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Elaboration of hybrid cotton fibers treated with an ionogel/carbon nanotube mixture using a sol-gel approach

Abstract: Ionic liquid (IL) synergy with other materials may influence their properties significantly. Nevertheless, their advantageous liquid state turns out to be an impediment for applications in devices which need stable solid state shaping. In the current study we present a novel method where new siloxane functionalized IL acts as a modifier for carbon nanotubes (CNTs) and titanium alkoxide-CNT coated hybrid cotton fibers. This elaborated route carried out by interconnected and entangled ionic liquid, sol-gel and solid carbon nanotube networks opens up opportunities for functionalization of sol-gel materials with different shapes and sizes. The comparison of properties of IL, ionogel, ionogel/CNT mixture and titanium alkoxide coatings is performed. Ionogel-modified cotton fibers have increased hydrophobicity, linear density, breaking force and ultimate strength as compared to the uncoated cotton fibers. These properties are ensured even after washing threads with water. A uniformly coated CNT network around the fibers strengthens the material and increases its electric conductivity.

New type of hybrids can be utilized in formulations which have UV-shielding and hydrophobic properties as well as for antibacterial properties. Characterization studies of the product were carried out by energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), optical microscopy and infrared (IR) spectroscopy.

Keywords: Ionogel; Homogeneous blending; Surface chemistry

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1 Introduction

Modifications of materials with ionic liquids (IL) have been in the focus of a rapidly growing number of studies in the last decade [1,2]. This became feasible due to the synthesis of first air- and moisture stable imidazolium salts by Wilkes group in 1991 [3]. ILs consist solely of ions and many of them are fluid at room temperature. Remarkable properties such as negligible vapour pressure, non-flammability, wide temperature range of liquid state and a wide electrochemical window [4,5] have kept IL studies continuously increasing [6]. Moreover, IL synergy with other materials may influence their properties significantly. Nevertheless, their advantageous liquid state turns out to be an obstacle for applications in devices which need solid state shaping. One possibility to confine IL into solid material is *in situ* polycondensation of the precursor (metal alkoxide, metal salt) through a sol-gel process in the presence of IL. Materials which consist of an ionic liquid and solid network (organic, inorganic or hybrid) are called ionogels. Ionogels are very attractive hybrid materials due to their tunability. It is possible to change the properties of ionogels by varying the ionic liquids and solid matrixes or by addition of a third component (nanoparticles, catalytic complexes) to elaborate functional materials for different applications [7,8].

In recent years modifications of materials with nanoparticles have also been in the focus of materials science [9]. Most commonly used additives are carbon nanotubes (CNTs), which have a unique spectrum of extraordinary mechanical, electrical, and thermal

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properties that guarantee them numerous potential applications in material science [10]. It is well-known that CNTs are hard to process due to their tendency to form agglomerates. To overcome this problem different approaches have been suggested in the literature to decrease the nanotube agglomeration, such as sonication, high shear mixing, and methods that change the surface chemistry of tubes either covalently (functionalization) or non-covalently (adsorption) [11].

In 2003, an alternative solution to the problem of low dispersibility of CNTs was found by Fukushima *et al.*, who reported that imidazolium-based ILs can separate the CNTs agglomerates without modification of the tube surface [12]. In this context materials based on CNTs and ILs, also called bucky gels, have attracted much attention due to the beneficial combination of properties of both components. CNT-IL mixtures have been intensively studied in the field of catalysis, electrochemistry, and composite materials with polymer matrices [13]. However, polymer materials have some disadvantages related to limited thermal and chemical stability. CNTs and IL incorporation into inorganic matrices by a sol-gel process definitely have advantages over organic polymer matrices in obtaining materials with desired shape and size [14]. A problem to be solved in this paper lies on the fact that it is hard to dissolve polar bucky gels in non-polar metal alkoxides, furthermore commonly used ILs may become unstable in air and moisture [15].

