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Monochlorotriazinyl-β-cyclodextrin grafting onto polyester fabrics and films

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ABSTRACT

The monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) grafting onto polyester fabrics and films was carried out in an alkaline medium (saponification conditions with Na_2CO_3 respectively NaOH) at different temperatures (20 and 130 °C) and treatment durations (30 min, 1 h, 3 h, 5 h, 24 h) through a discontinuous procedure. The saponification and grafting were accomplished in two variants: individually and simultaneously respectively. It was noticed that the alkaline medium produces chemical and superficial modifications which make possible the MCT-β-CD grafting onto the polyester supports. This was rendered evident through FTIR analysis and SEM electron microscopy. The degree of grafting depends on the saponification/grafting conditions (the concentration of alkaline agents, time, temperature, MCT-β-CD concentration) and is reflected by the nitrogen content, hygroscopicity, air permeability, as well as by mechanical properties (tensile breaking strength, breaking elongation, breaking mechanical work and the specific mass work).

1. Introduction

During the last years, many works were dedicated to the study of polyester (PES) behavior during the saponification operation (Asakuma, Nakagawa, Maeda, & Fukui, 2009; Kondratowicz & Ukielski, 2009; Mishra, Zope, & Goje, 2002; Ng, Zhang, Liu, & Yang, 2009; Partini & Pantani, 2007; Vigneswaran & Anbumani, 2007; Wada et al., 2007) carried out either only with alkaline agents, or with sodium hydroxide in the presence of an alcohol (methanol or ethanol) (Achwal, 1984a, 1984b; Nandy, Mishra, Thakker, & Bhattacharya, 1999). All these arrived at the conclusions that the alkaline medium results in the polyester de-polymerization, which in turn determines the amplification of antistatic properties, as well as of wetting and water retention. Aiming to improve the saponification effects, polymer grafting was carried out with chitosan (Matsukara, Kasai & Mizuta, 1995), in order to induce a "wash-fast antistatic effect" and/or germicidal effects: with poly-oxialkylene in various conditions, to improve the antistatic properties and to get a good dyeability with cationic dyes (Kim & Ko, 1986) with acrylic acid, which determines a modification of the electric conductibility (Hirotsu & Nakajima, 1987). Other attempts were based on the utilization of α-, β-, γ-cyclodextrin for the direct polyester grafting, but the results proved the impossibility of grafting without the existence of certain very reactive groups which are to be attached to the cyclodextrin structure. The β-cyclodextrin (β-CD) grafting on polyester fabrics is only possible when one makes use of cyclodextrine derivatives which migrate inside the polymer structure, or chlorine-type non-metals (bonded to a triazinic cycle) that can participate in substitution nucleophilic reactions (Denter, Buschmann, & Schollmeyer, 1991; Denter, Schollmeyer, Szejtli, & Szente, 1996; Ruppert, Knittel, Buschmann, Wenz, & Schollmeyer, 1997). Another working version is indicated by Martel and Co. (Martel, Morcellet, Ruffin, Ducoroy, & Weltrowski, 2002), by means of the poly-carboxyl acids playing the role of reticulant agents.

This work is dedicated to the investigation of the possibility of monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) grafting onto saponified polyester fabrics and films (either prior or simultaneous to grafting) through discontinuous depletion based procedures, at extreme temperatures: 20 °C and 130 °C, respectively. Basic mediums (NaOH and Na_2CO_3) at different concentrations and durations were used for saponification. It was noticed that the degree of MCT-β-CD grafting on polyester is much higher when the saponification and grafting occur in the same bath through discontinuous procedures, than through the pad-dry-cure technology (Abdel-Halim, Abdel-Mohdy, Al-Deyab, & El-Newehy, 2010).

The effects acquired through simultaneous saponification and grafting are: a high degree of grafting, shown off through a large amount of nitrogen, a higher hygroscopic sorption, and improved mechanical properties. The grafting diminishes the roughness produced by saponification and determines a decrease of air permeability.

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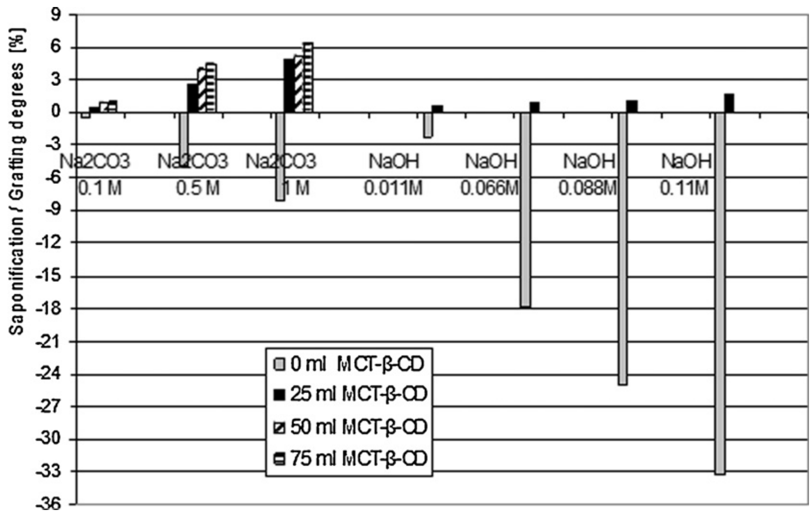


Fig. 1. Influence of the saponification formula (through alkaline agent type and concentration) on grafting with 25–75 ml MCT-β-CD at 130 °C for 1 h, onto a PES fabric.

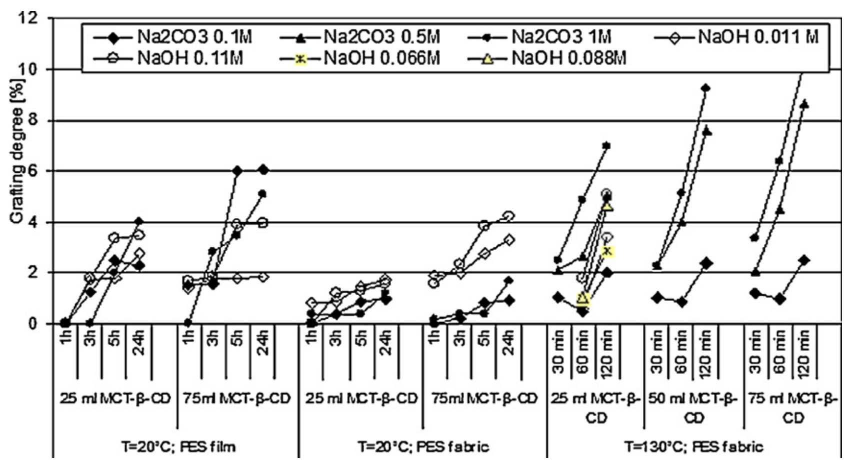


Fig. 2. Influence of processing conditions on the degree of grafting.

