

Study of the Effects by Tinctorial Method Obtained at Polyethylene Terephthalate Functionalization with Alcohols

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The fibers of recycled and virgin polyethylene terephthalate (PET) have been functionalized with three alcohols: ethanol, tetrol and polyvinyl alcohol (PVA). The chemical modifications generated by these alcohols have been relieved by spectroscopic analyses (FTIR, SEM, EDAX, XRD), calorimetric analysis (DSC) and thermogravimetric methods (TGA, DTG). The DSC analysis confirms the presence of a large amount of humidity on PET fiber after functionalizing it with PVA, and the TGA analysis offers indications on their thermal stability. The alcohols size and especially the number of hydroxyl groups influenced the tinctorial capacity; the CIE Lab Differences graphics reveal the values and positions of differences dL, da and db.

Keywords: PET, ethanol, tetrol, PVA, tinctorial capacity

PET is a synthetic polymer obtained through esterification reaction of ethylene glycol and terephthalic acid. Even if it contains the ester functional groups in the main chain, the polyester has a poor reactivity, because these functional groups are not free and able to react with other chemicals. The reactivity of the polymer from PET fibers can be improved if at fiber formation/synthesis one adds a co-polymer with many reactive groups, usually polar groups of -OH, -NH₂ or -COOH types [1].

In exchange, the reactivity of usual PET fibers can be modified by reactions that determine the breaking up of ester bond and appearance of free -OH and -COOH groups. This is possible using the following treatments: plasma treatment [2-5], when the appearance of some -COOH groups is noticed; grafting with agents rich in polar groups, on a support functionalized by plasma [6, 7]; saponification with NaOH [8-12] or a mixture of NaOH with methanol or ethanol [13-15]; PET treatment with amines [16-19]; grafting with various agents on a support functionalized by saponification [20]. The effects generated by the presence of the new functional groups of PET modified through physical/chemical treatments have been reported in literature as follows: wettability, by measuring the contact angle and longitudinal wicking [21]; surface roughness and pores effective diameter [22]; printing with anionic dyes (effect evaluated by means of the values of color strength and fastness tests) [23]; printing with pigments, type inkjet printing [24].

In this work, the PET functionalization was accomplished through treatment with NaOH or a mixture of NaOH and an alcohol. We have used ethanol, tetrol and PVA as alcohols. Tetrol is in fact ethylenediamide tetrakis (ethoxylate-block-propoxylate) tetrol, which can play the role of a good binder and for linear and cross-linked polymers (polyesters, polyurethane, and cellulose) [6, 25]. The alcohol size, type and functionality, as well as the treatment conditions determined chemical modifications of the PET structure. These modifications have been

relieved through spectroscopic, calorimetric, thermogravimetric methods, as well as through tinctorial method. By dyeing with non-specific dyestuffs (direct, acid, reactive and vat dyes), one can prove both the presence of new functional groups, and fastness of the new chemical modifications under severe dyeing conditions (100°C, 60 min).

Experimental part

Materials and methods

Virgin polyester fibers (3.3 den) and recycled PET fibers of fineness 3.3 den acquired from Green Fibers Buzau S.A., pure alcohol (ethanol, ethylenediamide tetrakis (ethoxylate-block-propoxylate) tetrol and polyvinyl alcohol) from Sigma Aldrich Co., auxiliary chemicals (NaOH, Na₂CO₃, Na₂S₂O₈, NaH₂PO₄) from Merck Co and the dyes: acid dye Eosin Y (C.I. Acid Red 87 from Merck), direct dye Bordo AN (C.I. Direct Red 13 from Colorom Codlea), reactive blue Bezaktive Brilliant grun V-6B and vat (CI Vat Orange 11) from Bezema were utilized. The characteristics of PET are presented in the table 1.

