

## Polyester-Polyvinylalcohol Hydrophilization Strategies

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**Keywords:** PET fabric, Poly (vinyl alcohol), Hydrophilicity, Soil-release

**Abstract.** Poly (ethylene terephthalate) (PET), also commonly called as polyester, is the most widely used polymer for the production of synthetic fibres over the past fifty years. The frequent use of this PET is due to its high mechanical strength combined with other properties such as the resistance to chemical products, stretching and abrasion. The fibre's hydrophobicity also impacts the difficulty of cleaning these materials [1, 2]. Previous works show that treatment with concentrated NaOH solutions can greatly improve hydrophilicity of PET fibre [1, 2, 3, 4]. However a significant decrease of mechanical properties takes place during this process. In this work, chemical strategies to counteract this negative effect and further increase the hydrophilicity of PET fibre's has been tested. In particular, the effect of polyvinyl alcohol (PVA) and N, N'-dimethylol-4, 5-dihydroxyethyleneurea (DMDHEU) chemically modified resin in the functionalization of saponified PET was carefully analysed. The treated fabrics were characterized by scanning electron microscopy (SEM), contact angle, ATR-FTIR spectroscopy and differential scanning calorimetry (DSC). When the best process conditions were considered for PVA-DMDHEU application, the modified PET presented a contact angle of 33.9°, stain release grade of 4 and a 45.6% increase in its mechanical properties when compared to saponified PET.

### Introduction

Polyester is a textile fibre of huge commercial importance. It is a polymer formed by polycondensation of terephthalic acid with ethylene glycol diol. The frequent use of this textile substrate is due to the fact that it has excellent properties such as high uniformity, mechanical strength, abrasion and resistance to chemicals. However, polyester fibres are hydrophobic leading to poor performance regarding moisture management, anti-static and washability properties [3]. Improving the hydrophilicity of PET fibres allows its wide application in various fields, such as biomedical and textiles areas. The dyeing, soil-release and comfort properties are improved when the fabrics hydrophilicity is increased [4].

Several strategies can be used to improve the surface energy and consequently change the hydrophilicity of the polyester structure. Chemical finishing, grafting, surface chemical hydrolysis with sodium hydroxide, physical surface treatment using plasma, biochemical treatment with enzymes and cyclodextrins-based PET fabric finishes are some examples of tested procedures [2, 5].

The most common chemical process is the saponification using concentrated sodium hydroxide solutions. However, this process needs careful control in order to avoid excessive fibre degradation and loss of its mechanical properties, compromising its use.

Water-soluble polyols can be insolubilized in fibrous materials by reacting with the tetrafunctional resin DMDHEU. In this context, Vigo and Bruno studied the application of low molecular weight PEGs to cellulosic and synthetic fibres and they found that several properties of the materials change, namely with regard to their thermal comfort, hydrophilic character and water sorption properties [6]. In the case of PET, it was found that the beneficial effect on mechanical and cleaning properties also occurred due to the deposition of the hydrophilic polymer resulting from the reaction of PEG with resin but such treatment is not durable to laundering. The fewer OH groups on PET reduces the yield of the crosslinking reaction [6].

More recently, Miranda and other investigators found that the durability of the PEG-DMDHEU resin on PET surface can be improved by a previous saponification of the textile [2, 7]. This previous hydrolysis process creates hydroxyl and carboxylic acid groups on polymer, which will be responsible for binding the other polymers to the textile structure [2, 7].

Poly (vinyl alcohol) (PVA) is a polyol with unique properties, such as hydrophilicity, flexibility, nontoxicity, resistance against chemicals, easy preparation and biodegradability [1, 8]. It is obtained *via* hydrolysis of poly (vinyl acetate) in which acetate groups are replaced by hydroxyls [8].

The aim of the present work is to develop a chemical functionalization of PET saponified fabrics with PVA and DMDHEU chemically modified resin in order to improve its mechanical properties, hydrophilicity and soil-release properties.

