Protein Textile Fibers Coated with Silica – azo Disperse Dyes Hybrid Film-forming Materials

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The paper presents experimental data regarding morphology and hydrophobic character of some film building silica hybrids containing disperse dyes embedded or covalently linked into the inorganic network, used as coating materials for protein textile fibers. Thermo-mechanical properties of the textiles coated with the colored film forming materials are studied in relation with the coating materials composition.

Keywords: thermo-mechanical properties, hydrophobic character, silica hybrids, disperse dyes, protein fibers

The most important type of hybrid materials, which has found wide application due to the different methods and properties obtained on different support materials, is the film-forming materials. Procedures of depositing hybrid materials on different supports together with their intrinsic properties and properties of the interface formed between the film-forming material and support are determinants for covered material characteristics.

Hybrid silica coatings are important for the functionalization of textiles due to the possibility of incorporation of functional compounds or to chemically grafting of additives on the surface of the fabrics[1,2]. It was proved that sols based on modified silica deposited on the textile materials formed transparent layers, which adhere strongly to their surfaces[3]. This type of film building materials obtained by sol-gel process in acidic catalysis lead to coatings which are very stable to heat, light and chemical agents [4-6] and improve some of the mechanical properties of the textiles [7], such as mechanical strength and abrasion resistance. Silica nanosols obtained by hydrolysis in acidic media result in weakly cross-linked condensation products which form denser layer structure, while a thermal post-treatment finally lead to a coating more stable and adherent.

Nanosols and sol-gel technology is increasingly attracting attention because can be used to modify textile attributes such as softness, hydrophobicity, thermal stability or mechanical durability [8]. Coating materials of the silica hybrid type are a viable alternative, which overcomes the limitations of conventional methods used in order to impart certain properties to textile materials [9,10]. The sol-gel method is widely used to obtain superhydrophobic surfaces by chemical modification of textile substrates. Superhydrophobic surfaces have been obtained by roughening surface of textile materials or by modifying rough surfaces with different compounds. This behaviour will determine water droplets to roll off and clean the coated surfaces. Silanes are well known as efficient coupling agents used in composites in order to create a bridge between the matrix and the reinforcement. There are many bifunctional silanes which improves the interfacial adhesion with one end of the molecule which is tethered to the reinforcement surface and with the other end capable to react with the network.

The goal of our study was to investigate in which way was modified the surface of protein fibres after coating with hybrid silica layers formed by acidic hydrolysis of organosilane and tetraethylortosilicate mixtures containing disperse dyes embedded or chemically linked to the inorganic network.

Experimental part

Materials and methods

The precursors used were of laboratory reagent grade and were obtained from Merck, Germany and Aldrich - USA. Hydrochloric acid (0.1 N), tetraethylortosilicate (TEOS), phenyltriethoxysilane (PhTES) diphenyldiethoxysilane (DPhDES), 3-glycidoxypropyltriethoxysilane, (GlyOPTES), vinyltriethoxysilane (VTES), 3-chloropropyltriethoxysilane (ClPTES), methyltriethoxysilane (METES), ethanol, 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), Disperse Brown 1 (DBr1) were previously obtained by us [11] and purified by extraction with toluene in a Soxhlet extractor, followed by recrystallization. The fabric used was 100% wool fabric with a specific weight of 220 g/m^2, ready for dyeing.

Preparation of the impregnation bath, impregnating-drying-crosslinking

A solution obtained from 3.25 mL of TEOS, 3.25 mL PhTES, 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 stirred vigorously at room temperature and used immediately for the impregnation of textile materials. A test sample of wool fabric of about 2 g was impregnated with an 80% 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

