

# Effect of Acetonitrile Pretreatment on the Physicochemical Behavior of 100% Polyester Fabric

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**ABSTRACT:** Acetonitrile pretreatment of 100% poly(ethylene terephthalate) fabric was performed over different lengths of time. The influence of solvent treatment on the dyeing behavior and some of the physicochemical properties were investigated.

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**Key words:** polyester fabrics; dyes/pigments; physicochemical properties; FTIR; differential scanning calorimetry (DSC)

## INTRODUCTION

Of all the man-made fibers, polyester fiber is widely used because of its outstanding properties such as high strength, high wear resistance, pleasant appearance, comfortable wearability, and ease of washing. However, dyeing of polyester fibers and fabrics with disperse dyes is a complex phenomenon and is often a challenge to the dyers, the main reasons for which are its high degree of crystallinity, its hydrophobic nature, the absence of dye sites, very low swelling, low diffusion of the dye molecules, high glass-transition temperature, and the absence of chemically reactive groups in the polymer. Extensive research has been carried out on modifying polyesters by solvents.<sup>1–7</sup> Solvent treatments did not have any adverse effect on the other textile properties of polyester.

Chemical modification of polyester polymer by solvent pretreatment before dyeing results in changes in the dyeability characteristics. When polyester polymer is pretreated with highly interacting solvents under suitable conditions, the internal structure—especially the amorphous region—is changed and thereby more voids, cracks, and the like are produced, which facilitate unhindered entry of dye molecules, even larger size molecules, into the polymer matrix. Besides, these solvents break the intermolecular bonds and loosen the fiber structure and thus enhance the dye uptake. The amount of dye uptake depends on the nature of solvents used for polymer modification and the degree of interaction between the solvent and the poly-

mer as well as the extent of structural modification effected by the treatment. The requirement of thermal energy for pretreatment and the toxicity of the solvents are some of the major drawbacks associated with the solvent-induced modification process. The aim of present study was to improve the dyeability by solvent pretreatment at room temperature.

## EXPERIMENTAL

### Dyes and chemicals

A plain woven polyester fabric of the following specification was used.

- Types of yarn: filament
- Ends per in: 119
- Picks per in: 60

Dyes: disperse dyes (M/s. Jaysynth Dyechem Pvt. Ltd., Mumbai-34, India).

- Terenix Scarlet F2RL
- Terenix Yellow F7GDL
- Terenix Blue F2RL
- Terenix Violet F3RL

### Chemicals required

Acetonitrile (Fischer, LR Grade) was used as the pretreater; phenol (Fischer, LR Grade) was used as carrier for conventional dyeing; and 3% acetic acid (Fischer, LR Grade) was used to maintain the pH at 5.5–6.

### Apparatus

A padding mangle was used to squeeze the pretreated fabric. Dyeing was performed using the rotadyer bath

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(rotadyer 18X100-N machine, R. B. Electronic & Engineering Pvt. Ltd., Mumbai-53, India).

### Pretreatment

Acetonitrile (AN) was used as pretreater. The pretreatments were carried out at room temperature for various time intervals (i.e., 2, 4, 6, 8, 10, and 30 min) in the rotadyer. The pretreated fabrics were then squeezed in the padding mangle and then air dried. Then the fabrics were subjected to dyeing.

### Color measurement

Color measurements were performed using a Systronic 20D spectrophotometer (Milton Roy).

### Dyeing

Recipe:

- Dye 2%
- Acetic acid 1–3 gpl
- MLR 1 : 50
- Temperature 40, 60, and 80°C, and boiling
- Time 45 min

The dye bath containing the required amount of acetic acid and water was set at 60°C. The pretreated sample was introduced into this dye bath and kept under these conditions for 10 min. Then the calculated amount of dye solution was added to the dye bath and the required temperature was set within 10 min. Dyeing was carried out for 45 min. After completion of the dyeing time, the dyed fabrics were removed and washed with cold water. In conventional dyeing, phenol was used as the carrier for dyeing untreated fabric.

### After treatment

The above dyed and washed fabrics were reduction cleared by using 2 gpl each of hydro- and sodium carbonate at 60°C for 20 min, after which they were washed with cold water and neutralized by acetic acid, washed twice with hot water and cold water, respectively, and then dried in a hot air oven.

