Polyester fibers coated with silica hybrid film forming materials containing non-ionic dyes

A. RADITOIU, V. AMARIUTEI, V. RADITOIU*, M. GHIUREA, A.N. FRONE, R.A. GABOR, L.E. WAGNER, M. ANASTASESCU[a]
National Research and Development Institute for Chemistry and Petrochemistry – ICECHIM, 202 Splaiul Independentei, 060021, Bucharest, Romania
[a]Institute of Physical-Chemistry "Ilie Murgulescu", 202 Splaiul Independentei, 060021, Bucharest, Romania

Polyester fabrics coated with hybrid silica film-forming materials containing non-ionic dyes were analyzed in view of structural and morphological properties of the coatings and in direct relationship with their wetting properties. Wettability of the coated textile materials was investigated by performing contact angle measurements and by the analysis of the influence of films morphology and surface roughness. Thermo-mechanical behavior of the coated polyester fabrics was investigated in relationship with the precursors of the coating materials.

(Received July 1, 2014; accepted January 21, 2015)

Keywords: Silica hybrids, Disperse dyes, Polyester fibers, Contact angle, Wettability, Roughness

1. Introduction

Among the methods used for the functionalization of textile fibers, the sol-gel method occupies a special place because it offers the possibility of depositing organo-ceramic materials on this type of surfaces under mild conditions [1]. The existence of a wide range of precursors such as organic substituted alkoxysilanes offers virtually unlimited possibilities for variations in the composition of coating materials, which can be obtained [2].

Depositing film-forming materials on textile substrates by simple and operational methods currently used in practice of textile finishing such as impregnation-thermo-fixation process, leads to the imposition of this process as a very viable for textile functionalization [3]. Thus, thin films consisting of polysiloxane networks of varying hardness and elasticity can be obtained on the surface of textile fibers by modifying agents used in the process of nanosols manufacture [4,5]. Furthermore, by incorporating in the silica network of various additives (dyes, pigments, organic polymers, biomolecules) it can be obtained various types of coatings with different functions and protective properties on textile fibers [6].

The application of the hybrid silica coating materials on the polyester substrates in order to improve dyeing properties has been a major concern in recent years [7,8]. Influence of modified silica coatings on the color of the polyester fabrics dyed with organic colorants has been investigated mainly in relationship to an increased washing fastness due to this type of treatments [9].

2. Experimental

2.1 Materials

The precursors used were of laboratory reagent grade and were obtained from Merck, Germany and Aldrich - USA. Hydrochloric acid (0.1 N), tetraethylorthosilicate (TEOS), phenyltriethoxysilane (PhTES) diphenyldiethoxysilane (DPhDES), 3-glycidoxypropyltriethoxysilane, (GlyOPTES), vinyltriethoxysilane (VTES), 3-chloropropyltriethoxysilane (ClPTES), methyltriethoxysilane (MeTES), ethanol, 1,4-diazabicyclo[2.2.2.]octane (DABCO), tetrahydrofuran (THF) were used in the study without further purification. Disperse dyes: Disperse Red 1 (DR1), Disperse Red 5 (DR5), Disperse Red 17 (DR 17), Disperse Orange 5 (DO5) and theirs triethoxysilyl derivatives were previously obtained by us [10] and purified by extraction with toluene in a Soxhlet extractor, followed by recrystallization. Disperse dyes were chemically modified by performing an addition reaction with 3-isocyanatopropyltriethoxysilane (NCOTEOS) in order to synthesize dyes containing trialkoxysilane groups, able to provide covalent bonds with the inorganic network. The fabric used was 100% polyester (PES) with a specific weight of 170 g/m^2 obtained from Matasea Romana, Romania.

