Colorimetric Evaluation of Chemical Modifications Generated by PAN Functionalization in Acid/ basic Medium and Grafting with Chitosan

VASILICA POPESCU[1]*, IRINA CRINA ANCA SANDU[2, 3], GABRIEL POPESCU[4]

[1] Gheorghe Asachi Technical University, Faculty of Textiles, Leather Engineering and Industrial Management, 29 Mangeron Blv.,TEX 1 Building, 700050, Iasi, Romania

[2] Universidade de Évora, Laboratório HERCULES, Palácio do Vimioso, Largo Marques de Marialva, 8, 7000-809, Évora, Portugal

[3] Romanian Inventors Forum, 3 Sf. P.Movila Str., L11, III/3, 700089, Iasi, Romania

[4] Gheorghe Asachi Technical University, Faculty of Mechanical Engineering, 43 Mangeron, Blvd., 700050, Iasi, Romania

The acrylic fiber from Romania - Melana (PAN) consists in a tertiary copolymer obtained through copolymerization of three comonomers: vinyl-acetate (AV), acrylonitrile (AN) and $\triangle\alpha$- methyl styrene (MS). PAN functionalization depends on the reaction medium: a strongly basic pH converts the acetate group from AV in hydroxyl group, and the nitrile group from (AN) in COOH group via amide group. This thing does not happen in weakly acid medium realized with acetic acid (pH= 4-5). Yet, in this acid medium occurs the protonation of acrylic fiber, which confers the possibility of establishing electrovalent bonds between the fiber and a basic compound, such as chitosan. In this paper, one evaluates colorimetrically all the chemical modifications appeared on PAN during functionalization in basic/acid medium and then grafting with chitosan (CS). Dyeing operations with non-specific dyes (reactive dyes) were performed using different concentrations, durations and pH. By comparing the tinctorial behaviour of the acrylic supports in the two mediums (acid and basic), it resulted that functionalization through saponification determines important chemical modifications. Through grafting, the contribution of NH_2 groups from CS makes possible dyeing in acid medium, a fact confirmed by the values of colour strength (K/S), as well as by the colour differences ($\Delta L^*, \Delta a^*, \Delta b^*, \Delta C^*, \Delta h^*, \Delta E^*$).The chemical modification produced during functionalization and grafting have been proved by qualitative methods (FTIR analyses and dropping colour test) and quantitative method (dyeing with reactive dyes when the values of K/S and of colour differences can also highlight the impact of these modifications).

Keywords: PAN, functionalization, grafting, chitosan, reactive dyes, colorimetry

The technology of acrylic fibers synthesis has improved in time, such that polymers with 100% acrylonitrile have been replaced by copolymers that contain 2 or 3 comonomers with groups more reactive than CN group from acrylonitrile [1-4].

Polyacrylic fibers are known under numerous forms of commercial presentation and they frequently accuse differences in their technological and tinctorial properties. These differences are partly due to the utilization of both different solvents during spinning, and wet or dry spinning procedure [5]. Fiber-producing technology influences the nature, properties and implicitly the quality of acrylic fibers. From this standpoint, the acrylic fibers differ in terms of copolymer composition, polymerization procedure, used solvent, fiber spinning and processing system, as well as according to utilization fields [6, 7]. As the monomers result from a large number of vinyl derivates, such as vinyl chloride, vinyl acetate, vinyl pyrazine, methacrylic acid and styrene-sulphonic acid, it follows that fiber properties differ from one another depending on the nature and proportion of utilized comonomers [1, 5].

Nevertheless, even if nowadays the acrylic fibers have a wide structural diversity, they are not as reactive as the natural fibers (cotton, wool, natural silk) [1], due in the first to the tinctorial behavior: they are only dyed with cationic dyes through an ionic and hydrophobic exchange between fiber and dye [8-10]. Reactivity can be improved by modifying fiber synthesis process (by using comonomers that possess strong reactive groups), or by a chemical modification of the already synthesized fibers [5, 6]. One can produce chemical modification of PAN fiber either by activation/ functionalization, or by grafting with a wide series of products, inclusively with natural or synthetic polymers that have several polar/reactive groups [11].

In this work, the chemical modification of the CN groups and of acetate from Melana was realized at the contact with two different mediums: a weakly acid solution and a strongly basic solution respectively. PAN functionalized in this way was then grafted with a natural polymer (chitosan). The chemical modification produced during functionalization and grafting have been proved both quantitatively and qualitatively. The qualitative results indicated by FTIR analyses and dropping colour test have been also confirmed by the tinctorial method, which also rendered evident the quantitative impact of these modifications.