## Materials and Methods

**Materials** A 100% taffeta polyester fabric made from cut fibre was used. It was supplied by the company Lemar (Portugal), already bleached with a mass per unit area of the 102g/m<sup>2</sup>, 7.5 tex (warp), 17.3 (weft) and a thickness of the 0.22 mm. PVA (average molecular weight 9000- 10000) with hydrolysis degree of 80% was purchased from MoleculAlchemy (Portugal). Adipret P-LF (modified DMDHEU resin with catalyst incorporated, from now on described as resin) was used as a crosslinking agent and kindly offered by ADI Group (Portugal).

**Methods** All samples (30x15 cm) were weighed after being stored in a conditioned atmosphere (30 ± 2 °C) for 24h.

The fabric PET samples were saponified in an Ahiba dyeing machine with NaOH aqueous solutions (3M), using a 1:20 liquor ratio, at 55 °C for 30 minutes [2, 7, 9, 10]. At the end, the samples were thoroughly washed in tap water to remove unreacted and soluble products, and dried.

The saponified PET samples were impregnated with the aqueous solution containing different concentrations of the modified resin (40 g/L and 60 g/L) and several concentrations of PVA (25, 50 and 70 g/L ) with average molecular weight of 9000–10000 and an hydrolysis degree of 80%. After impregnation, the samples were first dried at room temperature, then cured 90 s at 180°C and finally washed and dried during 24h at 30°C.

The thermal properties of the fabrics were measured with a DSC – 822° instrument (Mettler Toledo). The FTIR-ATR analyses were made on Fourier–transform infrared spectrophotometer SHIDMAZU IR Affinity S1. The FTIR spectra of treated and untreated PET fabric samples were recorded with 8 cm<sup>-1</sup> resolution and 45 scans, with a wavenumber range of 400-4000 cm<sup>-1</sup>. The FTIR spectra were obtained by attenuated total reflectance technique (ATR), with the Diamond being the ATR crystal material used in this work. The ATR correction was made with the software LabSolutionsIR.

The contact angle was carried out on system OCA 15 Plus, DataPhysics Instruments GmbH.

Soil release tests were performed according to AATCC Standard Test Method 130-2018.

The surface morphology of all PET fabric samples were observed in SEM (NOVA 200 Nano SEM, FEI Company).

Mechanical properties of fabrics were evaluated according to ISO Standard Test Method 13934. These tensile strength tests were performed by Hounsfield Tester, model H1OKS.

## Results and Discussion

Alkaline hydrolysis of polyester 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 functionalization. The nucleophilic attack of a base on the electron-deficient carbonyl carbon in polyester causes chain scissions at the ester linkages along the polyester chain, producing carboxylic acid and hydroxyl polar end groups [2, 6, 7, 10, 11]. Briefly, the functionalization process here described was carried out in two stages, one to hydrolyse the polyester in alkaline medium, through

the creation of hydroxyl and carboxylic acid groups on the surface and improve its hydrophilicity and the other to insolubilized the PVA-resin on PET.

The extent of the crosslinking reaction between polyols, namely the PVA and PEG and resin depends on many factors, such as the molecular weight and polymer solution concentration, the type and concentration of the crosslinking agent, catalyst and process conditions, such as, temperature and time [6]. In PVA's case, it should be noted that the reaction extent may also depend on the degree of hydrolysis. The range of average molecular weights that can be insolubilized is wide ( $M_n$  600 – 20.000) as well as the curing conditions (0.25 – 10 minutes at 80 – 200°C) [6]. It is expected that the hydrophilicity and the soil-release properties of PET fabrics can be improved with the use of polyols, namely PEG and PVA, since these polymers are hydrophilic [2, 4]. In fact, PEG molecules have two terminal hydroxyl groups and ester groups along the chains favouring hydrogen bonds with water molecules. PVA molecules have hydroxyl groups along the chains, allowing the establishment of hydrogen bonds with the water molecules. However, PET does not have enough chemically active groups capable of reacting with the -OH groups of polyols, with the exception of a few acid end groups.

In the second stage of material functionalization, the PVA resin polymer is formed and insolubilized in the saponified PET fabric samples. [6].