Table 1
THE MAIN CHARACTERISTICS OF PET

Characteristics	Virgin PET (code 0V)	Recycled PET (code 0R)
Title (dtex)	3.3 ±10%	3.3 ±15%
Tenacity (cN/tex)	35	31
Elongation (%)	30-50	40-70
Length (mm)	51 ±10%	51 ±10%
Crimps (No/inch)	11 ± 2	11 ± 2
Oil pick-up (%)	0.20-0.24	0.20-0.24
Shrinkage in hot air 180°C, 30min (%)	2	2
Moisture (%)	0.40 ± 0.2	0.40 ± 0.2
Defects (fused fibers)	max. 0.001	max. 0.1
Color measurement: Lightness (L*) (%)	85 ± 0.5	75 ± 0.5

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PVA presence	Treatment type	Codes	Functionalization conditions
Without PVA	without NaOH, without PVA	0V–untreated virgin PET 0R–untreated recycled PET	- -
	with NaOH, without PVA	0R+1NaOH 0V+1NaOH	25mL NaOH 1M T = 20°C, t = 48h
	with NaOH + ethanol, without PVA	0R+1NaOH+E 0V+1NaOH+E	25mL NaOH 1M 12.5 mL ethanol, T = 20°C, t = 48h
	with NaOH + ethanol + catalyst, without PVA	0R+1NaOH+E+H 0V+1NaOH+E+H	25mL NaOH 1M 12.5mL ethanol 0.2gNaH ₂ PO ₂ , T = 20°C, t = 48h
	With NaOH + tetrol, without PVA	0R+0.044NaOH+T 0V+0.044NaOH+T 0R+0.066NaOH+T 0V+0.066NaOH+T 0R+0.11NaOH+T 0V+0.11NaOH+T	25mL NaOH with 0.044M; 0.066M or 0.11M concentration 1mL tetrol, T = 20°C, t = 24h
	With PVA	with NaOH and with PVA	(0R+ 0NaOH)+PVA (0V+ 0NaOH)+PVA (0R+ 1NaOH)+PVA (0V+ 1NaOH)+PVA (0R+ 2NaOH)+PVA (0V+ 2NaOH)+PVA

Table 2
EXPERIMENT PLANNING AND SAMPLE CODIFICATION

PET functionalization with the three alcohols (ethanol, tetrol and PVA) that have 2, 4 or several -OH groups, has been accomplished on a polyester support pre-functionalized through saponification. It is well known that PET functionalization with NaOH is more efficient if one adds an alcohol (methanol) to the reaction medium. Yet, if an alcohol with bigger molecular mass (ethanol, tetrol, PVA) is added to the reaction medium, the resulted saponification reaction is less efficient. If, besides NaOH and alcohol (ethanol, tetrol, PVA), one adds a catalyst (NaH₂PO₂ or MgCl₂), the alcohol becomes an agent which is grafted on the saponified PET, irrespective on the working temperature, but using an adequate time (maintained for 24-48h at 20°C or 3 min at 160°C). In fact, in the first stage occurs the saponification, i.e. PET enrichment with -OH and -COONa groups; then, in the presence of an alcohol and an acid-type catalyst, polycondensation reactions occur, resulting in the generation of ether bridges between saponified PET and utilized alcohol molecules.

In this investigation, PET has been functionalized both through saponification, and through grafting on a pre-

saponified support, according to the treatment conditions indicated in table 2.

After saponification and/or grafting with alcohols, the virgin and recycled PET samples were dyed with four classes of dyes unspecific for this type of fiber (PET fiber is usually dyed with dispersion dyes): direct dye, acid dyes, reactive dye and vat dye. The conditions in which the dyeing operations were carried out are presented in table 3.

FT-IR analysis was carried out on a Multiple Internal Reflectance Accessory (SPECAC, SUA) with ATR KRS-5 crystal of thallium bromide – iodide, having 25 reflections and the investigation angle of 45 degrees. This accessory device was attached to the Spectrophotometer FTIR IRAffinity-1 Shimadzu (Japan), the spectra registration being realized with 250 scans in the 1800 -600 cm⁻¹ range. After the registration, the absorption spectra have been electronically superposed using Spekwin 32 soft.

