# Influence of Maleic Polyelectrolytes on the Variation of Colour Parameters at Dyeing Polyacrylonitrile Fibres with Victoria Blue B

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The present study pursues the influence of polyelectrolytes based on maleic co-polymers with styrene and vinyl acetate under the form of natrium salt, on the color parameters CIEL\*a\*b\* of the Melana type polyacrylonitrile fibers dyed with Victoria Blue B (VBB) dye - a triamino triarylmethane one. The colours attributes are analyzed in terms of the tinctorial conditions: polyelectrolyte character and concentration, structural parameters of the VBB, temperature and time of dyeing.

*Keywords: maleic polyelectrolytes, Victoria Blue B dye, Melana fibers, colour differences, tinctorial parameters* 

The affinity of the cationic dyes for acrylic fibers is very high due to the electrostatic attraction and hydrophobic interactions between the fiber and the dye, which represents quite an impasse when aiming to achieve uniform acrylic fibers dyeing. Anionic retarders act upon the dyes by forming a complex having a low diffusion rate in solution, and hence a slower sorption. These products are not selective, but determine a reduction in the tinctorial performance by retaining the dye in solution, and in extreme cases, by its precipitation [1].

Various studies have described the dyeing of the textiles with the anionic dyes using cationic retarders while only a few publications were focused on the dyeing of the textiles with cationic dyes using anionic polyelectrolyte retarders [1, 2]. Besides the structural and chemical characteristics of the dyes and polyelectrolytes chosen for this study, another selection criterion was the field of their utilization.

The remission spectral studies [3] on Melana dyeing with cationic dyes in the presence of the polyelectrolytes based on maleic acid with vinyl acetate (NaM-VA), or on maleic acid with styrene (NaM-S) respectively, showed the following aspects: (i) NaM-VA shows the acceleration effect of dyeing due to its hydrophilicity; (ii) NaM-S shows retarding effect (dyeing uniformization) of dyeing. These effects can be explained by the hydrophilicity / hydrophobicity balance of both polyelectrolytes.

In literature are many data regarding the applications of maleic copolymers in medical or pharmaceutical field. Most of them can be classified as: i) maleic copolymers with *perse* activity, ii) drug polymer systems (conjugates), iii) drug formulations [4]. The last two groups belong to the topic of controlled delivery systems. Other more recent applications of maleic copolymers are in the fabrication of biomaterials or in tissue engineering [5-7]. Thus, VBB was used in botanic, cytology, histology and neurohistology fields to dye certain types of fibers or textiles [8, 9]. VBB derivatives have applications in medicine, particularly in the field of photodynamic therapy, method that becomes widely accepted in treatment of neoplastic disorders [10].

The purpose of this study was to achieve information regarding the influence of maleic copolymers as retardation/acceleration agents, on colour variations of Melana samples, dyed with VBB. The novelty of this paper is to study the influences of the polyelectrolytes based on maleic anhydride on the dyeing capacity of Melana with VBB. The colors attributes are analyzed in terms of the tinctorial conditions: polyelectrolyte character and concentration, structural parameters of the VBB, temperature and time of dyeing. The results could by useful in finding new medical applications for these samples after assessing the toxicological properties.

# **Experimental part**

#### Materials and methods

The reagent dye: VBB (Merk, Dearmstadt, Germany) was used as received (scheme 1).



Scheme 1 Chemical structure of VBB dye

The polyelectrolytes used were: a copolymer of the maleic acid with styrene ( $M_v = 95,000$ ) and a copolymer of the maleic acid with vinyl acetate ( $M_v = 70,000$ ), both as sodium salt. The two polyelectrolytes were obtained from copolymers of the maleic anhydride with vinyl acetate or styrene, synthesized in laboratory according to the methods described in the literature [11-13]. The chemical structures of polyelectrolytes are presented in scheme 2.