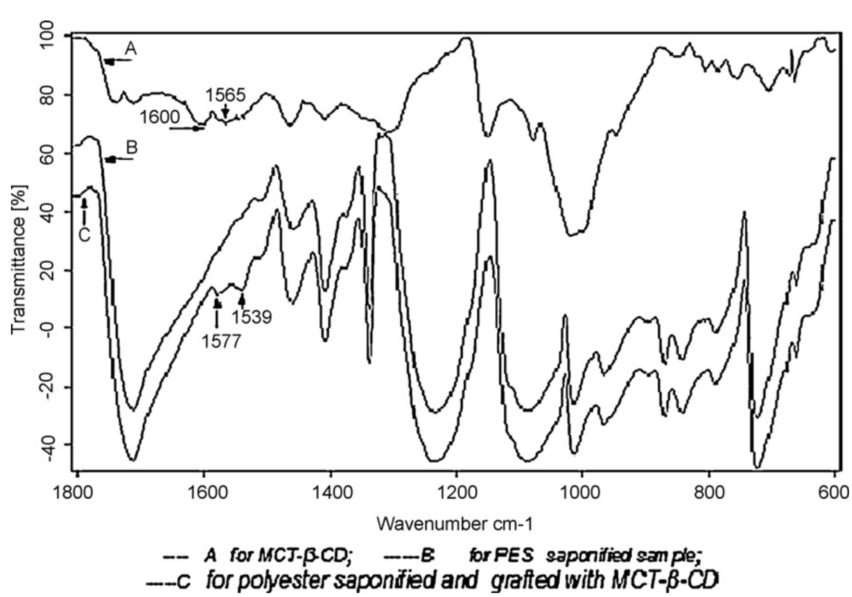


Fig. 3. FTIR-ATR spectra.

2. Experimental

2.1. Materials

Chemically modified cyclodextrin: monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) was supplied by Wacker-Chemie-Germany, and the alkaline agents (Na_2CO_3 p.a., NaOH p.a.) by Merck.

Polyester (PES) supports (fabrics and films), supplied by Romanian firms (Terom S.A), have the following characteristics: *fabric* has 70 dtex/23 filaments finesses on warp and 60 dtex/23 filaments finenesses on weft and the *films* have a thickness of 25 μm and an areal density of 15 g/m^2. The polyester fabrics and films were washed with a solution of non-ionic surfactant (1 g/l) for 30 min at 60 °C, liquor ratio 1:50, followed by rinsing in warm and then in cold water, and drying at room temperature.

Polyesters samples with the mass of 1 g each were used for experiments were treated with 50 ml alkaline agents ±25–75 ml monochlorotriazinyl-β-cyclodextrin of 10 g/l. The alkaline agents used were Na_2CO_3 and NaOH at different concentrations.

2.2. Saponification conditions of PES fabrics and films

The saponification was realized with each of the specified alkaline agents, by using solutions with increasing concentrations (for Na_2CO_3: 0.1; 0.5 and 1 M and for NaOH the concentrations 0.011 M; 0.066 M; 0.088 M and 0.11 M), both at 130 °C for limited durations of 30, 60 and 120 min, respectively, and at 20 °C (cold conditions) for higher durations: 1 h, 3 h, 5 h and 24 h.

Two different working variants were used: (I) saponification–drying–grafting; (II) simultaneous treatment of saponification and grafting. The treatments were carried out with a Mathies Polycolor 2002 machine from Bezema Company, and drying was done at the room temperature.

The degree of saponification D_s was calculated with the relation:

$$D_s = 100\frac{W_a - W_b}{W_b}[\%] \tag{1}$$

where D_s is the degree of saponification; W_b and W_a are the weights of PES supports before and after saponification.

2.3. Grafting conditions with MCT-β-CD onto PES support

The volumes of MCT-β-CD used both in the case of grafting onto the already saponified polyester supports, and in the case when the saponification and grafting were executed simultaneously, were of 25, 50 and 75 ml MCT-β-CD, respectively, at a concentration of 10 g/l.

In this case too, the treatments were carried out on Mathies Polycolor 2002 machine. Finally, after the grafting treatments, the samples were rinsed with distilled water at 40 °C and respectively at 20 °C and drying at room temperature.

The degree of grafting was calculated according to the relation:

$$D_G = 100\frac{W_{aG} - W_{aS}}{W_{aS}}[\%] \tag{2}$$

where: D_G is the degree of grafting (%); W_{aG} and W_{aS} are the weights of PES supports after grafting and after saponification, respectively.

2.4. Analysis methods

2.4.1. FTIR analysis

The FTIR analysis was carried out to reveal the MCT-β-CD presence onto the polyester supports as the result of the process of simultaneous saponification and grafting. FT-IR analysis was carried out on a Multiple Internal Reflectance Accesory (SPECAC, SUA) with ATR KRS-5 crystal of thalium bromide–iodide, having 25 reflexions and the investigation angle of 45°.

This accessory device was attached to the Spectrophotometer FTIR IRAffinity-1 Shimadzu (Japan), the spectra registration was realized with 250 scans in the 1800–600 cm^{-1} range.

After the registration, the absorption spectra have been electronically superposed (using the Bruker OPUS 5.5 soft) and they are presented in Fig. 3.

2.4.2. SEM analysis

A QUANTA 200 3DDUAL BEAM electron microscope was used, which is a combination of two systems (SEM and FIB), by whose means, by sending an electron beam on the treated samples, three-dimensional images could be obtained, with a magnification of 100,000×. Moreover, by using the ×radiation with dispersive energy (EDX), the elemental analyses were possible for the identification of the surface characteristics and a high resolution chemical analysis.

2.4.3. Home laundering testing

Another possibility for proving the durability effect of grafting is the home laundering test. According to the standard test SR EN ISO 105-CO6:1999, samples were subjected to five home laundering repeated cycles. The testings were carried out with a Mathies Polycolor 2002 machine from Bezema Company, followed by the rinsing with distilled water at 40 °C and then drying at the room temperature.

2.4.4. Hygroscopicity

The determination of the hygroscopic sorption property (the capacity of the samples to retain the water vapors) was made according to the standard test BS EN ISO 12571:2000. The hygroscopicity was determined based on the difference between the average weight of five samples with 50 cm × 50 cm dimensions, kept (for 24 h) into a atmosphere with a relative humidity of 100% and the average weight of the conditioned samples (for 24 h also) in a standard atmosphere (φ = 65%), The hygroscopicity was calculated with the relation (3) as follows:

$$H = 100 \times \frac{W_u - W_c}{W_c}[\%] \tag{3}$$

where H is the hygroscopicity; W_u is the average weight of the wet samples, expressed in grams; W_c is the average weight of the conditioned samples, expressed in grams.

2.4.5. Air permeability

The measurements for air permeability of simultaneously saponified and grafted polyester fabrics were carried out with an ATL-2 Metrimpex-Hungary apparatus, according to the ASTM D 737-96 standards. The calculation formula for air permeability is given by the relation (4)

$$P_a \cdot p = \frac{V}{60 \cdot A}\,[\mathrm{m^3/(min\ m^2)}] \tag{4}$$

where P_a is the air permeability; p is the pressure at which the air is passed through the polyester fabric, expressed in mm H_2O; V is the flow rate of the air passed through the polyester fabric, expressed in [dm^3/h]; A is the area of the air absorption section, expressed in [m^2].

2.4.6. Mechanical properties

According to the standard test DIN EN 13934-1:1999, the breaking force F_H, the elongation ε_H corresponding to the breaking force, the breaking work W_H and the specific mass breaking work $W_{H,m}$ were determined for the untreated fabric and for the sample treated

Table 1
The values of the grafting degree[a], expressed in [%].