2.2 Methods

2.2.1 Preparation of the nanosol film-forming material and coating of the polyester fabrics

A solution obtained from 3.25 ml of TEOS, 3.25 ml DPhDES, 3.9 ml of a solution containing 1.7 g of disperse dye, selected from those mentioned above, in 100 ml of THF, 0.65 ml water, 2.35 ml of ethanol and a few drops of hydrochloric acid was stirred for 1 h at room temperature. The mixture was used immediately for the impregnation of textile materials. Thus, a test sample of polyester fabric of about 2 g was impregnated with a 40% degree of uptake in several successive passes, on a laboratory impregnation device Ernst Bentz, at a constant speed of 0.5 m / min and a pressure of 0.4 Kg/cm^2. The coated materials were dried at room temperature for 2 h and then were subjected to heat treatment at 120^{0}C for 1 hour in a thermo-fixation oven.

2.3 Measurements

FTIR spectra were recorded on a JASCO FT-IR 6300 spectrometer equipped with a Specac ATR Golden Gate (KRS5 lens) in the range 400-4000 cm^{-1} (32 accumulations at a resolution of 4 cm^{-1}). SEM images were obtained with a scanning electron microscope FEI QUANTA 200 (Philips). Atomic force microscopy (AFM) was performed in noncontact mode on a Park Systems XE 100 microscope.

A goniometer optical device type CAM 200 for contact angle and surface tension (KSV Instruments) was used to determine the surface wetting properties. A 6.5 μl drop of deionized water was placed onto the surface of each sample in order to measure the static contact angle and the water absorbed in time [11]. Contact angles are measured by fitting a mathematical expression to the shape of the drop by means of a specialized program which is used to calculate the slope of the tangent to the drop at the liquid-solid interface. At least four different spots for each sample were measured and the average value was considered.

Dynamic mechanical analysis was performed on a TA Q 800 instrument, in multi-frequencies-strain mode using a shear sandwich clamp, operated at a fixed frequency of 1 Hz, oscillation amplitude of 20 μm, temperature ramp of 3^{0}C/min., in air, from room temperature to 200^{0}C, on specimens of 10x10x0.75 mm. By dynamic mechanical analysis, complex tensile modulus (G*) can be decomposed in its measurable components, the recoverable elastic component - storage modulus (G') and loss modulus (G") the energy of which is lost through viscous heating during the stressing process. Because the wave motion is sinusoidal, the stress and strain are out of phase by an angle δ, the phase angle [12,13]. Equations which describe the stress wave decomposed in two waves, one in phase with the strain and the other out of phase with the strain, are: $G^* = \sqrt{G'^2 + G''^2}$, $G' = \dfrac{\sigma\cos\delta}{\varepsilon}$, $G'' = \dfrac{\sigma\sin\delta}{\varepsilon}$, $\tan\delta = \dfrac{G''}{G'}$, where: σ is the tensile stress, ε is the tensile strain, δ is the phase angle and tan δ is the loss tangent.

3. Results and discussion

3.1 Structural characteristics of the coated fabrics by ATR-FTIR

From the structural point of view, in the ATR-FTIR spectra were identified characteristic bands of the coating materials precursors together with those belonging to the structure of the polyester substrate. As it can be seen from Fig. 1, the most important absorption bands in the spectra belong, as expected, to PES fiber. Thus, the intense band located at 1714 cm^{-1} correspond to the stretching vibration of the carbonyl group of the ester bonds, at 1578 cm^{-1} is found a relatively weak band corresponding to the stretching vibration of CO bond of carboxylate anion. At 1408, 1338, 1241 and 1094 cm^{-1} are identified absorption bands corresponding to bending vibration δ(C-O) and asymmetric stretching vibration ν_{as} (C-O-C). Other important bands of polyester fibers [14] are determined by the valence vibrations of the C-H and C-C bonds of the aromatic rings and are situated at 872, 793 and 721 cm^{-1}, respectively.

