

Soil-release behaviour of polyester fabrics after chemical modification with polyethylene glycol

T M R Miranda¹, J Santos¹ and G M B Soares¹

¹Minho University. 2C2T – Centre for Textile Science and Technology. Department of Textile Engineering. Guimarães. Portugal

Email: tmiranda@det.uminho.pt

Abstract. The fibres cleanability depends, among other characteristics, on their hydrophilicity. Hydrophilic fibres are easy-wash materials but hydrophobic fibres are difficult to clean due to their higher water-repellent surfaces. This type of surfaces, like polyester (PET), produce an accumulation of electrostatic charges, which favors adsorption and retention of dirt. Thus, the polyester soil-release properties can be increased by finishing processes that improve fiber hydrophilicity. In present study, PET fabric modification was described by using poly(ethylene glycol) (PEG) and N,N'-dimethylol-4,5-dihydroxyethylene urea (DMDHEU) chemically modified resin. Briefly, the modification process was carried out in two steps, one to hydrolyse the polyester and create hydroxyl and carboxylic acid groups on the surface and other to crosslink the PEG chains. The resulting materials were characterized by contact angle, DSC and FTIR-ATR methods. Additionally, the soil release behavior and the mechanical properties of modified PET were evaluated. For the best process conditions, the treated PET presented 0° contact angle, grade 5 stain release and acceptable mechanical performance.

1. Introduction

Polyester fabrics are made from poly(ethylene terephthalate) (PET), currently accounting for more than 50% of all fibrous materials, have high uniformity, mechanical strength and resistance against chemicals and abrasion.

The fibres cleanability depends, among other characteristics, on their hydrophilicity. So, hydrophilic fibres are easy-wash materials but hydrophobic fibres are difficult to clean due to their higher water-repellent surfaces. These type of surfaces, like that of PET fibres, produce an accumulation of electrostatic charges that attract and retain dirt. Thus, the polyester soil-release properties can be increased by finishing processes that improve fiber hydrophilicity [1, 2].

In order to increase their surface energy and hence their hydrophilicity, the PET chemical structure can be modified by different ways: by chemical finishing or grafting, chemical treatment with NaOH, superficial physical treatment using plasma or by a biochemical treatment with enzymes [1, 2, 3, 4, 5]. Poly(ethylene glycol) (PEG) can be used in chemical PET modification, due to its exceptional properties such as hydrophilicity, flexibility and nontoxicity [1]. This hydrophilic polymer has already been used to improve soil-release properties of PET fibres in the form of a copolymer with blocks of poly(ethylene terephthalate) and poly(oxyethylene terephthalate) that provide a structure with alternating hydrophilic and hydrophobic regions that have a strong attraction for the PET surface [2].

Alkaline hydrolysis of PET fibres is one of the most reported and widely used strategies to enhance PET reactivity, by increasing the number of reactive sites that can react during chemical modification. The nucleophilic attack of a base on the electron-deficient carbonyl carbon in PET causes chain



scissions at the ester linkages along the polyester chain, producing carboxylic acid and hydroxyl polar end groups (Figure 1) [2, 6, 7].

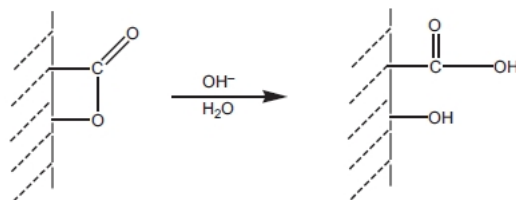


Figure 1. Hydrolysis of PET fibres in alkali solution.

The aim of the present paper, is to develop a chemical modification of polyester fabrics, in order to improve their Soil-Release properties by treatment with PEG and N,N'-dimethylol-4,5-dihydroxyethylene urea (DMDHEU) chemically modified resin.

2. Experimental

2.1 Materials and chemicals

A 100% polyester fabric was purchased from Lemar (Portugal). PEG (average molecular weight 1000 and 2000) was purchased from Merck (Portugal), Adipret P-LF (modified DMDHEU resin with catalyst incorporated) was used as a crosslinking agent and kindly offered by ADI Group (Portugal).

