Surface Energy Analysis of Polyester Fibers Modified by Graft Fluorination

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ABSTRACT: The modification of the PET fiber surface to render a higher degree of hydrophobicity by graft fluorination involves a surface layer of only a few nanometers thickness. The relatively low fraction of the modified surface layer presents difficulties in surface analysis. However, surface free energy characterization is of high importance in the evaluation of the degree of water repellency. This article will discuss the advantages of using wettability studies according to the Wilhelmy method to evaluate the degree of surface graft modification and its effects on the wetting properties. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 10–15, 2000

Key words: polyester fibers; grafting; fluorination; surface energy; wettability

INTRODUCTION

Fluorination of polyester fibers is of fundamental importance in oil resistance, water repellency, adsorption, adhesion, and composite materials. In our previous article, we studied the graft reaction of the polyester fibers with the perfluorooctyl-2 ethanol acrylic monomer (AC8) (C_8F_{17}—C_2H_4—O—CO—CH=CH_2)[1] from a kinetic overview. The surface of the grafted fibers was characterized by using the roughness analysis as determined by the atomic force microscopy measurements. In this article, we try to analyze the effects of the graft fluorination on the surface energy of fibers.

The free surface energy of the fibers is the main characteristic because it determines the potential level of physics interactions that the fibers are able to exchange, in particular, with others fibers. In fact, the knowledge of this parameter is necessary to understand and forecast many surface and interface phenomenon, such as, for example, the absorption, the wettability, the adhesion, and the friction.

Concerning the resistance of textile materials to the water and other liquids, we can say that the interactions of the macromolecules on the surface fiber with the water play a deciding role. Consequently, the exact determination of the surface energy is of special interest.

The absence of mobility of the macromolecules does not allow, as for a liquid, the direct determination of its surface energy, and it is necessary to study the interactions between the fiber and different liquids, in particular, by measuring the contact angles, fibers–liquids.[2]

METHOD OF SURFACE ENERGY MEASUREMENTS

There is no direct method of measuring the surface energy of the fiber (γ_s); thus, many indirect methods to estimate γ_s were proposed in the literature.[2–4]

The reversible work of adhesion between the liquid and the fiber (W_{sl}) is given by the modified Young's equation,[2]

$$W_{sl} = \gamma_l (1 + \cos \theta) \qquad (1)$$

where γ_l is the surface tension of the liquid, and θ is the contact angle, liquid–fiber.

Fowkes[2,5] showed that both the interfacial work of adhesion and the free surface energy can be decomposed into the nondispersive and dispersive component,

$$W_{sl} = W_{sl}^{nd} + W_{sl}^{d} \qquad (2)$$

$$\gamma = \gamma^{nd} + \gamma^{d} \qquad (3)$$

Fowkes showed that the dispersive attraction can be calculated as the geometric mean of the dispersion forces

$$W_{sl}^{d} = 2(\gamma_s^d \gamma_l^d)^{1/2} \qquad (4)$$

Furthermore, Owens et al.[2,4] developed a fruitful approach of the Fowkes theory by assuming that the nondispersive interactions could be described by a geometric mean expression of the polar components of the solid (γ_s^p) and the liquid (γ_l^p).

$$W_{sl}^{nd} = 2(\gamma_s^p \gamma_l^p)^{1/2} \qquad (5)$$

By using eqs. (1–5), the work of adhesion between a liquid and a solid can be described by:

$$W_{sl} = \gamma_l (1 + \cos \theta) = 2(\gamma_l^d \gamma_s^d)^{1/2} + 2(\gamma_l^p \gamma_s^p)^{1/2} \quad (6)$$

The introduction of $A^2 = \gamma^d$ and $B^2 = \gamma^p$ and rearrangement of eq. (5) give

$$\frac{\gamma_l (1 + \cos \theta)}{2 A_l} = A_s + B_s \left(\frac{B_l}{A_l} \right) \qquad (7)$$

Values of A_l and B_l are well known for several liquids. By using eq. (7) and measuring the contact angle for different liquids, we can determine graphically A_s and B_s (so γ_s^d and γ_s^p).

Surface energies of the grafted polyester fibers (with a different percent of grafting) were estimated according to this method (Fig. 1).