Working conditions	30 min treatment time		120 min treatment time	
	Separate treatment (variant I)	Simultaneous treatment (variant II)	Separate treatment (variant I)	Simultaneous treatment (variant II)
0.1 M Na_2CO_3				
25 ml MCT-B-CD	0.22	1.027	1.09	2.01
50 ml MCT-B-CD	0.12	1.052	0.63	2.40
75 ml MCT-B-CD	0.74	1.181	0.79	2.50
0.5 M Na_2CO_3				
25 ml MCT-B-CD	0.73	2.11	1.63	5.03
50 ml MCT-B-CD	0.70	2.25	1.36	7.64
75 ml MCT-B-CD	0.84	2.47	1.66	8.67
1 M Na_2CO_3				
25 ml MCT-B-CD	0.93	2.47	1.50	6.96
50 ml MCT-B-CD	0.90	2.29	1.45	9.24
75 ml MCT-B-CD	0.88	3.36	1.70	10.30
0.011 M NaOH25 ml MCT-B-CD	0.35	0.57	0.46	2.43
0.066 M NaOH25 ml MCT-B-CD	0.44	1.33	1.45	2.89
0.088 M NaOH25 ml MCT-B-CD	0.52	2.13	3.80	4.64
0.11 M NaOH 25 ml MCT-B-CD	0.72	3.67	5.43	7.10

[a] Working temperature 130 °C.

in alkaline medium in the presence of MCT-β-CD. The determinations were carried out in the weft direction using a ZWICK ROELL Z005 Germany 2008.

3. Results and discussions

3.1. MCT-β-CD grafting mechanism

Since the polyester, a polymer based on terephtalic acid and ethylene-glycol, contains a reduced number of terminal/end OH groups, the grafting reaction with MCT-β-CD does not occur. By previous treatment with Na_2CO_3 or NaOH (version I), the reaction of alkaline hydrolyze takes place, thus increasing the number of the end OH groups, able to react with MCT-β-CD. In the case of the simultaneous saponification and grafting (II treatment version), an alkaline hydrolyze reaction also occurs in a first stage, since both Na_2CO_3 or NaOH have the molecular mass much smaller as compared to MCT-β-CD, and therefore they have access to the fiber.

The possible mechanism could be illustrated through the chemical reactions (5):

3.2. Results of treatment variant I (saponification–drying–grafting)

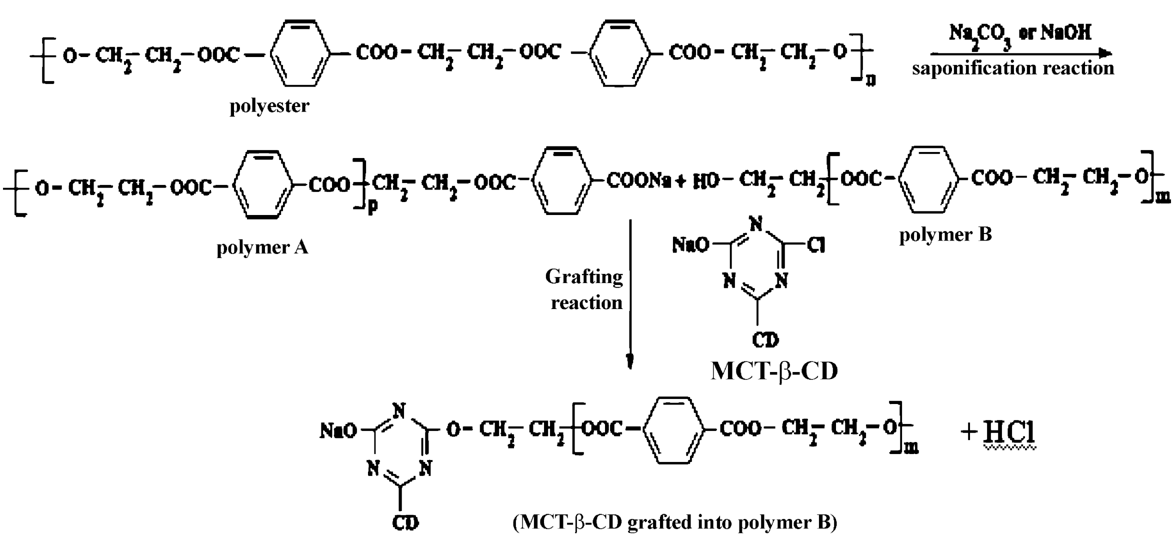
The experimental tests proved that no grafting occurs onto the unsaponified support, and according to the variant I, the degrees of grafting are smaller as compared to the variant II (Table 1). This proves that the intermediate drying (even at room temperature) results in the diminution of gaps, either in volume or in number, which in turn influences the value of grafting degree.

Based on the obtained results, the subsequent experiments on MCT-β-CD were carried out, according to the variant II (saponification and grafting in the same bath).

3.3. Results of treatment variant II (simultaneous saponification and grafting)

3.3.1. Factors that influence the degree of grafting

The degree of grafting is influenced by the conditions under which the two stages (saponification and grafting) occur in the same bath, as follows: the saponification is influenced by alkaline agent concentration and type, as well as by working parameters (time and temperature), while the grafting is influenced by the



(5)

Table 2
Influence of the saponification formula on the degree of saponification.

