

SURFACE TREATMENT OF POLY(ETHYLENE TEREPHTHALATE) FABRIC WITH POLYETHYLENEIMINE

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ABSTRACT

A branched polyethyleneimine (BPEI) was applied to poly(ethylene terephthalate) (PET) fabric to improve its surface moisture absorption so that the fabric becomes less liable to retention of electrostatic charge. The durability of this treatment was assessed by washing and followed by measurement of charge development on the fabric. The treated samples showed improved surface wetting compared to the untreated. The results are consistent with attachment of the BPEI to the PET surface by a cross-linking mechanism.

INTRODUCTION

The electrostatic charge propensity of textile fibres is a major problem in processing and in use. This problem is pronounced with hydrophobic synthetic fibres such as polyester, nylon and acrylic. Poly(ethylene terephthalate) (PET) fibre has a very low moisture regain, for example, 0.4% at 65% relative humidity (RH) and 20°C. Its hydrophobic nature contributes to its inability to conduct electrostatic charge^[1,2]. Much work has been carried out on the modification of PET fibre to improve its surface moisture absorption property by applying hydrophilic antistatic agents, which are intended to protect materials against accumulation of electrostatic charge^[3-6]. It is desirable that antistatic treatments should withstand long-term use, and especially should offer resistance to washing and dry cleaning^[5,6,7]. In this paper, we describe work in which a branched polyethyleneimine (BPEI), which contains a multiplicity of amino groups capable of reacting with ester groups at the surfaces of PET fibres, is applied to polyester fabric through pad-dry-heat treatment. As far as we are aware, this type of agent has not previously been used to modify the surface properties of PET.

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EXPERIMENTAL

Polyester fabric

A fine plain weave polyester fabric produced from multifilament yarns, of the following constitution:

Ends/cm=45

Picks/cm=30

Count: Ends (24 filaments)=4.0 tex (measured unextended)

Picks (36 filaments)=13.7 tex (textured yarn, measured unextended)

Branched polyethyleneimine (BPEI)

Polyethyleneimine of molecular weight 60,000 (50% in water) supplied by BDH.

Chemicals

Methanol, dichloroacetic acid (DCAA), and other chemical reagents were used as supplied.

Cleaning

The 100% PET fabric was Soxhlet extracted with methanol overnight. This was followed by thorough rinsing with de-ionized water and drying under normal room conditions. The dried fabric was stored in a vacuum desiccator over drying agents for further use.

Washing/laundrying

Washing tests were carried out in a CPA Wash Wheel at 60°C for 30 minutes using 2 g/l ECE (European Colourfastness Establishment) reference detergent^[8] in a bath at a liquor ratio (LR) of 200 : 1. This was followed with a warm rinse in the machine for 5 minutes and two further cold rinsing treatments with de-ionized water. Washed samples were all air-dried under normal room conditions.

Static honestometer test^[9,10]

All test samples were conditioned in a test room at 65% RH and 20°C overnight before measurement. The conditioned sample was clamped in the sample holder on the turntable of the Static Honestometer, which rotated at 1,750 revolutions/minute. A potential of 10 kV was applied to the sample through a needle electrode placed 22 mm above it. A detector probe located at 180° across the turntable from the discharge electrode measured the charge leakage from the sample through a similar air gap on each revolution. The charge potentials in milli-volts (mV) at 10 kV were recorded from a voltmeter (Keithley 177 microvolt DMM). Ten readings were noted from the voltmeter for each sample and averaged.

Reflectance measurements

Reflectance values were determined on a Macbeth Color-Eye 1500+ equipped with a Digital Rainbow 100 microprocessor using CIELAB colour difference formula. Each fabric sample was folded into four layers for this determination. Each reflectance tabulated was an average of ten readings from a single sample of the same fabric.

Absorption of methyl orange dye by the fabric samples

Dyeing of the samples was carried out using an 0.001% solution of methyl orange (sodium 4'-dimethyl aminoazobenzene-4-sulphonate) (orange III; C.I. acid orange 52). About 0.1 g of each sample was dyed in a steel pot in a Jeffreys Rotadyer Mark I at 20°C for 60 minutes in neutral liquor (liquor ratio of 250 : 1). The samples were rinsed thoroughly with distilled water and dried.