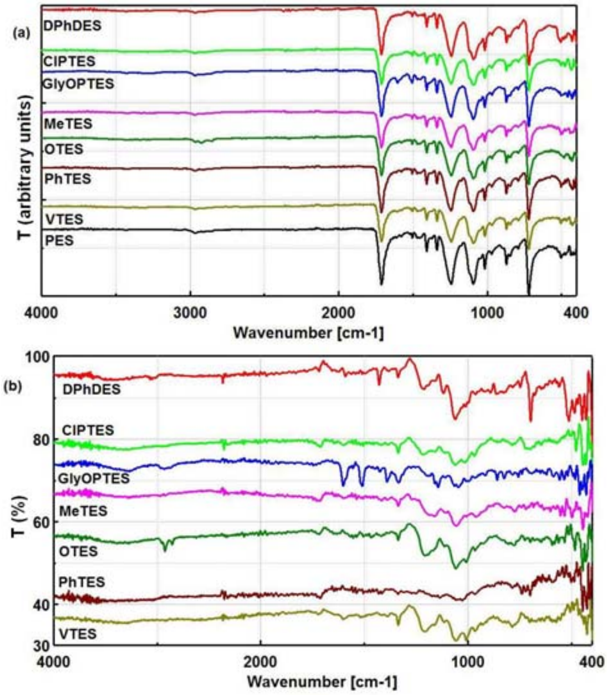

Fig.1. ATR-FTIR spectra of PES fabrics coated with nanosols (a) and of the coatings obtained by subtracting the PES spectrum (b)

It should be noted that in the FTIR spectrum of PES appear bands corresponding to asymmetrical and symmetrical stretching vibrations of methylene groups, located at 2964 and 2857 cm^{-1}, respectively. At 3430 cm^{-1} is situated a band of relatively low intensity which is due to the intermolecular hydrogen bonds between OH groups, without an important influence on the spectra of the coated materials [15].

Analyzing the FTIR spectra obtained by difference, it was found the characteristic absorption bands for each type of coating material as a function of the modifying agent used. Thus, the doublet at 2922 and 2852 cm^{-1} is assigned to asymmetric, respectively symmetrical stretching vibration of CH$_2$ group [16], due to the presence of OTES as a modifying agent. The peak located at

1417 cm^{-1} originates from the symmetric deformation of CH_2 group. At 1336 cm^{-1} was observed a band corresponding to deformation of OH group, and around 1100 and 1058 cm^{-1} are found bands that can be attributed to the stretching vibration of Si-O-Si group [17,18]. Also, at 964 cm^{-1} need to be mentioned a characteristic band of the silanol groups.

For coatings containing VTES, C=C stretching vibrations are found at 786 cm^{-1} together with a band which corresponds to the out of the plane vibration of the C=C-H bond. In the case of coatings derived from ClPTES, the stretching vibration of the C-Cl bond is found at 783 cm^{-1}, whereas in the case of PhTES the out of the plane deformation vibration of CH groups of the aromatic ring was located at 791 cm^{-1}. In the case of the coating generated from MeTES, the band located at 775 cm^{-1} corresponds to the deformation of $Si-CH_3$ group [19]. GlyOPTES modified silica coatings show a band at 912 cm^{-1}, which is due to the symmetric stretching vibration of the epoxy ring.

3.2 Morphology and hydrophobic character of the coatings

PES uncoated fabrics (Fig. 2a) show a uniform, regular and flat surface of the fibers which have an average diameter of about 20 µm. SEM images of the coated polyester fabrics obtained with an impregnation nanosol formed of TEOS/PhTES and containing DR5 showed the formation of a continuous silica film covering the walls of the fibers, without any visible cracks (Fig. 2b).