EXPERIMENTAL

Materials

Grafted polyester fibers with AC8 used in this study were prepared by using benzoyl peroxide as initiator. The procedure of the graft reaction and the mechanism were treated in our last article.[1]

Contact Angle Measurement

Many indirect methods were used by investigators to determine the contact angle on the thin fiber.[6–8] Techniques to measure contact angle are based on two methodologies, the first one static and the other dynamic.

In this work, we used the dynamic method[9] in which the wetting force (F) at the solid/liquid/vapor interface is automatically recorded via a Cahn electrobalance as a function of time and immersion depth.

Although the solid sample (typically a flat plate or single fiber) is held in a fixed position by the electrobalance, the wetting liquid contained in a beaker scans along the solid at a constant speed via a computer-controlled stage. The meniscus formed at the interface is characterized by theta (θ), the dynamic contact angle.

Contact angles are measured in two directions. In one direction, as the stage moves up, the liquid advances across the solid surface, advancing the contact angle θ_a, and in the opposite direction, as the stage moves down, the liquid recedes across the previously wetted surface, retreating contact angle θ_r.

The difference between these two extreme contact angles is known as contact angle hysteresis ($H = \theta_a - \theta_r$) and is a universal property of any surface because of the topographic or chemical heterogeneity.

Calculation from the Wilhelmy technique is derived directly from the Young equation described above . A simple equation relates the cosine of the contact angle to the magnitude of the wetting force recorded by the balance (F), the surface tension of the probe liquid (γ_l), and the wetted perimeter of the fiber (p) sample by the following equation:

$$F = p \gamma_l \cos \theta \qquad (8)$$

On immersion in the liquid, the wetting force will be partly balanced by the buoyancy force, but in the case of fine textile fibers, the buoyancy force will be less important than the general experimental noise level.

Experimental Conditions

To eliminate fiber resistance to immersion caused by buoyancy of the fine poly(ethylene terephthal-
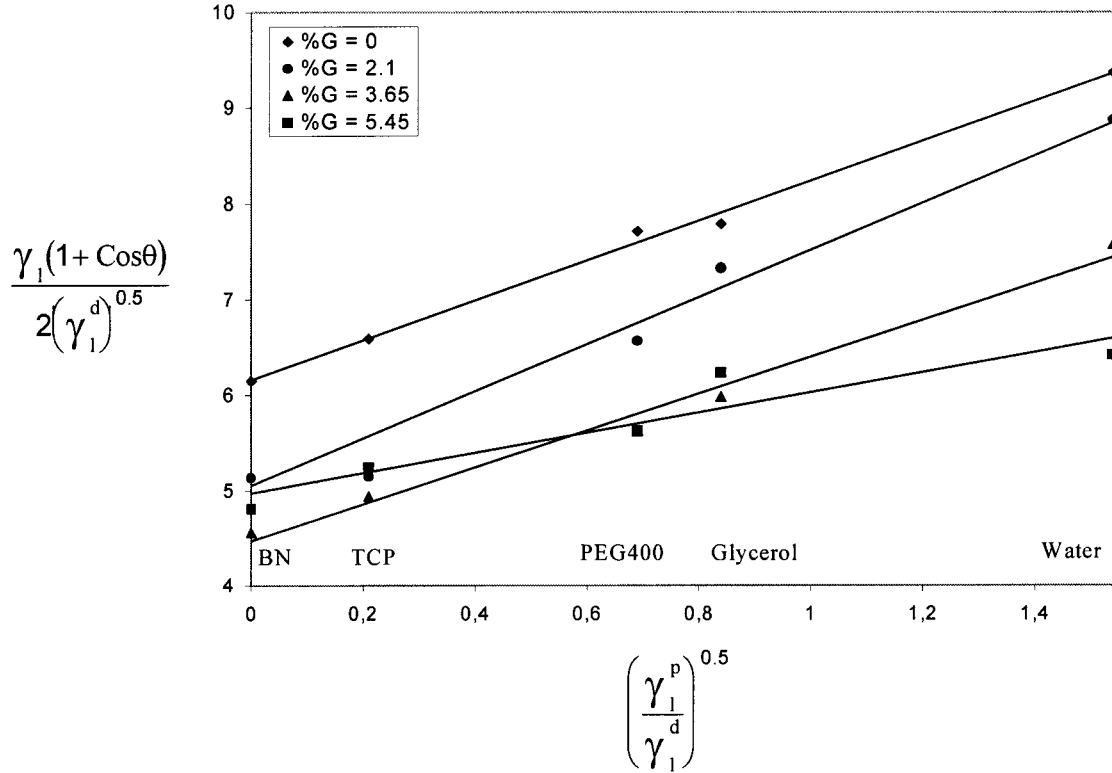
Figure 1 Plots of $\gamma_l(1 + \cos\theta)/2(\gamma_l^d)^{0.5}$ versus $(\gamma_l^p/\gamma_l^d)^{0.5}$ for fibers grafted with AC8 and original fibers. Linear regression analysis lead to the following equations: $y = 2.079x + 6.157$ ($R^2 = 0.996$) for $\%G = 0$; $y = 2.593x + 4.909$ ($R^2 = 0.978$) for $\%G = 2.1$; $y = 1.927x + 4.467$ ($R^2 = 0.986$) for $\%G = 3.65$; $y = 1.051x + 4.972$ ($R^2 = 0.886$) for $\%G = 5.45$.