Experimental part
Materials and methods

The acetic acid and NaOH acquired from Merck were used for functionalization. Chitosan 48165 (highly viscous)/ Commercial CS3 was acquired from Fluka; Chitosan was used for grafting after having been solved in acetic acid. Chitosan has a deacetylation degree DD= 77±4%. The oxalic acid used as grafting catalyst was obtained from Merck.

Textile support consisted in Melana-type PAN fibers, i.e. acrylic fibers (85% acrylonitrile (AN) + 10% vinyl acetate

(AV) + 5% α methyl styrene (MS)) obtained from Savinesti S.A. / Romania, whose chemical structure is illustrated in figure 1. The main characteristics of the Romanian PAN fibres are: 3.3 den finesse, 4.7×10^{-5} acid equivalent/g fibre, saturation index $S_F = 1.88$.
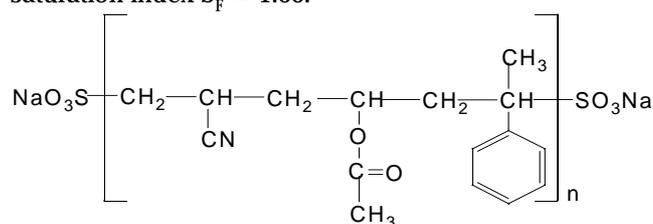

Fig. 1. Chemical structure of PAN synthetized in Romania

Three reactive dyes were used for dyeing: Procion Red H-E3B, Procion Red H-EXL and Procion Brilliant Red H-EGXL from the company Ciba-Geigy; the chemical structures and characteristics of these dyes are presented in table 1.

PAN functionalization was accomplished in two reaction mediums: weakly acid medium realized with CH_3COOH (pH=4-5), at 100°C for 30 min, liquor ratio M= 1:150; basic medium realized by the presence of 2.5 g NaOH for 100 g acrylic material, at 100°C for 30 min, and liquor ratio M=1:150. After these treatments, the samples were grafted with 2.5% CS (pK_b= 7.8) in the presence of oxalic acid (as catalyst) at a temperature of 100°C for 30 min (table 2). In this work, all the concentrations were expressed in percents that mean grams reagent/100 g textile material.

After each stage (of functionalization and grafting respectively), the samples were intensely washed with de-ionized water (at 40°C) and then with cold water at room temperature.

One can reveal the chemical modifications due to functionalization/grafting by means of tinctorial method; the samples are dyed with non-specific dyes (reactive dyes from table 1), in the condition of modifying the concentration (3, 9 and 15%), pH (1 ÷ 12) and dyeing duration (30 - 120 min.). After dyeing, the samples were intensely soaped (at 90°C, 15 min) and then rinsed with de-ionized water at 60°C and then with cold water at room temperature. One estimates the colour strength (K/S) and colour differences (ΔL^*, Δa^*, Δb^*, ΔC^*, Δh^* and ΔE^*).

All the treatments (functionalization, grafting and dyeing) have been carried out on Mathies Policolor machine.

FT-IR – analysis was performed on a Spectrophotometer FTIR IRAffinity-1 Shimadzu (Japan), but the spectra registration was realized with 250 scans in the 4000–600 cm^{-1} range. The overlapping spectra were performed using software Spekwin32.

Dropping colour test was performed according to the indications in the literature [12]. This test consists in treating of functionalized PAN samples with a solution of 1% HOCl for 5 min, in a basic medium. A thorough washing with distilled water followed. After adding one drop (20 mL) of 2% KI solution 1% starch we observe the colour appears. A brown-violet coloration indicates the presence of iodine which developed as a reaction product of chloramines formed into acrylic fibre with KI solution.

Colour measurements: Using a Spectrophotometer Spectroflash SF 300 from Data Color were realized many

Table 1
CHEMICAL STRUCTURES OF THE REACTIVE DYES

Code	Chemical structure and name	No. groups SO₃Na	No. chlorine atom	No. other groups (OH)
R1	Procion Red H-E3B (C.I. Reactive Red 120)	6	2	0
R2	Procion Red H-EXL	4	1	0
R3	Procion Brilliant Red H-EGXL	6	2	2

Table 2
CODING OF FUNCTIONALIZED/ GRAFTED SAMPLES

Code sample	Significance
FA	PAN functionalized in a low acid medium
FB	PAN functionalized in a strong alkaline medium
GA	CS grafted onto FA
GB	CS grafted onto FB

colour measurements: colour strength (K/S) and colour differences (ΔL*, Δa*, Δb*, ΔC*, Δh* and ΔE*).