The absorbances of dye removed from the samples by 50 ml of 0.1 mol/L NaOH solution were determined on a Pye Unicam SP 1800 (UV) spectrophotometer, at $\lambda_{\max}$ of 464 nm.

Solution viscosity

Solutions for viscometry were prepared using dichloroacetic acid (DCAA) at room temperature. The appropriate mass of each sample was weighed out and placed in a stoppered flask containing the acid. The flasks were mechanically agitated gently for 30 minutes to dissolve the samples. The solution was filtered through size 2 sintered glass before measurement. The flow times(s) of the solutions were determined in an Ostwald viscometer at a constant bath temperature of 25°C. The relative viscosities of the polymer solutions were thus evaluated.

Pad-dry-heat

The fabric samples were cut to size (32 cm by 22 cm) and impregnated with 5% BPEI solution in separate beakers for 5 minutes. The excess liquor was removed by mangling using an Ernst Benz laboratory padder (2 bowl vertical pad mangle) with a roller nip load of 35 kg/cm and at a speed of 1 metre/minute. The samples were then batched each in a separate air-tight bag for one hour to equilibrate. They were air-dried prior to high temperature heating in a Werner Mathis laboratory baking machine.

Wettability measurement

The wettability of samples was determined by modifying the standard drop wettability method^[11,12]. A drop of distilled water was formed using an 'Agla' micrometer-driven syringe (Burroughs Wellcome & Co., England) fitted with a calibrated glass capillary tube. The tip of the glass needle used to form the drop

of water was ground flat and polished (external diameter of 1.08 mm). The plunger of the syringe was operated by the micrometer head; a complete turn advanced the plunger by 0.5 mm, delivering a volume of 0.01 ml. The peripheral scale of the micrometer head was divided into fiftieths of a revolution; each step on this scale thus corresponded to a volume of 0.0002 ml^[13].

All test samples were conditioned in a test room at 65% RH and 20°C overnight before measurement. The sample (10 cm by 10 cm) was held flat by means of two wide clamps mounted on a rigid frame-work. To ensure that samples were held flat by the clamps, a T-type spirit level (11.5 g) was used. The micrometer and syringe arrangement was held vertically over the levelled test sample with a tip clearance of 1 cm. This clearance was used to avoid a possible collapse of the fallen drop of water under acceleration due to gravity on the sample surface.

The first drop of water formed per determination was always discarded by collecting it on a paper surface. This was done to determine the approximate volume of the liquid in a drop and most especially to ensure that each drop was freshly formed. About 90% of the volume was formed fairly rapidly, while the remaining 10% was formed carefully and slowly without exceeding a total drop formation time of 1 minute^[14]. The drop was then allowed to fall on the sample surface under the influence of gravity. The stop watch was started when the drop reached the fabric surface, and stopped when the specular reflection of the water on the surface of the test sample disappeared due to complete absorption of the water. The elapsed time(s), the volume of the drop of water in ml and comments on the spreading behaviour were recorded.

RESULTS AND DISCUSSION

Reflectance of the samples

The reflectance data in Table 1 were used to assess the colour change of the treated samples. Generally the lightness (L^*) values of the baked samples decreased compared to the control (untreated) sample. The treatment temperatures and times that produced the best results in terms of apparent brightness of the surface were those for samples PB-A, PB-B and PB-E, in that order of preference. Other samples were more seriously discoloured possibly as a result of long exposure to high temperature in the presence of oxygen, which could cause oxidative degradation of the antistat. The worst affected sample was PB-H as shown by its chromaticity (a^*b^*) values. Partial oxidation may also be a cause of its low percent add on.

Static charge

The static charging propensity of PET was greatly decreased in all the treated (PET/BPEI) samples, probably as a result of the hydrophilic property induced by the antistant. The charge values of the baked samples were further decreased after first washing (see Table 2). This may be a result of association of water molecules and some of the detergent anion with basic groups on the surface of the samples rendering the surface more solvated. As the number of washes increased, the charge values started increasing gradually for most of the samples as shown in Table 2. This effect may be an indication of surface removal of the finish. After six washes the charge values of samples PB-C, PB-E, PB-F, PB-G and PB-H had increased beyond their initial treatment (zero wash in Table 2) values while samples PB-A, PB-B and PB-D maintained their charges below it.