ate) (PET) monofilament, a short length (5–6 mm) of PET fiber studied was cut with a tweezers. It adhered to the end of a small handmade copper-wire hook. The fiber/hook was suspended on the arm of the microbalance. A beaker of probe liquid was moved up or down at 12.6 μm/s.

As soon as the fiber tip touched the liquid, the microbalance would detect a change in force due to the wetting of the fiber by the liquid. The result of each scan of the fiber immersion in the probe liquid is plotted as a trace of the weight in milligrams versus the height of immersion or the distance (Fig. 3). The reference liquids used in our study were water, glycerol, polyethylene glycol (PEG 400), tricresylphosphate (TCP), and 1-bromonaphtalen. Their surface tension components are listed in Table I.

RESULTS AND DISCUSSION

The variation of the surface energy of modified fibers in relation to the grafting percent is determined by measuring the advancing fiber/liquid contact angles and by using eq. (7). Figure 2 shows the variation of γ_s^d, γ_s^p, and γ_s^t via the

Table I Surface Tensions of Reference Liquids Measured at 20°C

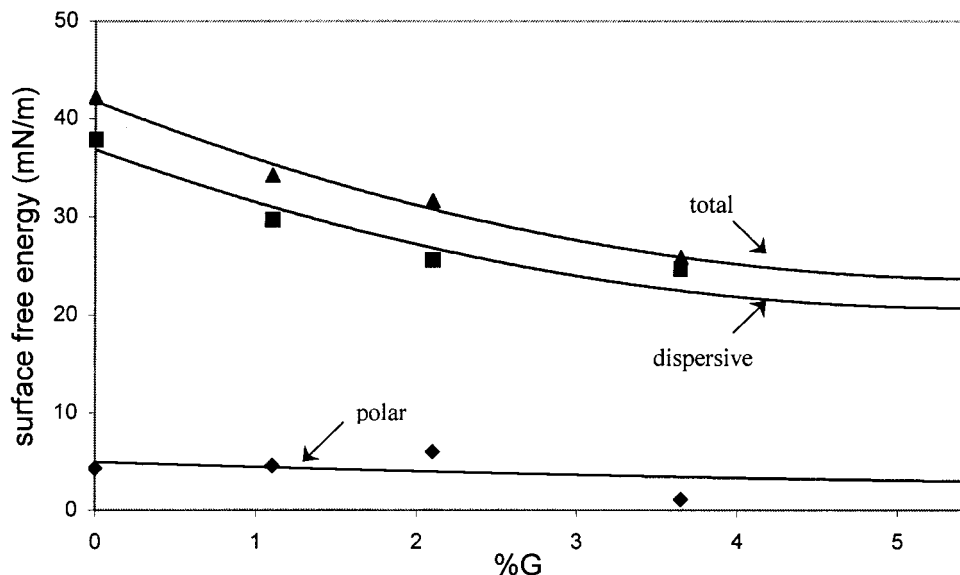|	Bromonaphtalen	TCP	PEG 400	Glycerol	Water
γ_l^t(mN/m)	44.6	40.9	44.5	63.4	72.6
γ_l^d(mN/m)	44.6	39.2	30.0	37.0	21.6
γ_l^p(mN/m)	0	1.7	14.5	26.4	51.0

Figure 2 Variations in surface free energies of polyester fibers versus the percent grafting.

percent of grafting. The variation decreases with the increase of the percent grafting. The dispersive component γ_s^d decreases remarkably from 37.9 ($\%G = 0$) to 19.9 mN/m for $\%G = 5.45$. However, the polar components are approximately similar; this can be explained by the fact that the polymer grafted on the fiber presents a very small polar component of the surface free energy (0.96 mN/m). The total surface free energy γ_s^t reaches a plateau value of 23.6 mN/m at $\%G = 5.45$.