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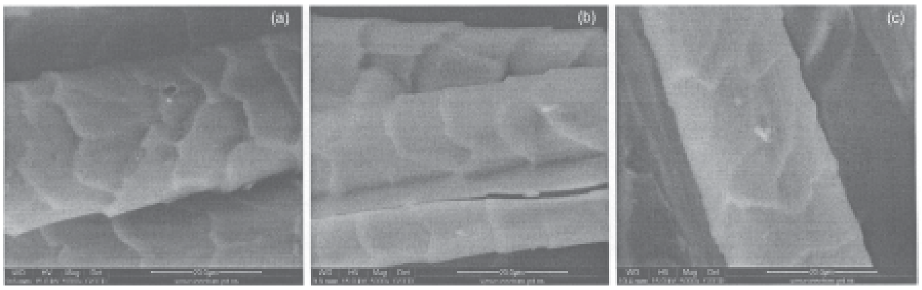

Fig. 1. SEM images of the wool fibers untreated (a),coated with TEOS/PhTES containing DR5 (b) and DR5-PTES (c)

at room temperature for 2 h and then were subject to heat treatment at 120^0C for 1 hour in a thermo-fixation oven.

Measurements

SEM images were obtained with a scanning electron microscope FEI QUANTA 200 (Philips). A goniometer optical device type CAM 200 for contact angle and surface tension (KSV Instruments) was used to determine the surface wetting. Atomic force microscopy (AFM) was performed in noncontact mode on a Multimode-8-AM microscope from Veeco Instruments. Dynamic Mechanical Analysis was performed on a Q800 TA Instrument in multifrequency mode, using a shear clamp and operated at a fixed frequency of 1 Hz, the amplitude of oscillation of 20μ at a heating rate of 3^0C/min. and in the temperature range of 25 - 200^oC.

Morphology and hydrophobic character of the coatings

SEM images of the uncoated wool fiber show a scaly uneven fiber; whereas the coating with an impregnation sol formed of TEOS/PhTES mixtures containing DR5 with the precursor composition identical to that applied in the case of cotton fibers, resulting in a uniform and continue film, with no visible cracks.

These coatings attenuate the scaly structure of the fibers, especially in the case of class II hybrids, where the network contraction of the coating material results in a good coverage of the irregular surface of the protein fiber. The composition corresponding to hybrids of the class I results in the formation of bridges between the wool fibers, as can be seen from figure 1, which would adversely affect the rigidity of the obtained materials.

In the case of the composition containing DR5-PTES it is likely that the solvent used to dissolve the dye action in order to reduce viscosity and to ensure simultaneously wetting characteristics needed for a better contact with the fiber and thus to achieve hybrid film adhesion to the surface of the fabric.

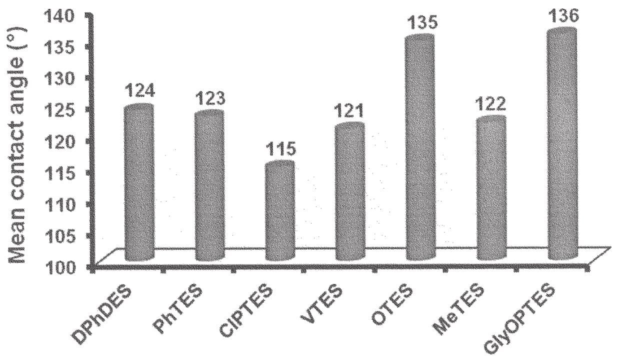

Fig. 2. The contact angle of water on the fabric of wool covered with nanosols containing TEOS and different modifying agents at a 1:1 molar ratio

Wool fibers are impregnated with water because of the existence of pores in the cuticle, the outer layer serving as a membrane that protects the hydrophilic core of the fiber. This is responsible for difficult wetting of the fiber in the first moments after the contact with water. Wool textile substrates impregnated with a composition containing OTES as network-modifying agent show hydrophobic surface with a water contact angle of 135^0. Almost the same value of the water contact angle is recorded when GlyOPTES is used as silica network modifier, probably due to the orientation of the obtained polymer with hydroxyl groups generated by epoxide ring opening to the inside network and with the organic chain to its exterior.

