Colorimetric Answer of Monochlorotriazinyl-β- cyclodextrin Grafted onto PAN Support Chemical Modified with NaOH and Amines

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The acrylic fibre Melana (a ternary copolymer, AN + AV + αMS abbreviated as PAN) was pretreated with NaOH ± amine. The effects caused by these pretreatments have a chemical nature (at AV and AN comonomers level) and were investigated. The results show that after the pretreatments with amines (in presence of NaOH), the acrylic fibre undergoes chemical changes, acquiring OH, COOH groups or amides and hydroxamic acids. Monochlorotriazinyl-β-cyclodextrin (abbreviated with - CD) grafting on functionalized acrylic support determined new chemical modifications. All the modifications occured by PAN are demonstrated by qualitative analysis (FTIR, SEM) and by quantitative analysis (EDAX, tinctorial method). The tinctorial method can be used to confirm the chemical modification of PAN functionalized with amines and grafted with CD, only if it is carried out with another class of dyes (reactive dyes), different from the specific dye class (cationic dyes). The tinctorial answer to these transformations is revealed by colour strength values K/S obtained after dyeing with three reactive dyes: Procion red H-E3B, Procion Red H-EXL and Procion Brilliant Red H-EGXL. The obtained values of K / S are dependent on the amine type used in functionalization stage but also on the parameters of dyeing with reactive dyes (concentration, pH, temperature, duration, and amine type).

Keywords: polyacrylonitrile fibre, monochlorotriazinyl-β-cyclodextrin , reactive dyes, dyeability

The first acrylics were of homopolymer type and they were characterized by remarkable textile properties but because of the extremely difficult dyeing process their manufacture was stopped. Gradually, acrylic fibres have been synthesised based on the binary acrylic copolymers which have acidic groups of carboxylic or sulphonic acid type in order to improve the dyeability [1, 2]. The introduction of methyl acrylate, vinyl acetate and methylstyrene, as the third comonomer in the copolymerization reaction, led to the drop in glass transition temperature, thus facilitating dyeing [3] and changed other properties: breaking elongation, contraction, thermal stability etc.).

Worldwide there is a wide variety of acrylics differentiated by ionic character (most are anionic but there are cationic also: Acrilan 41, Creslan 58, Leacril N1 Orlon 28, Orlon 44, Vonnel [4] whose properties depend on the type, the percentage of comonomers and method of spinning [5].

The improvement of tinctorial property and widening the scope of use (from textile products to those used in the medical area) has been the subject of numerous scientific research projects aiming to two directions: I) obtaining new acrylic polymers; II) chemical modification of acrylic polymers already synthesised. Regarding the first direction, the efforts of the research for synthesis of new acrylic polymers were directed to two possibilities: a) the AN polymerization with various monomers, in order to improve the capacity of dyeing with cationic dyes: acrylic and methacrylic acid [6], fumaric acid, hydrazide, itaconic acid [7, 8], allyl sulphonic acid, vinylsulphonic acid, p-vinyl benzene sulphonic acid [9, 10], sulphonic acid, 4-vinyl benzene phosphonic acid [11], cinamic acid [12], crotonic acid, unsaturated carboxylic acids [2, 13], ethyl acrylate + divinylbenzene [14]. Although these substances have improved the tinctorial ability of acrylic fibres they have not solved the unlevelling problems encountered in dyeing process; b) the copolymerization with a basic monomer, for dyeing with acid dyes: 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine [15], 1-vinyl-imidazole, N,N-dialilmelamine, N-ethyl-N-vinylGuamide [4, 5], chitosan [16].

Regarding the second direction, many options were investigated throughout the time for chemical modification of acrylic polymers, for dyeing with anionic dyes: a) saponification with bases (NaOH or KOH, Na_2CO_3) with or without ethanol or methanol [17]; b) the treatment with amines of the following type: dimethylaminopropylamine [18], ethylenediamine [19] hydrazine [20, 21], urea [22], hydroxylamine [23-26], aliphatic amines, acyclic, whether primary or secondary with no more than 10 carbon atoms (e.g. diethylamide, ethylenediamine, hexamethylene diamine [27, 28], diethylenetriamine [29]; c) the treatment with enzymes of Luteus type [30];

This paper aims to change the chemical structure of acrylic fibre Melana (abbreviated as PAN) using basic

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Table 1
CHEMICAL STRUCTURES OF THE REACTIVE DYES