2.2 Methods

2.2.1 PET alkali treatment. Before treatment, all fabrics were stored in conditioned atmosphere (20 ± 2 °C and 60% R.H.) during 24h, according to ISO139:1977 and then weighed. After that, bleached PET fabric samples with 30x15 cm, were treated in NaOH aqueous solutions at different concentrations and temperatures, namely, 2M, 2.5M and 4M at 90 °C and 3M at 90 °C and 55 °C. All treatments were developed in an Ahiba dyeing machine for 30 min, using a 1:20 liquor ratio. Finally, the samples are thoroughly washed in tap water, to remove unreacted and soluble products, dried and stored again in conditioned atmosphere during 24h and then again weighed in order to calculate loss weight.

2.2.2 PET chemical modification with PEG and modified DMDHEU resin by pad-dry-cure process. Before treatment, all PET fabrics previously hydrolyzed, were stored in conditioned atmosphere (20 ± 2 °C and 60% R.H.) during 24h, according to ISO139:1977. Samples were then impregnated into an aqueous solution with 250 g/L of PEG-1000 or PEG-2000 and 60 g/L or 120 g/L of chemical modified DMDHEU resin. After impregnation, two approaches were taken. In the first approach, the samples were dried during 7 minutes at 60 °C, then cured for 3 minutes at 160°C and finally washed and dried. In the second approach, the samples were first dried at room temperature, then cured for 90 s at 180 °C and then finally washed and dried.

2.2.3 Testing methods. Before being analysed, all fabrics were stored in conditioned atmosphere (20 ± 2 °C and 60% R.H.) during 24h, according to ISO139:1977. The thermal parameters of the fabrics were measured with a DSC –822° instrument (Mettler Toledo). The IR analyses were made on a Fourier-transform infrared spectrophotometer Nicolet-Avatar 360. The FTIR spectra of untreated and treated PET fabric samples were recorded with 4 cm⁻¹ resolution and 32 scans, with a wavenumber range of 400-4000 cm⁻¹. The FTIR spectra were obtained by attenuated total reflectance technique (ATR), with the zinc selenide being the ATR crystal material used in this work. The ATR correction was made with OMNIC 5.2 software (Nicolet, Izasa, Portugal). The contact angle can be defined as the angle

between a liquid droplet and the surface over which it spreads and measurement provides an indication of the nature of the surface. The evaluation of the contact angle was carried out on a system OCA 15 Plus, DataPhysics Instruments GmbH. Soil-Release tests were performed according to AATCC Test Method 130-2000. Tensile strength evaluation was performed on a Hounsfield Tester, model H1OKS, according to ISO Test Method 13934.

3. Results and discussion

3.1 PET surface modification in alkali solutions

It was observed that samples treated at 90 °C, in a 3M and 4M NaOH aqueous solutions, show high fibre degradation, with formation of visible holes in the material. On the other hand, PET samples treated with 2M and 2.5 M NaOH solutions, at the same temperature conditions, show not visible degradation and a very soft touch. The samples that did not show visible degradation, showed significantly different weight loss values, according to the Tukey test (Figure 2b). The sample treated with 3M NaOH aqueous solutions at 55 °C, was the one that presented less loss weight, as can be proven by the analysis of figure 2a). These results are in agreement with previous studies [6].

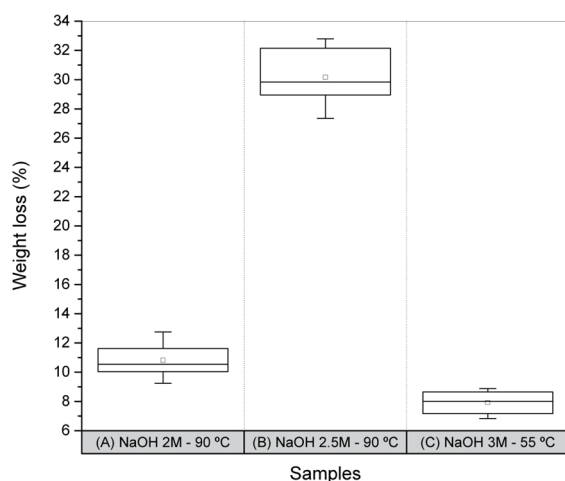


Figure 2a). Weight loss of the treated samples.