This complex study involves overcoming two interconnected barriers: First we prepared ionogels based on CNTs non-covalently modified with siloxane functionalized imidazolium salt – 1-methyl-3-(3'-triethoxysilyl)propyl]imidazolium chloride (MTICl) and titanium(IV)butoxide ($Ti(OBu)_4$) through an aqueous sol-gel reaction. Our aim was to achieve homogeneous dispersion of CNTs in the resulting material to ensure its good electrical and mechanical properties. The good miscibility of MTICl and alkoxide is known to play a crucial role in the formation of stable and homogeneous ionogels [16]. Homogeneous distribution of MTICl in alkoxide also contributes to uniform dispersion of CNT in resulting material. Moreover, confined IL helps to avoid the destructive shrinkage of the gel during the aging process due to its low vapor pressure. As it was described before, ionic liquid can act as a coordinating agent and prevent cracking, which is characteristic of sol-gel materials [17]. As a result, crack-free material can be obtained.

Secondly, usage of new hybrid ionogel for functionalization of cotton fibers has been shown for the first time. Organic-inorganic hybrids are a new type of composites with interesting mechanical, optical, electrical and thermal properties, rather different from those of the starting materials [18]. Generally, the inorganic phase confers thermal and mechanical resistance to the composite, whereas the organic phase governs the composite's flexibility, density and free volume [18]. Recently, modified cellulose synthesis by the sol-gel method has attracted much attention [18,19], but the main problem is the same that was mentioned before: organic and inorganic compounds do not interact enough to endure mechanical changes or mechanical washing with different solvents [18]. In our case we report a "green" and simple approach for modification of cellulose cotton fibers with the same ionogel that was used in the modification of carbon nanotubes. We assume that MTICl acts as a linker to retain nanoparticles on the surface. Synergistic effects from the chemical interactions between the organic and inorganic compounds and better mechanical properties make these hybrids attractive in applications such as in formulations which have UV-shielding and hydrophobic properties [20] as well as for antibacterial properties [19,21] or as a linker to retain nanoparticles on the surface.

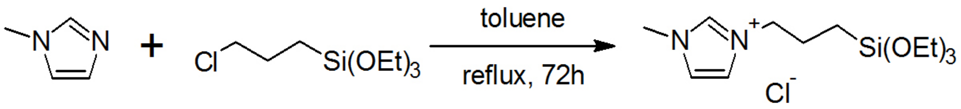
2 Experimental procedure

2.1 Materials

1-Methylimidazole (≥99%), 3-chloropropyl(triethoxy) silane (≥95%), titanium tetrabutoxide (≥97%) and hexane were purchased from Sigma Aldrich and used as received without additional purification. Diethyl ether was obtained from Lachner. n-butanol (≥99%, Sigma Aldrich) was dried and distilled over CaH_2. Cotton thread was extracted with petroleum ether (40-60°C).

2.2 Characterization

Infrared (IR) spectra were recorded on a Spectrum BXII FTIR spectrophotometer (Perkin Elmer). The scanning electron microscopy (SEM) was performed on a Vega microscope at 10 kV (Tescan). Carbon tape was used for sample preparation. Energy-dispersive X-ray spectroscopy (EDX) analyses were performed on a Helios NanoLab 600 SEM (FEI). Optical characterizations were carried out on a BX 51 optical microscope (Olympus).



Scheme 1: Synthesis of MTICl [16].

2.3 Synthesis of ionic liquid

1-methyl-3-(3’-triethoxysilyl)propyl]imidazolium chloride was synthesized according to the method reported previously [22] using the following reaction (Scheme 1).

MTICl was prepared using 1:1 mole ratio of 1-methylimidazole and 3-chloropropyl triethoxysilane through a one step synthesis (Scheme 1). In the experiment, 3-chloropropyl triethoxysilane (36.23 g; 0.15 mol) was added dropwise to 1-methylimidazole (12.29 g; 0.15 mol) dissolved in toluene (150 mL). Then the mixture was refluxed at 111°C for three days in Ar atmosphere. As a result, two layers were formed: brown MTICl at the bottom and toluene at the top. Layers were separated and the MTICl layer was purified from any unreacted starting materials by washing three times with diethyl ether (50 mL). After drying overnight at room temperature under vacuum ($^<$1 mm Hg) 17.23 g (36%) of MTICl as yellowish viscous liquid was obtained.