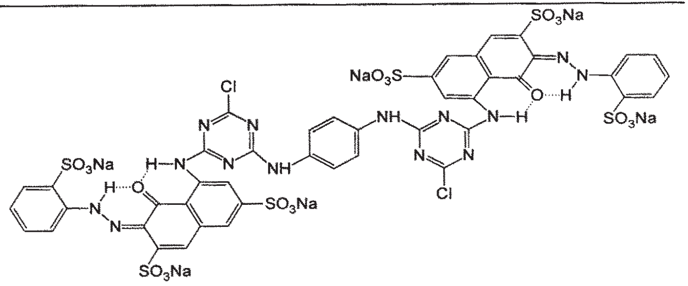
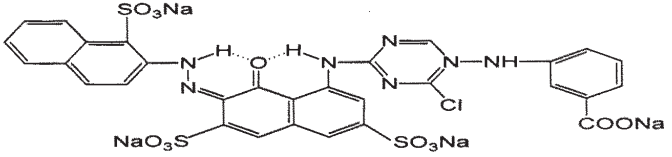
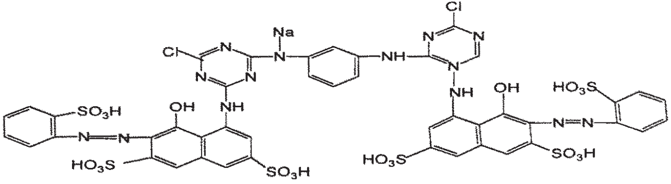
Cod Dye	Chemical structure
D1	 Procion Red H-E3B (C.I. Reactive Red 120)
D2	 Procion Red H-EXL
D3	 Procion Brilliant Red H-EGXL

Table 2
WORKING CONDITIONS AND SAMPLE CODIFICATION

Functionalization		***Grafting***	
Sample code	**Functionalization conditions**	**Sample code**	**Grafting conditions**
S01	2.5% NaOH	S1	2.5% NaOH+2% CD
S02	2.5% NaOH+2.5% CS	S2	2.5% (NaOH+2.5% CS)+2% CD
S03	2.5% NaOH+2.5% HA	S3	2.5% (NaOH+2.5% HA)+2% CD

substances/ amines with various pK_b in order to introduce amino groups which provide antibacterial properties [18, 31-36] to the textile support and thus enlarging the scope of textiles towards the medical field (dressing gowns for medical personnel, blankets, sheets, kits and seat covers for medical equipment).

Another objective aims to show that dyeing method may highlight chemical changes caused by functionalizations/ graftings. For PAN pretreatments two amines were used: chitosan (CS), hydroxylamine (HA) in the presence of NaOH. The parameters of functionalisations were: 2.5% amine, T= 100°C, 30 min period of time. Grafting with CD was performed at 100°C, in presence of NaOH as catalyst. All the changes are proved by qualitative analysis (FTIR, SEM) and quantitative analysis (EDAX analysis, tinctorial method). The answer to the changes made by functionalizations and CD grafting is given by the colour strength values K/S, which are dependent on one hand of amine type and on the other hand of dyeing parameters (type and concentration of the reactive dye used, *p*H, temperature, duration).

Experimental part

Materials and methods

The chemicals used were: hydroxylamine, HA (p.a with pK_b 8.02) and chitosan, CS (p.a with pK_b = 7.8) from Fluka, NaOH (pK_b = 0.2), acetic acid 2% (for dissolving chitosan) from Merck company. Acrylic fibre was obtained from a Romanian company (Savinesti SA) and is a ternary copolymer: acrylonitrile + vinyl acetate + α methyl styrene (85% AN+ 10% AV + 5% αMS). The main characteristics of PAN fibres are: 3.3 den finesse, $4.7x10^{-5}$ acid equivalent/ g fibre, saturation index S_F = 1.88 and 66.1% degree of remission of light. PAN fibres, as pales form were prepared for experiments through a cleaning process performed with 5 g/L non-ionic surfactant (Lavaton DSU from Bezema Company) at 60°C, 60 min. Then the samples were cooled, rinsed with deionised hot water and dried at room temperature.