Table 1 The heating conditions and reflectance data for BPEI treatment

Sample	Temp (°C)	Time (s)	Add on (%)	L^*	a^*	b^*	Remarks
PB-A	180	10	5.4	88.1	-1.1	+2.8	
PB-B	180	15	5.4	88.3	-1.4	+4.4	
PB-C	180	30	5.2	87.6	-1.8	+10.5	discoloured
PB-D ⁺⁺	180	60	5.7	87.3	-1.8	+11.3	discoloured
PB-E	150	60	5.6	88.1	-1.5	+5.6	
PB-F	150	90	5.3	87.6	-1.7	+12.0	discoloured
PB-G	150	120	5.3	87.1	-1.3	+15.0	discoloured
PB-H	150	300	4.5	84.4	+1.8	+23.0	discoloured
Control (untreated)				89.6	-0.8	+0.9	
Tile				95.7	-0.1	+1.1	

⁺⁺ 0.5 g of phosphorous acid (antioxidant) in pad liquor.

Table 2 The effect of BPEI on electrostatic charge development and its durability to washing

Number of washes	Samples and their average charge value (mV)							
	PB-A	PB-B	PB-C	PB-D	PB-E	PB-F	PB-G	PB-H
0	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
1	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.7
2	1.5	1.6	1.7	1.7	1.6	1.7	1.8	3.1
3	1.6	1.6	1.6	1.6	1.6	1.7	1.9	3.0
4	1.6	1.7	1.7	1.8	1.9	2.0	2.1	3.2
5	1.6	1.7	1.9	1.7	1.9	1.8	1.9	3.1
6	1.6	1.7	2.0	1.7	2.4	2.0	2.1	3.5

The charge value for untreated (control) PET fabric is 17.7 mV

Solution viscosity data

Sample solutions of 0.1 g/100 ml were used in the determination of viscosity. The

relative viscosity values for samples PB-A and PB-H were 1.08 and 1.07 respectively compared to the control PET which was 1.06. The relative viscosity results for the treated samples (PB-A and PB-H) are slightly increased, but not significantly higher than for the control sample. Also their solutions contained some undissolved material, whose presence is consistent with the expected cross-linking of BPEI during baking.

Absorption of methyl orange by the samples

Table 3 The absorption of methyl orange dye by the samples

Sample	Dye absorbed (mol/g) $\times 10^{-5}$
PB-A	2.5(4.7)
PB-B	2.8(5.3)
PB-C	4.4(5.0)
PB-D	7.2(6.2)
PB-E	2.2(2.6)
PB-F	4.1(3.8)
PB-G	6.0(4.4)
PB-H	10.2(5.5)
Control	0.0(0.0)

Values in parenthesis are for samples washed six times

Table 4 Changes in reflectance data for the fabric samples after six washes

Samples	L^*	a^*	b^*
PB-A	-1.7	-0.3	+11.0
PB-B	-1.5	+0.1	+9.5
PB-C	-0.6	+1.0	+4.4
PB-D	-0.1	+0.9	+4.9
PB-E	-1.2	+0.3	+6.3
PB-F	-1.0	+0.5	+1.7
PB-G	-0.8	+0.4	+0.6
PB-H	+1.1	-1.2	-4.2
Control	+0.7	-0.2	+0.1

Methyl orange absorption by polyethyleneimine was used as an indicator of the relative amounts of BPEI available on the surfaces of the samples. Table 3 shows that the untreated control sample did not absorb the dye, because of the lack of basic groups. All the treated samples absorbed the dye, but the group of samples PB-F, PB-C, PB-G, PB-D and PB-H absorbed more dye than PB-E, PB-A and PB-B in their initial heat treated state. The amount of dye absorbed by the samples washed six times has decreased in samples PB-D, PB-F, PB-G and PB-H while more is still retained in samples PB-A, PB-B, PB-C and PB-E. The values of dye uptake after six washes under quite severe conditions remain high, indicating that the retention of BPEI during an extended series of normal washes is likely to be good.

Changes in reflectance data of washed samples

The changes in reflectance data for the control (untreated) and the treated samples after six washes are shown in Table 4. The data for the control sample indicates that there was very little change compared to the treated samples. The increase in L^* value of sample PB-H after the sixth wash may be an indication that some of its

surface finish has been washed off. This was the sample on which there was already evidence for partial oxidation of the finish. The other samples all gave lower L^* and higher b^* values, showing some deterioration in colour during washing.