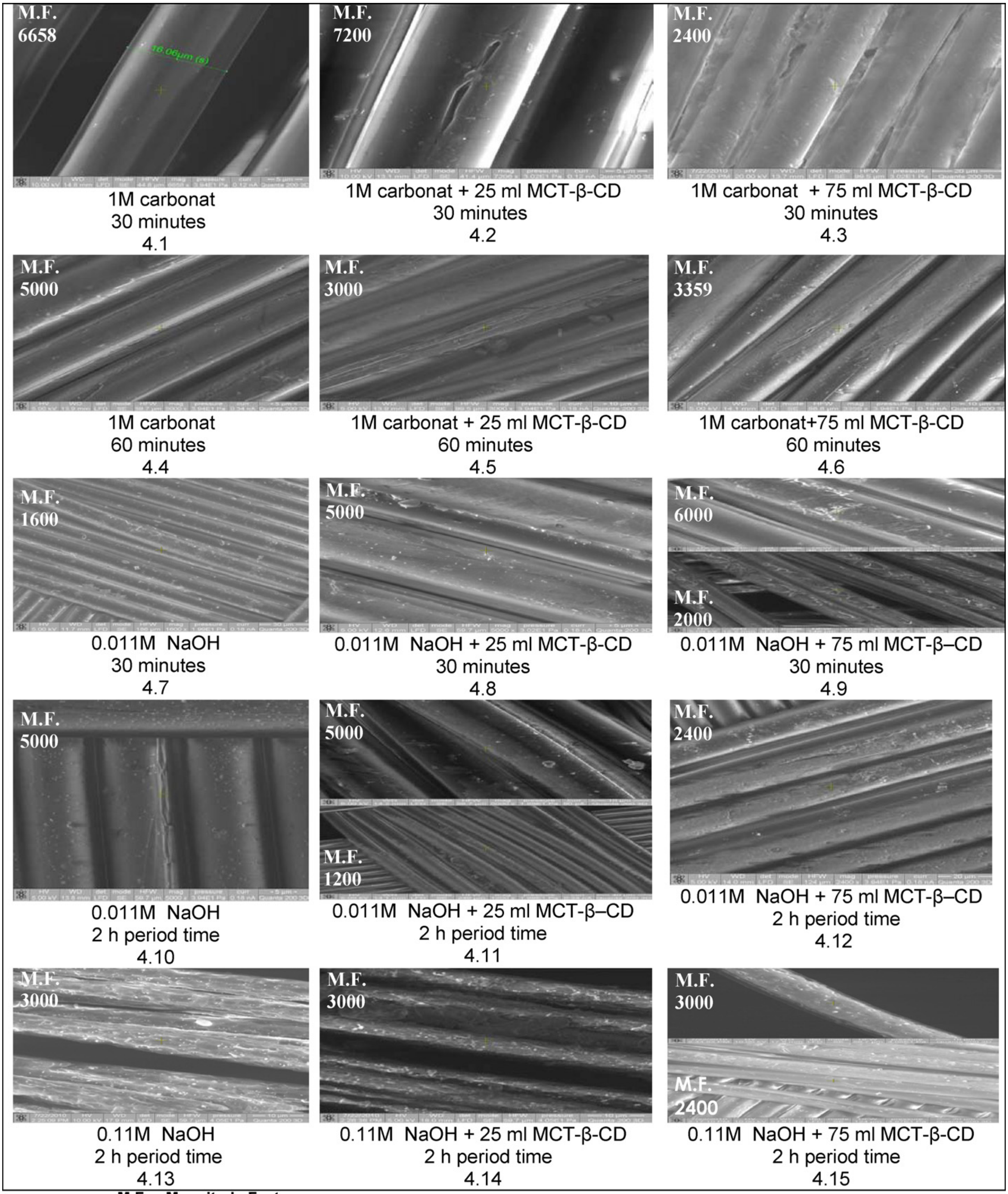
Sample type	Type alkaline agent	Molar Concentration (M)	Time (minutes or hours)	Temperature (°C)	Saponification degree in absolute value (%)
Polyester fabric	Na_2CO_3	0.1	30 min	130	0.480
		0.1	60 min	130	0.504
		0.1	120 min	130	2.000
		0,5	30 min	130	1.800
		0.5	60 min	130	4.920
		0.5	120 min	130	12.97
		1	30 min	130	2.470
		1	60 min	130	8.099
		1	120 min	130	18.64
Polyester fabric	NaOH	0.011	30 min	130	0.8900
		0.011	60 min	130	2.2000
		0.011	120 min	130	7.6800
		0.066	30 min	130	8.4800
		0.066	60 min	130	17.900
		0.066	120 min	130	33.350
		0.088	30 min	130	13.570
		0.088	60 min	130	25.050
		0.088	120 min	130	45.610
		0.11	30 min	130	17.610
		0.11	60 min	130	33.300
		0.11	120 min	130	60.300
Polyester fabric	Na_2CO_3	0.1	1 h	20	0.000
		0.1	3 h	20	0.850
		0.1	5 h	20	1.670
		0.1	24 h	20	1.750
		1	1 h	20	0.000
		1	3 h	20	1.600
		1	5 h	20	1.730
		1	24 h	20	1.840
Polyester fabric	NaOH	0.011	1 h	20	0.180
		0.011	3 h	20	0.290
		0.011	5 h	20	0.380
		0.011	24 h	20	0.450
		0.11	1 h	20	0.430
		0.11	3 h	20	0.650
		0.11	5 h	20	0.710
		0.11	24 h	20	0.940
Polyester film	Na_2CO_3	0.1	1 h	20	0.000
		0.1	3 h	20	0.900
		0.1	5 h	20	1.700
		0.1	24 h	20	1.770
		1	1 h	20	1.600
		1	3 h	20	1.700
		1	5 h	20	1.820
		1	24 h	20	1.900
Polyester film	NaOH	0.011	1 h	20	0.000
		0.011	3 h	20	1.360
		0.011	5 h	20	1.420
		0.011	24 h	20	1.880
		0.11	1 h	20	1.360
		0.11	3 h	20	1.440
		0.11	5 h	20	1.720
		0.11	24 h	20	1.500

degree of acquired saponification, MCT-β-CD concentration and working parameters (time, temperature). As the working parameters are identical for the two stages, since they occur in the same bath, yet at different moments, the conclusion is that the grafting degree is influenced by the working saponification formula, treatment parameters (time, temperature) and MCT-β-CD concentration.

3.3.1.1. Influence of the saponification recipe on the degree of saponification and implicitly grafting. Since the two saponification agents determine mass loss from the polyester supports, they result in degrees of saponification $D_s < 0$, according to Eq. (1), as the masses $W_a < W_b$.

By comparing the efficiency of sodium carbonate and NaOH during the saponification stage, it has been noticed that NaOH is more aggressive and determines advanced de-structuring, rendered evident by increasing (in absolute values) degree of saponification with increasing NaOH concentration and treatment duration, irrespective of the working temperature (Table 2).

The dependence of the grafting degree on the acquired degree of saponification (revealed at 0 ml MCT-β-CD through the type and concentration of the utilized saponification agent) is illustrated in Fig. 1. In the case of sodium carbonate utilization, the higher is the concentration, the closer to the absolute value of the saponification degree is the value of the grafting degree, this meaning that MCT-β-CD fills up almost all the holes created by saponification realized with this agent. In the case when NaOH, the other saponification agent, is used, the degradation through de-polymerization results in holes big in number and size, the longitudinal aspect of the filaments is course and MCT-β-CD no longer manages to cover all the



- **M.F. = Magnitude Factor**

Fig. 4. Longitudinal aspect of the saponified/grafted filaments in treatments at 130 °C.