SEM and EDAX analyses was used an electron microscope type QUANTA 200 3DDUAL BEAM, which is a combination of two systems (SEM and FIB), by whose

	Direct dye (C.I. Direct Red 13)	Acid dye (C.I. Acid Red 87)	Vat dye (C.I. Vat Orange 11)	Reactive dye
<i>Dyeing Recipe</i>	3% dye, 10%NaCl, M = 100:1, T = 100°C, t = 1h	3% dye, M = 100:1, T = 100°C, t = 1h	3% dye 5 g/L NaOH, 3 g/L Na ₂ S ₂ O ₄ , M = 100:1, T = 20°C, t = 1h	3% dye, pH = 10 (Na ₂ CO ₃), M = 100:1, T = 60°C, t = 1h
<i>Final stages</i>	Rinsing, Warm washing, Cold washing, Drying at room temperature	Rinsing, Warm washing, Cold washing, Drying at room temperature	Oxidation at 40°C: 1.5mL/L H ₂ O ₂ 35%, 1mL/L CH ₃ COOH. Warm washing, Cold washing, Drying at room temperature	Rinsing, Hot Soaping: 1g/L tensed, M = 50:1. Warm washing, Cold washing, Drying at room temperature

Table 3
DYEING CONDITIONS

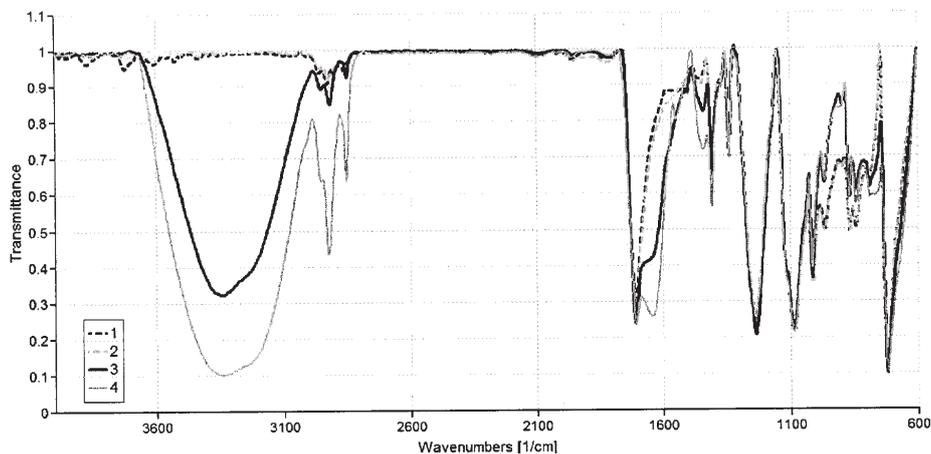


Fig.1. FTIR spectra for witness samples (1 is virgin PET (code 0V) and 2 is recycled (OR)) and for saponified PET treated with PVA (3 is (OV + 2NaOH) + PVA, and 4 is (OR + 2NaOH) + PVA); (the sample code being the same as in table 2)

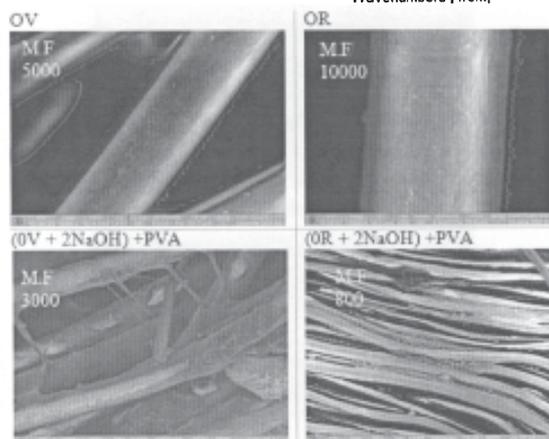


Fig. 2. The surface aspect of virgin/recycled PET samples before and after grafting with PVA

XRD results: by treating with PVA, the crystalline/amorphous ratio is modified, which is visible from both, the peaks intensity and the position of the corresponding 2-theta- angles, situated around the values 17.7, 22.6 and 25.8 degrees (fig. 3).