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Morphologically, the polyacrylonitrile fibers display an inhomogeneous fibrillary structure with several discontinuities (pores, channels) and non-uniform cross section. The Melana fibers manufactured in Romania are polyacrylonitrile fibers based on a ternary polymer (85% acrylonitrile, 10% vinyl acetate, 5%  $\alpha$  - methyl styrene) obtained through a radical polymerization reaction, initiated in the redox system of potassium persulfate-sodium metabisulphite. The polyacrylonitrile fibers are hydrophobic; the water sorption under standard conditions being 1- 2%, thus the swelling in water is reduced [1]. The chemical structure of Melana fibers is schematically represented in scheme 3.

The dyeing operations were performed with a Mesdan lab-dying device with 6 dyeing positions. We carried out dyeing operations (6 dyeing of 1 gram sample for each color position) of the Melana fibers in aqueous solutions (distilled water) with VBB in the presence of NaM-S and NaM-VA, at dye and polyelectrolytes concentrations of 0.5, 1.0, 1.5, 2.0, 2.5% and a liquor ratio of 1:50. The float pH was adjusted to 5.5-6.0 with 10% acetic acid solution. Practically, one adds at the dye solution polyelectrolyte in different concentrations, acetic acid some drops to adjust the pH. The dyeing flask is magnetically stirred for 5 minutes for homogenization, the solution left to rest for 30 min, after which the Melana fibers (1.0 g) are added. The solution is stirred again for 5 min, and then the dyeing flask follows a thermal regime. It starts by heating the dyebath up to 80°C and maintained for about 10 min. The heating continues until the temperature reaches 90, 95 or 100°C, at a heating rate of 1°C/min; this temperature is maintained for 75 min, after which the dyeing solution is slowly cooled. The dyed Melana is intensely washed for 5 min with cold water and 5 min with warm water, manually squeezed and dried at room temperature. Besides the dyeing operations performed in the presence of the two polyelectrolytes, witness operations of Melana dyeing were also carried out in the absence and presence of the polyelectrolytes at 90°C, for 75 min.

The color differences were measured with a portable Datacolor 2002 Check Plus spectrophotometer. We have thus determined the color differences  $\Delta E^*$ , evaluating at the same time the chromatic modifications which result from the components L\* (brightness coordinate), a\* (red/

green coordinate) and b\* (yellow/blue coordinate) [14-23]. The CIE chromatic diagram L\*a\*b\* [1] was used in order to interpret the colour modifications, considered as being due to the action of the following parameters such as, type of polyelectrolytes, temperature and time of dyeing on Melana. The total color difference was calculated using eq1:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$
(1)

where,  $\Delta E$  indicates the difference between the sample that reproduces in the present case the tinctorial determinations and specified witness (standard) sample (tables 1, 2 and 3).  $\Delta L^*$  represents the brightness difference (%), and the values  $\Delta a^*$ ,  $\Delta b^*$  indicate the differences between the sample positions in the chromatic diagram and a standard sample that are expressed in Adams-Nickerson (AN) units.

$$\Delta L^* = L^*_{sample} - L^*_{standard}$$

$$\Delta L^* > 0 \text{ means sample is lighter than standard}$$

$$\Delta L^* < 0 \text{ means sample is darker than standard}$$

$$\Delta a^* = a^*_{sample} - a^*_{standard}$$

$$\Delta a^* > 0 \text{ means sample is redder}$$

1	than standard
	$\Delta a^* < \theta$ means sample is greener
	than standard
$\Delta b^* = b^*_{and b} - b^*_{and b}$	$\Delta b^* > 0$ means sample is yellower
sample standard	than standard
	$\Delta b^* < \theta$ means sample is bluer
	than standard

The chromatic intensity or saturation, defined by the notion of chroma,  $C^* = (a^{*2} + b^{*2})^{1/2}$  is as higher as the bigger are the absolute values of the parameters  $a^*$  and  $b^*$ . The shade modifications ( $h^*$ ) can be evaluated according to the relation:  $h^* = tg(b^*/a^*)$ .