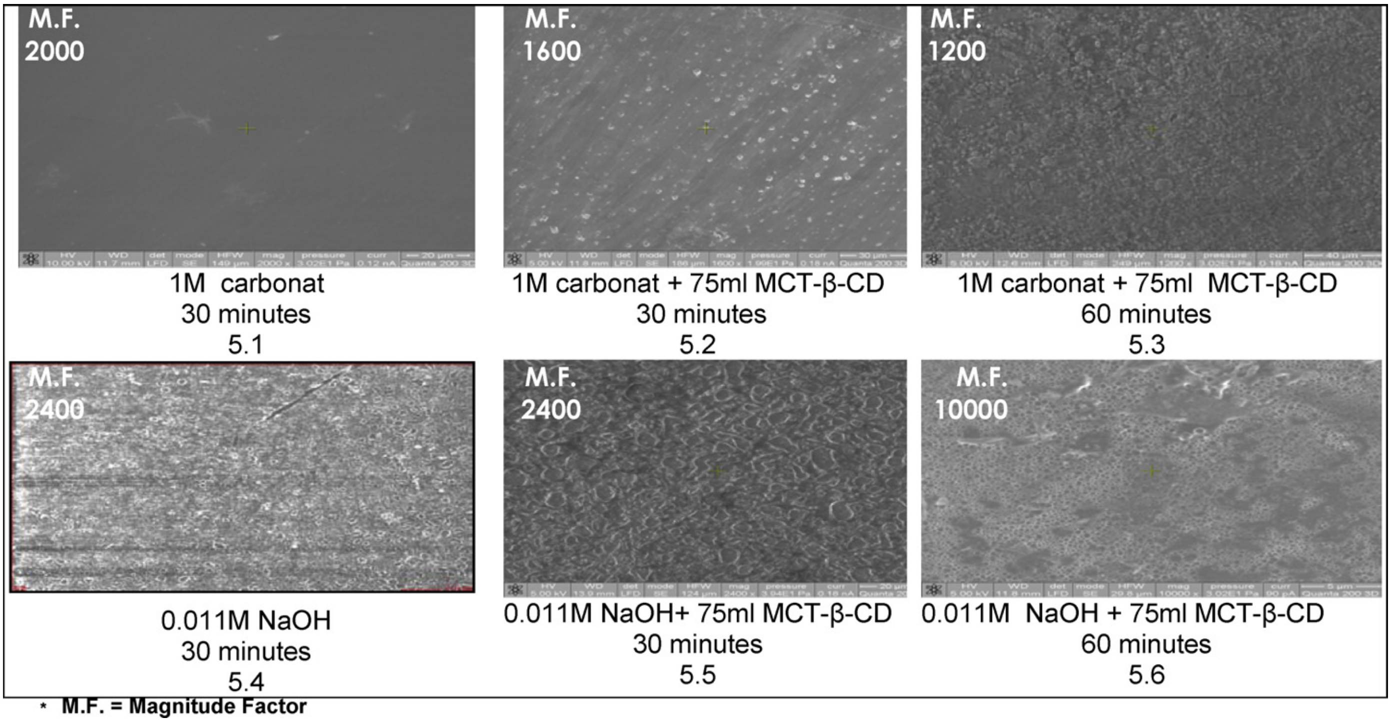


Fig. 5. Surface aspect of saponified/grafted films in treatments at 130 °C.

formed holes, and the degree of grafting is no longer able to reach values equal to the degree of saponification (Fig. 1).

3.3.1.2. Influence of treatment parameters (temperature, time) on the degree of grafting. The temperature significantly influences the degree of grafting, such that, at room temperature, small degrees of grafting are obtained, onto both fabric and film, irrespective of the concentration of the agent of saponification and grafting respectively. This can be explained by the fact that the low temperature does not confer the energy necessary to molecular chains to move out from the polyester support and to create those empty volumes which should constitute the entrance gate for the saponification agents that would determine the appearance of OH type reactive groups able to crosslink the MCT-β-CD through grafting. The high temperature of 130 °C accomplishes this thing and the grafting degrees considerably increase with increasing concentration of the alkaline agent and implicitly of MCT-β-CD (Fig. 2).

Table 3
The weight loss of the polyester samples (fabrics) after 5 cycles of home laundering.

Treatment conditions		Weight loss [%]
0.1 M Na_2CO_3		
T = 130 °C; 30 min	25 ml MCT-β-CD	0.43
	50 ml MCT-β-CD	0.49
	75 ml MCT-β-CD	0.58
T = 130 °C; 120 min	25 ml MCT-β-CD	0.36
	50 ml MCT-β-CD	0.47
	75 ml MCT-β-CD	0.59
1 M Na_2CO_3		
T = 130 °C; 30 min	25 ml MCT-β-CD	0.95
	50 ml MCT-β-CD	1.33
	75 ml MCT-β-CD	1.45
T = 130 °C; 120 min	25 ml MCT-β-CD	1.30
	50 ml MCT-β-CD	1.36
	75 ml MCT-β-CD	1.63

The treatment duration is the determinant factor with major influence on the degree of grafting; thus, under the treatment conditions of the two polyester supports at any of the two temperatures (20 or 130 °C), for a constant concentration of MCT-β-CD, one can notice a significant increase of the grafting degree (Fig. 2) as the treatment duration extends.

3.3.1.3. Influence of the MCT-β-CD concentration on the grafting degree. One can notice from Fig. 2 that an increase of the MCT-β-CD quantity in the treatment bath results in the increase of the grafting degree in any of the working variants individualized through the treatment conditions (time, temperature).

3.4. Analyses proving the grafting realization onto studied polyester supports

3.4.1. FTIR analysis

The analysis of the IR spectra showed the presence of the MCT-β-CD monochlorotriazinic nucleus grafted onto the polyester fabric. By comparison, Fig. 3 presents the FTIR-ATR spectra in the 1800–600 cm^{-1} range, for a fabric saponified with 1 M concentration sodium carbonate, for 30 min at 130 °C, for the product MCT-β-CD, and for a polyester fabric simultaneously treated for saponification and grafting with 75 ml MCT-β-CD.

The absorption spectrum of the polyester modified with the MCT-β-CD product compared with the spectrum of MCT-β-CD has the same characteristic bands, for the triazinic nucleus (i.e. stretching vibrations υ(C=N)) at 1577 and 1539 cm^{-1} for the functionalized polyester, respectively at 1565 and 1600 cm^{-1} for MCT-β-CD. That means the polyester has indeed been functionalized with the reactive product monochlorotriazinyl-β-CD. The small shifts of the characteristic bands for the triazinic nucleus are due to the substituent modification (from –Cl to –O–R), following the reaction of the MCT-β-CD with polyester substrate. The peaks

Table 4
The values of the hygroscopicity on PES supports after different treatments (saponification/grafting), in percents.

PES type	Treatment conditions (temperature, period time, concentration MCT-β-CD)	The concentration of alkali for saponification:			
		Na_2CO_3 0.1 M	Na_2CO_3 1 M	NaOH 0.011 M	NaOH 0.11 M
PES fabric	T = 130 °C; 30 min				
	0 ml MCT-β-CD	0.7850	1.4130	2.2850	3.4518
	25 ml MCT-β-CD	1.7638	1.7816	2.7350	4.8725
	50 ml MCT-β-CD	2.8407	2.7444	–	–
	75 ml MCT-β-CD	3.1590	4.3755	–	–
	T = 130 °C; 60 min				
	0 ml MCT-β-CD	1.5510	2.5416	3.3427	4.9983
	25 ml MCT-β-CD	2.8080	3.1921	4.5780	6.6044
	50 ml MCT-β-CD	3.0895	6.1019	–	–
	75 ml MCT-β-CD	4.3777	8.8290	–	–
	T = 130 °C; 120 min				
	0 ml MCT-β-CD	1.6727	9.6275	6.0489	6.5555
	25 ml MCT-β-CD	7.8242	12.9987	8.1789	16.5151
	50 ml MCT-β-CD	9.6085	17.4863	8.5941	–
	75 ml MCT-β-CD	10.085	19.0429	9.1352	–
	T = 20 °C; 3 h				
	0 ml MCT-β-CD	0.3316	0.3932	0.8349	0.7853
	25 ml MCT-β-CD	0.4947	0.5992	0.8893	0.8906
	75 ml MCT-β-CD	0.6837	0.7597	0.9782	0.9636
	T = 20 °C; 5 h				
	0 ml MCT-β-CD	0.5593	0.6499	0.5135	0.4748
	25 ml MCT-β-CD	0.6102	0.7560	0.5956	0.5817
	75 ml MCT-β-CD	–	–	–	–
PES Film	T = 130 °C; 60 min				
	0 ml MCT-β-CD	–	0.6148	–	–
	25 ml MCT-β-CD	–	0.6932	–	–
	75 ml MCT-β-CD	–	1.3502	–	–
	T = 130 °C; 120 min				
	0 ml MCT-β-CD	–	–	0.5938	–
	25 ml MCT-β-CD	–	–	0.7415	–
	75 ml MCT-β-CD	–	–	2.7390	–

marked with arrows prove the MCT-β-CD presence onto the treated fabric, therefore the grafting occurred.