Table 4
EDAX RESULTS

Sample*	Element	Weight Wt%	Atom At%
0V	C	49.39	56.24
	O	50.61	43.76
0R	C	48.14	55.28
	O	51.86	44.72
(OV + 2NaOH) + PVA	C	37.28	44.18
	O	62.72	55.82
(OR + 2NaOH) + PVA	C	31.11	37.56
	O	68.89	62.44

*same code as in table 2

The angles 2θ (Bragg's angles) were determined from diffractograms from figure 3, while the d- spacing of crystalline part of the PET were calculated from the relation: $d = n\lambda/2\sin\theta$ (from Bragg's law: $n\lambda = 2d\sin\theta$), and $n = 1$ ($n =$ order of reflection) and $\lambda = 1.542 \text{ \AA}$ (λ is radiation wavelength) [19, 26]. The XRD results are presented in table 5.

Figure 3 and the data from table 5 indicate the presence of a smaller crystalline zone in the treated samples than in the non-treated ones, while the inter-crystalline spacing increases, which could also mean an increase of PET fiber accessibility.

Calorimetric and thermo-gravimetric results: the DSC and DTG curves of the pre-saponified PET samples treated afterwards with PVA have each within the temperature

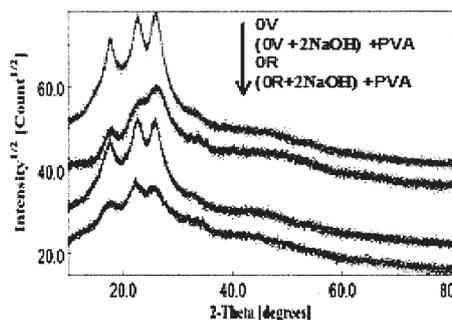


Fig. 3. Diffractograms of the witness samples (0V and 0R) and of the samples saponified and treated with PVA ((OV+2NaOH) + PVA and (OR+2NaOH) + PVA); same code as in table 2

Table 5
VALUES FOR BRAGG'S ANGLES (2θ) AND FOR d-SPACING OF A CRISTALLINE PART OF THE PET

Code	Peak no.	2θ (degrees)	$d = \lambda/(2 \sin\theta)$ (\AA^2)
0V	1	17.79	4.98
	2	22.66	3.92
	3	25.88	3.44
(OV+2NaOH) + PVA	1	17.55	5.05
	2	22.66	3.92
	3	25.86	3.45
0R	1	17.71	5.008
	2	22.62	3.93
	3	25.81	3.45
(OR + 2NaOH) + PVA	1	17.43	5.09
	2	22.15	4.01
	3	25.38	3.51

*same code as in Table 2

range 25- 135°C an endothermic peak whose size indicate the sample capacity to absorb humidity; water can penetrate through the pores/channels formed during saponification, and can form hydrogen bonds with the new functional groups (polar OH groups). The presence of the free OH groups also agrees with the information offered by the FT-IR analysis (fig. 1). None of the untreated samples (0V and 0R) shows an endothermic peak in the DSC curves within this temperature interval. The data taken from the DSC and DTG curves are presented in table 6 (the samples codes being same as in table 2).