The product used for grafting, CAVASOL W7 MCT (i.e. monochlorotriazinyl-β-cyclodextrin abbreviated as CD) was obtained from the company Wacker- Chemie, Germany. The reactive dyestuffs used for dyeing were Procion Red H-E3B, Procion Red H-EXL and Procion Brilliant Red H-EGXL from the company Ciba- Geigy. The structures of the three reactive dyes used to highlight the chemical modifications after functionalization and grafting respectively are presented in table 1.

The PAN samples were pretreated initially with 2.5% reagent at 100°C for 30 min, 1:150 liquor ratio, with the view to make them functional (table 2). The grafting was performed with the CD in the presence of NaOH (as catalyst) at a temperature of 100°C, 30 min, 1:150 liquor ratio (table 2). After each stage (functionalization and grafting respectively), the samples were intensely washed with de-ionized water (at 40°C) and then with cold water at room temperature. All the treatments (functionalizations and grafting respectively) were carried out on Mathies Policolor machine.

The dyeings have been carried out with the three reactive dyes in conditions of different concentrations (9-15%), *p*H (10-14), temperature (80-100°C) and duration (30-120 min). All dyeings have been carried out on Mathies Policolor machine.

In order to reveal the effects of these treatments both qualitative and quantitative methods were used.

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 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 4000–600 cm^{-1} range. After the registration, the absorption spectra have been electronically superposed (using Spekwin32 software).

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

Tinctorial method was applied to confirm the changes through functionalization/grafting. Dyeing was performed on the two series of samples: functionalized, and grafted respectively. Dyeing was carried out with 1:150 liquor ratio, changing the concentration (9 - 15% reactive dye), *p*H (10-14), temperature (80°C and 100°C) and duration (30-120 min). After dyeing, the samples were subjected to some final treatments, consisting in the repetition of the following stages: soaping at 90°C for 15 min, rinsing at 40°C, and cold water rinsing. Dyeing and hot soaping were performed at Mathies Policolor machine.

After drying at room temperature, the samples color was evaluated; color strength (K/S) [37-40] was measured on a Datacolor Spectrophotometer Spectroflash FS300.

Results and discussions

Functionalization mechanism: the chemical structure of PAN can be changed by some pretreatments with NaOH+amines for dyeing with reactive dyes. Nature of the substances/amines and especially the basicity (through pk_b values) are the main attributes which generate distinct changes, at the levels of AN and AV [41-48]. It is known that NaOH transforms the acetate group in a new functional group, OH type; nitrile group is transformed in COOH via amide group.

In equation (1) we have written the general reaction of functionalization of PAN with amine in an alkaline medium, at AN and AV levels.

In eq. (1) R_1 could be =O; R_2 could be: H (in amides from the reaction of NaOH) or OH (in hydroxamic acid from the reaction of NaOH+HA mixture); pyranozic ring (from chitosan) in amides; P could be some secondary products as CH_3COONa or CH_3-CO-NH-Y or Na^+.

The transformations of acetate groups from AV and CN groups from AN, in the presence of NaOH ± amine are summarized in table 3 [41-48].

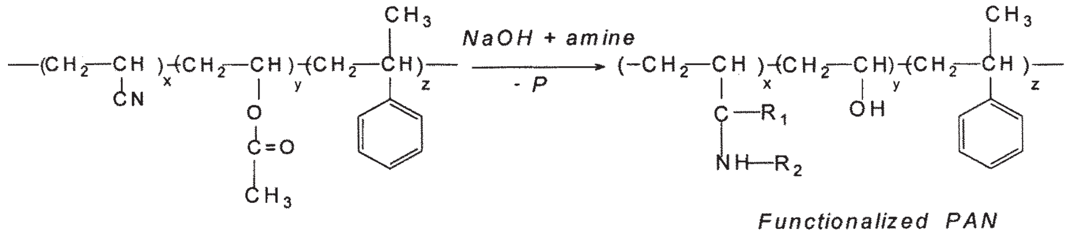
Grafting mechanism

MCT-β-CD can be grafted on functionalized PAN by means of new functional groups (OH type / table 3); appear etheric links. In table 3, one can notice that PAN is functionalized with two OH groups in the case of treatment with NaOH + HA.

FT-IR for functionalized PAN: the ester group in vinyl acetate, co-monomer existing in PAN, is converted by NaOH, in a secondary alcohol. This fact is confirmed by the modification of the height of the peaks at 3385 cm^{-1} (OH stretching), 1069 cm^{-1} (C-OH stretching (s), and near 1400 cm^{-1} for O-H in-plan deformation (m)) (fig. 1).