Several treatments were developed to modified PET samples. The conditions are described in Table 1.

**Table 1** Functionalization conditions of PET samples.

Treatments								
Untreated PET	X							
NaOH 3M		X	X	X	X	X	X	X
Resin	40 g/L		X		X	X		
	60 g/L			X			X	X
PVA	25 g/L				X			
	50 g/L					X	X	
	70 g/L							X
Tests	Samples							
	A	B	C	D	E	F	G	H
Number of Tests		10	6	6	8	7	8	6
Weight gain average (%)		-5.31	0.96	1.38	3.32	4.97	5.92	7.84

The weight gain samples after each treatment is shown in the boxplot of Fig. 1a). The differences between the average weight gain of the samples obtained by the various treatments are graphically represented in Fig.1b) considering a confidence interval of 95%.

Analysing the results, a weight loss can be observed in the case of saponified PET. This result was expected, since there was a break in the PET chains according to the previous described. However, an increase in weight was observed in all treatments performed with the application of PVA and resin, and the differences between the average weight gains between all treatments were statistically significant as can be seen in Fig. 1b).

In the test corresponding to saponified PET, an average weight loss of 5.31% was obtained. This result was expected, since there was a break in the PET chains according to the previous described.

In the case of saponified PET treated with resin 40g/L (test C), a weight increase was observed. Hydrolysed PET fibres have functional groups available (such as -OH) that can bond by grafting and/or react directly with the resin [6]. With the increase of the resin concentration, from 40 to 60 g/L (test D), a weight increase was obtained (1.38%), which indicates that there was a greater extension of the reaction by grafting and/or react directly with the resin.

In turn, the saponified PET sample and treated with PVA (25 g/L) in the presence of resin (40 g/L) showed a weight gain of 3.32% when compared to the samples from tests C and D. By increasing the PVA concentration from 25 g/L to 50 g/L and maintaining the resin concentration, a higher weight gain of 4.97% was obtained. In the samples of tests E and F, keeping the PVA concentration and

increasing the resin amount from 40 to 60 g/L, a greater weight gain (5.92%) was obtained. Finally, keeping the resin concentration (60 g/L) and increasing the PVA concentration from 50 g/L to 70 g/L, an even greater weight gain (7.84%) was observed. These results indicate that the PVA and resin was insolubilized in saponified fabric samples and cross-linked in the PET. Similar effect was described by Vigo and collaborators regarding the binding of PEGs to PET through DMDHEU resin using a pad-dry-cure process [6, 12].

As shown in Fig.2a the increase in weight of samples treated with PVA and resin is accompanied by an increase in the mechanical strength of the fibre, which undergoes an increase of about 45.6% when compared to saponified PET treated with 60g/L of resin and 70 g/L of PVA (648 N after treatment against 445 N before treatment).

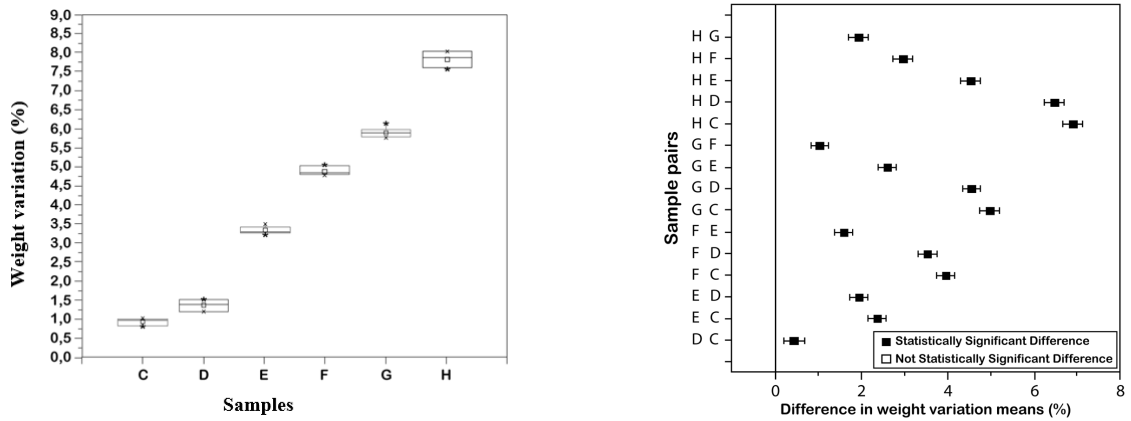


Fig. 1a) Weight gains of the treated samples. Fig. 1b) Weight gain mean values comparison (Tukey test).