Colour strength (K/S) was measured by the light reflectance technique using Kubelka-Munk equation (1) [13-15] on a Data Color Spectrophotometer Sprectroflash SF300. In this article all values of K/S have been indicated for the wavelength where the visibility of the red colour is maximum (500 nm).

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \qquad (1)$$

where: *K/S= colour strength; R= reflectance of the dyed sample [%].*

Colour differences were expressed by means of the parameters: ΔL*, Δa*, Δb*, ΔC*, Δh* and ΔE* [13 -18]. The parameters ΔL*, Δa*, Δb*, ΔC* are calculated by making the difference between the value read on the tested sample and that from the witness sample. The parameters ΔL* indicates the brightness difference: if ΔL* < 0, it means that the tested sample is darker than the witness, having a smaller brightness than this. The parameters Δa* and Δb* represent the chromatic parameter, indicating the position of the tested sample in the colour space. The parameters ΔC* indicate the saturation difference, and when ΔC* < 0 it means that the tested sample has a smaller saturation than the witness does. The parameters Δh* indicate the hue differences: when the witness is red, the parameters Δh* > 0 indicates that the tested sample is more yellow than the witness is; when Δh* < 0, it means that the tested sample is bluer than the witness is [13].

The values ΔE* and Δh* can be calculated using equations (2) and (3) [13-15, 19]:

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \qquad (2)$$
$$\Delta h^* = (\Delta E^{*2} - \Delta L^{*2} - \Delta C^{*2})^{1/2} \qquad (3)$$

where: ΔE* is the total colour difference; ΔL* is the difference in lightness; Δa* is the difference on the red-green coordinate; Δb* is the difference on the blue-yellow coordinate; Δh* is the difference in colour hue; ΔC* is the difference in chroma.

Fastness properties for functionalized/grafted and dyed samples were made according to ISO standard AO5-CO6 in 1999 using grey scale related (grey and grey change Stain Scales) to assess the change in colour of samples after a wash, respectively the degree of soiling / dye staining accompanying samples, undyed.

Results and discussions

PAN treatment in a low acid medium does not lead to chemical modification of acetate and nitrile groups. In exchange, PAN functionalization with 2.5% NaOH determines the conversion of acetate group into an OH-type functional group (through saponification reaction), and of the nitrile group into a COOH group (via amide group by a hydrolysis reaction) [11] (fig. 2).

In figure 2, one can notice the following chemical modifications [11]: 1) during functionalization in basic medium, acetate groups are converted into OH groups, and the CN groups in COOH groups via amide group (CO-NH₂); there are no transformations at the level of these groups in acid medium, but SO₃Na (final groups) are converted into SO₃H. 2) during grafting with CS using oxalic acid as catalyst and the temperature of 100°C, the following chemical modifications occur: a) the methylen- ether bond is formed between the primary OH group of CS and the new OH group from the functionalized PAN ; b) ester bond
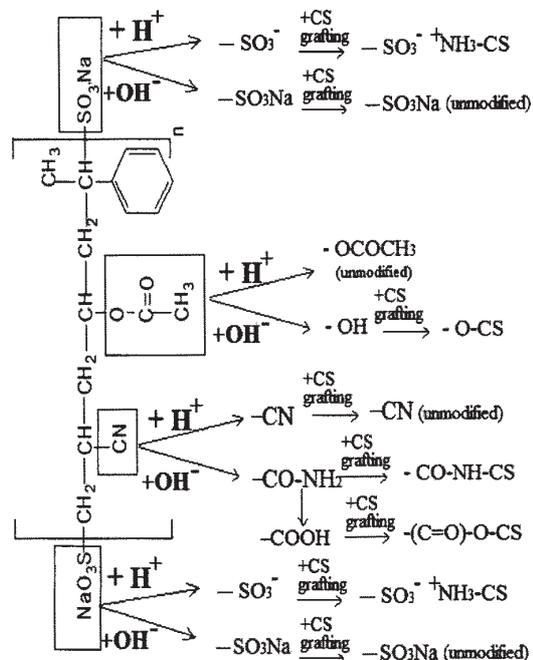

Fig. 2. Chemical transformations in PAN at levels of acetate, nitrile and final groups, during functionalization and grafting treatments

is formed between the primary OH group of CS and the COOH group of functionalized PAN; a group of mono-substituted amide (CO-NH-CS) type appears at the level of amide group (CO-NH₂); c) in acid medium, the electrovalent bond is formed between the sulphonic group of PAN and ⁺NH₃ group from CS solved in acetic acid.

