamide fiber as reinforcement, surface modification is essential to enhance its reinforcing effect. Extensive studies have been performed on this matter[7]. Enzymatic technology[8] was used recently to modify the fiber surface. The application

Received 29 April 2014, revised 8 May 2014, online published 20 May 2014

of enzymes to modify the surface of natural polymer, such as wool has been widely researched by industry[9]. Park[10], *et al.* reported that the chemical treatment of Kevlar surface by phosphoric acid significantly affected the degree of adhesion at interfaces between Kevlar fibers and epoxy resin matrix. Yue and Padmanabhan[11] improved the interfacial shear strength of Kevlar fiber/epoxy composites significantly through chemical treatment of the fiber with organic solvents. Saikrasun et al. used the hydrolysis techniques to modify the Kevlar surface[12]. Vaughan et al. studied the incorporation of coupling agents[13] while Takayanagi et al. reported the use of ionomer matrix[14]. Modification of the fiber surface by chemical treatment[15,16], and plasma treatment[16] was studied. Garbassi[18], *et al.* reported the hydrolysis techniques (one of chemical treatment techniques), allowing simple and easy modification of Kevlar surface.

Direct modification of polymer surfaces with fluorine[19] is particularly attractive since it is a simple and fast method that allows the simultaneous treatment of outer and inner surfaces of complex shaped polymer samples. The strong exothermal process can be controlled by lowering pressure (typically in the mbar range) and adjusting fluorine concentration (several vol. % of F_2 in N_2 or He). The fluorination induces large (about a factor of 2) and stable increases in the surface energy of most polymers including polyamides[20-23].

In this work, we performed surface modification of poly-*p*-phenylene terephthalamide fibers by direct fluorinaton using elemental fluorine and characterization of fluorinated and non-fluorinated poly-*p*-phenylene terephthalamide fibers was undertaken.

2. EXPERIMENTAL DETAILS

2.1 Materials Used

The fiber i.e. poly (p-phenylene terephthalamide), [grade 1055, 1610 dTex, diameter 12 µm, density 1.44 g/cc, manufactured by AKZO Netherlands] was used in this experiment. Fluorine gas supplied by Air Products and Chemicals Ltd., contains 20% F_2 and 80% He. He gas was supplied by Air Products and Chemicals. Nitrogen (XL grade) was supplied by BOC. The Chemicals used in this study were, Benzoyl peroxide (Merck), Maleic anhydride (Merck), Sodium fluoride (Merck), EDTA (Merck), Ammonium ceric nitrate (Loba Chemie), Eriochrome black T (Ranbaxy Lab. Ltd.), Calcium carbonate.

2.2 Fluorination of Poly (P-Phenylene Terephthalamide) Fiber and Prepared Composites

Surface fluorination of poly(p-phenylene terephthalamide) fiber was done in our laboratory (IIT, Kharagpur). The F_2-He mixture was introduced in to the vessels in which fibers were placed. Fluorination of the fiber was done by treating with (2% F_2 + 98% He) mixture in closed vessels at total mixture pressure of 95.59 kPa at temperature of 25 °C for 2 h. The gas mixture was diluted with He in a chamber before it entered into the reaction chamber.

2.3 Morphology by Scanning Electron Microscopy

In this investigation, the fibers were gold coated and the morphology visualized using a JEOL JSM-5800 Scanning Electron Microscope (SEM).

2.4 IR Spectroscopic Analysis

For structural analysis, IR study of the fibers was undertaken using a Thermo Nicolet NEXUS 870 FTIR spectrophotometer. The IR-spectrum was taken in the frequency range of 4000-500 cm^{-1}.

2.5 XRD Study

The XRD patterns of the fibers and composites were obtained using a PANalytical-X'Pert PRO-PW: 3040/60 X-ray diffractometer using CuKα radiation having wavelength 1.5418 Å at an operating voltage of 40 kV and 30 mA current. The samples were always kept in a holder and scanned in the 2θ range of 0 to 60° to cover most of the peaks. Step size of the scan was 0.05°.

2.6 Contact Angle Measurement

Contact angle measurement of the fibers was done by using dynamic contact angle measuring instrument (Model No. DCAT II) at 24.5 °C temperature.

2.7 Thermal Study

Thermal analysis was carried out using DSC Model No. 200PC NETZSCH, Pyris Diamond TG/DTA (Perkin-Elmer Instrument, Technology by SII).