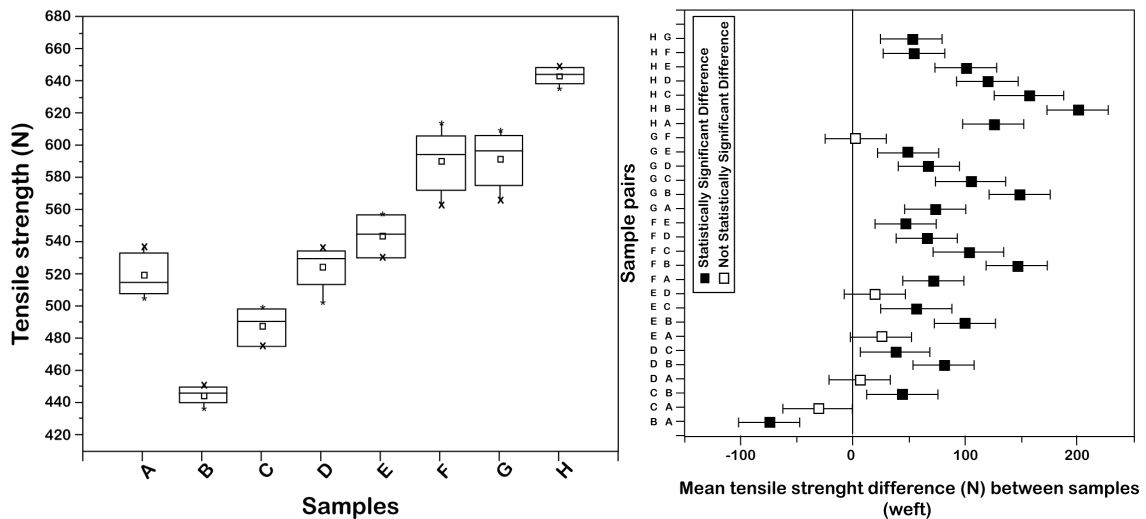
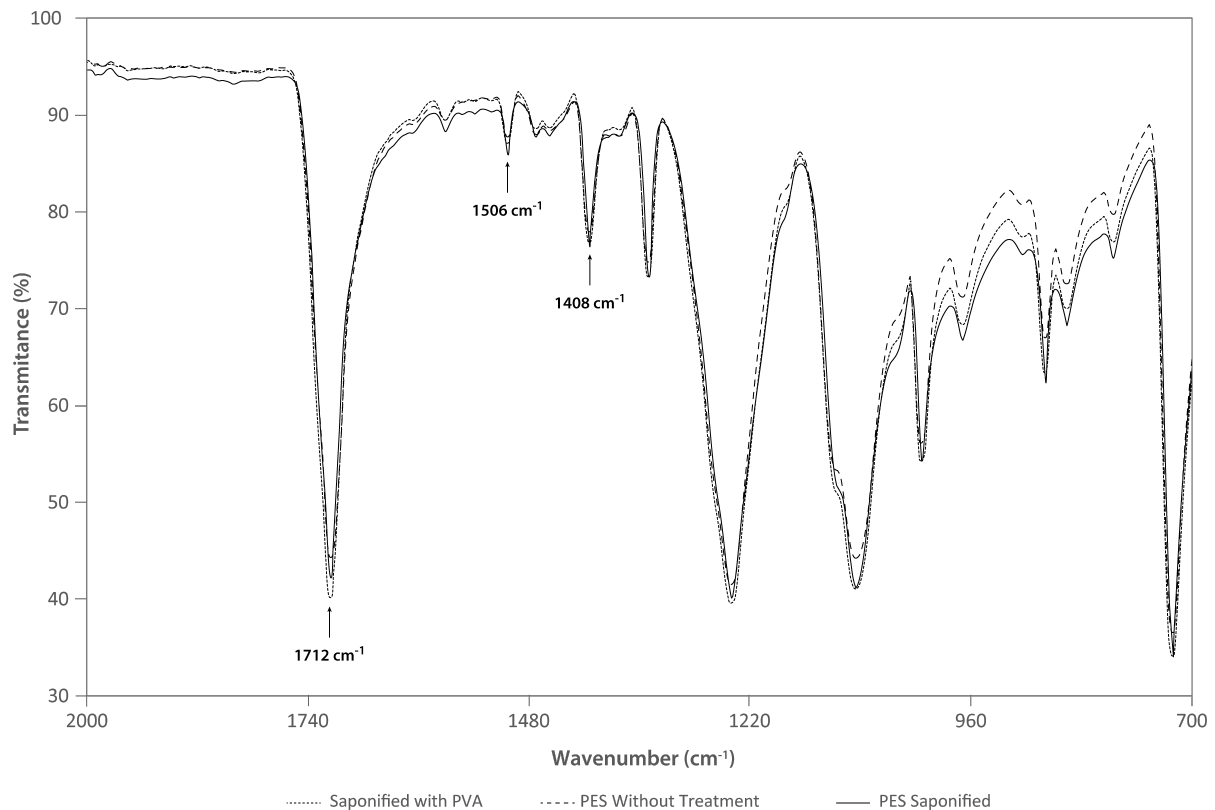