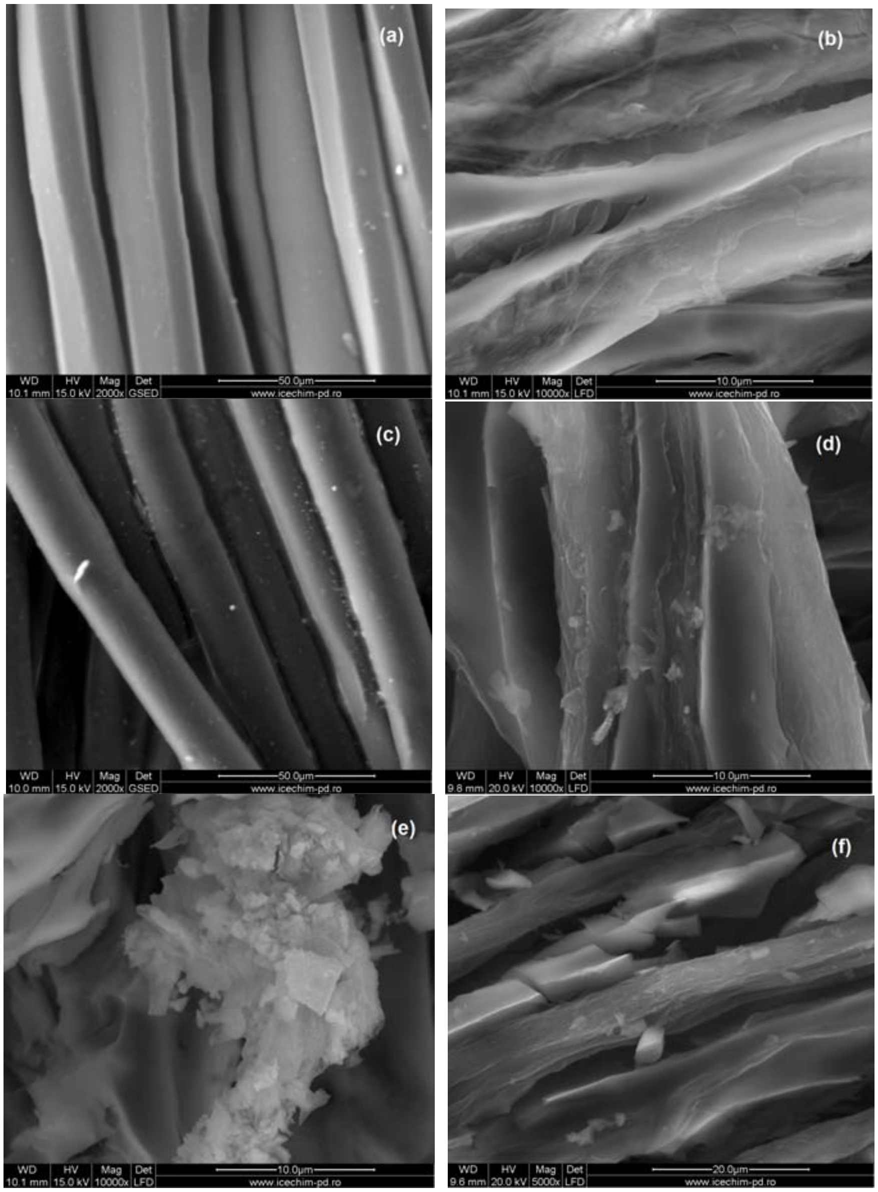

Fig. 2. SEM images of PES fabrics: uncoated (a), and coated with sols: TEOS/PhTES/DR5 (b,f), TEOS/PhTES/DR5-PTES (c,d,e)

Another situation was recorded in the case of the impregnation composition containing DR5-PTES, when the solvent used (THF), decreases the viscosity of the nanosol and ensure the wetting characteristics required for achieving good contact with the fiber and the adhesion of the hybrid film to the surface of textile material (Fig. 2c). In this case, the fibers are uniformly coated but on the surface are seen agglomerates likely to occur due to the premature formation of the particles in the impregnating nanosol, before its application to the fiber, as can be shown in Fig. 2d.