The data from table 6 indicate that out of the samples treated with PVA, the recycled PET sample realizes the most hydrogen bonds with water molecules; this statement is confirmed by the shift of the endothermic peak to bigger values (85.48°C), as compared to the sample (0V + 2NaOH) + PVA (72.76°C). This conclusion also results by comparing the content of humidity evaporated during the dehydration stage (when the samples are heated, namely the first stage from the DTG curves): 12.78% for (OR + 2NaOH) + PVA, and 7.72% for the sample (0V + 2NaOH) + PVA. The presence of PVA in the treated virgin and recycled PET samples is confirmed by TGA results, namely

Sample	From DSC curves			From DTG curves	
	T _i ^a °C	T _{peak} ^b °C	T _f ^c °C	ΔH ^d J/g	Moisture ^e %
(0V +2NaOH)+PVA	48.92	72.76	95.84	52,85	7.72
(0R +2NaOH)+ PVA	40.34	85.48	133.74	87.51	12.78

Table 6
MAIN PARAMETERS TAKEN FROM DSC
AND DTG CURVES

^aT_i is the temperature at which the dehydration stage begins;

^bT_{peak} is the temperature at which the dehydration reaction rate is maximum;

^cT_f is the temperature at which the dehydration stage is finished;

^dΔH is the dehydration heat (obtained by measuring the area of the endothermic peak);

^ePercent moisture is indicated by the size of the endothermic peak situated between 25-135°C

by the results of heating these samples within the interval 25 - 800°C. The data taken from the TGA and DTG curves have been presented in table 7 (the samples codes being the same as in table 2).

The data from table 7 indicate that the behavior to heating/pyrolysis of the untreated samples (0V and 0R) occurs in only one stage, called de-structuring stage (within the interval 380-465°C). The PET samples treated with PVA present three stages: I) dehydration (40-135°C); II) de-structuring through melting of pre-saponified PET grafted with PVA (380-465°C); III) de-structuring of the intermediate product formed at the end of the stage II (520-625°C). As the 1st stage offers indications on the percentage of evaporated humidity, the stage II (through the values of T_{onset}) offers indications on thermal stability of each treated sample. It has been noticed that the pre-saponified virgin and recycled PET samples, treated then with PVA, are less stable from a thermal point of view, as they have smaller T_{onset} than their untreated counterparts (0V and 0R). At the end of the heat treatment, the residues are bigger in the case of the samples treated with PVA than in the case of the untreated ones.

Dyeability: in our previous works we have shown that changes in natural or synthetic polymers, by various treatments including by grafting, can be highlighted through the tinctorial method [27-40].

Dyeing with direct dye (C.I. Direct Red 13).

The results of dyeing the samples saponified with NaOH in the presence of ethanol or tetrol are as follows:

When using ethanol as alcohol. From the comparison of the untreated virgin PET (yet dyed with C.I. Direct Red 13), with the samples dyed with direct dye after having been saponified with NaOH 1M (48 h at cold) in the presence of an inferior alcohol (ethanol) without catalyst or with a catalyst of hypophosphite (H) type, (fig. 4) one can notice that: the saponified virgin samples dye more intensely than

the recycled ones; the presence of ethanol in the saponification bath, without catalyst, leads to more intense dyeing than at the samples saponified only with NaOH, perhaps because the mixture (NaOH+alcohol) determines a stronger saponification; the presence of a hypophosphite-type catalyst in the treating bath with NaOH and ethanol confers ethanol the role of grafting agent (when working at T = 20°C, t = 48h), which attaches on the macromolecular chain of the saponified PET, forming with it an ether bond; dyeing with direct dye can be explained based on the hydrogen bonds that appear between the -OH groups of the saponified PET, and the -OH, -NH₂ and -SO₃ groups from the dye.

When using tetrol as alcohol: dyeing the recycled PET samples after a previous saponification with small, but increasing molar concentration of NaOH (from 0.044M to 0.11M), for 24 h, in the presence of a tetrol, leads to luminosity difference (dL) values that decrease as the NaOH concentration increases, the utilized tetrol concentration being the same in all the cases (fig. 5).

This behavior is assigned to tetrol; it is well known that an increase of NaOH concentration determines the increase of saponification efficacy, therefore the formation of a larger number of functional -OH groups onto the saponified PET.