Fig. 2a) Tensile strength mean values of samples. Fig. 2b) Tensile strength means comparison (Tukey test).

It should be noted that the mechanical strength traction results presented and discussed above are statistically significant (Fig. 2b) proving that the incorporation of PVA crosslinked with resin and insolubilized in saponified PET produces an improvement in resistance to mechanical strength traction of textile material.

In order to characterize the PET samples, FTIR-ATR analysis were recorded. Fig. 3 shows the obtained FTIR-ATR spectrum of unmodified PET. It can be observed several PET characteristic absorption bands. The absorption peak around  $1712\text{ cm}^{-1}$  is assigned to C=O stretching for the ester groups. The peaks at  $1465$  and  $1403\text{ cm}^{-1}$  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  $1245\text{-}1000\text{ cm}^{-1}$  are assigned to stretching vibrations of the C-O bond. It should be noted that the original PET spectrum shows two

bands around  $1506\text{ cm}^{-1}$  and  $1408\text{ cm}^{-1}$  attributed to asymmetrical and symmetrical elongation vibrations of the  $\text{COO}^-$  anion respectively [13]. The appearance of these peaks indicates that the supplied PET had already been through a physical treatment that led to fibre degradation.

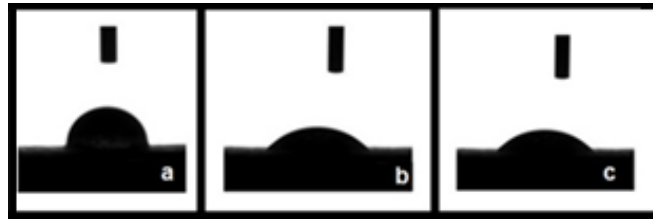


**Fig. 3** ATR-FTIR spectrum of untreated PET fabric, ATR-FTIR spectrum of saponified PET fabric and ATR-FTIR spectrum of hydrolysed PET fabric treated with PVA (9000-10000), hydrolysis degree of 80% (50 g/L) and resin (60 g/L).