### Calibration curve

The calibration graphs for the dyes Terenix Scarlet F2RL, Terenix Yellow F7GDL, Terenix Blue F2RL, and Terenix Violet F3RL were obtained by measuring the optical density of the dye solution of various known concentrations at their respective  $\lambda_{\text{max}}$  values (680, 575, 462, and 430 nm) using a spectrophotometer.

### Measurement of the dye uptake

The amount of dye absorbed by polyester fabrics during dyeing was determined spectrophotometrically. After each dyeing session, the optical density of the residual liquor was measured. From the optical density, the concentration of the residual liquor was determined by referring to the calibration graph. Because the initial concentration of the dye bath was known, the difference in concentration before and after dyeing was determined and hence the percentage dye uptake was determined.

### Test for color fastness

The washing fastness for dyed fabrics with and without pretreatment was assessed using the ISO4 method. The dyed fabrics were subjected to light fastness tests using test procedures ISO BS1006 (BO4/1) and BS 1006X12 (1978). The change in color and staining to adjacent fabric were assessed according to the SDC gray scales. The AATCC blue wool standards were used to assess the light fastness of fabric. A similar test procedure was also carried out for the untreated sample. The rubbing fastness was determined by using a Crock meter.

### Measurement of shrinkage

The percentage shrinkage was calculated using the following formula:

$$\text{Shrinkage (\%)} = \frac{I_0 - I}{I_0} \times 100$$

where  $I_0$  is the length of the sample before treatment and  $I$  is the length of the sample after treatment.

### Determination of weight loss

The initial and final weights of conditioned fabric before and after solvent treatments were measured using a single-pan balance and the loss in weight was calculated accordingly.

### Measurement of crimp

Percentage crimp is defined as the mean difference between the straightened thread length and the distance between the ends of the thread while in the cloth expressed as a crimp percentage, which was determined for both warp and weft yarns.

### Mechanical properties: tearing strength

The tensile strength of the fabric samples before and after solvent treatment was measured using a tensom-

eter (Type W 10241 by Monsanto, UK). Specimens were 20 cm long and 1 in. wide. The rate of extension was kept at 3.2 mm/min.

### SEM topography

SEM observations were carried out on treated and untreated samples with Au-coated vacuum ion sputter by the liquid hydrogen method (JEOL 840A). The rotating system was attached to the instrument and was also used for accurate measurements at various magnifications.

### FTIR analysis

IR spectra were recorded on an FTIR spectrometer (Perkin-Elmer, Paragon-500 model, Poole, UK) with built-in spectral-matching computerized software for surface analysis.

The samples were analyzed using a 2-mg powder pellet along with 300 mg KBr. The mixture was dried at 110°C for 4 h and pelletized using a 13-mm die under vacuum and a 10-tons pressure.

The FTIR spectra were recorded in the frequency range 3800–400  $\text{cm}^{-1}$ , in the mid-IR region. The resolution was set at 4  $\text{cm}^{-1}$  and the optical path differ-

ence velocity was set at 0.2 cm/s. For the KBr pellet technique, an average of 25 scans were taken.

### Differential scanning calorimetry

Thermal analyses of the samples were carried out using an Perkin-Elmer DSC-2. The temperature range of thermal analysis was between 100 and 400°C with a heating rate of 10°C/min. Nitrogen was used as the purge liquid at a flow rate of 10  $\text{cm}^3/\text{min}$ . After the DSC cell attained the initial set temperature, the weighed sample was placed in the cell. After allowing a 3-min settling time for the sample to equilibrate at the starting temperature, the temperature program was automatically initiated. After the run, various thermal parameters were evaluated.

## RESULTS AND DISCUSSION

The 100% PET fabrics treated with acetonitrile solvent under different conditions were dyed with four different disperse dyes to study the effect of solvent pretreatment on the dyeing behavior of the treated fabric. The untreated sample was also simultaneously dyed by carrier dyeing for comparison. The results are presented in Table I. It is evident from the table that

TABLE I  
Percentage Dye Uptake of 100% PET Fabric (AN-Treated and Untreated)