2.4 Prepration of carbon nanotubes

Multi-walled carbon nanotubes (MWCNTs) used in this work were prepared by hot-wall chemical vapour deposition on cobalt nanoparticles supported on aluminium oxide from acetylene/hydrogen/helium (6 sccm/100 sccm/100 sccm) mixture at 730°C. Length of the synthesized MWCNTs was in the range of 50-200 nm and diameter of 10 - 15 nm.

2.5 Preparation of MTICl-Ti(OBu)$_4$ ionogel

Ionogels were prepared using the following procedure after optimization of important parameters including water/Ti(OBu)$_4$ molar ratio, appropriate MTICl mass percent and hydrolysis temperature. Titanium(IV)butoxide was added into 50 mL borosilicate glass reaction bulb and closed with airtight septum. MTICl (0.05-0.30 g) was added directly to the Ti(OBu)$_4$ (1.80 g) [16]. The mixture was left to stir for 10 minutes. To initiate the sol-gel process H_2O/BuOH solution was added to the mixture portion-wise, 1 mL after every 5 minutes. As a result, a water/alkoxide ratio (R) of 0.8 was achieved. The mixture was left to stir overnight at room temperature. After that solvents and other low molecular mass organic compounds were removed portion-wise to get the requisite concentration (Table 1), using a rotary evaporator and 70°C water bath. Before detaching the bulb from the evaporator it was filled with argon until ambient pressure was achieved.

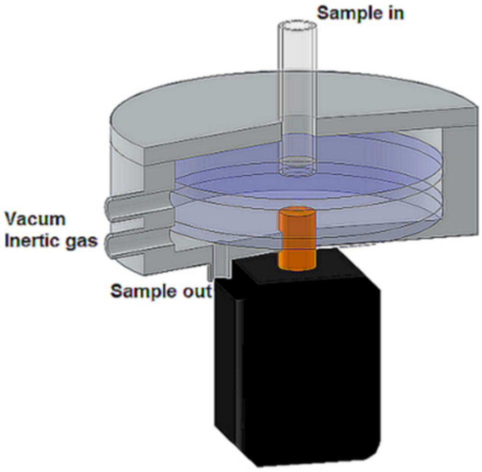


Figure 1: A figure of CNT-ionogel blender.

2.6 Preparation of iono-CNT gel

Hybrid CNT-ionogels were prepared through aqueous sol-gel reaction using MTICl-Ti(OBu)$_4$ ionogels preparared according to the routine described above. CNTs (0.015 g, 1.22 ww%) were added to the ionogel that contained 8% of MTICl [16] and mixed with a magnetic stirrer for 24 h at room temperature. Solvents and other low molecular mass organic compounds were removed portion-wise to get the requisite concentration (Table 1), using a rotary evaporator and 70°C water bath. The gels were obtained as black and highly viscous materials.

2.7 Device for dispersion of CNTs

A separate device was designed to disperse the CNTs’ agglomerates (Fig. 1). The glass plates were isolated by a spherical aluminium cover. The bottom glass plate was rotating as the sample passed through the machine. The motor controller had the option to vary the rotation speed from 1 rpm to 3000 rpm.