A more detailed investigation of this phenomenon led us to conclude that we obtained large particles, which agglomerate mainly due to DR5-PTES solution used as resulted from the synthesis. The DR5-PTES solution contained the catalyst used for the addition reaction, an amine (DABCO) which causes rapid condensation and formation of large particles and agglomerates (Fig. 2e). To counteract this phenomenon we used a technical solution that consists of introducing the dye into the impregnation nanosol mixed with hydrochloric acid solution used as a catalyst for the sol-gel process.

Unfortunately, in the case of coating materials obtained with DR5 the relatively high viscosity of the impregnating composition leads to the formation of bridges between fibers, which will not allow the fibers to maintain flexibility within acceptable limits. Coating materials between fibers showed multiple cracks as can be seen in Fig. 2f.

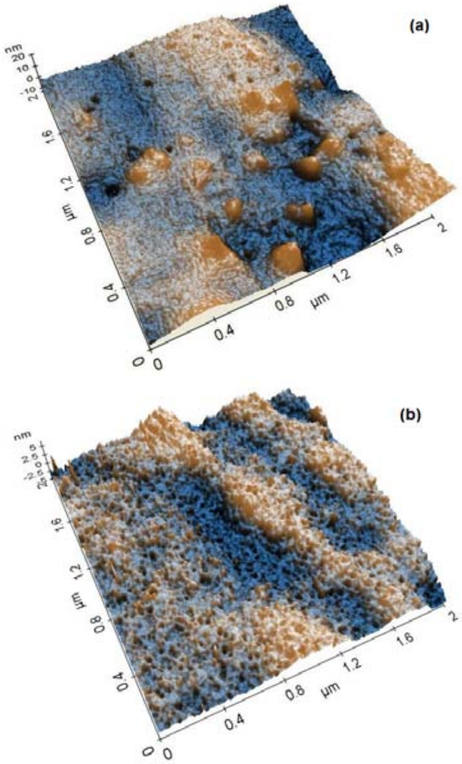

Fig. 3. AFM images of PES surfaces coated with DR1-TEOS-PhTES (a) and DR1-PTES-TEOS-PhTES (b)

AFM images of the surface of polyester fibers coated with silica hybrids show different behaviors of the hybrid films of class I (corresponding to the entrapped dyes) comparatively with those of class II (corresponding to the chemically linked dyes). As in the case of cotton and for the same reasons, the root mean squared roughness is 37 nm in the case of coatings obtained with DR1 , while in the case of DR1 - PTES the value of the roughness is only 20 nm , as can be seen from Fig. 3. The higher roughness obtained in the case of class I hybrids is due to the nanosol formation, which as noted in the case of cotton substrate [20,21], shows particles with a hydrodynamic diameter larger than those obtained in the case of class II hybrids. Contraction of the network manifested in the last case is due to covalent bonds formed between the dye and the inorganic network and ultimately leads to the formation of films with a lower roughness. This behavior has a large influence on the contact angle, the most illustrative example being the coating formed of TEOS and PhTES and containing DR1, respectively DR1 - PTES. In the first case, the contact angle of water is 111^0, significantly higher than that measured in the second case, for which the value measured is only of 84^0. An influence in this case has the difference between the roughnesses of the surfaces.

It is well known that a water droplet deposited onto a rougher surface exhibit a decreased contact area at the liquid-solid interface. The droplet contacts the coating only on the peaks of the profile, while the valleys which are not wetted contain air. It is obviously that the contact area between liquid and air is much higher than with the coating material [22] and as a consequence will mainly influence the resulting contact angle. Therefore, a rough hydrophobic coating with the same chemical composition with a smoother one will have a higher water contact angle [23,24].