Contact angle data are shown in Table II. The values of θ listed were calculated from eq. (8) and represent the average of measurements made on each type of fiber with the indicated liquid. In general, contact angles decrease with the decrease of the surface tension liquids. It was anticipated that the contact angle measured with a polar liquid would be high for a relatively hydrophobic surface due to bad wetting and vice versa.

Variations of the fiber/water contact angles with the increase of the percent grafting show that a hydrophobic fiber surface is reached at a grafting yield of 3.65% (contact angle > 90°).

On the other hand, for a qualitative analysis of the contact angle hysteresis ($H = \theta_a - \theta_r$), we use the typical trace of the wetting force as a function of the immersion depth (Fig. 3). The variation of the wetting force is extremely sensitive to the surface characteristics, because it reflects the effect of functional groups in a surface layer < 10 Å thick and in direct contact with the liquid phase. The wetting cycle (2) in Figure 3 ($\%G = 5.45$) shows a very fluctuating trace at both advancing and receding processes; as a consequence, exceptional peaks are observed with a

Table II   Contact Angles in Degree of Various Liquids on Grafted PET Fibers

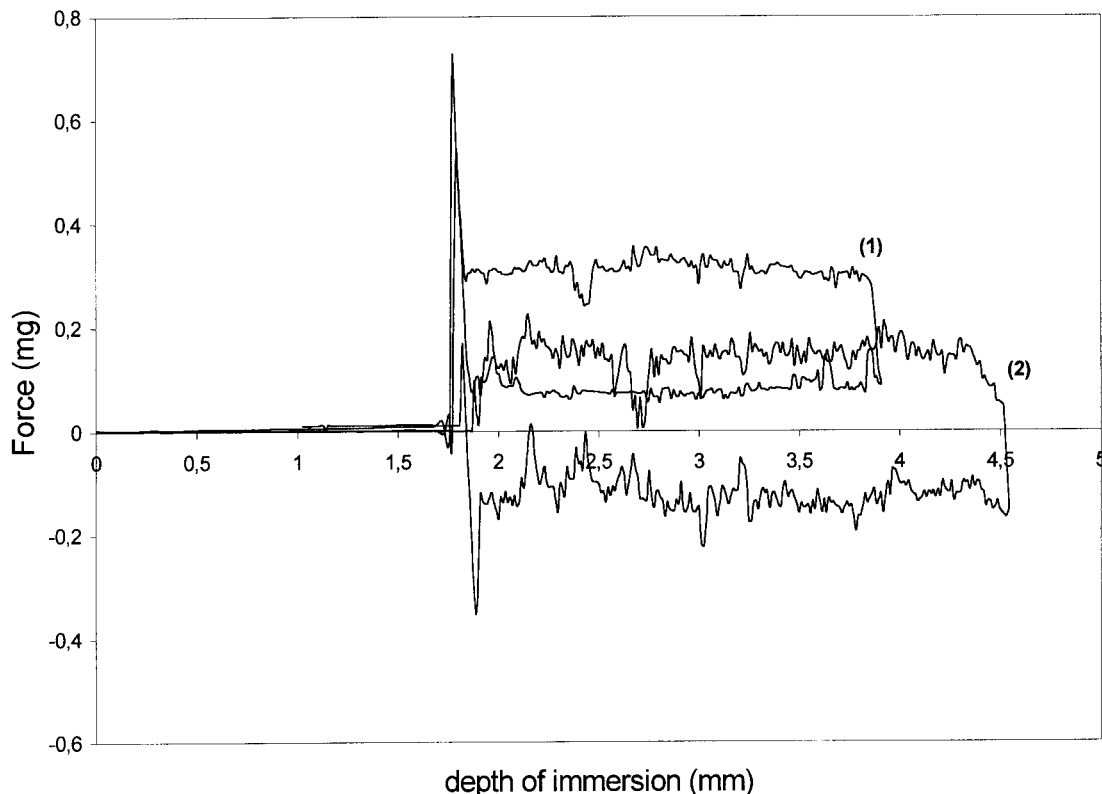| Liquid	%G				Polymer PAC8
	0	2.1	3.65	5.45	
Water	79 ± 2	83 ± 4	92 ± 4	101 ± 5	119 ± 4
Glycerol	60 ± 3	66 ± 3	81 ± 1	79 ± 4	—
Bromonaphtalen	33 ± 5	57 ± 4	69 ± 2	64 ± 6	—
Polyethylene glycol	26 ± 3	52 ± 4	68 ± 3	67 ± 4	—
Tricresylphosphate	0	55 ± 6	60 ± 4	53 ± 8	—