Dye	Treatment time (min)	% Dye uptake			
		40°C	60°C	80°C	100°C
Terenix Scarlet F2RL	2	21.7	32.1	48.4	38.8
	4	22.5	36.6	49.2	40.5
	6	33.5	44	50.6	42.2
	8	44.6	54	55.1	46.8
	10	33.6	49.3	48.6	42.3
	30	22.1	37.8	46	37.4
	Untreated			32	
Terenix Yellow F7GDL	2	30.7	42.3	53.5	42.4
	4	31.6	45.1	58.6	46.6
	6	34.5	47.7	65.2	52.1
	8	36.4	51.8	68.2	56.9
	10	34.3	48.3	62.8	53.9
	30	31.3	45.3	55.4	51.8
	Untreated			46.5	
Terenix Blue F2RL	2	23	35.6	48.5	38
	4	26	39.4	52.3	42.8
	6	28.8	41.8	56.3	46.8
	8	31.7	44.8	58.9	53.4
	10	27.5	42	53.7	52.2
	30	26.5	40.6	47.7	48.8
	Untreated			42.2	
Terenix Violet F3RL	2	27.3	32.5	56.7	44.6
	4	29.4	38.1	60.1	47.9
	6	31.5	39.4	66	50.5
	8	32.1	42.4	69.9	54.4
	10	29.9	38.4	67.4	52.2
	30	28.8	37.8	62.4	48.4
	Untreated			41.4	

TABLE II  
Washing Fastness of Dyed PET Fabric

Dye	Dyeing temperature (°C)	Pretreatment time (min)					
		2	4	6	8	10	30
Terenix Scarlet F2RL	40	4	4	4-5	4-5	5	5
	60	4-5	4-5	5	5	5	5
	80	4-5	4-5	5	5	5	5
	Boil	4-5	5	5	5	5	5
Terenix Yellow F7GDL	40	4	4	4-5	4-5	5	5
	60	4	4-5	4-5	5	5	5
	80	4-5	4-5	5	5	5	5
	Boil	4-5	4-5	5	5	5	5
Terenix Blue F2RL	40	4	4	4	4-5	5	5
	60	4	4-5	5	5	5	5
	80	4-5	4-5	5	5	5	5
	Boil	4-5	5	5	5	5	5
Terenix Violet F3RL	40	4	4	4-5	5	5	5
	60	4-5	4-5	5	5	5	5
	80	4-5	4-5	5	5	5	5
	Boil	4-5	5	5	5	5	5
Untreated				5			

the dye uptake increases with increase in time of pretreatment and the dyeing temperature. The dye uptake increases up to a pretreatment time of 8 min, beyond which the dye uptake decreases.

The dyeing temperature also has an effect on the dye uptake of the fabric. As the dyeing temperature increases, up to 80°C there is an increase in dye uptake, although it decreases for samples dyed at 100°C. The reason for the above behavior may be attributable to the fact that the solvent diffuses into the fiber structure and results in a breakdown of intermolecular forces of attraction between molecular chains so that the molecular chains become free for relaxation. This

relaxation results in increased penetration of dye molecules into the fiber matrix.

The improvement may also be attributable to the large increase in intersurface area by swelling; greater segmental mobility of polymer molecules; decreased glass-transition temperature ( $T_g$ ); and formation of microvoids, cracks, and so on as a result of solvent pretreatments.<sup>8,9</sup> The relaxation may decrease beyond 80°C and therefore the dye uptake would decrease for the fabric pretreated at above 80°C.

Tables II-IV show the wash, light, and rubbing fastness properties of the treated and untreated polyester fabrics. The results indicate that the solvent treatment

TABLE III  
Light Fastness of Dyed PET Fabric

Dye	Dyeing temperature (°C)	Pretreatment time (min)					
		2	4	6	8	10	30
Terenix Scarlet F2RL	40	4.5	4.5	5	5-6	6	6
	60	4.5	5	5-6	6	6	6
	80	5	5	5-6	6	6-7	7
	Boil	5	5-6	6	6-7	6-7	7
Terenix Yellow F7GDL	40	4	4-5	5	5	5-6	6
	60	4-5	5	5	5-6	6	6
	80	4-5	5	5-6	6	6-7	6-7
	Boil	5	5	5-6	6	7	7
Terenix Blue F2RL	40	4-5	4-5	5	5	5-6	6
	60	4-5	5	5	5-6	5-6	6
	80	5	5	5-6	6	6-7	6-7
	Boil	5	5-6	5-6	6	6-7	7
Terenix Violet F3RL	40	4	4-5	5	5	5-6	5-6
	60	4-5	4-5	5	5-6	5-6	6
	80	5	5-6	5-6	6	6-7	7
	Boil	5	5-6	6	6-7	7	7
Untreated				6-7			