Therefore, figure 2 clearly indicates that, out of the two mediums used for functionalization, PAN is only sensitive to the basic medium, resulting the sample FB, in which the acetate group from AV and nitrile groups from AN were converted into more reactive functional groups [11]. During the grafting with CS, these functional groups (from the FB sample) react with the primary OH group of CS and form ether bridges and a small number of ester groups in GB (the esterification reaction needs more severe conditions to be produced with a higher yield).

The acid mediums in which functionalization (leading to the FA sample) and grafting with CS (with oxalic acid as catalyst, at 100°C) occur, result in the protonation of acrylic fiber, which confer the possibility to establish electrovalent bonds between the PAN fiber and chitosan solution (obtained by solving in acetic acid).

The large number of bonds established between PAN functionalized in basic medium (FB sample) and CS will result in more intense dyeing with reactive dyes; for these reasons the GB sample will dye more intensely than the GA sample.

FTIR for PAN functionalized in acid medium and grafted with CS

In figure 3, one can notice that the FTIR spectra of untreated PAN and that treated with CH₃COOH are completely overlapped. This indicates that the acetic acid cannot convert the acetate and nitrile groups from PAN in other more reactive functional groups. Grafting with CS in the presence of oxalic acid as catalyst brought no modifications at the level of acetate groups (1730 cm⁻¹) or nitrile group (2242 cm⁻¹), which leads to the idea that CS formed only electrovalent bonds with the acid groups (obtained by the conversion of SO₃Na into SO₃H in acid medium) from the end of the macromolecular chain of the acrylic polymer [11, 20, 21].
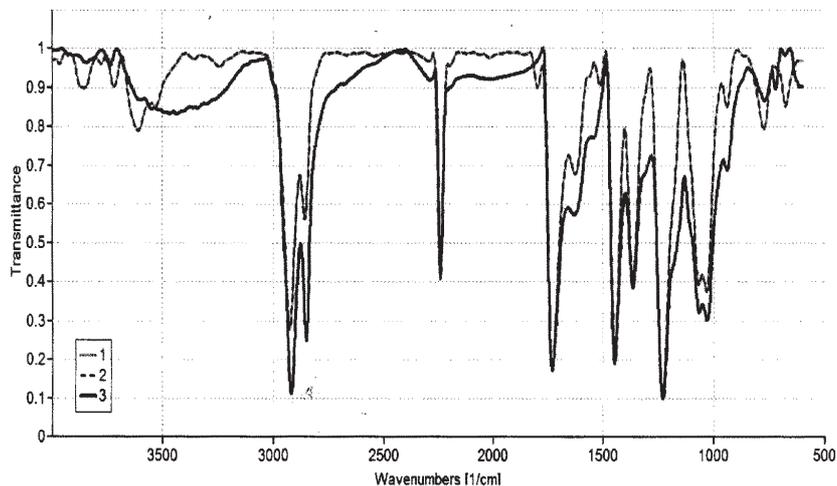
Fig. 3. FTIR spectra for untreated PAN (1), PAN+CH_3COOH (2) and PAN functionalized in acid medium but grafted with CS (3)

It is known that PAN fibers are ternary copolymers (85% acrylonitrile (AN) + 10% vinyl acetate (AV) + 5% α methyl styrene (αMS)) obtained by a radical polymerization reaction initiated in redo system (potassium persulphate and sodium metabisulphite) having an acide equivalent E_a = 47 µE/g [11, 22-27].

The CS presence in the final samples is proved by the appearance of absorption bands assigned to some groups specific for CS [11, 20, 21], such as: OH (3436 cm^{-1} for OH (which remains free, not involved in any chemical bond), 1026 cm^{-1} for C–O stretching of C(6)-OH (s), 1060 cm^{-1} for C - O stretching of C(3) - OH (s); $^+NH_3$ (1537 cm^{-1} for overlapping of $^+NH_3$ symmetric deformation with CN stretching (m-s)), 1628 cm^{-1} for overlapping of $^+NH_3$ asymmetric deformation with NH deformation, amide II (m-s), 3408 cm^{-1} for $^+NH_3$ asymmetric and symmetric stretchings, near 2500 cm^{-1} (for $^+NH_3$ combination bands (w)) and at 722 cm^{-1} for NH, wagging (broad peak)).

Moreover, CS grafting is proved by the increase of the absorption bands for C-H stretchings (2854 cm^{-1} and 2920 cm^{-1}), as well as by the modification of absorption bands specific to sulphonic/the final acid groups (1250 - 1000 cm^{-1} for S=O asymmetric and symmetric stretchings, these overlapping with C-O-C stretching from AV, which in this case does not modify).