## **Results and discussions**

Our studies intended to establish the influence of various factors, such as polyelectrolyte concentration, optimal time and temperature dyeing process of Melana fibers with VBB. The chromatic diagram CIE  $L^*a^*b^*$  was used for results interpretation [1].

# Influence of polyelectrolyte concentration

The table 1 presents the technological parameters and the values of color components obtained at dyeing Melana with VBB, in the presence of NaM-S or NaM-VA at different concentrations.

From table 1, one can notice that with the increase of polyelectrolyte concentration in the dyebath, the values of

No.	VBB	Polyelectro	Dyeing	Tempe	Chroma	Hue							-
	concen	lyte concen	period	rature	C*	h*	$\Delta L^{\star}$	∆a*	Δb*	$\Delta C^{\star}$	$\Delta h^{\star}$	$\Delta E^{\star}$	
	tration	tration											
	(%)	(%)	(min)	(°C)	(AN)	(º)	(%)	(AN)	(AN)	(AN)	(°)	(AN)	Table 1
	CVBB	C NaM-S											TECHNOLOGICAL PARAMETERS
Std	1.5	0	75	90	49.13	274.35							COMPONENTS OBTAINED AT
1	1.5	0.5	75	90	63.88	280.54	-5.69	7.95	-13.81	14.75	6.04	16.92	DYEING MELANA WITH VBB IN
2	1.5	1.5	75	90	60.13	279.21	-8.21	6.18	-10.32	11.00	4.86	14.36	THE PRESENCE OF NAM-S OR
3	1.5	2.5	75	90	66.72	282.11	-9.29	10.27	-16.25	17.60	7.75	21.35	NAM-VA AT DIFFERENT
	CVBB	C NaM-VA											CONCENTRATIONS
Std	1.5	0	75	90	49.13	274.35							-
1	1.5	0.5	75	90	64.21	281.69	-9.31	9.27	-13.89	15.08	7.18	19.12	
2	1.5	1.5	75	90	62.74	280.46	-7.84	7.31	-13.07	13.61	6.11	16.85	
3	1.5	2.5	75	90	63.64	280.95	-8.56	8.35	-13.50	14.52	6.43	18.03	



(C)

shade h\* and saturation C\* do not differ significantly; presence of polyelectrolytes in the system containing Melana dyeing with VBB generates color differences between the samples dyed and the witness sample.

One can notice that the highest values of the saturation (C\*) were obtained in the case of Melana samples dyed at a concentration of 2.5% NaM-S solution and 0.5% NaM-VA solution, respectively. The color differences  $\Delta E^*$  of Melana samples dyed with VBB in the presence of NaM-S or NaM-VA are reflected in the color component variations L\*, a\*, b\* and are presented in figure 1.

By analyzing the brightness of Melana samples dyed with VBB in the presence of NaM-S or NaM-VA, one can notice that this is compared to that of the witness sample. The values of L\* corresponding to Melana samples dyed with VBB in the presence of the NaM-S, continuously decrease with increasing of concentration (fig. 1a). The brightness value of the Melana samples dyed with VBB in the presence of NaM-VA increase with increasing polyelectrolyte concentration in the dyebath up to 1.5%; further increments of the polyelectrolyte concentration up to 2.5% do not result in significant changes of the brightness values (insignificant reduction was recorded).

The values of a\* corresponding to Melana samples dyed with VBB in the presence of the NaM-S or NaM-VA (fig. 1b) are positive, and higher than those of the witness sample.

The values of b\* corresponding to Melana samples dyed with VBB in the presence of the NaM-S or NaM-VA (fig. 1c) are negative and increase initially with increasing of polyelectrolyte concentrations (up to 1.5%). When the concentration of NaM-S or NaM-VÅ increase up to 2.5%, the values of b\* insignificantly decrease, the color of these samples being bluer than of witness sample.