3.4.2. SEM analysis

3.4.2.1. Surface aspect of the polyester supports after saponification/grafting. The electron microscope was used to visualize the longitudinal aspect of the polyester fabric filaments treated apart with saponification agents (Na_2CO_3 and NaOH), as well as after simultaneous saponification and grafting treatment with MCT-β-CD.

Figs. 4 and 5 show off the degradation relieved through mass loss suffered by the polyester fabric/films under the influence of saponification agents. Following the saponification with sodium carbonate, one can notice the appearance of pores in the PES film, and of pores and cavities/cracks along the filaments (Fig. 4, points 1 and 4), the bigger in size the more severe is the saponification formula.

After saponification with NaOH, one can notice a depolymerization of PES filaments (Fig. 4, points 7, 10 and 13) and films (Fig. 5, point 4) the more advanced the higher the hydroxide concentration.

The sodium hydroxide determines a degradation shown off in the diminution of the diameter of the saponified filament and in significant mass loss, which results in the appearance of a rough surface. The sodium hydroxide is more aggressive than the sodium carbonate, resulting in a much higher saponification degree with increasing concentration of saponification agent and the time.

Starting from the premise that in the simultaneous saponification/grafting treatment the first developed stage is the attack of the alkaline agent on the polyester support, followed by grafting with MCT-β-CD, the formations appeared after saponification (pores, micro-cavities, holes, cracks) are filled up with MCT-β-CD, and the mass loss are annihilated and positivated even if the grafting deposits are non-uniform.

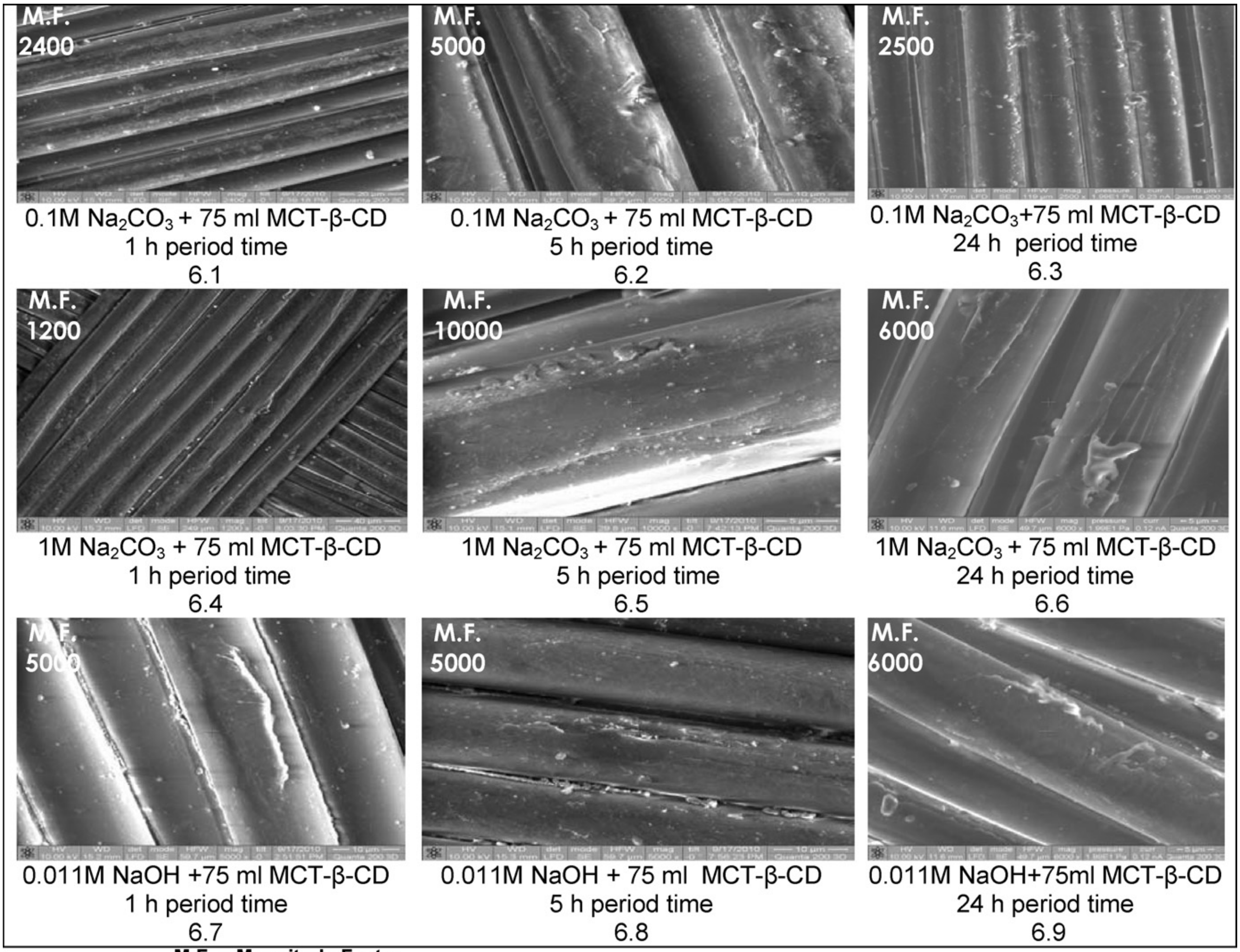
In Fig. 6 the treatment temperature was 20 °C; under the condition of a treatment extended from 1 h to 24 h, the degree of saponification was smaller in value than that obtained for the treatment at 130 °C. At 1 h treatment time, the grafting degree was smaller than that corresponding to warm treatment for the same time interval, but extending the time between 5 and 24 h results in grafting degrees comparable in size with those from the 2 h treatment at 130 °C. The advantage of cold treatment consists in a smaller roughness of the polyester support surfaces.

3.4.2.2. Quantitative and qualitative microanalyses. By means of the electron microscope, advanced qualitative (using EDAX 32/SEM) and quantitative (through elemental or atomic mass analysis) microanalyses were carried out, which proved the MCT-β-CD presence onto the polyester supports. Fig. 7 shows the presence of the nitrogen and sodium atoms, as an evidence of MCT-β-CD grafting onto the polyester supports which were treated with saponification agents and MCT-β-CD, both under cold and warm conditions.

The higher the MCT-β-CD concentration, the higher is the nitrogen content onto both polyester fabrics and films for the two treatment temperatures, 20 °C and 130 °C (Fig. 8).

3.4.3. Home laundering durability

Weight loss (expressed in percents) of some samples with 40 mm × 100 mm dimensions, after five home laundering cycles at 60 °C (according to the standard test EN ISO 105-CO6:1999 and using AATCC Standard Detergent 1993 and a liquour ratio 1:50)



- **M.F. = Magnitude Factor**

Fig. 6. Longitudinal aspect of the saponified/grafted filaments at 20 °C.

are presented in Table 3. Lower values mean a strong link between MCT-β-CD and polyester, so a durable effect.

3.5. *Effects of monochlorotriazinyl-β-cyclodextrin onto polyester fabrics and films*

3.5.1. *Hygroscopicity*

The pores, cracks and fissures obtained by the saponification action, represent the ways of water access inside the polyester supports. If the treatment was carried out at 130 °C, their volume and number are higher as the result of the thermal agitation which determines the motion of the macromolecular chains and the creation of empty volumes that can be filled with solutions.