FTIR for PAN functionalized in basic medium and grafted with CS

In basic medium (fig. 4), PAN suffers chemical modifications both at the level of ester group from AV, and at the CN group from AN. The conversions of ester groups from AV into OH groups, and of nitrile groups into carboxyl groups (via amide groups) are accompanied by modifications that can be revealed in the IR range.
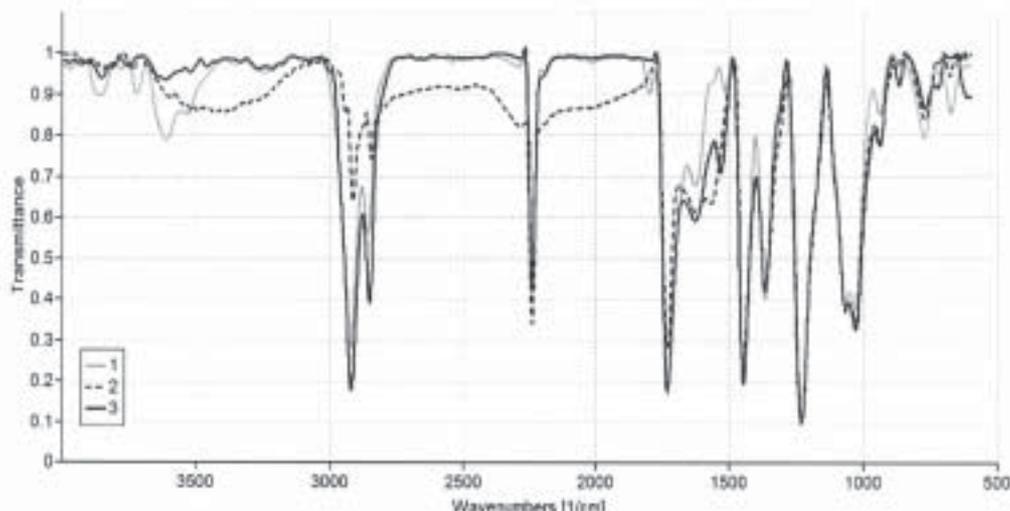
CS grafting is proved, first of all, by the increase of the peaks assigned to the new bonds between CS and functionalized PAN [11, 20, 21]: the ether bonds established between the new functional OH group of PAN and primary OH group of CS (1231 cm^{-1}); the ester bonds between the new COOH functional group of PAN and primary OH group of CS (at 1732 cm^{-1} assigned to C=O stretching (s)). Secondly, the presence of the NH_2 primary group in the IR spectra confirms the CS presence. This group is specific to CS and it determines the appearance of the absorption bands from 1537 cm^{-1} (N-H bending), 720 cm^{-1} (NH, wagging (broad peak)).

Moreover, the peak at 869 cm^{-1} (assigned to pyranosic ring stretching) confirms CS presence. The implication of OH primary group from CS in the reaction of the formation of ether bridge with OH from PAN functionalized is given by the diminution of the absorption band at 3436 cm^{-1}, assigned to the OH free group.

Dropping colour test results

Normally, acrylic fibres do not contain amino groups but after functionalization with NaOH they acquired an NH_2 group's content (in amide group), which depends on the alkalinity of the reaction [11, 12]. After a 5 min contact with a solution of HOCl, the amino compounds which are present in FB sample (that was chemically altered), can generate chloramines, R-NHCl. When these chloramines coming into contact with a solution of KI and starch, the potassium iodide will extract chlorine in the form of KCl and I_2 will be issued. Iodine is highlighted in presence of starch when it will generate a brown-violet coloration for PAN functionalized with NaOH. In FA sample does not appear the brown-violet coloration because the PAN was not chemical modified by a low acid medium. On the

Fig. 4 FTIR spectra for untreated PAN (1), PAN functionalized with NaOH (2) and PAN functionalized in alkaline medium but grafted with CS (3)
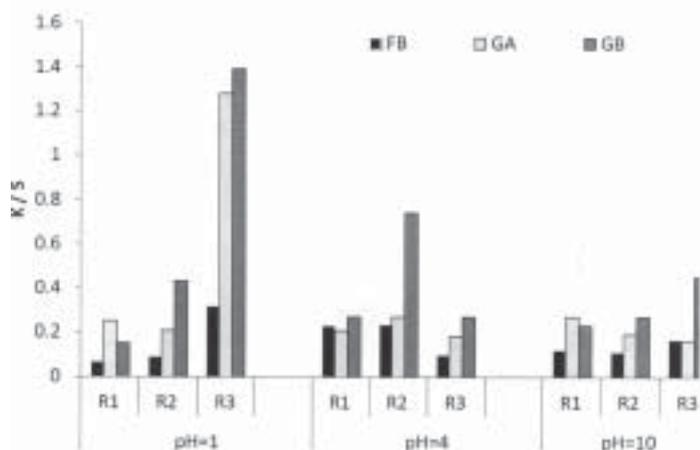
Fig. 5. Colour strength dependence on pH and the structure of the three reactive dyes; (dyeing conditions: 9% reactive dye; 30 min)

samples GA and GB appear intense brown-violet colorations that confirm the presence of CS because have NH2 groups (at the level of C2 atom).