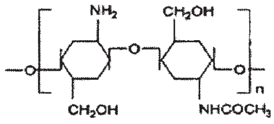
In S01-S03 samples, NaOH acts as hydrolysis agent for the CN group, converting it to a certain extent in COOH groups (via amidic groups).The presence of some COOH groups is confirmed by the height of the peaks at 1732 cm^{-1} (assigned to C=O stretching (s) and 1233 cm^{-1} for C-O stretching vibration (s)), taking into account that the number of CN groups decreases as the result of the degradation generated by NaOH. The presence of amidic groups is confirmed by the bigger height of the peaks near 1630 cm^{-1} (C-O stretching (s), 1565 cm^{-1} (N-H out of plane (m)), if is made the comparison with the witness. The decrease of the absorption band from 2239 cm^{-1} (CN stretching) is the bigger, as its conversion in COOH groups was stronger [41, 49-51].

Still another effect of functionalization in alkaline medium is the diminution of macromolecular chain length as the effect of degradation produced during the saponification reaction; this can be especially noticed at the samples functionalized with NaOH or with NaOH+HA,



(1)

Table 3
CHEMICAL TRANSFORMATIONS AT NITRILE AND ACETATE GROUPS IN PAN

Pretreatment		**Transformation after pretreatment**			
		Nitrile group		**Acetate group**	
NaOH ± Amine	**Abreviation**	**Reaction type**	**Transformation in:**	**Reaction type**	**Transformation in:**
NaOH	NaOH	Alkaline hydrolysis	-CO-NH$_2$ and -COOH	Saponification	-OH
NaOH+ NH$_2$-OH	NaOH+HA	N-acylation	| C=O | NH—OH Hydroxamic acid	Saponification	-OH
NaOH+ 	NaOH+CS	N-acylation	| C=O | NH - CS Amide monosubstituted	Saponification	-OH