The smallest contact angle of about 115^o is seen when the coating was obtained from a mixture of TEOS and ClPTES. As in the case of applying this type of coating material on cotton fabrics, the value is the lowest in the series, due to the higher polarity obtained from the difference of electronegativity existent between the halogen and carbon atoms. For the other compositions the coatings obtained are more hydrophobic with a water mean contact angle situated in the range of 121-124^o, which is less influenced by the volume of organic substituent (methyl, vinyl and phenyl) from the network modifying agents.

AFM images of the wool fabrics coated with silica hybrid film-forming materials shows different behaviour in the case of class I comparatively to class II hybrids. For the same reason, the mean square roughness is 84 nm in the case of coatings obtained with DR1, while in the case of DR1-PTES, roughness value is only 44 nm, as can be seen in figure 3. The higher roughness obtained for hybrids of

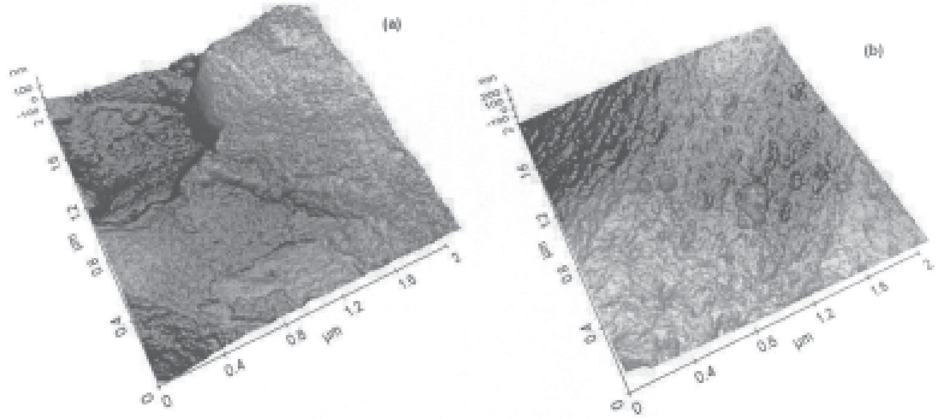

Fig. 3. AFM images of the surface of the wool fibers coated with TEOS/DR1/PhTES (a) and TEOS/DR1-PTES/PhTES (b)

Table 1
RESULTS OF THE DYNAMIC MECHANICAL ANALYSIS

Sample (coating)	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	
Wool (reference)	989.5	265.6	134.7	157.1	92.08	0.4368	112.59	2474030
TEOS/PhTES 50/50	757.3	149.9	91.03	149.3	63.36	0.6036	117.45	2322440
TEOS/ClPTES 50/50	974.3	290.4	213.7	166.7	94.54	0.5444	122.45	3020260
TEOS/VTES 50/50	877.2	230.9	146.2	151.6	86.88	0.5522	115.75	2690070
TEOS/MeTES 50/50	963.3	302.3	186.4	161.4	99.19	0.5170	121.32	3018260
TEOS/OTES 50/50	1083	570.1	524.8	165.4	109.04	0.3090	148.71	3253570
TEOS/ GlyOPTES 50/50	654.1	204.2	130.7	133.3	105.76	0.6275	119.77	2311010
TEOS/DPhDES 50/50	836.5	215.7	131.3	145.1	69.32	0.4900	119.26	2593240

class I comes from the formation of the nanosol particles, which have a hydrodynamic diameter larger than those obtained for hybrids of class II. Contractions of the hybrid network of class II is owed to covalent bonds formed between the dye and the inorganic network and ultimately lead to the formation of films less roughness. However, it should be noted that unlike the film obtained in the case of cotton substrate, on wool, the roughness of the coatings obtained is significantly higher in both cases of colored film-forming materials.

Thermo-mechanical behaviour of coated protein fibers

Storage modulus shows minor differences between the values obtained regardless of the type of coatings used. This leads to the idea that in this case, the storage modulus is strongly influenced by the structure of the fiber and less by the type of hybrid coating applied to the surface. This dramatically decrease up to 120°C in all cases is mainly due to the decrease in the degree of the fiber crystallinity because of the water removal from the structure. This cause structural disruption due to the breaking of some existing hydrogen bonds with amide groups from the macromolecular chains.