TABLE IV  
Rubbing Fastness of Dyed PET Fabric

Dye	Dyeing Temperature (°C)	Pretreatment time (min)											
		2		4		6		8		10		30	
		Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Terenix Scarlet F2RL	40	3	4	3	4	3-4	4-5	3-4	4-5	4	5	4	5
	60	3	4	3-4	4-5	3-4	4-5	4	5	4	5	4	5
	80	3-4	4-5	3-4	4-5	4	5	4	5	4	5	4	5
	Boil	3-4	4-5	3-4	4-5	4	5	4	5	4	5	4	5
Terenix Yellow F7GDL	40	3	4	3	4	3-4	4-5	3-4	4-5	4	5	4	5
	60	3	4	3	4	3-4	4-5	4	5	4	5	4	5
	80	3-4	4-5	3-4	4-5	4	5	4	5	4	5	4	5
	Boil	3-4	4-5	3-4	4-5	4	5	4	5	4	5	4	5
Terenix Blue F2RL	40	3	4	3	4	3-4	4-5	4	5	4	5	4	5
	60	3-4	4-5	3-4	4-5	3-4	4-5	4	5	4	5	4	5
	80	3-4	4-5	3-4	4-5	3-4	4-5	4	5	4	5	4	5
	Boil	3-4	4-5	3-4	4-5	4	5	4	5	4	5	4	5
Terenix Violet F3RL	40	3	4	3	4	3-4	4-5	4	5	4	5	4	5
	60	3	4	3-4	4-5	3-4	4-5	4	5	4	5	4	5
	80	3-4	4-5	3-4	4-5	4	5	4	5	4	5	4	5
	Boil	3-4	4-5	3-4	4-5	4	5	4	5	4	5	4	5
Untreated													

involving acetonitrile did not affect the fastness properties. It seems that the solvent did not disturb the stability of the dye-fiber bond.

The results of studies on physical properties of solvent-treated and untreated fabrics are presented in Tables V and VI. It is seen from the tables that there is not much difference in the physical properties; in particular, there is no appreciable weight loss of the treated fabric.

### Modification of surface topography

Scanning electron micrographs of polyesters treated with AN along with their respective untreated samples are presented in Figures 1-3. In the treated sample, it appears that the solvent attacks almost the entire surface of the fiber and causes the erosion. With progress of the attack erosion propagates inside the

fiber, resulting in the formation of elongated pits or cavities on the surface. Both depth and frequency of occurrence of pits increased with increasing weight loss in the treatment.<sup>10</sup>

In all the solvent-treated polyester materials, as the time of treatment increases, migration of the oligomer to the surface of the polymer was found (Figs. 1-3). Surface pitting attributed to solvent-assisted removal of delustering agents was also observed. This is further supported by the fact that during strength measurements of the treated fabric, only a slight decrease in the strength was observed.

### FTIR spectroscopic study

FTIR studies of treated and untreated 100% polyester fabric were made to assess any structural change, creation of any new functional groups, or the alter-

TABLE V  
Properties for 100% Polyester Fabric

Sample no.	Property	Untreated	Treated
1	Ends per inch	119	122
2	Picks per inch	60	66
3	Weight/m <sup>2</sup>	1.1 g/m <sup>2</sup>	—
4	Crimp of the weft	8%	8.8%
5	Crimp of warp	6.8%	7.2%
6	Tenacity (g/d)	4.2	3.8
7	% Shrinkage	6.46%	6.62%
8	Weight loss		0.099% (2 min) 0.105% (4 min) 0.118% (6 min) 0.145% (8 min) 0.16% (10 min)

TABLE VI  
Tearing Strength of 100% Polyester Fabric

Solvent system	Pretreatment time (min)	Maximum load applied (kg)	True extension (cm)	Percentage elongation	Percentage strength
AN-treated	2	18	2.325	25	5.8
	4	16	2.45	25	5.8
	6	16	1.87	25	5.8
	8	14	2.15	25	17.6
	10	14	2.5	25	17.6
	30	14	2.25	25	17.6
Untreated		17	2.375	25	

ation of existing groups in the fabric as a consequence of solvent treatment.

