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THERMO-MECHANICAL BEHAVIOR OF CELLULOSIC TEXTILES COATED WITH SOME COLORED SILICA HYBRIDS

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In this article we present results of thermo-mechanical analysis obtained in the case of some cellulosic textile materials coated with silica hybrids modified with organic dyes.

Keywords: thermo-mechanical, silica, hybrids, coatings, dyes

1. Introduction

Modification of textile fibers with organosilanes is an interesting topic in the physics and chemistry of coating materials due to its applications mainly for obtaining composite materials [1-5]. Numerous research groups developed investigations on a large scale regarding the adsorption of various siloxanes onto the surfaces of textile fibers [6-8]. There are several studies on mechanisms of reaction between siloxane and functionalized surface of the fibers. Different strategies were envisaged for carrying out chemical grafting of silica coatings on textile surfaces through different coupling agents [9-12].

The purpose of the study was to explore the influence of the components and working conditions on the final coated cellulosic textiles and their thermo-mechanical properties [13]. Initial studies were made in relationship with the coloring process but the obtained coated materials could be studied also as composite materials [14].

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Organosilanes are well known reagents used industrially to modify the surface of glass fibers. Using suitable bifunctional anchoring agents the surface of organic fibers can be modified in the same manner. The fiber-coating interface is a key factor for mechanical properties of composites and is largely influenced by the composition of the coating material in order to obtain good adhesion properties. Unfortunately, in the particular case of cellulosic fibers, hydrophilicity is an undesirable property, which alters their dimensional properties and stability leading to mechanical failure, but silanes are agents used in practice for hydrophobization treatments especially in construction structures.

2. Experimental

The coating material was obtained starting from a mixture of tetraethylortosilicate (TEOS), phenyltriethoxysilane (PhTES), 3-glycidyltriethoxysilane (GlyOPTES), dyestuff (DR1 or DR1PTES, as was reported in [15]) dissolved in tetrahydrofurane (THF), N-methylimidazole (NMI), water, ethanol and hydrochloric acid, which was allowed to react at room temperature. The mixture was used for the impregnation of a cellulosic test-piece in a laboratory Ernst BENTZ padding mangle. Coated materials were dried at room temperature and then subjected to heat treatment in a thermo-fixation oven following a procedure previously reported [14].

Thermal analysis was conducted on samples of 5-10 mg, from room temperature to 700°C, using a SDT Q600 apparatus (TA Instruments) at a heating rate of 10°C/min, in alumina crucibles and in air as purge gas (50ml/min).

Dynamic mechanic 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 3^0C/min., in air, from room temperature to 200^0C, 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 [16,17].

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:

$$G^{*} = \sqrt{G^{''2} + G^{''''2}}\ ,\ G^{''} = \frac{\sigma\cos\delta}{\varepsilon},\ \ G^{''''} = \frac{\sigma\sin\delta}{\varepsilon},\ \tan\delta = \frac{G^{''''}}{G^{''}} \qquad (1)$$

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 discussions

Coating mixtures used in this study contain TEOS as a network forming agent, PhTES as a network modifier used to achieve compatibility with organic dyes and GlyOPTES involved in homo-polymerization during heating in the presence of a catalyst rather than for reaction with alcoholic groups from cellulose chains. The control of composites properties depend on the possibility of modifying the interfacial adhesion through the improvement of the fiber-matrix interactions.

The existence and integrity of silica coatings on textile materials was proved by performing SEM analysis on cotton fabric before and after the impregnation with silica coatings and on silica residues obtained after thermal decomposition at 700^0C. As it can be observed (Fig. 1) the cellulosic material can be considered as a template for silica coatings. After thermal decomposition of the organic part, silica residue mimics the fabric structure. This is a strong evidence of the uniformity and homogeneity of the coating.

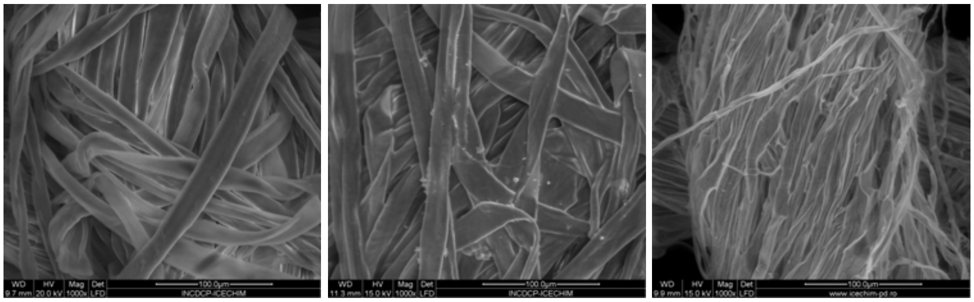

a) b) c)

Fig. 1. SEM images of : a) cotton; b) coated cotton ; c) silica residue at 700^0C (in air)

Thermal stability is one of the most important properties in relationship with this type of coating materials. For the evaluation of the thermal stability comparative experiments were developed. The mass loss observed as a result of thermal decomposition is evidenced as four stages, depending on the coating composition (Table 1). The first stage is due to dehydration and releasing of residual solvents, while the second stage is the most important and is due to thermal decomposition of the organic residues into carbon dioxide, carbon monoxide and carbonaceous char.