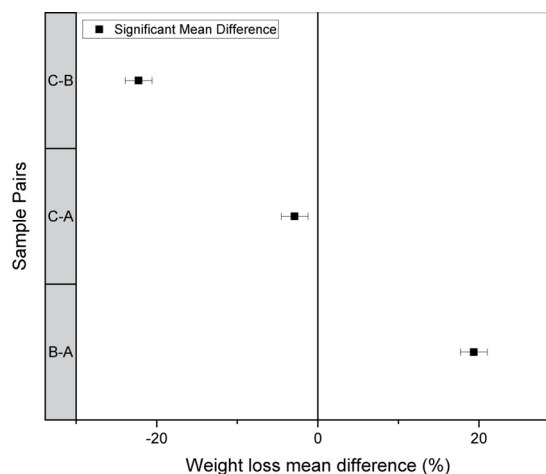


Figure 2b). Tukey test - Weight loss means comparison.

3.2 FTIR spectra

The obtained spectra are presented in the Figure 3, where we can observe several absorption bands characteristics of the untreated PET. So, the absorption peak around 1708 cm^{-1} is assigned to C=O stretching for the ester groups. The peaks at 1465 and 1403 cm^{-1} may correspond to the bending vibration in the plane of the C-H bond of the benzene ring. The absorption bands in the region of 1245-1000 cm^{-1} , are assigned to stretching vibrations of the C-O bond [8].

From the analysis of Figure 3, we can also observe an absorption peak at 1506 cm^{-1} that appears in the PET sample treated with NaOH (3M) at 55°C, which is assigned to an asymmetric stretching vibration of the COO^- anion, which shows that some carboxylic acids salts have been formed and there was effectively an alkaline hydrolysis of the polyester [8].

3.3 Contact angle of hydrolysed PET

The contact angle measurement is the main characterization method of hydrophobic and hydrophilic surfaces. Based on these results, it was possible to conclude that alkaline hydrolysis makes the PET samples more hydrophilic. Thus, we observed that the untreated polyester has the highest contact angle values (99.1°), which confirms the hydrophobic character of this fibre and in general, the contact angle decreases with saponification, regardless of the conditions used. The best results correspond to the PET sample hydrolyzed with NaOH 3M, at 55°C, with a contact angle of 23,8°.

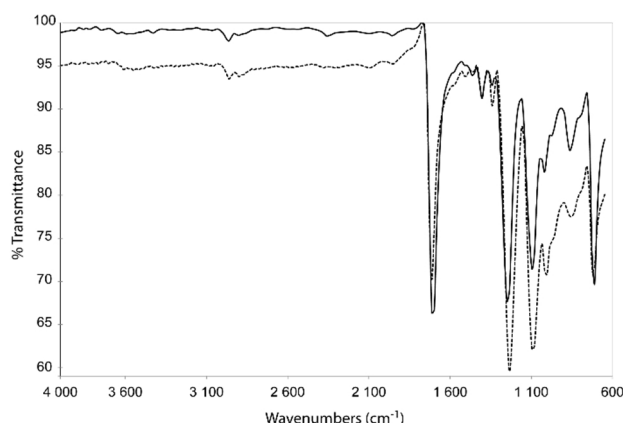


Figure 3. FTIR spectra of untreated PET (—) and PET treated with NaOH (3M) at 55 °C (---).

3.4 Basic thermal properties of hydrolysed PET

A DSC equipment was used to evaluate melting temperature and fusion enthalpy of untreated and treated PET samples during the exothermic process. Figures 4 and 5 show the DSC thermograms of untreated and hydrolysed PET

In Table 1 we can see the melting enthalpy and the melting point of untreated (A) and hydrolysed PET with NaOH 3M at 55 °C (B).