Figure 4 shows the IR spectrum of 100% PET fabric before and after solvent treatments. The observed absorption peaks are presented in Table VII. Although the spectra of treated samples appear similar to the spectrum of the untreated sample, the peak at  $1722\text{ cm}^{-1}$  is characteristic of the carbonyl group ( $>\text{C}=\text{O}$ ). According to the spectral data of poly(ethylene terephthalate) of  $>\text{C}=\text{O}$ , stretching is at  $1684\text{ cm}^{-1}$ . The intensity of this peak is high for the solvent-treated samples, whereas in the untreated sample the corresponding peak is observed at  $1672\text{ cm}^{-1}$ . Also additional bands are observed in the case of the AN-treated sample at  $1032$ ,  $936$ ,  $602$ , and  $462\text{ cm}^{-1}$ . On comparing the FTIR spectra of the untreated and treated 100% polyester fabrics it is evident that no drastic change in the spectral pattern is observed. Even in the fingerprint region very slight shifts in the absorption peaks are observed. Also from the spectral data one could infer that there is a slight increase in the amorphous region of treated fabric. The same trend is also reflected by SEM studies discussed earlier.

#### Thermal studies of polyester fabric

DSC curves obtained for PET fabric samples under study treated with AN when heated at a rate of  $10^\circ\text{C}/\text{min}$  ( $20\text{ K}/\text{min}$ ) are shown in Figure 5. The melting

temperature was determined by DSC in a Perkin-Elmer DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT). The starting, peak, and melting temperatures are noted.

	Untreated ( $^\circ\text{C}$ )	Treated ( $^\circ\text{C}$ )
Starting temperature	252	249
Peak temperature	268	264
Melting temperature	272	269
$T_g$	72	64
Heating rate	$10^\circ\text{C}/\text{min}$	

On comparison, the DSC thermograms are found to be almost identical, with small changes in terms of starting temperature, peak temperature, melting temperature, and melting range. The interaction of the polymer with the solvent is strongly influenced by morphological and structural parameters. In general, the solvent enters into the polymer structure, weakens polymer-polymer interaction, replaces it with polymer-solvent interaction, induces extensive segmental motion, and lowers the effective glass-transition temperature of the material. Polymer chains will rearrange themselves into a lower free-energy state. As a consequence of this there is a small increase in the amorphous region of the treated materials.<sup>11,12</sup>

In the present study, the interaction of solvent with the fiber material was found to be intracrystalline interaction. This is evident from a small decrease in the starting temperature, peak temperature, and melting temperature.

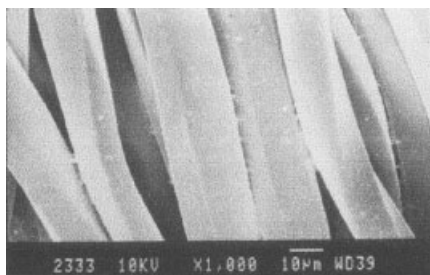


Figure 1 Untreated PET fiber (magnification  $\times 1000$ ).

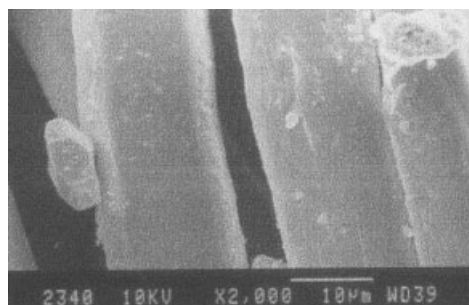


Figure 2 AN-treated PET fiber (magnification  $\times 2000$ ).

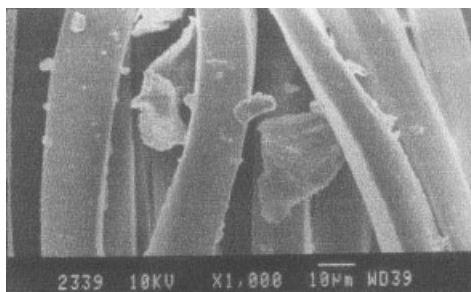


Figure 3 AN-treated PET fiber (magnification  $\times 1000$ ).