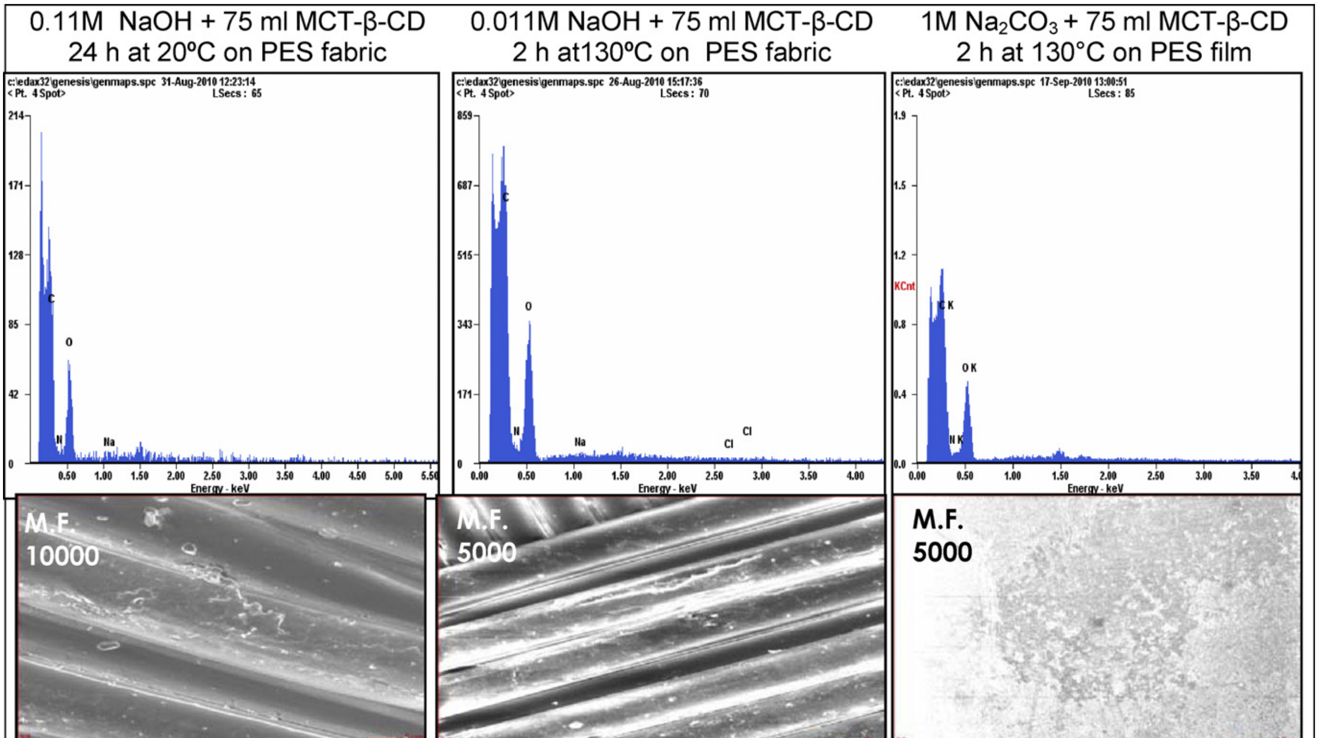
The grafting leads to an even bigger hygroscopicity (Table 4) than in the case of the supports only saponified because the exterior of MCT-β-CD cavity is very hydrophilic and has affinity for the polar molecules of water (Grigoriu, Luca, & Grigoriu, 2008; Harada & Kchi, 1990; Rusa, Luca, &Tonelli, 2001).

3.5.2. *Air permeability*

The air permeability is an index calculated as the average of 10 determinations, which reveals the PES fabric capacity to permit the air to pass through it. As compared to a calibrated untreated support, all the saponified fabrics have higher permeabilities, irrespective the saponification conditions. Yet, grafting determines a diminution of air permeability, the bigger, the higher is the MCT-β-CD content fixed onto the fabric. This justifies the supposition that MCT-β-CD can fill up part of the holes and cracks realized by the saponification agents inside the structure of polyester filament (Table 5).

Table 5 indicates that the air permeability increases with increasing concentration of the saponification agent (0 ml MCT) and the extension of the duration of saponification treatment, when working both at 130 °C and at 20 °C.

When the saponification and grafting occur simultaneously at 130 °C, one can notice that any increase of the MCT-β-CD concentration results in a decrease of permeability (for the same treatment duration), explicable through the capacity of the MCT-β-CD product to fill up, through grafting, the holes and cracks resulted under the action of alkaline saponification agents. Extending the treatment time from 30 to 120 min (for every formula of simultaneous saponification/grafting) results in increased permeability, due to the fact that the high temperature of 130 °C together with the saponification agent determine a large number of pores, holes and cavities, both inside the filament and at its external surface, holes that can not be completely filled up through grafting. The temperature of 20 °C does not determine significant modifications inside the filament (irrespective of the treatment time), the pores and holes only appearing at the filament external surface. These pores and cavities are covered by MCT-β-CD grafting, the reason why



Element	Wt%	At%
C	53.33	59.83
N	10.94	10.52
O	33.99	28.63
Na	01.74	01.02
Matrix	Correction	ZAF

Element	Wt%	At%
C	54.98	61.33
N	09.53	09.12
O	34.82	29.16
Na	00.66	00.39
Cl	00.00	00.00
Matrix	Correction	ZAF

Element	Wt%	At%
C	57.84	63.89
N	09.77	09.25
O	32.40	26.86
Matrix	Correction	ZAF

• M.F. = Magnitude Factor

Fig. 7. Qualitative (EDAX32/SEM) and quantitative (elemental and atomic mass analysis) analyses that prove the MCT-β-CD grafting onto polyester supports.

the permeability diminishes as the grafting agent concentration increases.

3.5.3. Mechanical properties after saponification/grafting

The mechanical properties vary according to the subjected treatments: the saponification or saponification and grafting in the same bath. The values obtained are presented in Table 6.

One can notice that the presence of the saponification agent leads to an alteration of the mechanical properties, irrespective of the treatment temperature. At 20 °C, a time of maximum 3 h is necessary to carry out the saponification stage, for which reason any shorter treatment (with or without MCT-β-CD addition) results in an alteration of the mechanical properties. By continuing the treatment with carbonate and MCT-β-CD, as the polyester is already saponified, the premises are created to start the grafting stage with MCT-β-CD, and thus the tensile breaking strength will increase, which shows that by grafting, the holes and cracks are covered, the roughness is less obvious, and polyester filaments get more rigid (Figs. 4.3, 6.3 respectively 6.6 – little wings made of MCT-β-CD appear between the PES filaments).