Table 1. Differential scanning calorimetry results of untreated (A) and treated PET (B)

	Melting enthalpy (J/g)	Melting point (°C)
A	48.11	253.62
B	45.93	253.56

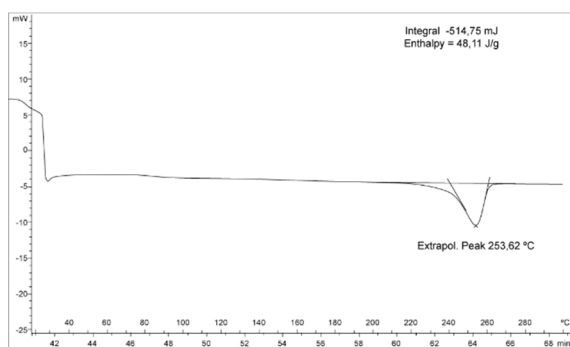


Figure 4. DSC heating curve of untreated PET.

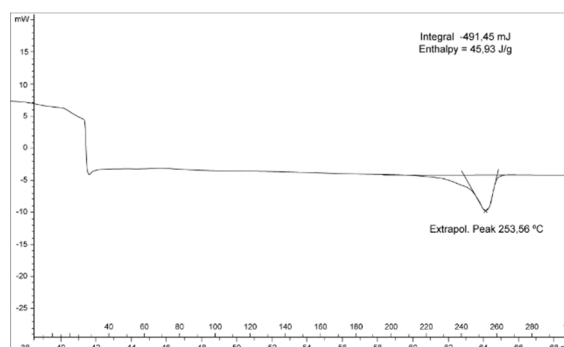


Figure 5. DSC heating curve of PET treated with NaOH solution (3M) at 55 °C.

Analyzing the Table 1, it can be concluded that alkaline hydrolysis promotes a polymer chains breaking, leading to a decrease in crystallinity. Thus, a slight decrease in melting enthalpy was observed for the PET samples hydrolyzed with NaOH 3M at 55 °C, when compared with the untreated PET. It should be noted that, the melting point for the treated and untreated PET samples are similar. These results are in agreement with the results obtained in the evaluation of the tensile strength of the hydrolyzed PET which are closest to the untreated PET (results not shown). So, we can conclude that the best conditions to develop PET saponification with a minimum fibre degradation is a treatment with NaOH 3M at 55 °C for 30 minutes.

3.5 Chemical modification of hydrolyzed PET fibres with PEG and DMDHEU resin

The chemical modification of PET fibres was studied in terms of PEG and resin concentrations as well as process conditions. Under suitable conditions the application of a crosslinking agent (modified DMDHEU resin), that can act as a bridge, the chemical crosslinking reaction between the low molecular weight PEG and the fibre can be promoted.

It was observed that by performing a pre-drying at 60 °C, after impregnation and before the curing process, a PEG degradation occurs as described by J. Glastrup [9]. He noted that PEG degradation can occur under air stream at 70°C, with formation of formic acid. Under dry conditions, this acid reacts with the terminal hydroxyl group of the PEG, resulting in formic acid esters. Under wet conditions the acid stays in solution or evaporates. Therefore, the pre-drying step previously described by T. L. Vigo and J. S. Bruno [10], in their PET modification process with DMDHEU and adopted in our first trials, was changed by a simple room temperature drying process. The PET samples were thus treated by this process, with PEG of different molecular weights (1000 and 2000) in the presence of a modified DMDHEU resin (Adipret P-LF). After the treatment, we evaluated the changes produced in terms of weight gain, contact angle, mechanical and soil-release properties.

Several treatments were developed in conditions described in Table 2. In Figure 6a) we can see the weight gain obtained in each treatment. According to the Tukey test presented in Figure 6b) the best results are obtained in the case of sample D, which are significantly different from the results obtained in other samples. The increase in the hydrophilicity of treated PET surface was confirmed by decrease of contact angle from 99° to 0° (Figure 7).