#### Influence of dyeing time

The increase of the dyeing time determine color modifications in the Melana samples dyed with VBB in the presence of the two polyelectrolytes, that are proven by the value of color difference  $\Delta E^*$  (table 2). With the increase of the dyeing time up to 75 min, the color differences decrease to 14.36 (AN), and then increase at 16.03 (AN) with the increase of the dyeing time to 120

No.	VBB	Polyelectr	Dyeing	Tempe	Chroma	Hue							
	concen	olyte	period	rature	C*	h*	$\Delta L^{\star}$	∆a*	∆b*	$\Delta C^{\star}$	$\Delta h$	$\Delta E^{\star}$	
	tration	concen											Table 2
		tration											TECHNOLOGICA
	(%)	(%)	(min)	(°C)	(AN)	(°)	(%)	(AN)	(AN)	(AN)	(°)	(AN)	PARAMETERS AND T
	CVBB	C NaM-S											VALUES OF THE CO
std	1.5	0	75	90	49.13	274.35							COMPONENTS OBTA
1	1.5	1.5	30	90	63.89	280.04	-5.99	7.41	-13.93	14.77	5.56	16.88	IN THE CASE OF MEI
2	1.5	1.5	75	90	60.13	279.21	-8.21	6.18	-10.32	11.00	4.86	14.36	IN THE PRESENCE
3	1.5	1.5	120	90	68.24	283.80	-14.88	12.55	-17.29	19.12	9.54	26.03	NAM-S OR NAM-VA
	CVBB	C NaM-VA											DIFFERENT DYEIN
std	1.5	0	75	90	49.13	274.35							DURATIONS
1	1.5	1.5	30	90	64.05	281.19	-10.33	8.70	-13.84	14.92	6.69	19.34	
2	1.5	1.5	75	90	62.74	280.46	-7.84	7.31	-13.07	13.61	6.11	16.85	
3	1.5	1.5	120	90	62.11	279.05	-4.86	6.04	-12.35	12.98	4.53	14.58	



min. One can notice that the highest values of saturation (C\*) were obtained in the case of Melana samples dyed with VBB in the presence of NaM-S, at a dyeing time of 120 min (maximum), while in the case of Melana samples dyed with VBB in the presence of NaM-VA this was achieved at a dyeing time of 30 min. These results confirm the previous findings concerning the acceleration effect determined by the presence of NaM-VA in the dyeing system, and the retardation effect determined by the presence of NaM-S [3].

Also, can be observed that the increase of dyeing time of Melana with VBB in the presence of NaM-VA lead to the decrease of the color differences  $\Delta E^*$  and the saturation (C\*) values.

Table 2 presents the values of the technological parameters and color components in the case of Melana fibers dyeing with VBB in the presence of NaM-S or NaM-VA, at different dyeing times.

The colour differences of the Melana samples dyed with VBB in the presence of NaM-S and NaM-VA are reflected in the variations of the color components  $L^*$ ,  $a^*$  and  $b^*$  (fig. 2).

In figure 2a one can notice that the brightness values of Melana samples dyed with VBB in the presence of the NaM-S decrease with the increase of the dyeing time, while in the presence of the NaM-VA they slightly increase with increasing of the dyeing time, being lower than those of the witness sample.

Figure 2b points out that the values of a\* corresponding to Melana samples dyed with VBB in the presence of the NaM-S and NaM-VA are positive and bigger than those of the witness sample. In the case of Melana – VBB - NaM-S system is observed that with increasing of dyeing time until t = 75 min, the values of a\* slightly decrease, while the values of a\* significantly increase when the dyeing time increase up to 120 min. In the case of Melana– VBB -NaM-VA system is observed that an increase of the dyeing time lead to a continuous and insignificant downward tendency of a\* levels. When the dyeing time increases, the shade of Melana samples dyed in the presence of NaM- S and NaM-VA are redder compared to standard dyed Melana. Melana samples dyed in the presence of NaM-S are redder than those dyed in the presence of NaM-VA.