2.8 Determination of Fluorine Percentage of the Fiber after Surface Fluorination

4-6 mg of fluorinated poly(p-phenylene terephthalamide) fiber was taken into an L-shaped piece of Whatman No. 40 filter paper. The packet was folded and placed in the platinum basket of the combustion flask. The absorption solution, which contains of 5ml water, 15 ml of cerium (III) nitrate solution and 5 ml of 10% glycerol solution, was placed in the combustion flask and then the flask was filled with pure oxygen. After ignition, the flask was allowed to cool for 10 min and then the flask was shaken vigorously for complete absorption of the combustion products. Then the flask was opened, and the stopper assembly rinsed with a little water, 20 ml of ethanol was added. Then 3 drops of 0.2% xylenol orange solution and 2 drops of 0.1% methylene blue solution followed by 75 mg of hexamethylenetetramine were added to develop a violet color for the indicator and the pH was maintained in the range 5.5-6.5. This was further titrated with 0.002 M EDTA to a sharp color change to green at the end point (V_1 ml). A blank (V_2 ml) experiment was run in the same way.

The percentage of fluorine in the sample was calculated by using the following equation:

$$\% F = \frac{(V_2 - V_1)M}{W} \times 5700$$

where M is the molarity of the EDTA and W is the weight of sample in mg. V_2 is the volume of EDTA solution with the fluorinated sample V_1 is the volume of EDTA solution for blank titration (without fluorinated sample). The above procedure was repeated for five times and the average percentage of fluorine determined from this experiment was almost five percent.

3. RESULTS AND DISCUSSION

3.1 Morphology by Scanning Electron Microscopy

Figure 1 shows SEM photographs of poly(p-phenylene terephthalamide) fibers with and without surface treatment by elemental fluorine. It can be seen that surface treatment by direct fluorination does lead to a significant change in surface morphology. Also, the photographs in Fig. 1 illustrate how the roughening of the fiber surface occurs in the case of modified fiber. This is probably due to the results of fluorine attack on fibers and changes the nature of bonds. Hence, there are local distributions in the morphology of surface (changing from crystalline to amorphous in nano and micro regions) with consequent roughing of the surface.

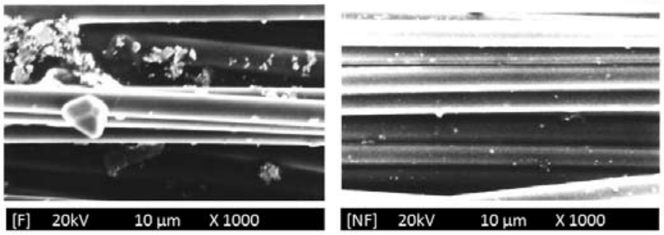

Figure 1. SEM image of the fibers, before [NF] and after [F] fluorination.

3.2 Infrared (IR) Spectroscopy

FTIR spectroscopy was also used to observe the effect of fluorination on the fiber surfaces. The FTIR transmittance spectra of the fibers before and after fluorination are shown in Fig. 2. The strong band at 3310 cm^{-1} is the N-H stretching vibration. The band at 3038 cm^{-1} is due to C-H stretching of the aromatic compound. The bands at 1650-1651 cm^{-1} and 1538-1539 cm^{-1} are the so-called ν(C=O) and ν(C-N) stretching frequency of amide bands. The amide band consists mostly of the ν(C=O) and ν(C-N) stretches, and it also involves contributions of the ν (N-H) bending vibration. The series of bands below 1500 cm^{-1} concern -C-H (1400 cm^{-1}), -CH (1388 cm^{-1}), and ν(C-N) (1110 cm^{-1}) modes. The band at 723 cm^{-1} is the –C-H rocking vibration of aromatic ring. Some important changes occur in the infrared spectra of the fiber after fluorination. The frequency appearing at 1014 cm^{-1} is a characteristic frequency of the C-F bond. The C-F stretching frequency is absent in case of non-fluorinated fiber. All other peak values remain almost at the nearly same position in both the cases. We also observed from FTIR analysis that the intensities of the treated fiber improved significantly compared to the spectrum of the virgin fiber, which suggest that the fluorine has been introduced onto the polymer surface.

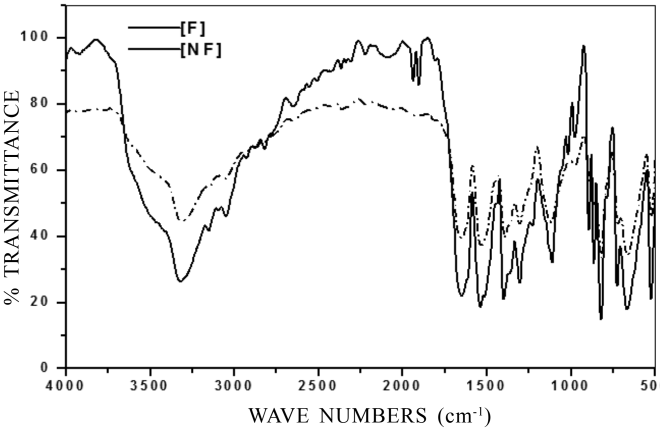

Figure 2. IR spectra of the fibers, before [NF] and after [F] fluorination.