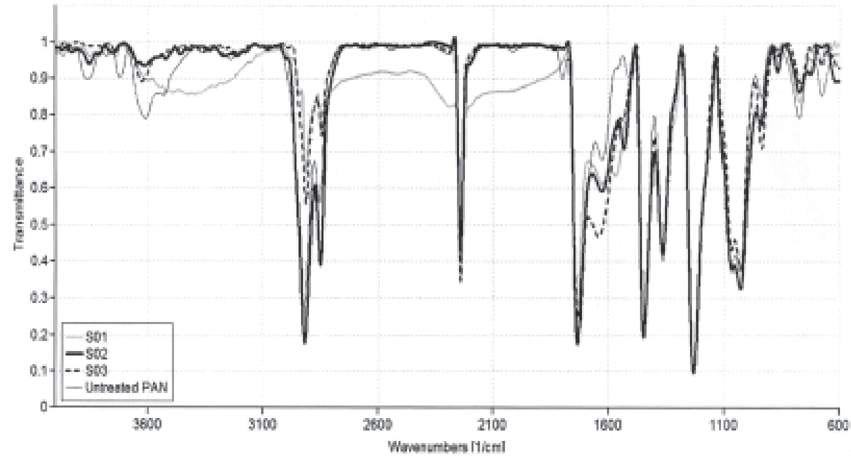


Fig.1. FTIR spectra for functionalized samples

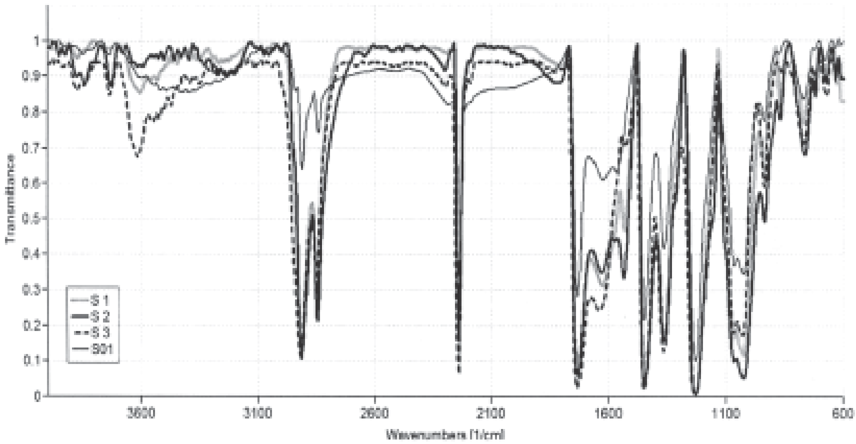
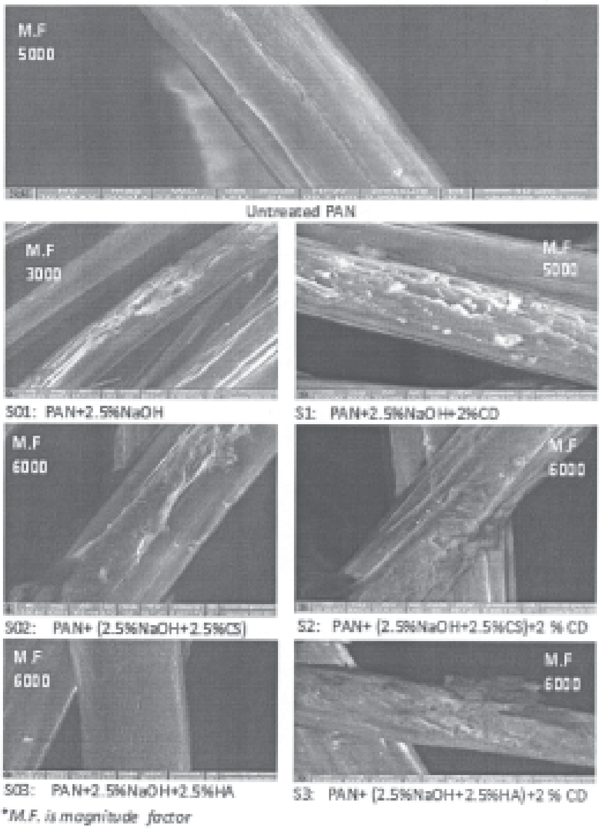


Fig. 2. FTIR spectra for grafted samples



*M.F. is magnitude factor

Fig. 3. SEM images

within the range 2930-2857 cm^{-1} (s), 1445 cm^{-1} (m) and 1366 cm^{-1}, afferent to C-H stretching vibrations.

In S02 sample, the presence of the NH_2 (from CS), overlapped with amide monosubstituted group, is proved by the appearance of the peak at 1535 cm^{-1}, which does not exist in the witness sample.

The presence of the hydroxamic acid in the sample S03 (functionalized with NaOH + HA) is confirmed by the absorption bands from 1670-1600 cm^{-1} for combination of C-N and C=O stretching (m-s), 1534 cm^{-1} for N-H deformation and C-N stretching (m), and near 937 cm^{-1} for N-O stretching (w).

FT-IR for grafted samples: the product with which each functionalized sample was grafted (according to the conditions from table 2) was CD. This is in fact a β-cyclodextrin that has attached a reactive system consisting of three triazine cycles, each cycle having one chlorine atom and one –O$^-$Na$^+$ group. The chlorine atom is the one by whose means the CD can be grafted on the functionalized sample (the presence of the unreacted chlorine is confirmed by the new peak appeared at 722 cm^{-1}). The grafting is possible at the secondary OH group (obtained in the functionalized PAN), when ether groups are formed; The formation of ether groups between the functionalized samples, and CD was possible in the presence of the catalyst (NaOH) and the high temperature, and it implied each time the HCl elimination, as secondary reaction product.

All the samples grafted with CD preserve the characteristics of functionalized samples, but they also have some characteristics which confirm the CD presence, through: the appearance of the peak at 1530 cm^{-1} (assigned to C=N from the triazine group attached to CD); the increase of the absorption bands from the range 1028-1241 cm^{-1} (assigned to OH primary and secondary groups from β-cyclodextrin, and the ether bond C-O-C, which is in fact the bonding bridge between each functionalized sample and the CD); the increase of the absorption bands specific to C-H vibration (the range 2844-2920 cm^{-1}).

SEM: figure 3 illustrates the morphological aspects of functionalized/grafted samples.