In the case of the Melana samples dyed with VBB in the presence of the NaM-S and NaM-VA (fig. 2c), the values of b\* are negative and smaller (therefore the samples are bluer) than those of witness sample. In the Melana samples dyed with VBB in the presence of NaM-S, with the increase of the dyeing time, the values of b\* do not change significantly compared to Melana samples dyed in the presence of NaM-VA.

Therefore, the results we presented are in good agreement with visual appreciations of Melana samples dyed in this way.

#### Influence of the dyeing temperature

We have found that the increase of the dyeing temperature induces color modification of Melana samples dyed with VBB in the presence of the two polyelectrolytes, set off by the values of the color difference  $\Delta E^*$ .

From table 3, one can notice that the increase of dyeing temperature lead to the increase of the values of following parameters:  $\Delta E^*$ ,  $C^*$  and  $h^*$ . For Melana samples dyed with VBB in the presence of the two polyelectrolytes, the highest values of  $\Delta E^*$ ,  $C^*$  and h have been achieved at the maximum dyeing temperature of 100°C.

Table 3 presents the technological parameters and the values of color components in the case of dyeing Melana samples with VBB in the presence of NaM-S or NaM-VA, at different dyeing temperatures.

Figure 3 illustrates the values of the parameters L\*, a\* and b\* corresponding to Melana samples dyed with VBB in the presence of the NaM-S or NaM-VA, as function of dyeing temperature.

The values of brightness for Melana samples dyed with VBB (fig. 3a) in the presence of NaM-S or NaM-VA are lower at 80 and 100°C than those of the witness samples, but higher at 90°C. This still un-encountered phenomenon can be due to the clearness of Melana samples dyed in the presence of the two polyelectrolytes, the aspect being visually noticed too.

No.	VBB	Polyelectro	Dyeing	Tempe	Chroma	Hue						
	concen	lyte concen	period	rature	C*	h*	$\Delta L^{\star}$	∆a*	Δb*	$\Delta C^*$	Δh*	ΔE*
	tration	tration										
	(%)	(%)	(min)	(°C)	(AN)	(º)	(%)	(AN)	(AN)	(AN)	(°)	(AN)
	CVBB	C NaM-S										
Std	1.5	0	75	90	49.13	274.35						
1	1.5	0.5	75	90	45.90	273.05	8.90	-1.29	3.15	-3.22	-1.08	9.53
2	1.5	1.5	75	80	60.13	279.21	-8.21	6.18	-10.32	11.00	4.86	14.36
3	1.5	2.5	75	100	65.28	280.79	-8.73	8.49	-15.14	16.15	6.36	19.43
	CVBB	C NaM-VA										
Std	1.5	0	75	90	49.13	274.35						
1	1.5	0.5	75	90	40.61	272.81	9.24	-1.74	8.42	-8.52	-1.20	12.62
2	1.5	1.5	75	80	62.74	280.46	-7.84	7.31	-13.07	13.61	6.11	16.85
3	1.5	2.5	75	100	65.65	281.13	-10.02	8.95	-15.43	16.52	6.71	20.46



# Table 3TECHNOLOGICALPARAMETERS AND THEVALUES OF COLOURCOMPONENTS OBTAINED INTHE CASE OF DYEING THEMELANA FIBERS WITH VBBIN THE PRESENCE OF NAM-SOR NAM-VA AT DIFFERENTDYEING TEMPERATURES

Fig. 3. The values of the parameters L\* (a), a\*
(b) and b\* (c) corresponding to dyeing of
Melana samples with VBB in the presence of
the polyelectrolytes NaM-S and NaM-VA as
function of dyeing temperature

Figure 3c points out that the values of b\* corresponding to Melana samples dyed with VBB at 80-100°C in the presence of NaM-S or NaM-VA are negative, smaller than those of witness dyed Melana samples at the same temperatures and continuously decrease with increasing dyeing temperature. Melana samples dyed with VBB in the presence of the two polyelectrolytes are bluer than the witness dyed Melana samples.