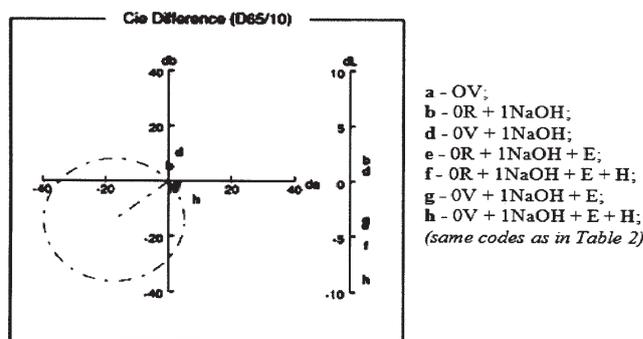


Fig. 4. Color Difference for PET dyed with a direct dye after a pre-treatment with NaOH + ethanol +/- catalyst

Sample code	Stage	From DTG curves			From TGA curves	
		T _{onset} ^a (°C)	T _{peak} ^b (°C)	T _{endset} ^c (°C)	W ^d (%)	R ^e (%)
0V	I	387.91	427.55	456.25	96.68	3.32
(0V+2NaOH)+PVA	I	48.92	72.76	95.84	7.72	
	II	376.95	431.78	450.24	67.28	3.91
	III	527.95	560.00	622.57	21.09	
0R	I	392.77	432.11	462.51	93.62	6.38
(0R+2NaOH)+PVA	I	40.34	85.48	133.74	12.78	
	II	390.94	429.36	454.07	67.28	14.28
	III	564.28	580.00	595.44	5.66	

Table 7
MAIN PARAMETERS TAKEN FROM TGA
AND DTG CURVES

^aT_{onset} is the temperature at which the each stage begins;

^bT_{peak} is the temperature at which the reaction rate is maximum for: dehydration (I), melting (II), and decomposition of grafted agents (III);

^cT_{endset} is the temperature at which each stage is finished;

^dW is the weight loss (expressed in percent) during each stage;

^eR is the residue (the mass remaining after heating of the samples) at 800°C.

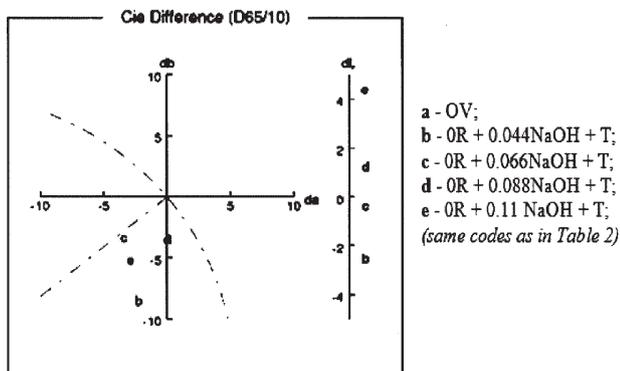


Fig. 5. Color Difference for PET dyed with a direct dye after a pretreatment with NaOH + tetrol

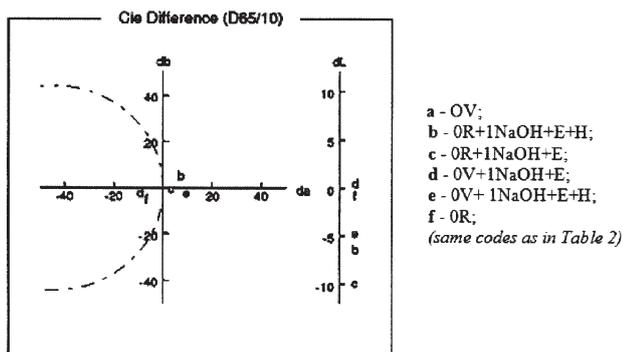


Fig. 6. Color Difference for PET dyed with an acid dye after a pretreatment with NaOH + ethanol +/- catalyst

The tetrol can form (by means of the four -OH groups) hydrogen bonds with the new functional groups of the saponified PET (the -OH groups), thus eliminating the possibility of their interaction with dye molecules from the dyebath. Therefore, the presence of a poly-functional alcohol does not improve the saponification degree of PET; and accordingly, it cannot work as a saponification co-agent.