The existence of the peak loss factor almost invariably located at 110-120°C supports this assertion. There is one exception and it is related to the fabrics coated with hybrid material obtained with OTES. In this case, perhaps through van der Waals bonds with the hydrophobic cuticle on the surface of the fiber is produced a coating with good adhesion and a decrease in apparent mobility of the system.

The loss factor values confirm the high mobility of the systems, which is maintained irrespective of the type of coating material, with the possibility of dissipating energy mainly by friction between the fibers, the intensity increasing lightly, as can be seen from table 1.

In terms of stiffness, it should be noted that in all cases there is a slight increase of its value depending on the coating material. It is important to notice that in all cases the stiffness is lower than that recorded for the same type of hybrid film forming materials used as coatings on cellulose substrates.

Conclusions

As in the case of cotton substrates, coatings obtained with hybrids of class I have a surface roughness greater than that of the coatings obtained with hybrids of class II, from the same considerations relating to the interactions established during the nanosol synthesis, previously mentioned.

Hydrophobic properties on protein fibers are obtained by modifying the inorganic structure of the hybrid film forming materials with different organic moieties. The wettability of the surface is dependent on the chemical composition of the coatings and less on the topography of the surfaces.

The influence of the dyestuff on the roughness of the coatings was demonstrated by AFM studies and it was observed that compositions containing embedded dyes lead to rougher surfaces.

Thermo-mechanical behaviour shows a high mobility of the systems, despite the existence of coating bridges between fibers. The stiffness of the coated materials is situated around the value recorded in the case of the uncoated substrate, which is good in terms of maintaining the original properties of textile materials.

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References

1. MAHLTIG, B., FIEDLER, D., BÖTTCHER, H., J. Sol-Gel Sci. Technol., **32**, 2004, p. 219
2. MAHLTIG, B., J. Text. Inst., **102**, 2011, p. 455
3. HRIBERNIK, S., SMOLE, M.S., KLEINSCHEK, K.S., BELE, M., JAMNIK, J., GABERSCEK, M., Polym. Degrad. & Stabil., **92**, 2007, p. 1957
4. RADITOIU, A., AMARIUTEI, V., RADITOIU, V., GHIUREA, M., NICOLAE, C.A., WAGNER, L.E., Rev. Chim. (Bucharest), **63**, no. 6, 2012, p. 612
5. RADITOIU, A., RADITOIU, V., AMARIUTEI, V., GHIUREA, M., NICOLAE, C.A., GABOR, R., FIERASCU, R.C., WAGNER, L.E., J. Optoelectron. Adv. Mat., **14**, 2012, p. 846
6. RADITOIU, A., RADITOIU, V., AMARIUTEI, V., NICOLAE, C.A., GABOR, A.R., FRONE, A.N., FIERASCU, R.C., GHIUREA, M., WAGNER, L.E., HUBCA, G., Mat. Plast., **50**, no. 4, 2013, p. 241
7. RADITOIU, A., RADITOIU, V., GABOR, R., NICOLAE, C.A., GHIUREA, M., HUBCA, G., U.P.B. Sci. Bull. Ser. A, **75**, 2013, p. 285
8. ALONGI, J., CIOBANU, M., TATA, J., CAROSIO, F., MALUCELLI, G., J. Appl. Polym. Sci., **119**, 2011, p. 1961
9. CHENG, T., LIN, T., BRADY, R., WANG, X., Fibers Polym., **9**, 2008, p. 521
10. CHENG, T., LIN, T., FANG, J., BRADY, R., Textile Res. J., **77**, 2007, p. 923
11. WAGNER, L., RADITOIU, V., RADITOIU, A., ARDELEANU, P., AMARIUTEI, V., RADULY, M., Rev. Chim. (Bucharest), **60**, no. 5, 2009, p. 444

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