Dyeing with reactive dyes

Normally, the PAN fibers do not dye with reactive dyes, but with cationic dyes [1, 4, 5, and 11]. Yet, in order to reveal the chemical modifications generated by PAN functionalization in acid/basic medium and by grafting with CS, one resorted to dyeing with non-specific anionic dyes, i.e. to the three reactive dyes presented in table 1.

In our previous works, the PAN chemical modifications were rendered evident by means of tinctorial methods. It is important to choose the adequate dyes class for dyeing, such that to permit the formation of chemical/electrovalent bonds between dyes and the new reactive groups obtained by PAN through functionalization or grafting, namely: 1) acid dyes [27] for dyeing the samples functionalized with certain amines; 2) acid dyes for dyeing PAN grafted with CS [11]; 3) reactive dyes for dyeing PAN functionalized with amines and grafted with monochlorotriazinyl-β-cyclodextrin [24]. In these works, the utilized dyes were selected very carefully, such that to lead to good color strength. Consequently, the number of groups solubilized from dye, the number of active groups (acid groups at acid dyes, and reactive groups at reactive dyes), as well as the size and planarity of dye molecules have been taken into account.

The target of the present work is to search the dyeing conditions (pH, concentration and duration) which lead to the highest color strengths (K/S) and which confirm the chemical modifications generated by functionalization in acid/basic medium and grafting with CS.

pH Influence

Even if dyeing with reactive dyes needs an alkaline medium, dyeing operations in acid mediums ($pH= 1$ and $pH= 4$) were also performed, in order to evaluate the protonation of the NH_2 group from CS grafted onto PAN, which will result in electrovalent bonds with the SO_3^- groups from reactive dye.

As one can see in figure 5, dyeing with 9% reactive dye (30 min) at an acid pH leads, indeed, to higher K/S values than in alkaline medium, which confirms the hypothesis of additional bonds formation between grafted acrylic support and reactive dye. The K/S values from 500 nm indicates that the most intensely dyed sample is GB, dyed with R3 dye at $pH= 1$ (fig. 5). This agrees with the number and nature of the functional groups from FB and GB. While

in the FB sample there are NH_2 groups obtained through the conversion of the nitrile group in basic medium, in GB the number of NH_2 groups is much higher (table 2), due to chitosan grafted (by means of the primary OH group, leaving free the NH_2 groups situated at the C2 atom) onto functionalized PAN.

Figure 5 indicates that pH significantly influences the K/S values. Yet, this influence depends on the structure of the utilized reactive dye, namely: R1 and R3 have 6 solubilized groups, while R2 has only 4; yet R1 and R3 have each two substituible reactive atoms (chlorine-type), and R2 has only one chlorine atom that can react with the chemically-modified acrylic support (table 1). R3 has two OH groups more, which can influence favorably the dyeing capacity (table 1).

At these acid pH values (especially at $pH = 1$, and less at $pH = 4$) occur both the protonation of NH_2 group from chitosan, and the protonation of the NH groups from the reactive dye. In this last case, the dye gets ionic valences, therefore it transforms in a basic/cationic dye and can interact with the anionic groups (SO_3^-) located at the end of PAN macromolecular chain (this is more marked at the R3 dye).

Dyeing with the three reactive dyes at $pH = 10$ leads to the formation of covalent bonds; this process is toilsome, but the covalent bonds are much more resistant that the electrovalent bonds realized at dyeing in acid mediums.

Influence of dye concentration

Figure 6 indicates that concentration increase from 9% to 15% (irrespective of the utilized reactive dye) leads to the increase of K/S values for each tested sample, in the following order: FB, GA and GB. The FA samples do not dye at all with any of the reactive dyes from table 1. One obtains the most intense dyeing with the dye R3, which has a structure reacher in chlorine atoms, as compared to R2, and reacher in OH groups as compared to R1.

Influence of duration

Figure 7 was plotted for dyeing with 15% reactive dye, $pH= 12$, and K/S values correspond to the wavelength of 500 nm, where red color visibility is maximum.