Figure 3 Wetting cycles of PET fibers in water as obtained by Wilhelmy microbalance. (1) %G = 0, (2) %G = 5.45.

high difference in the wetting force values (cycle 2). Because the original fiber presents a relatively normal wetting cycle (1), we can suggest that obvious fluctuations at the treated fiber are due to the fluorinated macromolecules grafted on the surface. By observing these exceptional areas at the surface of the treated fiber, we can assume that we have a heterogeneous distribution of fluorinated macromolecules on the fiber surface that causes a local change in the surface tension.

Previous researchers have studied the several possible causes of hysteresis.[5,10] The most commonly cited are chemical nature[11,12] and roughness of the surface. It is shown that hysteresis increases with increasing roughness.[13] Later, Yasuda et al.[14] show another cause of contact angle hysteresis, the mobility and the reorientation of the grafted macromolecules on the fiber surface.

In our last article,[1] we have studied the roughness of grafted fibers by the atomic force microscopy and concluded that untreated PET fiber presents a rougher surface than the grafted fiber.

In our case, the grafted fiber presents an important hysteresis with enormous fluctuations of the wetting force; this can be explained by the important contribution of the surface chemical nature (fluorinated surface) and probably by the amount and the mobility of grafted fluorine macromolecules. However, in the original fiber, the main cause of the hysteresis is the roughness factor.

CONCLUSION

The performed investigations show that wettability studies according to the Wilhelmy method can give qualitative and quantitative indications about the degree of water repellency and of the surface free energy distribution in a graft-modified surface. The variability in wetting force, the calculated averages of the advancing and receding forces, and the hysteresis between these values provide information on the surface heterogeneities and on the extent of the graft yield on the fiber surface.

REFERENCES

1. Louati, M.; El Achari, A.; Ghenaim, A.; Caze, C. Text Res J to appear.
2. Schultz, J.; Carre, A.; Simon, H. Double liaison-Chimie des peintures, 1982, 322, Jul/Aug, 263/9–14/268.
3. Martin-Martinez, J. M., Fernandez-Garcia, J. C., and Orgiles-Barcelo, A. C., in Contact Angle, Wettability and Adhesion; Mittal, K. L., Ed.; 1993; pp 397–419.
4. Gillberg, G.; Kemp, D. J Appl Polym Sci 1981, 26, 2023–2051.
5. Good, R. J. in Contact Angle, Wettability and Adhesion; Mittal, K. L., Ed.; VSPBV: The Netherlands, 1993; pp 3–36.
6. Adamson, A. W. in Physical Chemistry of Surfaces, 5th ed.; Wiley: New York, 1990; Chapter X.5, pp 389–402.
7. Adamson, A. W. in Physical Chemistry of Surfaces, 5th ed.; Wiley: New York, 1990; Chapter II.8, pp 25–28.
8. Brendan, J. C. Contact Angle, Wettability and Adhesion; Mittal, K. L., Ed.; 1993; pp 235–246.
9. Domingue, J. Spectroscopy/Process Analytical Chemistry Am Lab 1990; 22(15), 50, 52, 54–55.
10. Vergelati, C.; Perwuelz, A.; Vovelle, L.; Romero, M. A.; Holl, Y. Polymer 1994, 25, 262–269.
11. Johnson, R. E., Jr.; Dettre, R. H. J Phys Chem 1964, 68, 7, 1744–1750.
12. Johnson, R. E., Jr.; Dettre, R. H. J Phys Chem 1965, 69, 5, 1507–1515.
13. Johnson, R. E., Jr.; Dettre, R. H. Adv Chem Ser, Ed Am Chem Soc 1964, 43, 136–144.
14. Yasuda, H.; Sharma, A. K.; Yasuda, T. J Polym Sci: Polym Phys Ed 1981, 19, 1285–1291.