3.3 Crystallinity from X-ray Diffraction (XRD)

The X-Ray diffraction plot is given in Fig. 3. From XRD analysis the percentage of crystallinity was calculated. The crystallinity decreased although very small from 77% to 76% after fluorination. From the crystallinity data, it is seen that the percentage of crystallinity becomes slightly lower (although not very significantly) for fluorinated fiber than the non fluorinated fiber. The decrease in crystallinity after fluorination may be due to the disturbance of the regular structure. The crystallinity decrease after fluorination is also confirmed from DSC analysis (see Table 1). From DSC (Fig. 4) analysis, it is seen that enthalpy of fusion (ΔH_m) has decreased after fluorination, which is directly proportional to the crystallinity. From DSC thermogram, it is also observed that the crystalline melting peak shifts from 582 °C to 584 °C after fluorination.

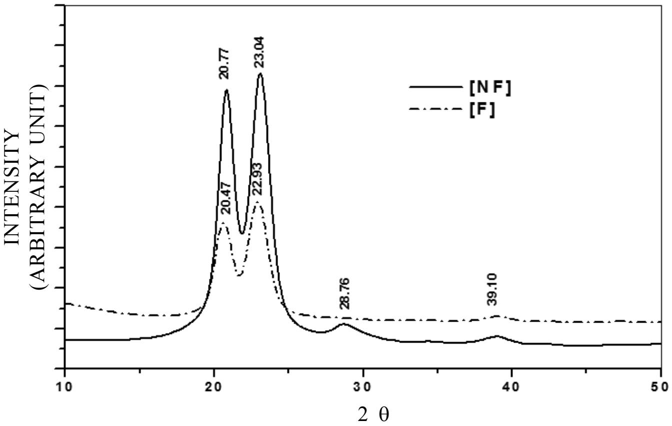

Figure 3. XRD plot of the fibers, before [NF] and after [F] fluorination.

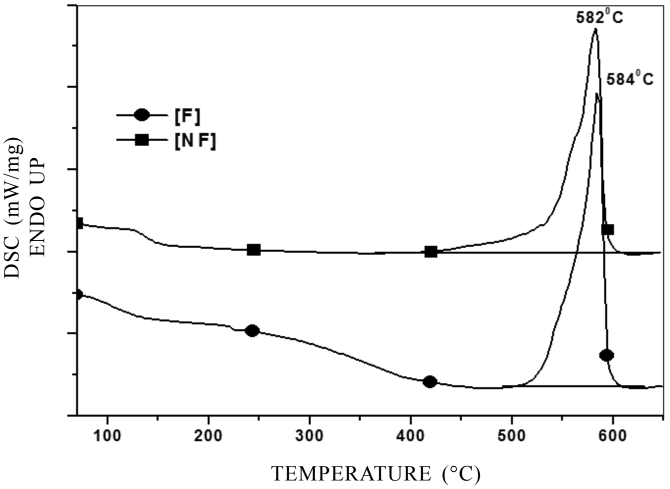

Figure 4. DSC heating thermogram of the fibers, before [NF] and after [F] fluorination.

Table 1. Melting temperature (T_m) and enthalpy of fusion (ΔH_m) obtained from DSC analysis

Sample name	ΔH_m (J/g)	T_m (°C)
[NF]	501	582
[F]	489	584

3.5 Thermogravimetic Analysis

Thermal stability of the fibers was evaluated by TGA technique. The plot of TG vs. temperature is shown in Fig. 5. From this figure, it can be observed that in case of the fluorinated fiber no significant weight loss occurred up to 470 °C but in case of non fluorinated fiber there is a significant weight loss starting from above 200 °C. This could be attributed to the fact that the energy required to break the C-F bond is very high compared with C-H bond. Thus, the fluorinated fiber is more thermally stable than the non-fluorinated fiber.

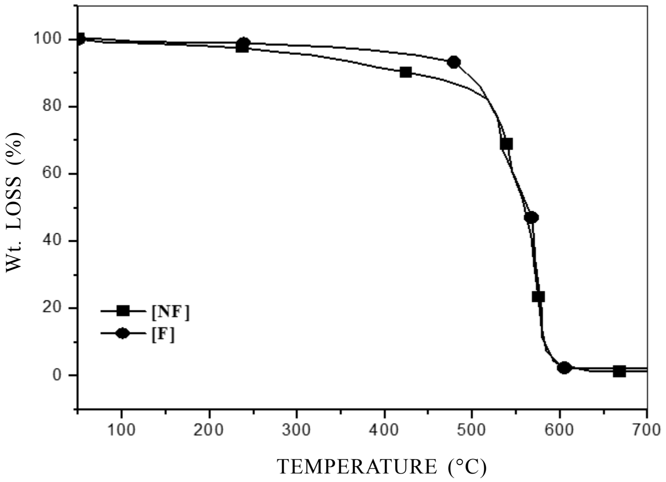

Figure 5. TG plot of the fiber, before [NF] and after [F] fluorination.