Table 1

Composition of coating materials

Sample	Composition, % (weight)			Dye	Catalyst
	TEOS	PhTES	GlyOPTES		
1	50	50	---	DR1	---
2	50	50	---	DR1PTES	---

3	40	50	10	DR1	NMI
4	40	50	10	DR1PTES	NMI
5	50	25	25	DR1	NMI
6	25	50	25	DR1	NMI
7	25	25	50	DR1	NMI
8	25	25	50	DR1PTES	NMI
9	50	---	50	DR1	NMI
10	50	---	50	DR1PTES	NMI

The char content undergoes oxidative decomposition in the third stage resulting in another important mass loss, which is characteristic for both uncoated and coated fabrics (Fig. 2). The fourth stage is characteristic only for coated fabrics in which aromatic residues are found at a sufficiently high level in the composition of the coatings. It is interesting to notice that thermal stability is strongly influenced by the content of phenyl residues.

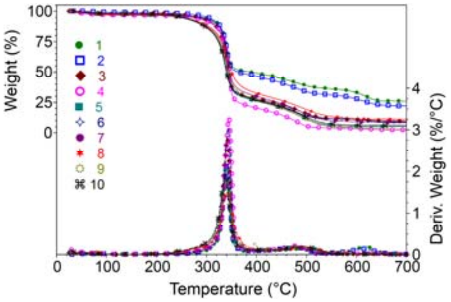


Fig. 2. Thermo-gravimetric analysis of coated fabrics

The organic groups attached to silicon are primarily involved in the thermo-oxidative degradation and if we compare the temperature for a degree of decomposition of 5%, we can conclude that phenyl group lead to a thermal stabilization of the coatings (Table 2). The stability of the phenyl residue is due to the aromatic character, which determines to consume a considerable amount of energy in disrupting the electronic cloud for destabilization of the molecules sufficiently to occur a bond breaking. The resulting aromatic radicals could combine creating a very stable cross-linked polyaromatic carbonaceous residue. This behavior results in different degradation pathways of the coating materials and is important in view of their usage to obtain fire retardant materials.

Table 2

Results of Thermo-gravimetric Analysis

Sample	Temperature range								Residue at 700°C (%)	T (5% Weight Loss) (°C)
	RT - 130°C		130 - 400°C		400 - 550°C		550 - 700°C			
	Peak max I (°C)	Weight Loss (%)	Peak max II (°C)	Weight Loss (%)	Peak max III (°C)	Weight Loss (%)	Peak max IV (°C)	Weight Loss (%)		
1	48.89	3.14	340.49	47.05	482.75	13.27	617.51	10.49	25.98	286.00
2	67.32	1.03	340.50	51.53	479.76	15.79	612.35	9.58	22.07	301.70
3	55.95	2.42	341.08	69.73	484.54	16.79	619.25	1.44	9.61	282.17
4	45.87	3.24	344.37	76.60	481.96	16.34	625.70	1.60	2.20	264.13
5	54.12	2.87	338.39	71.39	489.03	20.70	---	---	5.03	244.47
6	52.98	2.32	343.05	71.59	483.11	14.39	622.96	2.92	8.76	281.44
7	55.17	2.68	341.13	68.78	489.46	20.26	---	---	8.27	247.58
8	59.60	2.68	342.13	67.93	495.27	18.41	---	---	10.98	251.03
9	57.34	1.95	339.54	73.26	490.68	21.30	---	---	3.49	252.15
10	57.75	2.12	336.99	71.74	490.27	20.19	---	---	5.95	251.98

Two types of interactions take place and influence the thermo-mechanical properties of coated fabrics. On the one side are interactions between components in coatings and on the other side are forces established between coatings and cotton fabrics. The DMA studies indicate that the motion of the cellulose chains is constrained by the inorganic matrix.