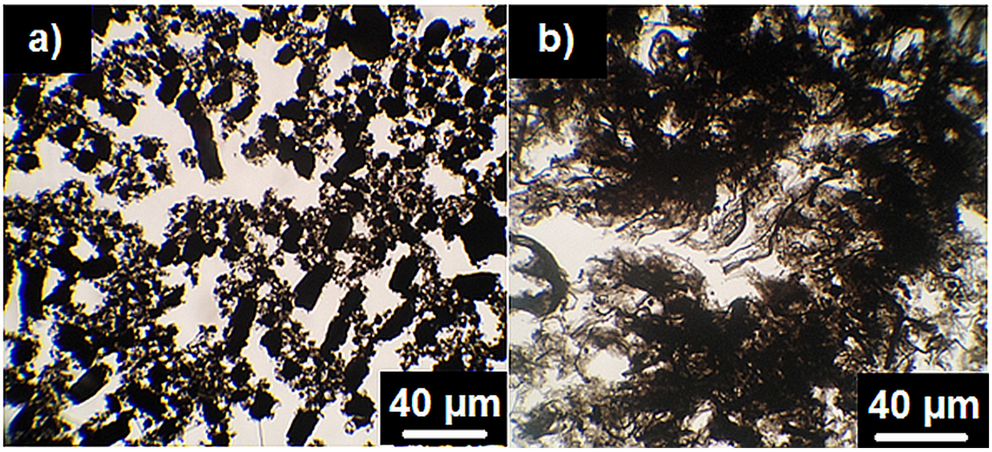


Figure 2: (a) Ti(OBu)$_4$-CNT gel, different phases of the material are clearly observed; (b) MTICl-Ti(OBu)$_4$-CNT, separation of phases is much less obvious.

2.8 Electrical measurements

The electrical resistance of the prepared materials was measured using a classical four point method. The surface of borosilicate glass was coated with thin ionogel films using precursors of different concentration. Conditions and the distances between electrodes were the same during all the measurements. Standard deviations were not estimated and the results should be taken as a rough estimation demonstrating the general nature of the system, rather than an exact measurement.

2.9 Preparation of modified cotton fibers

Cotton threads with 200 µm diameter, were used as a starting material source. Various experiments with the different concentrations of MTICl were carried out. The concentration of Ti(OBu)$_4$ and CNTs was equal in all experiments. Cotton threads were cut into 10 mm long fibers and left to stand in tightly closed bulbs filled with 5 mL of precursor (diluted with solvent MTICl-Ti(OBu)$_4$-CNT or MTICl-Ti(Obu)$_4$ ionogels) for 24 h at room temperature. After that coated threads were left to dry at room temperature (21°C, relative humidity 18.4%) for two weeks.

3 Results and Discussion

The sol–gel method is suitable for obtaining a wide range of ceramic materials, although many properties of different organometallic precursors vary to some extent [23]. Thus, we expected that this general route could be applied for ionogels to obtain materials of different shape and size. Modified ionogel mixed with CNTs from the above described procedure appeared much more monolithic and black than the gel without ionic liquid added, but the separation of phases still occurred (Fig. 2). Thus we used separately constructed devices to ultimately separate CNTs.

The key to development of a methodology for the preparation of uniformly distributed nanotube mixtures lies on the presence of MTICl in the mixture and the separation of the mixture. Ionic liquid with siloxane moiety mixes very readily with titanium tetrabutoxide resulting in homogeneous sol. NMR and EDX analyses were done in our previous work to show homogeneous nature and presence of Ti-O-Si bonds in the material [16]. Uniform dispersion of MTICl leads to exfoliation of the CNT ropes without any sonication (Fig. 3). Despite the fact that sonication is a common method for destroying CNT agglomerates, ultra sonication and high shear mixing can also fragment the CNTs, decreasing their aspect ratio [11]. Methods that include covalent treatment of the CNT surface, for example aggressive functionalization with acids, might introduce structural defects causing inferior properties of the tubes [11]. In our case MTICl is a non-covalent dispersant for CNTs that can effectively disperse them and protect their electronic properties. Nowadays there is an on-going discussion about the mechanism of the interactions between IL and CNTs [24,25].