In figure 7, one can see that increasing the durations of dyeing with R1 and R2 resulted in the increase of K/S values on the grafted samples (GA and GB). One can explain the higher values of K/S in the case of dyeing with R2 by a smaller structure/volume ratio of the R2 dye, and a smaller number of SO_3Na groups. This dye has a smaller capacity to give secondary reactions with water, because it has only 4 groups SO_3Na, and not 6, as in R1 and R3 (it is known that the SO_3Na groups have a bigger water affinity).
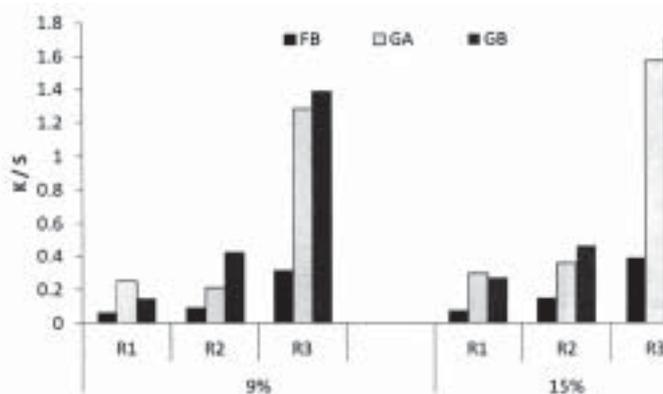

Fig. 6. Dependence of colour strength on concentration and chemical structure of the reactive dye used for dyeing in acid medium ($pH=1$) for 30 min
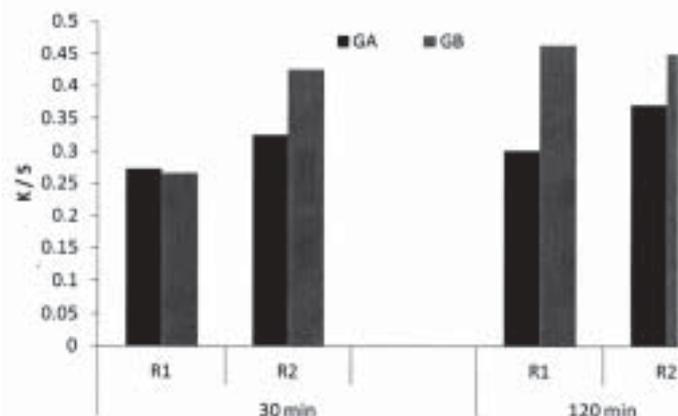
Fig. 7. Dependence of K/S values on dyeing duration

Fig. 8. Colour difference between GB and FB samples after dyeing
with 3% Procion H-E3B,
at 100°C for 30 min

Colour difference

Colour differences between the samples GB and FB (sample functionalized in basic medium, FB being considered as witness) dyed with 3% Procion red H-E3B, $pH = 1$ and 2 (to favor the protonation of aminic groups from CS or even from the dye) and a duration of 30 min are illustrated in figure 8. One can notice that $\ddot{A}L^* < 0$, which means that the sample GB has dyed more intensely than FB. The positive values for Δa^* and Δb^* indicates that the sample GB (grafted with CS onto FB support) has stronger red hues and weaker yellow hues. The sample GB is less yellow and has a slightly blue hue, a fact confirmed by the values $\Delta h^* < 0$. Colour difference ΔE^* between the two samples is quite big ($\Delta E^* = 7.1$), which confirms indirectly the CS grafting onto the sample FB.

In the case of this dye (Procion H-E3B), the increasing of the pH acid value ($pH=2$) used in dyeing leads to the decreasing of the protonation capacity (at PAN and dye) and hence, at the decreasing of the dL value.

Figure 9 presents the colour differences between GB and FB samples after dyeing with 3% Procion red H-EGXL for 30 min. at different pH values. Dyeing with the reactive dye Procion red H-EGXL leads to more intense dyeing on GB ($\Delta L^* < 0$) than on FB, regardless the pH value used during dyeing. This behavior confirms that the chemical modifications of the GB sample are more marked that those of FB, therefore one can confirm CS grafting onto FB. The most intense dyeings were obtained at $pH = 2$ and $pH = 10$. The acid/basic medium used for dyeing influenced also the red hues of the samples: they are red with yellow reflections, or red with blue reflections, as indicated by the values of Δa^* and Δb^* ($\Delta a^* > 0$ indicates more red, $\Delta a^* < 0$ indicates the green reflections, $\Delta b^* > 0$ indicates more yellow, and $\Delta b^* < 0$ shows more blue). The values $\Delta h^* < 0$ show that dyeings at $pH = 1$, 2 and 10 lead to bluish hues of the GB samples. The big colour differences ΔE^* for dyeing at the four pH values indicate indirectly significant chemical modifications between the sample functionalized in basic medium, and the sample grafted with CS. When dyeing in acid pH, one form mainly electrovalent bonds between the two dyeing partners (reactive dye and PAN functionalized and grafted with CS). At pH basic, dyeing with reactive dyes is based on the formation of chemical covalent bonds between the Cl atom from the reactive dye and the primary OH group from CS grafted onto FA (in GA), or with the primary OH groups (not involved in grafting process) from the CS grafted onto FB (in GB).