3.4 Contact Angle Measurement and Determination of Surface Energy by Geometric-mean Equation

The contact angle is defined as the angle between the solid surface and a tangent, drawn on the drop surface, passing through the triple-point air-liquid-solid. Surface tension (surface free energy) of the prepared sample was determined by contact angle measurements at 24.5 °C temperature using dynamic contact angle measuring instrument (Model No. DCAT II). Ten measurements of contact angle were taken on each sample to minimize the experimental error. Accuracy of contact angle determination is ± 0.1°. The surface tension (γ) of the materials was obtained from a combination of the dispersive (γ_s^d) and non-dispersive (γ_s^{nd}) components of the surface tension i.e. $\gamma = \gamma_s^d + \gamma_s^{nd}$

Although the surface energy cannot be measured directly, various indirect methods have been proposed in the literature. In this work, the geometric-mean[24,25] approximations were used to get the dispersive and the non-dispersive contributions to the total surface energy, as shown below.

The geometric-mean equations were employed to calculate the surface energy of the base, modified and the unmodified fiber. This approximation was proposed first by Girifalco and Good[25] and later modified by Owens and Wendt[24]. According to Owens and Wendt, the surface energy of a given solid can be determined by using the following equation applied to two liquids:

$$(1+\cos\theta)\gamma_l = 2(\gamma_s^d\,\gamma_l^d)^{1/2} + 2(\gamma_s^{nd}\gamma_l^{nd})^{1/2} \qquad (1)$$

where γ_s and γ_l are the surface free energies of the solid and pure liquid, respectively. The superscripts 'd' and 'nd' correspond to dispersive and non-dispersive contributions to the total surface energy, respectively. The contact angle, θ, obtained by the following equation as proposed by Uragami[26] et al., is used in Eq. (1):

$$\theta = \frac{\cos^{-1}(\cos\theta_a + \cos\theta_r)}{2} \qquad (2)$$

where, θ_a and θ_r are the advancing contact angle and the receding contact angle, respectively. By measuring the contact angles of two liquids on the surface, two simultaneous equations are obtained for Eq. (1), which can be easily solved for γ_s^d and γ_s^{nd}. Consequently, by assuming the linear additivity of the intermolecular forces (i.e. dispersive and non-dispersive forces), the sum of the two components, γ_s^d and γ_s^{nd}, provides an estimated value of the total surface free energy, γ_s. Owens and Wendt[5] employed water and methylene iodide as test liquids.

The single liquid method using distilled water (surface tension (γ_l) = 72.75 mN/m, γ_l^d = 21.80, γ_l^{nd} = 51.0) and N,N-dimethylformamide (surface tension (γ_l) = 37.30 mN/m, γ_l^d = 32.40, γ_l^{nd} = 4.90) as reference liquids was employed. Table 2 shows the results of surface energy measurement. Compatibility between polymers is very much dependent on the interaction parameter which is also related with surface energy[27]. The contact angle decreased greatly after modification, suggesting that the wettability of the treated fiber increased significantly.

Table 2. Surface energy of the non-fluorinated [NF] and fluorinated fiber obtained from contact angle measurement

Sample name	Contact angle (degree)		γ_s^d (mJ/m²)	γ_s^{nd} (mJ/m²)	γ_{Total} (mJ/m²)
	θ_{water}	θ_{DMF}			
NF	71.9	65.9	7.4	24.0	31
F	56.3	49.2	9.9	34.4	44

4. CONCLUSIONS

In this study, the effect of surface fluorination of poly (p-phenylene terephthalamide) fiber was investigated. Various analyses were performed for both fluorinated and non fluorinated fiber to characterize the chemical nature. FTIR spectroscopy indicates that the fiber gets fluorinated which is also confirmed from titrimetric methods. The crystallinity decreases slightly in case of fluorinated fiber. After fluorination, the smooth surface of the fiber becomes very rough. Characterization of the fiber found that the polar content of the surface increased significantly and the modified fiber become rougher compared to the untreated fiber, and thus is expected to improve the adhesion of fiber to other polymers. Surface fluorination also increased the thermal stability and surface energy.

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