EDAX analysis (table 4) confirms the chemical modifications also shown off by the FTIR analysis (figs. 1 and 2). The presence of CD on the grafted sample is

Table 4
ELEMENTAL ANALYSIS (At%)

Sample code*	Treatment conditions	Element C	O	N	Na	S	Cl
W	Witness sample	76.10	10.53	12.39	0.49	0.49	0.00
S01	(PAN+2.5% NaOH)	75.58	12.00	11.65	0.39	0.38	0.00
S1	(PAN+2.5% NaOH)+2%CD	75.74	9.70	13.46	0.36	0.32	0.42
S02	(PAN+2.5% NaOH+2.5%CS)	76.12	10.87	12.41	0.30	0.30	0.00
S2	(PAN+2.5%NaOH+2.5%CS)+2%CD	76.32	9.98	12.72	0.23	0.30	0.45
S03	(PAN+2.5% NaOH+2.5%HA)	76.05	10.01	13.13	0.69	0.12	0.00
S3	(PAN+2.5%NaOH+2.5%HA)+2%CD	76.12	9.56	13.24	0.34	0.28	0.46

**Sample codes are the same as in Table 2.*

confirmed by: the chlorine atoms not involved in chemical reactions; the increase of nitrogen content, as compared to the saponified sample (S01) at all the treated samples; preservation of the same sequence of carbon content increase in functionalized samples, as in the FTIR spectra: S01, S03 and S02; the increase of the carbon content in all the grafted samples, as compared to their functionalized correspondents.

Colorimetric measurements: in this paper, three heterocyclic dyes with nitrogen were used for dyeing; these form covalent bonds through nucleophile substitution reactions with chemically modified PAN. The general chemical structure of a reactive heterocyclic dye can be schematically represented as **S–Dye–P-X;** where **S** is the solubilized sulphonic group; **Dye** is the skeleton of acid dye with azoic, anthraquinonic or phthalocyaninic structure; **L** is the atom or group which binds the dye with the characteristic reactive group; **P** is the reactive system; **X** is the substituible reactive atoms.

The three dyes used for dyeing have the reactive system (P) of monochlortriazine type, being considered in the series of reactive dyes, as low reactivity dyes. Yet, they are able to dye the chemically modified acrylic support (*symbolized as HO-PAN*) (eq. 2) and, at the same time, they form secondary reactions with water, when large part of the reactive dye gets hydrolyzed (eq. 3):

$$\text{S-Dye–P–X} + \text{HO-PAN} \rightarrow \text{S-Dye–P–O-PAN} + \text{HX} \qquad (2)$$

$$\text{S-Dye–P–X} + H_2O \rightarrow \text{S-Dye–P–OH} + \text{HX} \qquad (3)$$

It is known that dyeing with reactive dyes is influenced by the following parameters: chemical structure of dye, concentration, *p*H, temperature, duration, electrolyte, liquor ratio and presence of auxiliary substance. In order to evaluate only the dyeability of these dyes without being supported by the electrolyte and chemical auxiliaries, we have used them in dyeing formulas without any other chemical agent, excepting NaOH, necessary to produce an alkaline *p*H.

Influence of dye concentration

The dependence of the K/S values on the dye concentration is illustrated in the figures 4-6.

Generally, the increase of dye concentration used for dyeing results in the increase of the color strength; in the case of reactive dyes, this can only be accomplished if the dye hydrolysis reaction occurs more difficult (eq. 3), the priority being the reaction of reactive dye binding to the textile support (eq 2). The D1 and D3 dyes used in this work have each six solubilizing sulphonic groups (table 1), which makes their affinity for water much higher than at the D2 dye; thus the dyeings with 15% D1 or D3 result in smaller color strength values comparison to the dyeing with 9% dye (figs. 4-6).

Figure 4 shows that CD grafting determines the decrease of K/S at all the samples S1, S2 and S3, as compared to their witnesses (S01, S02 and S03). The highest K/S values are obtained on the sample functionalized with NaOH + HA, because it sets at the disposal of the reactive group from the reactive dye, two new reactive groups (OH type) in each structural unit: by one OH group (coming from the transformation of the ester group of AV) and one OH group in hydroxamic acid. Grafting CD on functionalized PAN support consisted in the reaction of the new functional groups with the chlorine from tryazine cycle of cyclodextrin, which resulted in the generation of a voluminous architectonic system that made more difficult for the reactive dyes to get closer in order to react with the treated cellulose. Accordingly, these grafted supports dyed much poorer than the functionalized ones.