Dyeing with acid dye (Eosin Y or C.I. Acid Red 87).

From figure 6 one can notice that, from all the samples, those functionalized with NaOH + ethanol +/- catalyst (H) dye more intensely than the virgin sample (0V), therefore they have negative dL values.

The acid dye has as functional groups -COO⁻, -O⁻, =O, -Br, therefore there cannot be electrostatic attractions for the -OH or -COO⁻ groups from saponified PET; probably, between the two partners (acid dye and saponified PET) other bonds, less strong, are established, namely the hydrogen bonds.

Dyeing with a vat dye (C.I. Vat Orange 11).

From figure 7, one can infer that through saponification with NaOH + ethanol +/- catalyst, all the virgin and recycled PET samples are dyed more intensely than the witness sample of virgin PET (0V), having the brightness difference dL < 0. The explanation is because holes and microcracks appear inside the textile support through saponification. Therefore, all the samples become more accessible for the insoluble dye molecules; by means of the alkaline-reducing medium, the dye molecules will be solubilized and developed, dyeing the textile support, and then, after the oxidation phase, they will pass in the initial insoluble form.

What concerns the hue; one can say that the samples **d** and **b** have more yellow and a little red, sample **e** has red and yellow in equal quantities and the sample **c** has slight green hues.

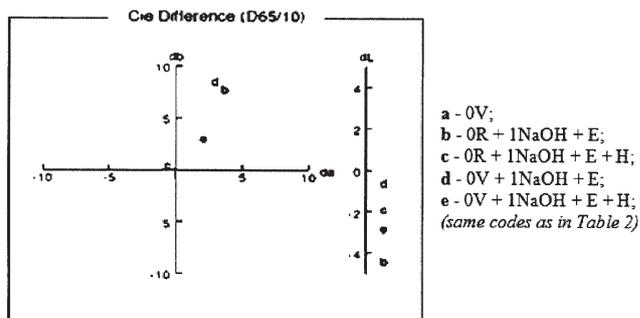


Fig. 7. Color Difference for PET dyed with a vat dye after a pretreatment with NaOH + ethanol +/- catalyst

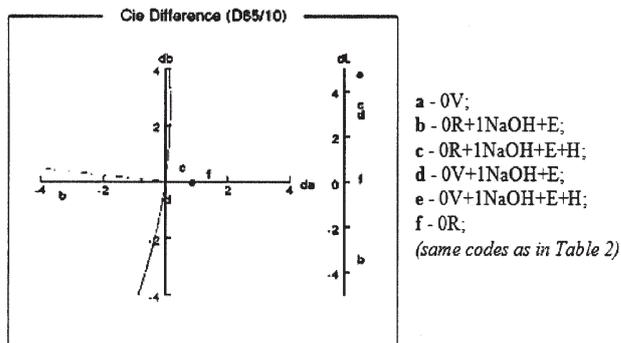


Fig. 8. Color Difference for PET dyed with a reactive dye after a pretreatment with NaOH + ethanol +/- catalyst

Dyeing with a reactive dye (Bezaktive Brilliant grun V-6B)

The reactive dye leads to values dL > 0, therefore all the functionalized PET samples dye poorer than the witness 0V, except for the sample **b**. In this case, it is possible that the saponification degree is higher; therefore, the number of functional -OH groups acquired from PET through saponification is bigger (fig. 8) and they form ether bridges with the reactive dye molecules.

It is known that all the reactive dyes determine the formation of a covalent bond of ether type, between the textile support (which usually contains -OH groups) and the dye (which contains 1 or 2 halogens, usually -Cl).

Dyeing the PET samples after grafting with PVA

Dyeing with direct dyes

When dyeing with a direct dye the PET samples saponified and then grafted with PVA (fig. 9), one obtains values dL < 0, which means that they dye more intensely than the witness sample 0V (namely the sample **a**).