Table 3

Results of Dynamic Mechanical Analysis

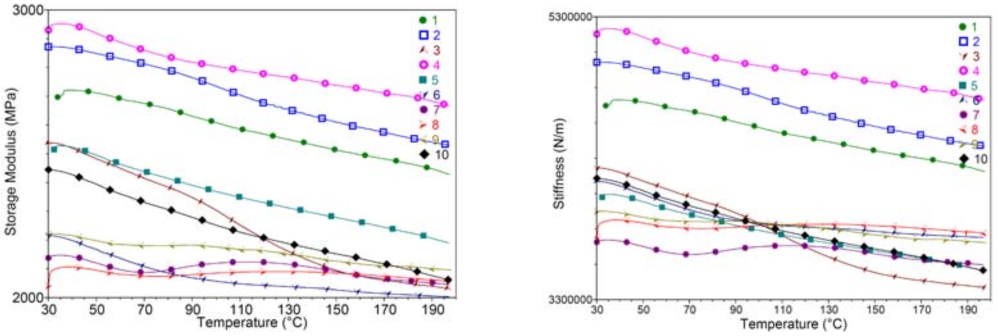
Sample	Storage Modulus		Loss Modulus		Loss Factor		Stiffness (S) N/m x10^6
	G' at 30°C, MPa	Signal change, MPa	G" (peak max.) MPa	Temp, °C	Tan δ (peak max.)	Temp, °C	
1	2719	292.2	67.81	74.72	0.02573	103.57	4.712
2	2872	336.0	61.87	101.49	0.02276	108.98	4.978
3	2538	492.2	116.6	63.86	0.04814	74.15	4.230
4	2953	285.3	92.18	51.86	0.03169	54.44	5.216
5	2582	324.6	101.7	60.62	0.04143	63.12	4.045
6	2216	260.0	90.85	56.31	0.04237	61.75	4.137
7	2147	101.7	133.9	53.86	0.06362	58.15	3.722
8	2107	51.39	90.04	51.29	0.04295	53.29	3.862
9	2220	124.3	140.8	52.71	0.06417	52.17	3.925
10	2444	378.6	93.83	74.24	0.04082	93.09	4.154

There are three main factors affecting the elastic and the viscous response of the coated fabric. Thus, storage modulus as a measure of recoverable elastic component is high when the rigidity of the sample is increased, as in case of using large quantities of TEOS in coating composition (Table 3).

The same trend is observed when DR1-PTES was used as a coloring material, comparatively with DR1. An explanation for this behavior was a rigidity of the hybrid coating obtained when the organic dyestuff was chemically linked to the inorganic matrix. If DR1 was used as coloring material, it acts as an organic filler and storage modulus decrease slightly. In this case loss modulus becomes higher because the energy lost through viscous heating is more important during the stressing process. A more pronounced effect was recorded when GlyOPTES was used as network modifier, due to organic chains obtained through homo-polymerization of epoxy groups. Rigidity was encountered when the mixture of TEOS and PhTES was used as coating material and storage modulus values became the highest in the entire series. If PhTES was changed with GlyOPTES, the storage dropped with about 15-20%, while loss modulus was increased with about 50-100% and temperature peak maximum was shifted to lower values with about 20-30^{0}C.

A good stability in the storage modulus value as a function of temperature was observed from signal change, which did not, exceeded 15% of the initial value overall range of temperature.

As it was seen, higher flexibility can be obtained in the studied systems even when a rigid component is implicated. By the inclusion of organic groups in the inorganic network, a large volume is occupied and the mobility of the system is assisted. Therefore, it was expected a decreasing in the storage modulus as the organic content increased (Fig. 3). This is probably due mainly to changes in the average crosslinking of the coating.



(a) (b)

Fig. 3. DMA plots of coated materials

Since the loss modulus is the dissipation component, higher values means that the system is more flexible due to more energy being dissipated. This can be explained by the formation of linear epoxy polymers and the presence of organic dye lead to a more flexible system through an increase in the free volume.

Epoxy groups in homo-polymerization could generate only linear polymers and thus crosslinking is obtained only in the inorganic rest due to the presence of TEOS. A higher degree of crosslinking of the inorganic network means a broader loss factor curve, which is synonym with lower mobility and more time for relaxation, shifting the temperature of the maximum to higher values. The peak high is indicative of the energy dissipated in the system. A high value means a poor interface in composites.

As we can see from SEM micrographs cellulosic fibers are uniformly covered with a thin coating. A composite with poor interface bonding should tend to dissipate more energy, because the greater the transferred stress from the fiber to the matrix the lower could be the energy dissipation. Strong interaction of fibers and matrix tends to reduce the mobility of the molecules chains at the interface and reduce tan δ values. However, the broader peaks recorded in all cases suggests molecular relaxations in the composites.

Stiffness is an important property of the coated textile fibers. Because the initial target was to obtain colored cotton-polyester blends using dyes, which are suitable in practice for dyeing polyester it was important to obtain values of the stiffness at least similar to those of polyester fibers.

The addition of GlyOPTES resulted in a decreased stiffness owing to the improved fiber-matrix interfacial adhesion. This can be ascribed to the fact that epoxy homo-polymer is located at the interface between silica matrix and cellulosic material, giving rise to more hydrogen bond interactions between hydroxyl groups from cellulose chains and hydroxyl groups formed during homo-polymerization of glycidyl groups [18].

4. Conclusions

From the SEM micrographs we can conclude that silica coatings reproduce exactly the fabric structure and the obtained coverings are uniform and crack free.

Thermal stability of the coated materials is considerably improved with greater amount of aromatic residues.

The hydrogen bonds formed between the adsorbed silanols and hydroxyl groups of cellulosic fibers may be further converted into covalent bonds by heating. The interactions between the hybrid matrix and cellulosic fibers are dominated by the network characteristics. To improve the interfacial adhesion on the one-side chemical bonds between the organo-silanes and the matrices is required and on the other side strong interactions or even covalent bonds between the hybrid matrix and the cellulosic fibers are necessary.

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