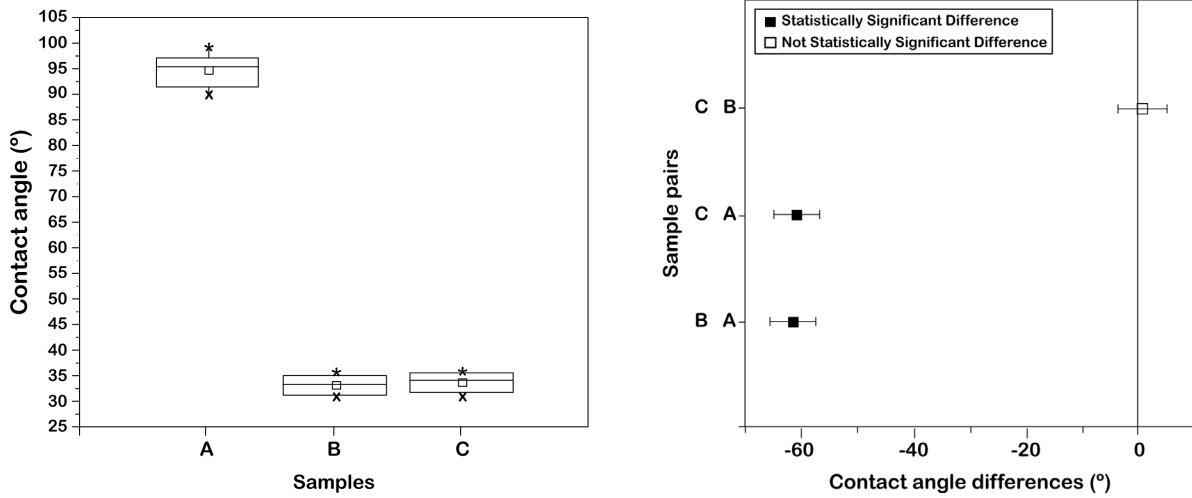
The FTIR-ATR spectrum of saponified PET fabric shows an additional peak at  $2359\text{ cm}^{-1}$  (not considered in Fig.3). This is assigned to carboxylic group introduced on the PET surface due to hydrolysis of the ester linkage [14].

Comparing the spectra of saponified PET with PET treated with a combination of 50 g / L of PVA and 60 g / L of resin, it is possible to observe a slight increase in peak intensity at  $1700\text{ cm}^{-1}$  which corresponds to the vibration of the carbonyl group of the tetrafunctional resin ring DMDHEU, which may result from the incorporation of the PVA-resin polymer in the PET fabric during the functionalization process [6].

The contact angle measurement is the main characterization method of hydrophobic and hydrophilic surfaces. The Fig. 4 shows respectively the static contact angles of the distilled water drops on the surfaces of untreated (a), hydrolysed (b) and treated with resin and PVA (c) PET samples. Fig. 5a) presents the contact angle mean values obtained for the different samples. The fibres become more hydrophilic ( $36.2^\circ$ ) by alkaline hydrolysis due to the break of the PET chains and the formation of acidic and hydroxyl groups. However, the slight increase in the mean hydrophilicity of saponified PET treated with PVA and resin ( $33.9^\circ$ ) is not statistically significant when compared to saponified sample (Fig. 5b)).

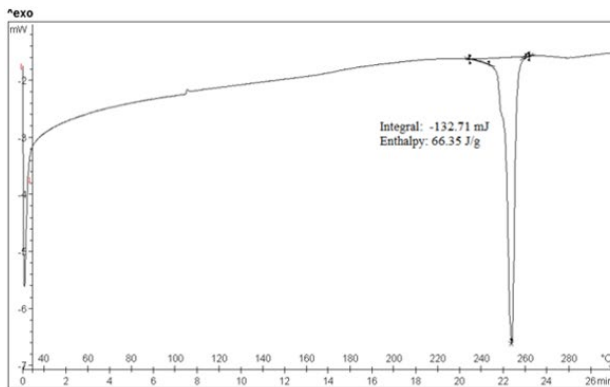


**Fig. 4** Static contact angles of water drop on a) Untreated PET; b) Saponified PET c) Saponified PET treated with PVA (9000-10000) and DMDHEU (40 g/L).