Fastness properties

Table 3 presents the values of washing fastness of the grafted samples (after functionalization in acid/basic
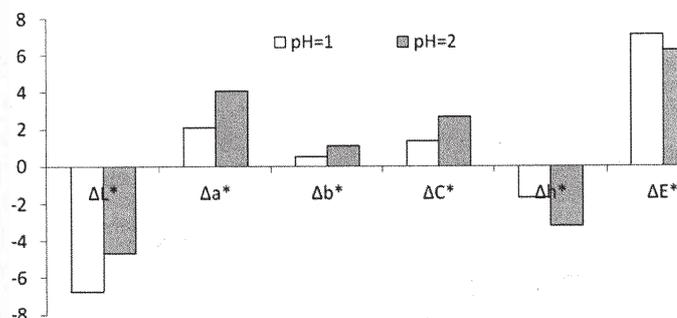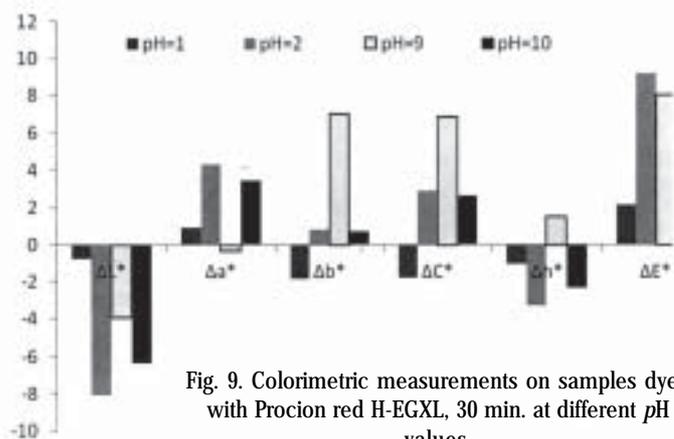

Fig. 9. Colorimetric measurements on samples dyed
with Procion red H-EGXL, 30 min. at different pH
values.

Table 3
THE VALUES OF FASTNESS TO WASHING

Reactive Dye	Samples after grafting and dyeing processes	
	GA*	GB*
Procion red H-EGXL	4/4/4	4-5/4-5/4-5

*The digits signification: the changing of colour after
washing / the staining of PAN / the staining of wool.

medium, GA and GB), and dyed with Procion red H-EGXL ($pH = 10$). At this pH, covalent bonds between PAN and reactive dye are formed both in GA and GB. However, the fastness of the sample GA is smaller than that of GB samples. This fact can be explained only based on the strength of the bonds between the PAN fiber and the grafting agent: electrovalent bonds in FA, and covalent bonds in FB (fig. 2). Perhaps part of electrovalent bonds is torn apart during the dyeing, which determines diminutions of colour strength and fastness properties.

Conclusions

One can increase PAN reactivity by functionalization in strongly basic medium, as the weakly acid medium does not have the power to convert the acetate and nitrile groups into other more reactive groups. Chitosan grafting onto functionalized samples in acid/basic medium makes possible PAN dyeing with reactive dyes (it is well known that untreated PAN does not dye at all with reactive dyes, but only with cationic dyes). Chemical modifications during functionalization and grafting with CS have been rendered evident both in the IR range, and by means of the dropping colour test. The FTIR spectra confirm the conversion of the initial groups from PAN (acetate, nitrile) in other, more reactive groups, able to form bonds with some reactive dyes. Dropping colour test confirms the presence of NH_2 groups in PAN samples functionalized in basic medium

(FB), as well as on the samples grafted with CS (coded as GA and GB). The presence of NH_2 groups from CS in the GB samples was also proved by the high values of colour strength obtained after dyeing with reactive dyes in acid medium, when these groups get positive and form electrovalent bonds with the SO_3 groups from reactive dye. At dyeing of GB in basic medium, a more difficult formation of covalent bonds leads to smaller K/S values, but at better washing fastness. Regardless of pH, the GA samples are dyed less intense than the GB samples. All the tested dyeing parameters (pH, dye concentration and duration) led to higher K/S values on the grafted samples than on the functionalized ones.

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