

The Evaluation of the Surface Characteristic of the PET Film and Fabric Treated with PEG–Diamine

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Synopsis

PET film treated with PEG–diamine at 130°C was investigated for the aminolysis reaction and the pseudografted PEG content was measured with FTNMR. The hydrophilic properties of the PET film and fabric treated with PEG–diamine were estimated by their surface free energies, water-wicking time, oily soil releasing, and static electricity. Results obtained indicated that the PEG unit was pseudografted to the PET chain end as a result of the aminolysis reaction of the ester bond of PET by the primary amine radical of PEG–diamine. The pseudografted PET content increased with the aminolysis time [PEG wt % = $2.1147 \times t \text{ (h)}^{0.4593}$]. γ_S^P increased very much, γ_S^d decreased a little, and consequently γ_S , I_{SW}^d , and the work of adhesion of water W_a increased with the increasing PEG content. γ_{FW} decreased very much, γ_{FO} increased a little, and consequently the difference between adhesion tensions of oily soil and water to the specimen ($A_{FO} - A_{FW}$) increased as the PEG content increased. The contact angle of oily soil to the specimen θ_O immersed in water increased and consequently θ_W and $W_{FO/W}$ decreased. Therefore, the PET fabric treated with PEG–diamine had very good water-wicking, oily soil releasing, and antistatic properties.

INTRODUCTION

It is well known that the PEG-containing or PEG derivative-blending polymer product, and the hydrophobic polymer film or fiber chemically after-treated with PEG derivatives have very good water-wicking, sweat absorbing, soil releasing, and antistatic properties. Therefore, PEG derivatives have been and are still being used to improve the hydrophilicity and antistaticity of the synthetic hydrophobic polymer.^{1–4} However, to the authors' knowledge, no report has been yet made concerning the investigation of the principal mechanism with which PEG derivatives can enhance the hydrophilic and antistatic properties of the hydrophobic polymer.

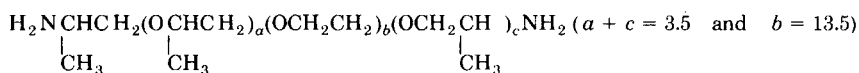
In this report, the authors elucidated the mechanism with which PEG derivatives make the hydrophobic polymer hydrophilic by means of the evaluation of the surface free energy of the PET-*b*-PEG film obtained when the PET film was aminolyzed with PEG–diamine at 130°C.

EXPERIMENTAL

Material

The biaxially drawn PET film, whose thickness and intrinsic viscosity are 24 μm and 0.8988, respectively, was used. It was kindly supplied from Sun

Kyung Co., Ltd. PEG diamine (Jeffamine ED-600), kindly supplied from Texaco Chem. Co, was used as the aminolysis reagent of PET. Its chemical structure is as follows:



Other reagents of extraordinarily pure grade were used without further purification.

Aminolysis Reaction

The PET film was aminolyzed in the PEG–diamine bulk solution at 130°C for different lengths of treating time. The sample code for the aminolyzed PET was expressed as $J - t$, where t means aminolysis time (h).

NMR Measurement

The proton NMR spectra were obtained with 80 MHz FTNMR spectrometer (Model FT-80A, Varian) using trifluoroacetic acid- d_1 as a solvent. The number of scans ranged from 20 to 200.

Contact Angle Measurement

Contact angles were measured by a goniometer-telescope type contact anglemeter (Model G-1, Erma Co., Japan) at 20°C using the two-liquid method.⁵ The specimen surfaces were cleaned with ether and dried *in vacuo* at 20°C. Saturated hydrocarbons for the two-liquid method were cyclohexane and isooctane saturated with water.

Wicking Time Measurement

This was measured by allowing a drop of water to fall on the sample and the time needed for this drop to disappear was then measured.

Frictional Electrostaticity Measurement

This was measured on the rotary static tester under 43% RH at 20°C.

Half-Decaying Time Measurement

This was measured on the static honestometer (Shishido and Co., Ltd.). The initially applied voltage was 10 kV.