Wettability

The drop wettability values of some of the PET/BPEI samples including control PET, for comparison, and of typical cotton samples, are shown in Table 5. The wettability is the average time in seconds(s) used in the absorption of the drop (0.02 ± 0.0002 ml) of distilled water by the sample. The wettabilities of the treated PET/BPEI samples initially have slightly improved over that of the untreated PET. With an increased number of washes, the wettabilities of these samples have markedly improved. This may be due to improved accessibility to the hydrophilic BPEI after washing. The wettability of all the samples, including the untreated PET, has in general improved with washing possibly due to improved pore size of the sample surfaces resulting in enhanced absorption of water. The hydrophilic cotton as expected had an excellent wettability, which was still better after a series of washes. The untreated PET has a poor absorption and spreading (more spreading of liquid on the weft than on the warp). This weft-way spreading of liquid can be attributed to the textured structure of the weft yarns, which enhances the flow of liquid by capillary action compared to the warp yarn. After treatment of the PET fabric with BPEI polymer, the spreading of the liquid became oval, indicating that the extent of spreading was still slightly greater in the weft than in the warp direction. In the case of the mercerized cotton, the spreading of liquid was circular indicating equal spreading in both warp and weft directions.

Table 5 Wettability(s) of PET, PET/BPEI and cotton samples

Samples	Number of washes		Comments
	0	5	
PET (untreated)	300	83	weft-way
PB-A	206	17	oval
PB-B	232	15	oval
PB-E	212	26	oval
Cotton (bleached)	7	2	oval
Cotton (mercerised)	4	1	circular

Mechanism

BPEI is a branched polymeric base of high molecular weight, containing primary amine groups at the branch ends, secondary amine groups within linear segments of

the chain between branch points, and tertiary amine groups at the branch points. Because of its high molecular weight, it should not diffuse into the fibres, so reaction should be confined to the fibre surface. The primary amine groups are known to have high reactivity with the ester groups of PET, whereas secondary amine groups have relatively low reactivity and tertiary amine groups at these temperatures are unreactive. Consequently the BPEI should become attached to the PET mainly through formation of a multiplicity of secondary amide (RCONHR') groups, and no reduction in average molecular weight of the surface polymer should occur. The results are consistent with this mechanism.

CONCLUSIONS

BPEI has been found to be a durable antistat for PET fibre when applied by a pad-dry-heat technique. Treatment at 180°C for a period of 10 to 15 seconds is suggested to avoid the oxidative discolouration of the fabrics. The wettability of PET fabrics treated with BPEI was also improved. The results are consistent with attachment of the BPEI to the PET surface by a cross-linking mechanism.

Keywords:

Surface modification; Polyester; Antistatic; Polyethyleneimine treatment

REFERENCES

- [1] Uyama, Y. and Ikada, Y., *J. Appl. Polym. Sci.*, **1990**, *41*: 619.
- [2] Warburton Jr., C.E., *J. Appl. Polym. Sci.*, **1991**, *42*: 207.
- [3] Williams, D.J. and Greib, G.M., *Melliand Textilberichte, (Eng. Ed.)*, **1983**, *12*: 157.
- [4] Uchida, E.; Uyama, Y. and Ikada, Y., *J. Appl. Polym. Sci.*, **1993**, *47*: 417.
- [5] Robert, W.R., E.I. du Pont de Nemours, *U.S. Pat.*, 2,839,431, **1958**.
- [6] Venkatesh, G.M.; Das, T.K. and Pal, S., *ATIRA Techn. Digest*, **1979**, *13*: 4.
- [7] Valko, E.I. and Tesoro, G.C., *Textile Res. J.*, **1959**, *29*: 21.
- [8] BS EN 20105: Colour Fastness to Domestic and Commercial Laundering, **1993**: C06, 6.
- [9] Shishido & Co. Ltd., Static Honestometer: Static Charge and Attenuation Measuring Instrument, Tokyo, undated manual.
- [10] Slade Jr., P.E., *Modern Textiles*, **1973**, *54*(3): 68.
- [11] BS 4554: **1991**, Methods of Test for Wettability of Textile Fabrics.
- [12] AATCC Test Method 79-**1992**, Absorbency of Bleached Textiles.
- [13] Trevan, J.W., *Biochem. J.*, **1925**, *19*: 1111.
- [14] Ateiza, O.J., MPhil. Thesis, University of Bradford, U.K., **1980**.