Electrical measurements were not the main objective of this work, rather a rough estimation demonstrating the overall properties of the system. The measurements showed that heated MTICl-Ti(OBu)$_4$-CNT hybrid films have quite good conductivity (up to 450 S m^{-1}, Table 1) Compared to other works [26,27], where CNTs were dispersed in metal

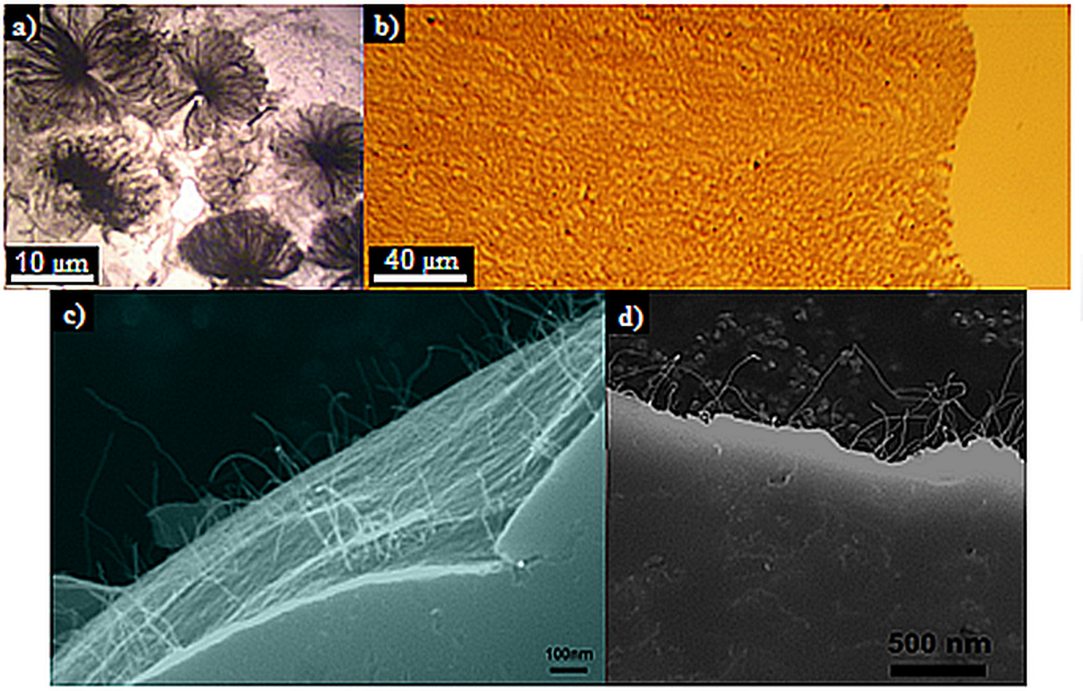


Figure 3: (a) Dispersed CNT ropes, MTICl-Ti(OBu)$_4$-CNT mixture is pressed between two glass plates; (b) MTICl-Ti(OBu)$_4$-CNT hybrid film, CNTs are separated; (c),(d) SEM images of MTICl-Ti(OBu)$_4$-CNT ceramic films, single CNTs are shown.

Table 1: Different parameters of experimental series.

Material/film thickness	Heating time, temperature	Added solvent (BuOH)	Condctivity (S m^{-1})
MTICl-Ti(OBu)$_4$-CNT, 200 nm	21°C	50	0.08
	10 min; 100°C		4.5
	1 h; 100°C		98
	24 h; 200°C		200
MTICl-Ti(OBu)$_4$-CNT, 1 μm	21°C	100	10.5
	10 min; 100°C		59
	1 h; 100°C		105
	24 h; 200°C		450
MTICl-Ti(OBu)$_4$, 1 μm	21°C	90	Very low
	10 min; 100°C		
	1 h; 100°C		
	24 h; 200°C		

alkoxide without ionic liquid, we achieved better values of conductivity due to the better dispersion of CNTs in the sol-gel-ionic liquid matrix. Heating was needed to remove organics and water still present in the material after polymerization. The heating temperature was carefully selected to avoid decomposition of ionic liquid [16] and oxidation of carbon nanotubes [28] while other organics could be removed. The results show the general nature of the system in which case lower CNT concentrations are needed to achieve desired properties of the materials.