Table 2. Chemical modification conditions

Sample	PEG 1000 (g/L)	PEG 2000 (g/L)	DMDHEU resin (g/L)
A	250		60
B	250		120
C		250	60
D		250	120

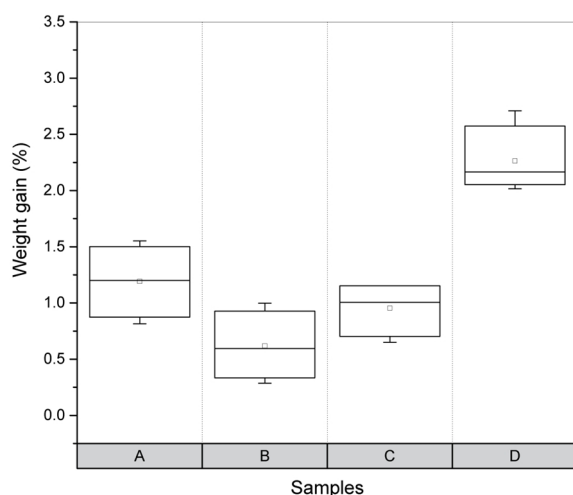


Figure 6a). Weight gain of the treated samples.

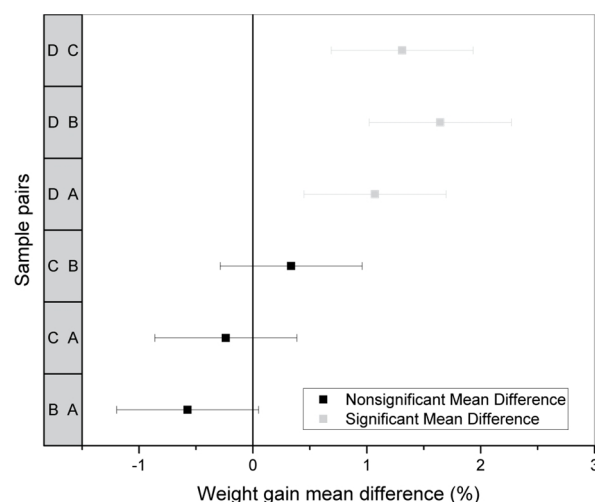


Figure 6b). Tukey test - Weight gain means comparison.



Figure 7. Dynamic contact angles of water drop on a) untreated PET; b) PET treated with PEG (1000) and DMDHEU (60 g/L); c) PET treated with PEG (2000) and DMDHEU (60 g/L).

The treated PET samples showed better soil-release properties, increasing the stain release degree from 3-4 in case of untreated PET, to stain release grade 5 for PET fabric treated with PEG (2000) and modified DMDHEU (60 g/L) (Figure 8).

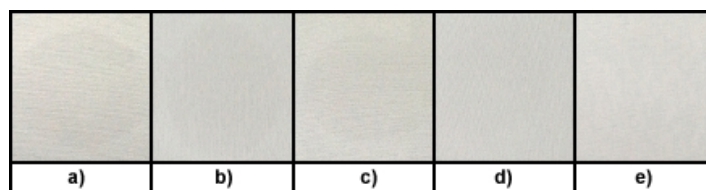


Figure 8. PET samples used in the evaluation of soil-release properties. a) untreated PET; b) PET fabric treated with PEG (1000) and DMDHEU resin (60 g/L); c) PET fabric treated with PEG (1000) and DMDHEU resin (120 g/L); d) PET fabric treated with PEG (2000) and DMDHEU resin (60 g/L); e) PET fabric treated with PEG (2000) and DMDHEU resin (120 g/L).

4. Conclusions

This work allowed to conclude that, PET chemical modification with PEG and modified DMDHEU resin was effective. The best results were obtained with PET fabric treated with PEG 2000 in presence of resin (60 g/L). This sample presented a 0° contact angle, acceptable mechanical performance (results not shown) and good soil-release properties.

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