The absorption of cationic dyes is accomplished after an Langmuir-type isotherm with saturation limit. Starting from the modified equation of Langmuir isotherm and using the classical Donnan or modified Donnan models, numerous authors have shown that the dyeing of acrylic fibers with cationic dyes can be explained by an ionic and hydrophobic exchange between the fibers and the dye. The dyeing of the polyacrylonitrile fibers with cationic dyes occurs in three stages [4, 24]:

- adsorption of dye cation on the external fiber surface;
- dye diffusion inside the fibers;

- formation of electrovalences between dye cations and fibers anions.

(C)

The values of L\* decrease insignificantly with the increase of dyeing temperature within 80-90°C range, in the presence of both NaM-S and NaM-VA; within 90-100°C, the increase is very slow. The difference of tinctorial behavior between the two polyelectrolytes is insignificant.

For Melana fibers dyed with VBB in the presence of NaM-S or NaM-VA (fig. 3b), the values of a\* are positive and higher than of the witness sample. It is interesting to notice that the negative value of a\* corresponds to the Melana samples dyed with VBB according to witness sample at 80°C, the sample being greener than those dyed with VBB at 80°C in the presence of the two polyelectrolytes, while in the case of positive a\* values the sample color tends to red. Based on the obtained chromatic variations, one can state that the temperature is the main factor in this tinctorial system.

With the increase of the dyeing temperature from 80 to 100°C, the values of a\* corresponding to Melana samples dyed with VBB in the presence of the NaM-S or NaM-VA are higher than of Melana samples dyed according to witness sample. The difference between a\* values corresponding to Melana samples dyed with VBB in the presence of the two NaM-S and NaM-VA does not differ significantly.

The first and the third stages occur at very high velocities, the speed of the second stage being decisive for the entire dyeing process.

The factors governing the first stage are: temperature, dye liquor stirring and fibers electric potential [5].

Around the acryl fiber, a limit static layer of float is formed, its thickness varying inversely proportional with the velocity of float passing by the fiber; the dye molecules must cross this layer first and then they rich the fiber surface. Once at the fibers surface, the cationic dye diffuses inside the fibers, making possible the dye depletion in the float; this can be explained by the fact that the spots left free on the external fiber surface (by inward diffusion) remain vacant and can be easily occupied by other dye molecules from the float. The diffusion stage is the slowest, determining the dyeing velocity. Both, dye diffusion and dyeing velocity are influenced by the temperature. At the beginning of dyeing, when the dye concentration in the bath is high, the absorption rate is also high, but when the balance is reached, the dye concentration in the float is much smaller. This is true irrespective of the initial dye concentration in the float (small under 1%, or big over 1%). At initial large concentrations, the depletion rate is no longer influenced by the dye concentration in the float [5].

The depletion rate changes depending on the dye concentration in the float, is similar to the variation of the concentration in the fiber, in terms of the dye concentration in solution. The modification of the dye concentration at the fiber surface determines the variation in the same direction and of the same importance of the gradient concentration (dc/dx) responsible for dye raising rate on the fiber.

The maleic acid copolymers behave as polyelectrolytes and many of their applications are common with those of other weak polyelectrolytes. The specific properties of the maleic acid copolymers derive from the presence of two adjacent carboxylic groups. Thus, they have specific applications that include the binding of divalent cations. The pH of the medium determines the conformation of the maleic acid copolymers, influencing their properties and their applications in solution. The dissociation constants of the weak polyelectrolytes are also important. In order to determine the dissociation of both carboxylic groups, the use of a supporting electrolyte is necessary [4, 6, 11]. The second acidity was observed only for the copolymers with hydrophilic comonomers NaM-VA. The dissociation of the first carboxylic group can be detected for both these copolymers. The apparent dissociation constants increase with the increase of the comonomer hydrophobicity. The peculiar behavior indicates a conformational transition from a tightly coiled configuration, stabilized by hydrophobic forces, to an extended coil due to the increase of the electrostatic repulsion [5, 6, 11]. The electrostatic repulsion between the ionized groups competes with some shortrange attractive forces, such as hydrophobic interactions and hydrogen bonds between the carboxyl groups. At low neutralization degrees, the tightly coiled conformation of the polyelectrolyte is stabilized by the short-range attractive forces. During the neutralization, the electrostatic energy accumulates on the polyelectrolyte and, at a certain value of the neutralization degree; a conformational transition from a compact coil to a loose or extended form occurs 4