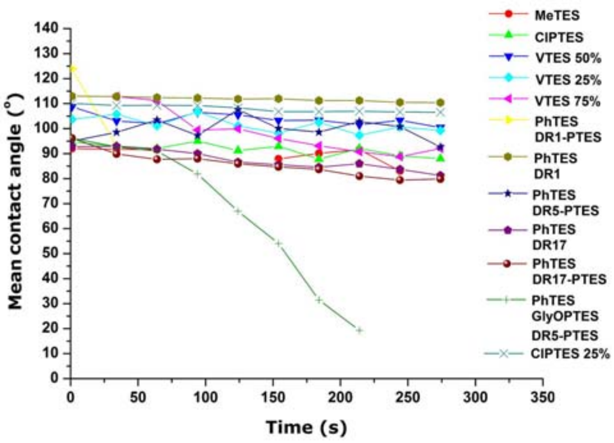

Fig. 4. The mean contact angle on PES fabrics coated with nanosols

PES fibers possessed hydrophobic properties, but the existence of fibrous and porous structure makes the water contact angle to be different on the fabric than on the fibers [25]. Paradoxically for the original PES fabric used in our experiments the water drops penetrated rapidly into the fabric although the fibers are hydrophobic. As can be observed in Fig. 4, PES substrate impregnated with a composition containing PhTES, as network modifier, has the most pronounced hydrophobic character, with a water contact angle of 111^0. When a short aliphatic chain is used to modify the inorganic silica network, as in the case of MeTES, was obtained a low contact angle of about 90^0.

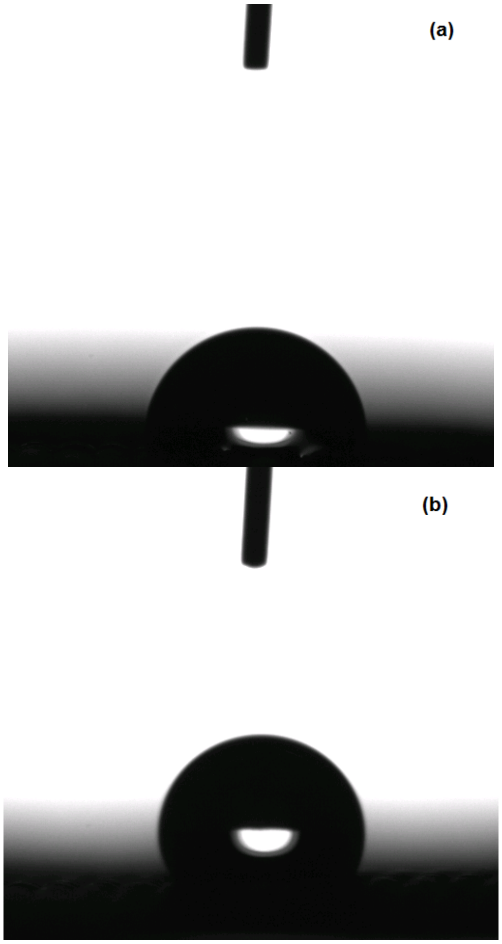

Fig. 5. Images of water drops on the surface of PES fibers coated with hybrids containing (a) PhTES/GlyOPTES=25/25 and (b) ClPTES

For coatings derived from VTES was obtained a value of the contact angle situated in the range $103\text{-}112^0$, the higher the more increases the amount of network modifier, while when GlyOPTES was used as modifying agent, the contact angle is of 88^0 only. A high value of the contact angle of about 110^0, was measured in the case of coatings obtained when ClPTES was used as network modifier, as can be seen in Fig. 4.

3.3 Thermo-mechanical behavior of the PES fibers coated with hybrid materials

The storage modulus is closely related to rigidity, which is observed from the higher values obtained for coatings derived from DPhDES or PhTES compared with those obtained when OTES was used as network modifier. If we analyze the behavior of the storage modulus with temperature, it was found that it is maintained within normal limits, with no significant variations up to 120^0C, after which, due to exceeding the transition temperature of polyester fibers, takes place a significant decrease of its value. In the case of the coating obtained using DPhDES it was found that this phenomenon occurs much earlier, around the temperature of 100^0C, as can be seen from the Table 1.