The figure 5 indicates the following aspect: the increase of the concentration of the dye Procion Red H-EXL from 9% to 15% results in the increase of K/S. Responsible for this behavior is the small number of the solubilizing groups and the lower molar volume of D2 dye [52, 53]. As

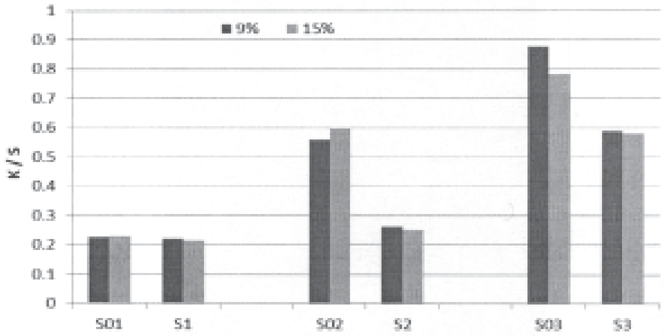


Fig. 4. Dependence of K/S on the concentration of D1 dye used for dyeing (at *p*H=14, 100°C, 30 min) of the functionalized and grafted samples (the same codes as in table 2)

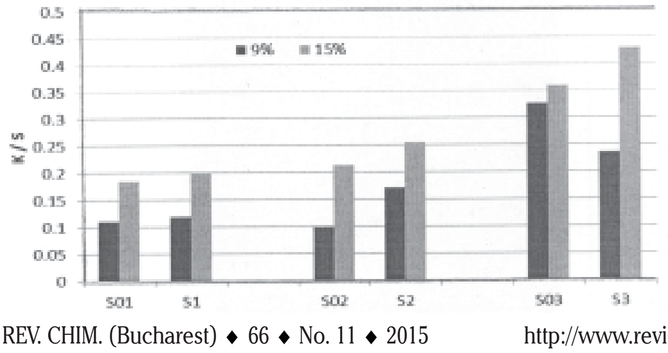


Fig. 5. K/S dependence on the concentration of D2 dye used for dyeing (at *p*H = 14, 100°C, 30 min) of the functionalized and grafted samples (the same codes as in table 2)

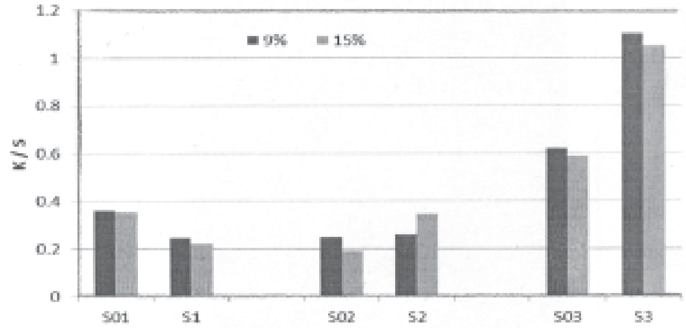


Fig. 6. K/S dependence on the concentration of D3 dye used for dyeing (at pH = 14, 100°C, 30 min) of the functionalized and grafted samples (the same codes as in table 2)

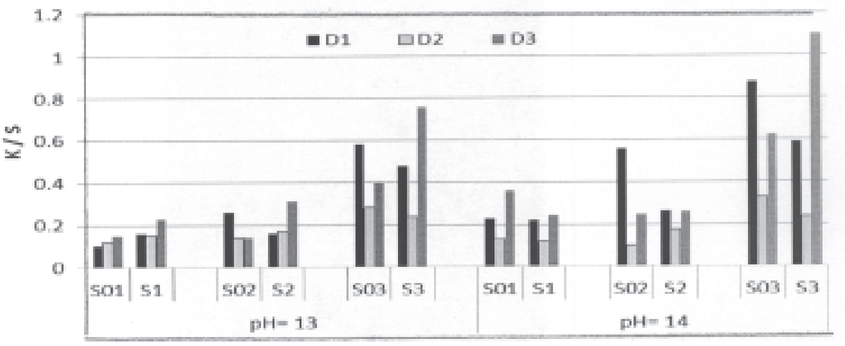


Fig. 7. Color strength dependence on the pH used in the dyeing (with 9% dye at 100°C, 30 min) of the functionalized and grafted acrylic supports (the same codes as in table 2)