There is a correlation between the behavior of dyes in solution and dye-fiber interaction. Typically, dye-dye interactions are achieved by forces of association and are of the same nature with dye-fiber interactions. Therefore, this explains why the association is a property of basic dyes, available for those connected by electrovalence with fibers. The studies carried out on the VBB interaction with NaM-S or NaM-VA in aqueous solutions, pointed out that the electrostatic interaction between VBB and NaM-S takes place as a result of the monomer dye concentration reduction; yet, a phenomenon of aggregation in form of dimmers also occurs. The problems specific to dimmer generation in dyes with charges opposed to those of polyelectrolytes, to non-stoichiometry of interactions in some systems, are due to the predominant hydrophobic interactions [25, 26]. This event might not occur due to the steric hindrance conferred, by the styrene radical and by the size of VBB molecule, on one side. On the other side, the aggregation of VBB molecule is favored by the relatively high hydrophobicity of the system (scheme 4) [25-27].



Scheme 4 Non-planar structure of VBB dye

We can appreciate that the orientation of VBB molecules toward charged positions from the polyelectrolyte and from the ends of Melana fibers is more ordered in the case of Melana fibers dyeing in the presence of NaM-S, than in the case of NaM-VA.

In case of NaM-VA/VBB system, it has been stated that the degree of dye molecules stocking is bigger than in the case of NaM-S/VBB system, because the shift of the metachromatic band corresponding to this system is bigger.

When adding NaM-S in the dyebath, the values of the color differences get modified: at small NaM-S concentrations, the VBB aggregates from solution break off, the dye ions interact, part of them orientating toward the charged positions of the polyelectrolyte, and others toward the anionic positions from the ends of the Melana fibers chains, to form ionic bonds. On the other side, given the high hydrophobia of these systems, hydrophobic, hydrogen, van der Waals, non-ionic bonds can be formed between the Melana fibers, VBB and polyelectrolyte [26]. When the NaM-S concentration in the dyeing bath increases, the hydrophobicity of the three partners, the steric hindrance (due to styrene residues) and the size of VBB molecule, determine together a slowdown or a blocking of dye monomers or dimmers bonding to the charged positions from the ends of the Melana fibers. Under these circumstances, the Melana fibers saturation with dye is weaker, and dyeing gets non-uniform, which is a visually confirmed aspect [28, 29].

Taking into consideration that the biggest weight is detained by the electrostatic and hydrophobic interactions in the tinctorial system, the possible interactions between the dyebath parameters determine the generation of a complex system, hard to detect through known investigation protocols. The presence of polyelectrolytes, depending on thermal level, duration or chemical and structural characteristics of the partners, as well as their concentration, can determine either dyeing acceleration or retardation.

#### Conclusions

The present results made us assert that at Melana fibers dyeing with VBB in the presence of the two polyelectrolytes, modifications of the color parameters appear; the intensity depends upon concentration, the nature of the two weak polyelectrolytes, the pH of the medium that determines the conformation of the maleic acid copolymers, dissociation constants of these polyelectrolytes and the other side structural parameters of the VBB: steric hindrance, molecular dimension, hydrophobicity of the systems.

The presence of polyelectrolytes in the system of Melana dyeing with VBB generates small color differences between the samples dyed in the presence of the two polyelectrolytes and witness sample. With the increase of the dyeing time, the Melana fibers dyed with VBB in the presence of NaM-S or NaM-VA are redder than the standard dyed Melana samples, and the samples dyed in the NaM-S presence are redder than those dyed in the presence of NaM-VA.

Despite the studied tinctorial system which is very complex, one cannot exclude the possibility that these color modifications have only a metachromatic nature.

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