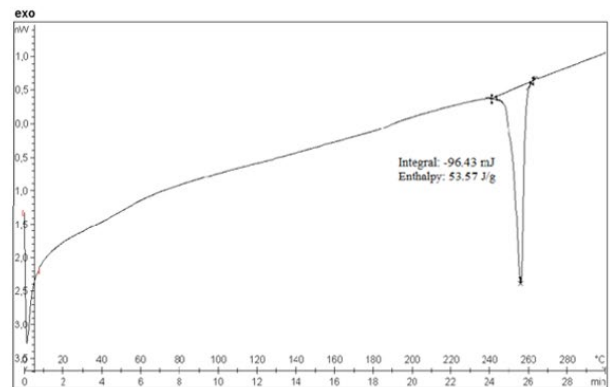


**Fig. 5a)** Contact angle mean values of samples. **Fig. 5b)** Contact angle means values comparison (Tukey test).

The thermal parameters of the treated and untreated PET fabrics are studied using differential scanning calorimeter (DSC). The melting temperature and fusion enthalpy of samples during the exothermic process were recorded (Fig. 6 and Fig. 7). DSC thermograms analysis show that there is a decrease in the enthalpy of fusion of treated PET when compared to the untreated one, obtaining 53.57 J/g and 66.35 J/g respectively. The enthalpy of fusion is the energy involved in the formation and melting of crystalline regions and it is proportional to the percentage of crystallinity of the sample. Fusion's enthalpy decreases in the case of PET samples treated with PVA and resin, indicating a loss in the degree of crystallinity of the fabric and, consequently, the loosening of compact structure [1]. It should be noted that there are no significant differences regarding the melting temperatures values of untreated and treated PET with PVA and resin.



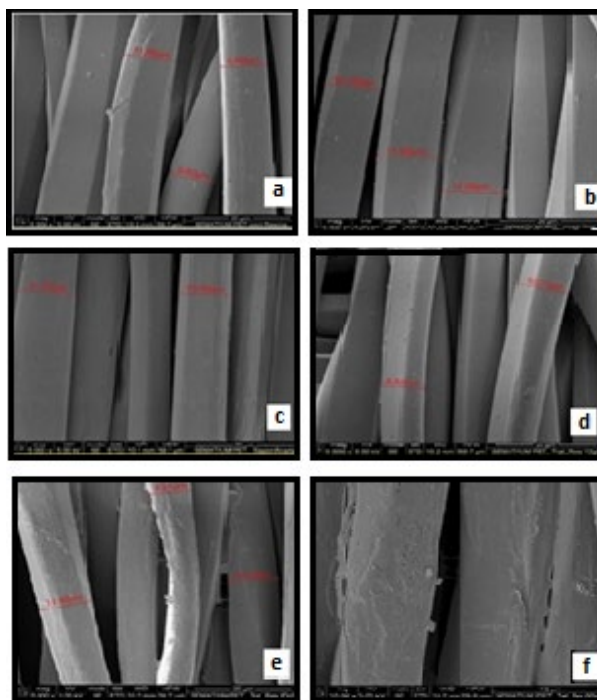
**Fig. 6** DSC heating curve of original PET.



**Fig. 7** DSC heating curve of PET treated with PVA (50 g/L) and resin solution (40 g/L).

The Scanning Electron Microscopy (SEM) technique has significantly contributed to the polymers characterization [14]. The surface morphology of original PET and the treated PET samples are shown in Fig. 8. It can be observed that untreated PET fibres are smooth. In SEM image that shows saponified PET with NaOH (3M) there are no fissures. These results are in line with those presented by Kish and other investigators [15].

The analysis of Fig. 8 allows us to observe a clear and accentuated change in the morphology of the hydrolysed PET fibres treated with PVA (50 g/L) and with resin (60 g/L). Regarding the image with a magnification of 10000x (f) it is possible to note the rough appearance and the deposition of the PVA- resin polymer on the fibres surface.



**Fig. 8** SEM photographs with a magnification of 5000x (except f): a) untreated PET; b) saponified PET c) saponified PET with resin (60 g/L); d) saponified PET with PVA (50 g/L) and resin (40 g/L); e) saponified PET with PVA (50 g/L) and resin (60 g/L) and f) PET treated with same conditions of e) but with a magnification of 10000x.