It is well known that natural cotton fibers, which have a cellulose content of 90% [29], possess abundant hydroxyl groups on their surface, and provide a suitable substrate for metal oxide deposition [19]. In our study covalently modified cotton threads were obtained by covering cotton fibers with MTICl/Ti(OBu)$_4$/CNT gels. MTICl is involved in sol-gel processes through ethoxy groups, giving covalent bonds with a titanium alkoxide matrix [16]. Ti-OH and Si-OH groups of the product of hydrolysis of titanium and silicon alkoxides plays a key role in interaction with OH groups located on the cotton surface, forming a chemical network between polymer and inorganic phases. It has been shown before that TiO$_2$ gels form stable chemical bonds with wood substances by sol-gel treatment [30]. Recent studies revealed that cotton fabrics treated with sol–gel titania hydrosols have improved UV radiation protection [31], thermal stability and flame retardancy [32]. The novelty of our work is in addition of ionic liquid functionalized with Si(OEt)$_3$ moiety into titania gel network that consequently will cover the surface of cotton fiber.

Hydroxyl groups of cellulose are targeted to undergo different types of reactions with silanes, for example esterification, carbamoylation, etherification, alcoholysis and condensation [33,34]. Moreover, the study has investigated silane oligomer formation in primers, the extent of reaction occurring between cellulose and

Table 2: EDX analysis of MTICl- $Ti(OBu)_4$ modified cotton fiber surface.

Element	Weight (%)	Atomic (%)
C	26.8	52.8
O	21.4	18
Si	1.3	1.2
Cl	1.2	0.9
Ti	46.8	24.9
N	2.5	2.2

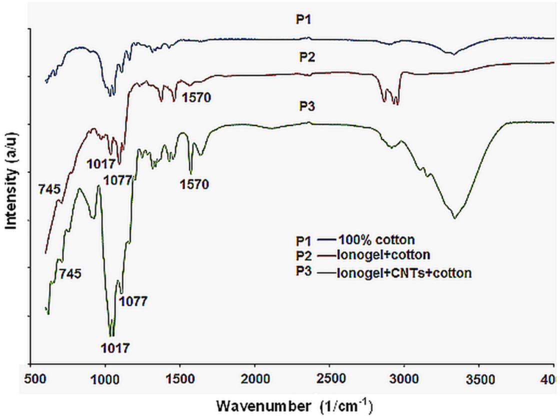


Figure 4: FTIR spectrum of P1) pure cotton; P2) cotton/MTICl/$Ti(OBu)_4$; P3) cotton/MTICl-$Ti(OBu)_4$/CNT in the 400-4000 cm^{-1} spectral range. Only major peaks are numbered.

silanes, and the type of polysiloxane network formed inside the wood structure [35]. In our case reaction of cotton OH groups with BuO(Ti) is preferred to EtO(Si) due to the faster reaction time of the metal alkoxide. The major difference in reactivity of metal alkoxides from those of silicon lies in their very easy and rapid reaction with water in the absence of catalysts. The reaction times for hydrolysis of titanium alkoxides are 10^5-10^8 times shorter than those for silicon alkoxides [36]. The combination of metal alkoxide and functionalized IL is beneficial, because IL behaves as a plasticizing agent, creating stronger, crack free, hydrophobic and more stable coatings for fibers. To prove this hypothesis, a number of chemical and physical parameters were clarified.

According to the energy-dispersive EDX analysis the material surface consisted of C, Si, O, N, Ti and Cl atoms. The presence of ionogel on the surface of the fibers was detected in every case and every concentration, even if the fibers were mechanically shaken or washed with water. The results of EDX analysis using the lowest concentration of ionogel are shown in Table 2. Elemental composition clearly demonstrates the presence of the IL imidazolium ring in the sample and Si-Ti coexistence on a cotton thread surface.

FTIR spectra (Fig. 4) indicate the existence of ionogel in cotton fibers. The spectrum of P1 vibrations of the pure cotton thread is presented. P1 and P2 are comparable to treated cotton. The band centered at 745 cm^{-1} corresponds to the vibration of the Ti–O bond [25]. Moreover, several signals at 1017-1170 cm^{-1} (C2H, C4H, NPr, NMe), 1600 cm^{-1} (sh-N1C2N3, C2H) demonstrated the presence of the imidazolium ring in the sample. The peak at 1570 cm^{-1} can be attributed to C=C stretching of the imidazole ring and the peak at 1077 cm^{-1} appears due to Si-O vibration. The peak at 1017 cm^{-1} in MTICl and MTICl/CNTs containing cotton fibers can be attributed to Si-O-Ti bond vibrations.