The  $T_g$  of the treated material was found to decrease. A similar decreasing trend in  $T_g$  as a consequence of solvent treatments was previously reported by many researchers.<sup>13-17</sup>

### CONCLUSIONS

- Pretreatment of 100% poly(ethylene terephthalate) fabric using acetonitrile solvent was found to increase the dye uptake. The magnitude of increase in dye uptake depends on the duration of pretreatment and the temperature of dyeing.
- The optimum pretreatment duration was found to be 8 min and the dyeing temperature, 80°C.
- The improvement may be attributed to an increase in the intersurface area by swelling and greater segmental mobility of polymer molecules.
- Assessment of wash, light, and rubbing fastness properties of the treated and untreated polyester fabrics shows that the solvent treatment did not affect the fastness properties.
- The solvent treatment did not affect the physical properties such as shrinkage properties, percentage crimp, and tearing strength.

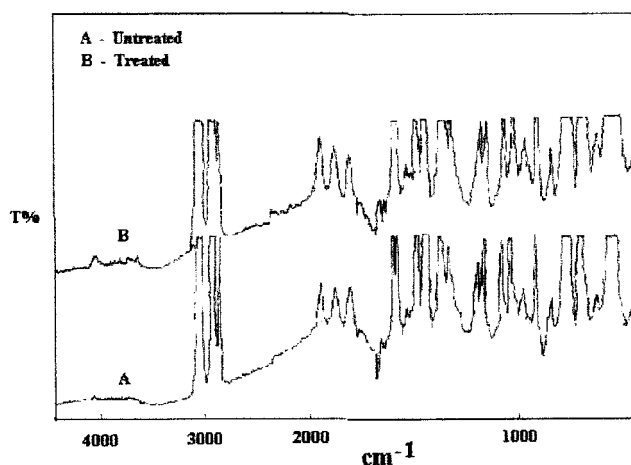


Figure 4 FTIR spectra of (A) untreated and (B) treated PET fabric.

TABLE VII  
Spectral Data of Untreated Polyethylene Terephthalate

Band (cm <sup>-1</sup> )	Assignment
3072, 3043	Aromatic C—H stretching
2985, 2920, 2914, 2868	Methylene C—H stretching
1917, 1824	Weak combination bands and overtone bands attributed to aromatic C—H
1684	C=O stretch
1588	Ring C—...C stretching in plane
1559, 1540, 1522, 1566, 1472, 1417	Skeletal vibrations involving C—C stretching within the ring
1339, 1237, 1171, 1124, 994	In-plane bending of aromatic C—H "C—C(=O)—O"—C—O stretching vibrations O—C—...C stretch
930, 880, 825, 754, 750, 720, 699, 652	Out of C—H plane bending of aromatic system

- SEM studies showed that the solvent treatment modified the surface of the fabric and only slightly affected the fabric structure.
- FTIR studies showed there was no introduction of any new functional groups or the alteration of existing groups.
- DSC studies showed a slight increase in the amorphous region of the treated materials.

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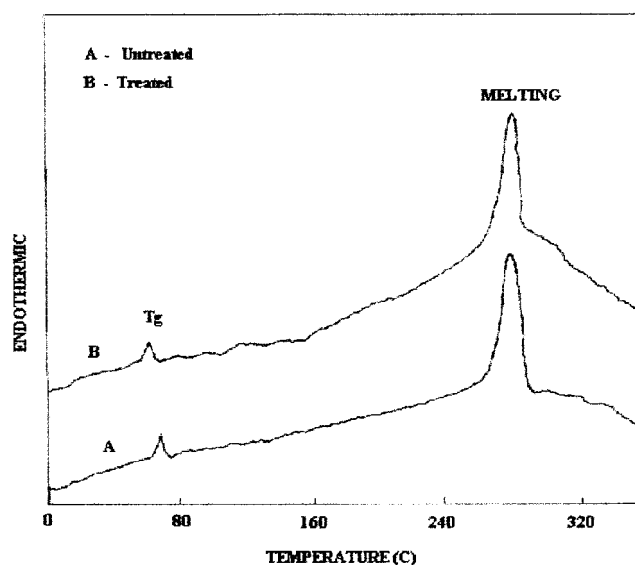


Figure 5 DSC curves for (A) untreated and (B) treated PET fabric.

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