As the loss modulus is the component of dissipation, its high values indicate that the system is more flexible. This is verified in the case of the coatings obtained with DPhDES when it was recorded the highest value of the loss modulus. This is mainly due to the large volume of the aromatic substituents that lead to an increased free volume of the network and consequently to more flexible systems.

Since the peak height of the loss factor is associated with mobility of the systems, it was observed that after applying the hybrid coatings, molecular mobility was reduced. Thus it is decreased the possibility of energy dissipation by fiber-network interactions or friction between the fibers and consequently the intensity of tan δ decreases. Because are established stronger interactions between the coating and polyester fabric, the peak was shifted to lower temperatures, as a direct result of improving the adhesion of the coating to the substrate fabric. It is obvious that the strongest interactions are established when DPhDES was used as a modifying agent of the inorganic network.

Regarding the stiffness of the coated materials, it is noted that in all cases there is a decrease of its value, which is similar with those recorded for cotton fibers covered with the same types of coating materials [26].

Table 1 Results of dynamic mechanical analysis on PES fabrics coated with hybrid materials

Coating precursors (%/%, by weight)	**Storage modulus (G'), MPa**			**Loss modulus (G"),MPa**		**Loss factor**		**Stiffness (S) N/m**
	30 °C	**120 °C**	**200 °C**	**G" peak max, MPa**	**Temp, °C**	**Tan δ (peak max)**	**Temp, °C**	
Uncoated sample	2500	2248	1286	455.6	143.98	0.2547	147.64	4333660
TEOS/PhTES (50/50)	1558	1422	908	162.0	150.62	0.1320	154.68	3687780
TEOS/ClPTES (50/50)	1858	1689	579	134.8	147.41	0.1066	155.01	3902850
TEOS/VTES (50/50)	1422	1266	754	156.3	155.82	0.1534	158.78	3412070
TEOS/MeTES (50/50)	1577	1428	928	127.2	156.79	0.1134	168.01	3678510
TEOS/OTES (50/50)	1261	1137	698	144.3	149.80	0.1547	166.22	2900380
TEOS/GlyOPTES (50/50)	1565	1476	733	91.14	148.55	0.08035	156.05	3364210
TEOS/DPhDES (50/50)	1560	954	525	365.2	135.25	0.4992	143.46	3485080

4. Conclusions

Polyester fibers were colored with silica hybrid film-forming materials by means of impregnation-thermofixation method, which is currently used in textile dyeing. The coatings obtained by this method provide a good contact with the fiber and adhesion of the hybrid film to the surface of textile fabric.

SEM images show uniform and continuous coatings deposited on the surface of polyester fibers and confirm that there are no major structural defects such as cracks or exfoliations of the hybrid coatings.

The contact angle measurements reveal that the most hydrophobic character was obtained with hybrid coatings derived from organosilanes containing aromatic groups, while when GlyOPTES was used as network modifying agent a more hydrophilic coating was obtained on the polyester fabrics.

Dynamic mechanical analysis confirm that more flexible coatings are obtained when DPhDES was used as modifying agent due to the large volume of the aromatic substituents. In the case of DPhDES are established stronger interactions between the hybrid coating and polyester, which improved the adhesion to the substrate, due to the structural similarities.

Acknowledgements

This work was performed through the Partnerships in priority areas Program – PNII-PCCA-2013-4 – developed with the support of MEN–UEFISCDI, project number 0864 - CLEANPHOTOCOAT.