The most saponified (with NaOH 2M) samples are dyeing the most intensely. By comparing brightness difference (dL) for the PET samples only saponified (samples **b** and **d** from figure 4, which have dL > 0) with that of the PET samples saponified and grafted with PVA (fig. 9), one can notice that all the samples from Fig. 9 are less bright after dyeing, therefore they dyed more intensely (have dL < 0). The large number of polar functional groups (-OH) that are attached to the new polyester support can explain this fact; these groups can form polar hydrogen bonds with direct dyes, making possible their more intense dyeing.

Dyeing with vat dyes

Saponification with NaOH 2M of the virgin or recycled PET and their grafting with PVA do not result in a more intense dyeing than for the witness samples 0V and 0R, when vat dyes are used (fig. 10). Perhaps PVA restricts through grafting the penetration of dye molecules into the saponified PET; having a big macromolecular chain, PVA covers most of the pores and holes acquired through saponification.

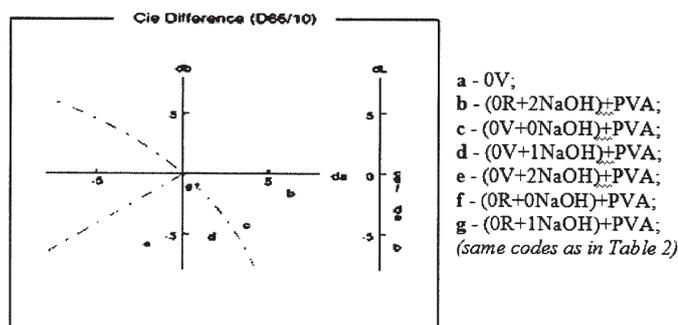


Fig. 9. Color Difference for PET dyed with a direct dye after a pretreatment with NaOH + PVA +/- catalyst

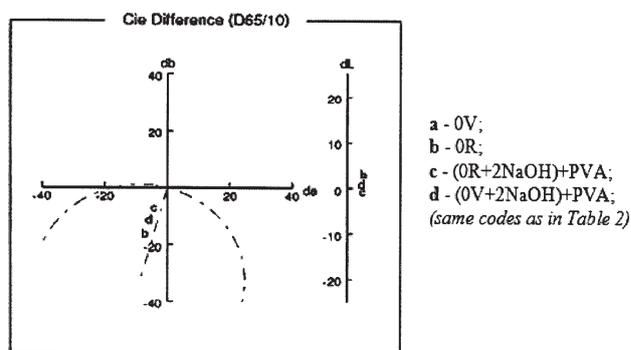


Fig.10. Color Difference for PET dyed with a vat dye after a pretreatment with NaOH + PVA +/- catalyst

Conclusions

PET can be functionalized through saponification with NaOH. The presence of an alcohol in the saponification bath influences the saponification degree in terms of size, reactivity and number of OH groups from alcohol, as follows: an inferior alcohol (for instance, ethanol) determines the increase of saponification degree, while tetrol does not act favorably to saponification. The higher the number of functional groups of an alcohol, the stronger is the functionalization conferred by the alcohol to a pre-saponified PET, only through a grafting reaction. The grafting reaction of a PVA-type poly-functional alcohol occurs at high temperature (160°C, 3 minutes) in the presence of an acid-type catalyst. PET functionalization through pre-saponification and grafting has been confirmed by spectroscopic analyses (FTIR, SEM/ EDAX, XRD), calorimetric analyses (DSC) and thermo-gravimetric (TGA and DTG), as well as by the tinctorial method. PVA grafting onto the pre-saponified PET leads to a more intense dyeing than that of 0V only when using anionic dyes. The CIE LAB Difference graphics have shown that darker colors than for the witness sample (0V) are obtained at saponified/ungrafted samples dyed with direct dye, acid dye and vat dye.

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Manuscript received: 23.01.2015