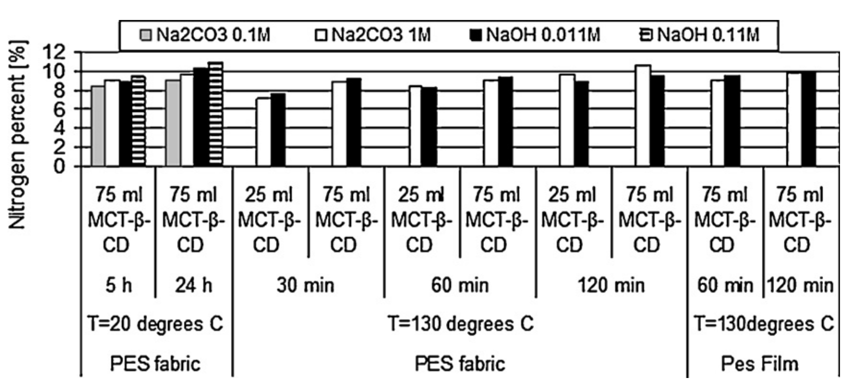


Fig. 8. Nitrogen content for PES fabric/film under the condition of simultaneous saponification and grafting at 20 °C and 130 °C.

Table 5
The values of air permeability ($P_s \cdot p$, mm H_2O) of simultaneously saponified and grafted PES fabrics, expressed in $m^3/(m^2$ min).

Saponification/grafting conditions	Saponification/grafting parameters (temperature/period time)						
	$T = 130\,^{\circ}C$			$T = 20\,^{\circ}C$			
	30 min	60 min	120 min	1 h	3 h	5 h	24 h
0.1 M Na_2CO_3							
0 ml MCT-β-CD	13.75	15.00	16.25	14.16	15.00	16.25	16.66
25 ml MCT-β-CD	11.66	12.08	13.99	13.08	12.50	11.91	11.66
50 ml MCT-β-CD	11.00	11.50	13.33	–	–	–	–
75 ml MCT-β-CD	10.00	11.25	12.41	11.75	11.26	10.41	8.75
0.5 M Na_2CO_3							
0 ml MCT-β-CD	14.75	15.47	17.50	–	–	–	–
25 ml MCT-β-CD	10.75	12.33	14.08	–	–	–	–
50 ml MCT-β-CD	9.16	10.83	13.16	–	–	–	–
75 ml MCT-β-CD	8.33	10.08	11.66	–	–	–	–
1 M Na_2CO_3							
0 ml MCT-β-CD	15.33	15.75	19.16	14.75	15.25	15.85	17.08
25 ml MCT-β-CD	12.08	14.25	16.66	13.33	13.16	11.66	10.41
50 ml MCT	11.08	13.50	15.83	–	–	–	–
75 ml MCT-β-CD	10.83	13.08	15.00	13.16	12.92	10.83	9.58
0.011 M NaOH							
0 ml MCT-β-CD	9.83	11.25	12.46	12.50	13.00	13.75	14.70
25 ml MCT	9.75	11.00	12.08	11.66	11.33	11.25	10.83
75 ml MCT-β-CD	–	–	–	10.83	10.40	10.00	10.50
0.066 M NaOH							
0 ml MCT-β-CD	10.75	20.83	24.44	–	–	–	–
25 ml MCT-β-CD	10.41	19.16	23.33	–	–	–	–
0.088 M NaOH							
0 ml MCT-β-CD	11.12	21.66	30.00	–	–	–	–
25 ml MCT-β-CD	10.83	20.03	28.75	–	–	–	–
0.11 M NaOH							
0 ml MCT-β-CD	12.50	25.83	34.16	12.16	12.42	13.16	13.25
25 ml MCT-β-CD	12.11	25.00	32.75	12.08	12.08	11.91	11.66
75 ml MCT-β-CD	–	–	–	11.45	11.33	11.25	11.00

Table 6
Mechanical properties in the weft direction.

Treatment conditions		Mechanical properties			
		F_H [N]	ε_H [%]	W_H [J]	$W_{H,m}$ [J/g]
Untreated sample		293	93.6	1.64	53.17
Treated sample (boiling in pure water) at 130 °C; 30 min		284	87.6	1.54	43.54
0.1 M Na_2CO_3 $T = 20\,^{\circ}C$					
1 h	0 ml MCT-β-CD	280	82.4	1.58	51.61
	25 ml MCT-β-CD	267	75.0	1.14	36.28
3 h	0 ml MCT-β-CD	268	77.6	1.18	37.26
	25 ml MCT-β-CD	308	99.4	1.83	60.60
24 h	0 ml MCT-β-CD	238	65.6	2.41	76.83
	25 ml MCT-β-CD	327	111.4	2.21	70.58
0.1 M Na_2CO_3 $T = 130\,^{\circ}C$					
30 min	0 ml MCT-β-CD	278	87.2	1.73	54.45
	25 ml MCT-β-CD	282	87.6	1.74	53.54
	50 ml MCT-β-CD	326	108.2	2.07	59.42
	75 ml MCT-β-CD	335	120.0	2.43	74.88
120 min	0 ml MCT-β-CD	208	70.6	0.85	26.85
	25 ml MCT-β-CD	239	76.8	1.04	31.91
	50 ml MCT-β-CD	249	76.0	1.06	31.63
	75 ml MCT-β-CD	285	95.4	1.58	48.63
1 M Na_2CO_3 $T = 20\,^{\circ}C$					
1 h	0 ml MCT-β-CD	270	83.0	1.27	42.00
	25 ml MCT-β-CD	260	73.6	1.09	35.93
3 h	0 ml MCT-β-CD	260	80.5	1.78	57.25
	25 ml MCT-β-CD	280	82.4	1.84	63.88
24 h	0 ml MCT-β-CD	250	60.2	1.27	38.99
	25 ml MCT-β-CD	282	80.6	1.34	42.35
1 M Na_2CO_3 $T = 130\,^{\circ}C$					
30 min	0 ml MCT-β-CD	264	87.3	1.34	42.77
	25 ml MCT-β-CD	246	79.8	1.14	35.60
	50 ml MCT-β-CD	263	87.0	2.58	79.80
	75 ml MCT-β-CD	273	89.8	1.45	45.32
120 min	0 ml MCT-β-CD	197	79.8	1.25	40.48
	25 ml MCT-β-CD	200	72.6	0.81	29.14
	50 ml MCT-β-CD	175	66.8	0.68	22.79
	75 ml MCT-β-CD	186	70.4	0.76	26.40

With treatments carried out at 130 °C, the mechanical properties are diminished as compared to those obtained at 20 °C, which proves the destructive effect of the alkaline agents used for saponification. For example, for a severe saponification formula (T = 130 °C, 2 h, 50 ml Na_2CO_3 1 M), the so-called natural silk touch is obtained for the treated polyester fabrics.

The alkaline agent concentration and the treatment time are the parameters which determine the diminution of the mechanical properties when one works without MCT-β-CD. The presence in the treatment bath of a concentration of 25–75 ml MCT-β-CD confers an increased stiffness, manifested through a rougher touch and increases of the mechanical properties.

4. Conclusions

The permanent anchorage of MCT-β-CD through grafting on polyester supports is possible by means of the alkaline agents, who act as saponification agents and create reactive–OH groups, able to bond the MCT-β-CD molecules by means of the chlorine atom from the triazine cycle.

A compromise is necessary between the tensile breaking strength of the polyester supports and the hygroscopicity, as this balance can be modified according to the user's requirements and the utilization field. The treatment time and temperature can be chosen depending on the future destination of the polyester support, as follows: if the purpose is to have a small air permeability, a higher hygroscopicity and a smaller breaking strength than the untreated polymer, then the treatment at 130 °C is the option; yet, if one aims at an increased resistance as compared to the untreated polyester and a lower roughness, the option is the treatment at 20 °C.

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