References

[1] E. Feresenbet, D. Raghavan, G.A. Holmes, J. Adhesion, **79**, 643 (2003).
[2] P. Stenstad, M. Andersen, B.S. Tanem, P.Stenius, Cellulose, **15**, 35 (2008).
[3] A.P.S. Sawhney, B. Condon, K.V. Singh, S.S. Pang, G. Li, D. Hui, Text. Res. J., **78**, 730 (2008).
[4] B. Kusuktham, J. Met. Mat. Min., **20**, 85 (2010).
[5] S.S. Latthe, H. Imai, V. Ganesan, A.V. Rao, J. Porous Mater., **17**, 565 (2010).
[6] A. Raditoiu, V. Amariutei, V. Raditoiu, M. Ghiurea, C.A. Nicolae, L.E. Wagner, Rev. Chim., **63**, 612 (2012).
[7] T. Nedelcev, I. Krupa, D. Lath, M. Spirkova, J. Sol-Gel Sci. Techn., **46**, 47 (2008).
[8] A. Hou, B. Chen, K. Zhang, Color. Res. Appl., **37**, 72 (2012).
[9] D. Juan, Z. Li, C. Shuilin, Color. Technol., **121**, 29 (2005).
[10] V. Raditoiu, A. Raditoiu, L. Wagner, V. Amariutei, M. Raduly, C.A. Nicolae, Rev. Chim. (Bucharest), **62**, 409 (2011).
[11] S.S. Latthe, h. Imai, V. Ganesan, A. Venkateswara Rao, J. Porous Mater., **17**, 565 (2010).
[12] J.V. Koleske, Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd., New York (2006).
[13] V. Carlier, M. Sclavons, R. Legras, Polymer, **42**, 5327 (2001).
[14] X. Xiao, F. Chen, Q. Wei, N. Wu, J. Coat. Technol. Res., **6,** 537 (2009).
[15] S.S. Latthe, H. Imai, V. Ganesan, C. Kappenstein, A. Venkateswara Rao, J. Sol-Gel Sci. Technol., **53**, 208 (2010).

[16] C.H. Xue, S.T. Jia, J. Zhang, L.Q. Tian, H.Z. Chen, M. Wang, Sci. Technol. Adv. Mater. **9**, 035008 (2008).

[17] T.C. Chang, T.M. Tsai, P.T. Liu, Y.S. Mor, C.W. Chen, Y.J. Mei, J.T. Shen, T.Y. Tseng, Thin Solid Films, **420**, 403 (2002).

[18] M. Messaoud, M. Houmard, S. Briche, F. Roussel, M. Langlet, J. Sol-Gel Sci. Technol., **55**, 243 (2010).

[19] N. Hering, K. Schriber, R. Riedel, O. Lichtenberger, J. Woltersodorf, Appl. Organomet. Chem. **15**, 879 (2001).

[20] A. Raditoiu, V. Raditoiu, V. Amariutei, M. Ghiurea, C.A. Nicolae, R. Gabor, R.C. Fierascu, L.E. Wagner, J. Optoelectron. Adv. Mater., **14**, 846 (2012).

[21] A. Raditoiu, V. Raditoiu, V. Amariutei, C.A. Nicolae, R.A. Gabor, A.N. Frone, R.C. Fierascu, M. Ghiurea, L.E. Wagner, G. Hubca, Mater. Plast. **50**, 241 (2013).

[22] N.A. Patankar, Langmuir, **20**, 8209 (2004).

[23] C. Su, J. Li, H. Geng, Q. Wang, Q. Chen, Appl. Surf. Sci., **253**, 2633 (2006).

[24] H.M. Shang, Y. Wang, S.J. Limmer, T.P. Chou, K. Takahashi, G.Z. Cao, Thin Solid Films **472**, 37 (2005).

[25] L. Frunza, I. Zgura, M. Enculescu, S. Frunza, C.P. Ganea, O Rasoga, F. Cotorobai, A. Dorogan, J. Optoelectron. Adv. Mater., **16**, 176 (2014).

[26] A. Raditoiu, V. Raditoiu, R. Gabor, C.A. Nicolae, M. Ghiurea, G. Hubca, U.P.B. Sci. Bull. Ser. A, **75**, 285 (2013).

---

[*] Corresponding author: vraditoiu@icechim.ro