Soiling and Soil Removal Measurement

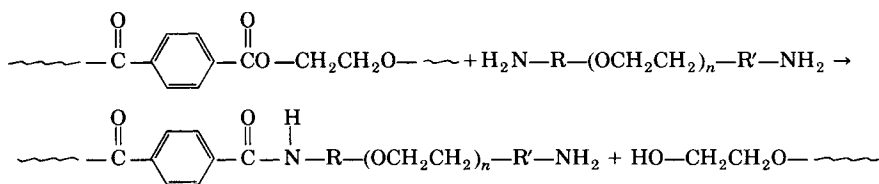
These were carried out as previously described.^{3,6}

RESULTS AND DISCUSSION

PEG Content with Aminolysis Time

The NMR spectrum of the PET film aminolyzed with PEG–diamine (PET-*b*-PEG film) showed three singlets. The singlets at 3.6, 4.6, and 8.2 ppm

correspond to ethylene unit of PEG-diamine, ethylene unit of PET, and aromatic ring of PET, respectively. From this result, it could be ascertained that the PET chain end is blocked with PEG-diamine as a result of the aminolysis reaction of the ester bond of PET by the amine radical of PEG-diamine. The reaction can be described as follows:



The PEG content of PET-*b*-PEG was calculated from the area of each singlet at 3.6 and 4.6 ppm.⁷ The experimental equation of the PEG wt % against aminolysis time *t*(h) was determined as follows: wt % = 2.1147 × *t*^{0.4593}.

Change in the Surface Free Energy of PET-*b*-PEG Film with PEG Content

The dispersion force component of surface free energy γ_S^d , the polar force component of surface free energy γ_S^P , and the nondispersion interaction free energy between water and PET-*b*-PEG film I_{SW}^n could be obtained from the contact angles of the two-liquid method and eqs. (1)–(3). The surface free energy of PET-*b*-PEG film γ_S was obtained from eq. (4). The work of adhesion of water to PET-*b*-PEG W_a was obtained from eq. (5)^{7,8}:

$$\gamma_S^d = \left(\frac{(\gamma_{H_1} - \gamma_{H_2}) - (\gamma_{H_1W} \cos \theta_1 - \gamma_{H_2W} \cos \theta_2)}{2[(\gamma_{H_1})^{1/2} - (\gamma_{H_2})^{1/2}]} \right)^2 \tag{1}$$

$$\begin{aligned} I_{SW}^n = & \left([(\gamma_{H_2})^{1/2} - (\gamma_W^d)^{1/2}] \{ \gamma_{H_1} - \gamma_W - \gamma_{H_1W} \cos \theta_1 - [(\gamma_{H_1})^{1/2} - (\gamma_W^d)^{1/2}] \right. \\ & \left. \times (\gamma_{H_2} - \gamma_W - \gamma_{H_2W} \cos \theta_2) \right) / [(\gamma_{H_1})^{1/2} - (\gamma_{H_2})^{1/2}] \tag{2} \end{aligned}$$

$$\gamma_S^P = (I_{SW}^n)^2 / (4\gamma_W^P) \tag{3}$$

$$\gamma_S = \gamma_S^d + \gamma_S^P \tag{4}$$

$$W_a = 2(\gamma_S^d \gamma_W^d)^{1/2} + I_{SW}^n \tag{5}$$

where θ_1 = contact angle of water in isooctane, θ_2 = contact angle of water in cyclohexane, γ_{H_1} = surface free energy of isooctane, 18.9 erg/cm², γ_{H_2} = surface free energy of cyclohexane, 25 erg/cm², γ_{H_1W} = interfacial free energy between water and isooctane, 49.3 erg/cm², γ_{H_2W} = interfacial free energy between water and cyclohexane, 50 erg/cm², γ_W^d = dispersion force component of surface tension of water, 23 erg/cm², γ_W^P = polar force component of surface tension of water, 49.7 erg/cm², γ_W = surface tension of water, 72.7 erg/cm².