The presence of hydrophobic $Si(OEt)_3$ groups confers hydrophobicity to the cotton hybrids and consequently weight and volume variation is very low. The hydrophobic nature and thermal stability of these new hybrid cotton materials make them suitable for preparation of packing or insulating materials. Therefore linear density (Tt), breaking force (Bf), ultimate strength (Us) presented as a breaking tenacity, and particular swelling capacity of cotton yarns as dimensional stability were measured (Table 3). Dimensional stability in the presence of water was ascertained by weight (ΔW) after submersion in water for 24 h at room temperature. Cotton fibers increased its weight by 286%. Ionogel treated cotton fibers are more stable towards water, especially the hybrids prepared with a uniformly dispersed CNT network around the fibers.

The results showed that the lower bending strength for Ct/$Ti(OBu)_4$ hybrid is strongly related to the absence of MTICl. Ct/MTICl hybrids show great hydrophobicity due to the presence of hydrophobic $Si(OEt)_3$ groups [37], but a weak breaking strength. It can be concluded that the best results in all cases are achieved using ionogel precursors for preparation of hybrid cotton fiber-thread.

4 Conclusions

In this study we presented a novel method of using ionogels as modifiers for CNTs and cotton fibers. Problems of dissolving polar bucky gels in non-polar alkoxides and of covalently modifying organic-inorganic hybrids were solved. MTICl helps to avoid CNTs' natural tendency to self-form ropes and bundles. This simple route, carried out by ionic liquid and carbon nanotube network in titania matrix, opens up opportunities for functionalization of differently shaped and sized sol-gel

Table 3: Mechanical properties and dimensional stability of different cotton hybrids.

Material	°C, time	MTICl %	ΔW%	Tt (Tex)	Bf (N)	Us (cN/Tex)
Cotton treads (Ct)	21, 2 weeks	-	286	36 ± 3	4.7 ± 0.1	13.0
Ct+MTICl/ $Ti(OBu)_4$	21, 2 weeks	3	51	57 ± 3	8.8 ± 0.2	15.4
Ct+MTICl/ $Ti(OBu)_4$	21, 2 weeks	8	45	59 ± 3	9.4 ± 0.2	15.9
Ct+MTICl/ $Ti(OBu)_4$	21, 2 weeks	12	28	61 ± 3	10.3 ± 0.2	16.9
Ct+MTICl/ $Ti(OBu)_4$	100, 4 hours	12	34	49 ± 3	7.5 ± 0.2	15.3
Ct+MTICl/ $Ti(OBu)_4$+CNTs	21, 2 weeks	8	20	62 ± 4	12.2 ± 0.3	19.7
Ct+MTICl/ $Ti(OBu)_4$+CNTs	100, 4 hours	8	26	56 ± 4	8.9 ± 0.3	15.9
Ct+ $Ti(OBu)_4$	21, 2 weeks	-	180	55 ± 3	7.9 ± 0.2	14.4
Ct+MTICl	21, 2 weeks	-	32	45 ± 3	5.9 ± 0.1	13.1

materials. We prepared ionogels based on imidazolium salts and titanium alkoxide. MTICl can be involved in sol-gel processes through ethoxy groups with a titanium alkoxide network by covalent bonding. Coating cotton fibers with ionogel, IL behaves as a plasticizing agent and as compared to the classical sol-gel coatings - stronger, crack-free, hydrophobic and more stable coatings for cotton fibers are achieved. Ionogel modified cotton fibers can be utilized in formulations which have UV-shielding properties as well as for antibacterial properties. Long-lasting treatment in a washing machine didn't damage the ionogel coating on the fibre. The hydrophobic nature and thermal stability of these hybrid cotton materials makes them suitable for the preparation of packing or insulating materials; addition of CNTs improves the mechanical and electrical properties of the fibers.

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