The soil-release properties of PET samples were determinate and a change from grade 2 of PET to 4 to PET after saponification was observed. The treatment of saponified PET with PVA 9000-10000 (50 g / L) and resin (40 g / L) did not change its soil-release behaviour.

## Conclusions

This work allowed to conclude that the chemical modification of saponified PET with PVA and modified DMDHEU resin results in:

1. Better soil release properties than untreated polyester but similar to saponified PET.
2. Rough appearance of PET fibres by the deposition of the PVA-resin polymer, confirmed by SEM results.
3. PET materials less crystalline, but similar to saponified fibres.
4. PET with acceptable mechanical properties, analysed in terms of tensile strength.

## Acknowledgment

Programme - COMPETE and by national funds through FCT – Foundation for Science and Technology within the scope of the project POCI-01-0145-FEDER-007136.

**References**

- [1] S. Natarajan, J.J. Moses, Surface modification of polyester fabric using polyvinyl alcohol in alkaline medium, *Indian Journal of Fibre & Textile Research*. 37 (2012) 287-291.
- [2] T.M.R., Miranda, J. Santos, G.M.B Soares, Soil-release behaviour of polyester fabrics after chemical modification with polyethylene glycol. *IOP Conference Series-Materials Science and Engineering*. (2017) 254 (3).
- [3] V. Takke, N. Behary, A. Perwuelz, C. Campagne, Surface and adhesion properties of poly(ethylene glycol) on polyester (polyethylene terephthalate) fabric surface: Effect of air-atmospheric plasma treatment. *Journal of Applied Polymer Science*. 122 (2011) 2621–2629.
- [4] B.S Butola, Polyesters and polyamides, in: B.L. Deopura, R. Alagirusamy, M. Joshi, B. Gupta Eds.), *Surface modification textiles*, Woodhead Publishing Limited Cambridge England, 2008, 272.
- [5] J. Wang, L.J. Zhejiang, *Surface modification of textiles*, Cambridge: Woodhead Publishing Limited, 2009.
- [6] T.L Vigo, J.S. Bruno. Textile Research Institute. Temperature - Adaptable Textiles Containing Durably Bound Polyethylene Glycols. *Textile Research Institute*. 57 (1986) 427-429.
- [7] R.F.M. Castro, Optimization of soil-release finishing processes for polyester fibers. *Universidade do Minho, Guimarães* 2017.
- [8] J-S. Park, J-W. Park, E. Ruckenstein. A Dynamic mechanical and thermal analysis of unplasticized and plasticized poly (vinyl alcohol)/methylcellulose blends. *Journal of Applied Polymer Science*. 80 (10) (2001) 1825-1834.
- [9] A.B.S. Barros, R.F. Farias, D.D. Siqueira, C. B. B. Luna, E.M. Araújo, M.S. Rabello, R. M. R. Wellen, The Effect of ZnO on the Failure of PET by Environmental Stress Cracking. *Materials*. 13 (2020) 2833-2844.
- [10] Q. Wey, *Surface modification of textiles*, Woodhead Publishing in Textiles: Number 97, New York 2009.
- [11] S.M. Burkinshaw, *Chemical Principles of Synthetic Fibre Dyeing*, First ed., published by Chapman Halli 1995.
- [12] X. Tao, *Handbook of Smart Textiles*, published by Springer Science+Business Media Singapore 2014.
- [13] X. Gu, D. Raghavan, T. Nguyen, M.R VanLandingham, D. Yebassaa, Characterization of polyester degradation using tapping mode atomic force microscopy: exposure to alkaline solution at room temperature. *Polymer degradation and stability*. 74 (2001) 139-149.
- [14] S. Pitchai, J. Moses, S. Natarajan. Study on the improvement of hydrophilic character on polyvinylalcohol treated polyester fabric. *Polish Journal of Chemical Technology* 16, (4)(2014)21-27.
- [15] M.H. Kish, M. Nouri. Effects of sodium hydroxide and calcium hydroxide on polyester fabrics. *Journal of Applied Polymer Science*, 72 (1999) 631-637.