TABLE I
Surface-Free Energy, Nondispersion Interaction Force, and Work of Adhesion of PET Control
and PET Treated with PEG-Diamine

Sample code	PEG content (%)	Contact angle (°) for		I_{SW}^d (erg/ cm ²)	γ_S^d (erg/ cm ²)	γ_S^P (erg/ cm ²)	γ_S (erg/ cm ²)	W_a (erg/ cm ²)
		Isooctane	Cyclohexane					
Control	0.00	112.41	114.55	29.45	38.32	4.36	42.68	88.83
J-1	2.00	109.45	111.50	31.88	37.65	5.11	42.76	90.73
J-3	3.60	105.40	107.50	35.18	37.98	6.23	44.21	94.29
J-5	4.60	103.16	105.26	37.00	37.90	6.91	44.81	96.10
J-7	5.21	98.85	100.92	40.73	37.44	8.34	45.78	99.42
J-10	6.42	95.80	97.87	43.35	37.23	9.45	46.68	101.87
J-15	7.41	94.56	96.60	44.43	36.89	9.93	46.82	102.69
J-24	8.40	92.24	94.00	46.61	34.45	10.93	45.38	102.90

All the data characterizing the surface of the PET-*b*-PEG film are listed in Table I.

The contact angle of water and γ_S^d decreased but γ_S^P increased with the increasing PEG content. The increasing range of γ_S^P was larger than the decreasing one of γ_S^d , so that the surface-free energy γ_S , the work of adhesion of water W_a , and the polarity increased with the PEG content.

Therefore, the PET fabric aminolyzed with PEG-diamine can be also presumed to have good water wicking and oily soil releasing properties.

Water Wicking Property

The PET-*b*-PEG fabric was obtained by aminolyzing the PET fabric under the same condition of aminolysis of the PET film with PEG-diamine. The wicking time of the PET fabric aminolyzed for over 1 h was less than 2 s irrespective of aminolysis time, while it took the water over 180 s to wick completely into the control PET fabric.

The rate of advancement of water in horizontal fiber capillary (length L per time t) is given by⁹

$$\frac{dL}{dt} = \frac{R_e \gamma_W \cos \theta_{app}}{4L\eta} \quad (6)$$

where R_e is the effective capillary radius of the interfiber spaces, η the viscosity of water, and θ_{app} the apparent advancing contact angle of water to fiber surface in air. $\cos \theta_{app}$ is given by

$$\cos \theta_{app} = r \cos \theta \quad (7)$$

where r is roughness and θ the real contact angle of water to fiber surface in air. θ cannot be measured precisely, but can be calculated approximately from eq. (8) using W_a data obtained from the two-liquid method⁷:

$$\theta = \cos^{-1}(W_a/\gamma_W - 1) \quad (8)$$

θ decreased but $\cos \theta$ increased with the PEG content. According to eq. (6), the higher PEG content enhanced dL/dt and shortened the water-wicking time.

Oily Soil Release

When an oily-soiled film or fiber in air is immersed into water, the new equilibrium state is formed at film-oily soil-water boundary as shown in Figure 1. Equations (9) and (10) can be given by Young-Dupré law. γ_{FW} , γ_{FO} , and γ_{OW} are given by eqs. (11)–(13), respectively, using an extended Fowkes' equation^{7,10}

$$\gamma_{FW} = \gamma_{FO} + \gamma_{OW} \cos \theta_O \tag{9}$$

$$\gamma_{FO} = \gamma_{FW} + \gamma_{OW} \cos \theta_W \tag{10}$$

$$\gamma_{FW} = \gamma_F + \gamma_W - 2(\gamma_F^d \gamma_W^d)^{1/2} - 2(\gamma_F^P \gamma_W^P)^{1/2} \tag{11}$$

$$\gamma_{FO} = \gamma_F + \gamma_O - 2(\gamma_F^d \gamma_O^d)^{1/2} - 2(\gamma_F^P \gamma_O^P)^{1/2} \tag{12}$$

$$\gamma_{OW} = \gamma_O + \gamma_W - 2(\gamma_O^d \gamma_W^d)^{1/2} - 2(\gamma_O^P \gamma_W^P)^{1/2} \tag{13}$$

Combinations of eqs. (9)–(13) can make the values of θ_O and θ_W calculated. The film or fiber specimen which makes θ_O larger for the same oily soil is thought to have better soil releasing property, because the larger θ_O makes oily soil rolled up during laundering more easily.