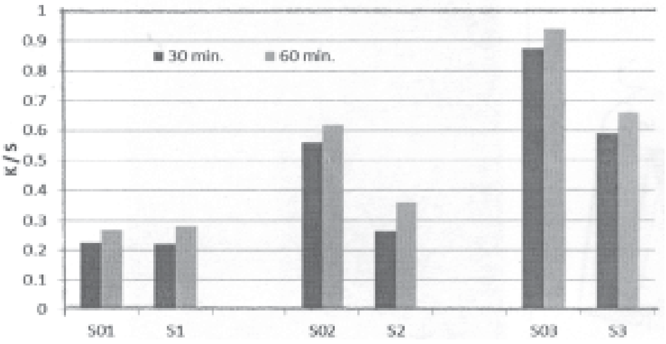


Fig. 8. Color strength dependence on the duration of dyeing (in case of 9% D1, pH = 14, 100°C); the same codes as in Table 2

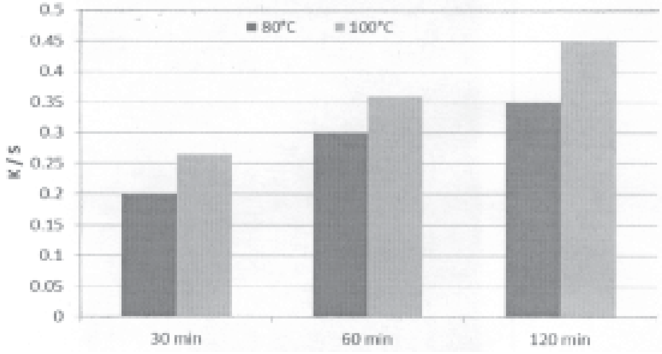


Fig. 9. Color strength dependence on temperature dyeing (for S2 dyed with 9% D1, pH = 14).

compared with S01, all the samples functionalized in alkaline medium and then grafted, resulted in bigger K/S.

In figure 6 one can notice that the utilization of a concentration of 15% results in smaller K/S than at 9%, and CD grafting results in higher K/S than at functionalized samples [52, 53].

By Comparison of the K/S values for functionalized and grafted samples we can observe that CD grafting on a PAN support functionalized with NaOH + CS (sample S2) leads to higher K/S values than on S02 sample; CD grafting on a PAN support functionalized with NaOH + HA (sample S3) results in higher values of K/S than on S03.

Influence of pH

In this work we performed dyeing operations with three dyes for pH = 10÷14, but the best values were obtained for pH = 13 and pH = 14 (fig. 7). This can be explained by the low reactivity of the dyes chosen for dyeing, and the big stability of these dyes in alkaline mediums. We found that a pH increase during the fixing period corresponds to an acceleration of the reaction between the dye and the textile support. Yet, this depends on the chemical structure of the utilized reactive dye.

Influence of dyeing duration

Dyeing duration favorably influences the color strength (fig. 8) in both series sample: functionalized or grafted samples; in the case of dyeing with D1, the increase of dyeing duration from 30 to 60 min resulted in a slight improvement of the color strength and in a higher color uniformity.

Influence of dyeing temperature

In dyeing with reactive dyes, the temperature has deep effects on both, the dye, and the textile support in aqueous solution. Temperature increase can result in a better dye penetration, a faster diffusion, a better color uniformity; yet, it can diminish the dye substantivity and increases the risk of its hydrolysis. A high temperature leads to a high dye-fiber interaction. Therefore, the dyeing temperature and color strength are influenced by the substantivity/reactivity of the dye and by the chemical modified structure of PAN. As one can notice in figure 9, the temperature of 100°C provides the highest values of K/S, irrespective of dyeing duration.

Conclusions

PAN functionalization was performed in basic medium with two primary amines: hydroxylamine and chitosan. CD was grafted on the functionalized support. The effects of these treatments were shown off through quantitative (spectroscopic analyses (FTIR and EDAX) and tinctorial methods) and a qualitative method (SEM). The tinctorial method can reveal the chemical modifications appeared during the functionalization or grafting treatments. Chemical modifications depend mainly on the nature of functionalization agent, its concentration and working conditions (concentration, temperature, duration). The structure of utilized reactive dyes influences the K/S values: the K/S values are the higher, the fewer solubilizing groups are in the dye and the less voluminous it is. The best colorimetric results were obtained on the samples functionalized in basic medium with HA and grafted with CD, being followed by the samples functionalized with CS. In each series, the samples grafted with CD (S1, S2 and S3) suffered more chemical modifications, as compared to their witness samples (S01, S02 and S03), which was also confirmed by the tinctorial method.

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