The work of adhesion of water and oily soil for the film or fiber is given by the Dupré equations (14) and (15) referred to the system film-oily soil-air⁹:

$$W_{FW} = \gamma_{FA} + \gamma_{WA} - \gamma_{FW} \tag{14}$$

$$W_{FO} = \gamma_{FA} + \gamma_{OA} - \gamma_{FO} \tag{15}$$

The difference between the two works of adhesion is obtained by subtracting eq. (15) from eq. (14). Substituting into eq. (1) and rearranging results in

$$(W_{FW} - \gamma_{WA}) - (W_{FO} - \gamma_{OA}) = \gamma_{FO} - \gamma_{FW} = \gamma_{OW} \cos \theta_W \tag{16}$$

or in terms of adhesion tension ($A_{FW} = W_{FW} - \gamma_{WA}$ and $A_{FO} = W_{FO} - \gamma_{OA}$):

$$A_{FW} - A_{FO} = \gamma_{OW} \cos \theta_W = \gamma_{FO} - \gamma_{FW} \tag{17}$$

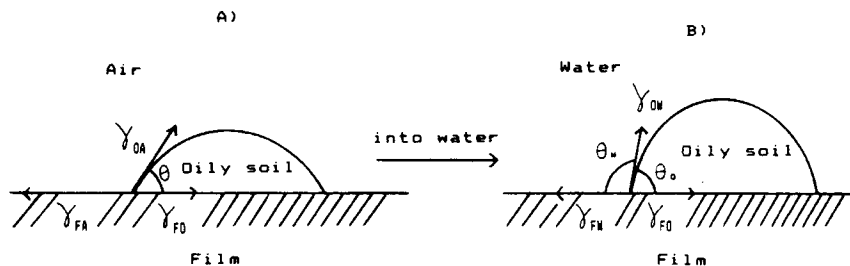


Fig. 1. Force diagram at film-oily soil-air boundary (A) and film-oily soil-water boundary (B) under the equilibrium state.

The adhesion tensions, rather than the works of adhesion of the two liquids on the fiber in air, are the important parameter in the rolling up of oily soil by the aqueous solution. The specimen which makes the value of $A_{FW} - A_{FO}$ larger for the same oily soil also has better oily soil releasing property.

The work of adhesion of the oily soil to film or fiber immersed in water is given by eq. (18) applied in analogy to eq. (15):

$$W_{FO/W} = \gamma_{FW} + \gamma_{OW} - \gamma_{FO} \quad (18)$$

Substitution of eq. (9) into eq. (18) yields

$$W_{FO/W} = \gamma_{OW}(1 + \cos \theta_0) \quad (19)$$

$W_{FO/W}$ is a measure of the affinity of the oil for the fiber relative to the affinity of water for fiber. $W_{FO/W}$ decreases as the fiber polarity increases, because θ_0 increases and, consequently, $\cos \theta_0$ decreases as the polarity of the fiber surface increases.

All the data about interfacial free energy, contact angle, and work of adhesion at film-oily soil-water boundary are listed in Table II. When data were calculated, the oily soil was presumed to be a tricaproinglyceride. As shown in Table II, γ_{FW} decreased very much, γ_{FO} increased a little, and, consequently, $A_{FW} - A_{FO}$ increased with the increasing PEG content, i.e., the increasing polarity of the surface. As the PEG content increased, θ_w decreased, θ_0 increased, and, consequently, $W_{FO/W}$ decreased. From these results, the PET fabric treated with PEG-diamine or chemically modified or finished with PEG derivatives can be thought to have very good oily soil releasing property.

Figure 2 shows the percentage of soil removal against laundering cycles for the PET fabric treated with PEG-diamine at 130°C. After 1 cycle of laundering, the percentage of soil removal for the control PET fabric was 45%, but the PET-*b*-PEG fabric had over 83% of soil removal irrespective of the PEG content. The control PET fabric had at most 79% of soil removal even after 10 cycles of laundering, while the PET-*b*-PEG fabric had over 97% of soil

TABLE II
Data about Interfacial Free energy, Contact Angle, and Work of Adhesion at Specimen-Oily Soil-Water Boundary^a

Sample code	PEG content (%)	γ_{FW} (erg/cm ²)	γ_{FO} (erg/cm ²)	θ_W (°)	θ_O (°)	$A_{FW}-A_{FO}$ (erg/cm ²)	$W_{FO/W}$ (erg/cm ²)
Control	0.00	26.56	1.29	156.93	23.07	-25.27	52.74
J-1	2.00	24.74	1.29	148.56	31.44	-23.44	50.91
J-3	3.60	22.61	1.61	139.85	40.15	-21.00	48.47
J-5	4.60	21.40	1.80	135.53	44.47	-19.60	47.07
J-7	5.21	19.07	2.21	121.87	52.13	-16.86	44.33
J-10	6.42	17.51	2.61	122.86	57.14	-14.90	42.37
J-15	7.41	16.83	2.75	120.83	59.17	-14.08	41.55
J-24	8.40	15.17	2.83	116.70	63.30	-12.34	39.81

^a $\gamma_O(\gamma_{OA}) = 29.2$ (erg/cm²), $\gamma_O^d = 25.9$ (erg/cm²), and $\gamma_O^p = 3.3$ (erg/cm²) for tricaproin-glyceride.¹⁰ $\gamma_{OW} = 27.47$ (erg/cm²) calculated from eq. (13), using $\gamma_W = 72.7$ (erg/cm²), $\gamma_W^d = 23.0$ (erg/cm²), $\gamma_W^p = 49.7$ (erg/cm²), and the surfacial free energy data for tricaproinglyceride.

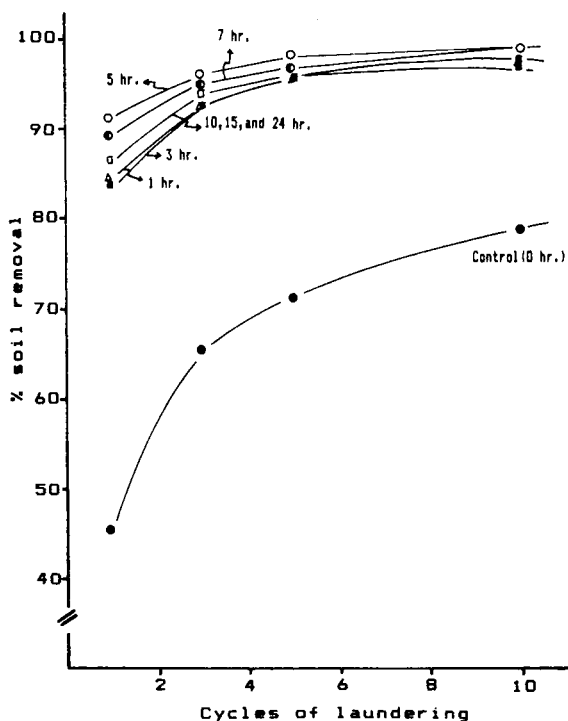


Fig. 2. Percentage of soil removal vs. cycles of laundering for PET fabric treated with PEG-diamine at 130°C.

removal. According to these experimental results, oily soil release could be proved to have a very close relation to the hydrophilicity or the polarity of the fiber surface.

Antistaticity

The frictional electrostatic voltage of the PET-*b*-PEG fabric was less than 1000 V irrespective of the PEG content, while that of the control PET fabric was over 7000 V. The half-decaying time of the PET-*b*-PEG fabric was about 2 s irrespective of the PEG content, while that of the control PET fabric was over 100 s. Therefore, the PEG derivatives can be known to give the hydrophobic synthetic polymer product good antistaticity as well as good hydrophilicity, i.e., good water-wicking and oily soil releasing.

CONCLUSION

The PET chain end was blocked with PEG-diamine as a result of the aminolysis reaction of the ester bond of PET with the amine radical of PEG-diamine, i.e., PEG unit was pseudografted to the PET chain end. The pseudografted PEG content increased with the aminolysis time (PEG wt % = $2.1147 \times t^{0.4593}$). The polar component of the surface-free energy γ_S^P increased and the dispersion component γ_S^d decreased with the increasing PEG content. The increasing range of γ_S^P was larger than the decreasing one of γ_S^d , so the surface-free energy γ_S , the work of adhesion, W_a , and the polarity increased as the PEG content increased. γ_{FW} decreased very much, γ_{FO} increased a little, and, consequently, $A_{FW} - A_{FO}$, which is an important parameter in the rolling up of oily soil by the aqueous solution, which increased as the PEG content became higher. As the PEG content increased, the contact angle of oily soil to the specimen immersed in water θ_O increased and, consequently, θ_W and $W_{FO/W}$ decreased. Therefore, the PET fabric treated with PEG-diamine had very good water-wicking, oily soil releasing, and antistatic properties.

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