CELLULOSE CHEMISTRY AND TECHNOLOGY

FABRICATION AND CHARACTERIZATION OF CELLULOSE/CNT NANOCOMPOSITE PAPERS

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In this research, cellulose/carbon nanotube (CNT) nanocomposites were prepared by a papermaking process. The nanocomposites containing different amounts (1-7 wt%) of CNTs were obtained from Kraft pulp. An anionic surfactant, sodium dodecyl sulfate (SDS) was used for CNTs dispersion. Bleached Kraft pulp was dispersed in water. Cationic surfactant, cetyltrimethylammonium bromide (CTAB), was used as fixer. The structural, electrical and mechanical properties of the nanocomposites were studied by field emission scanning electron microscopy (FESEM), and using a Keithly microprobe (current-voltage measurement system). The obtained results showed that the electrical conductivity of handmade nanocomposite papers changed from 5×10^{-11} to 5×10^{-7} S/m for 1-7 wt% of CNTs. The effect of CNT amounts were studied on different properties, such as tensile, tear and burst indices. The tensile, bursting and tearing strengths of the nanocomposites decreased when the added amount of CNTs was increased. This phenomenon can be explained through the role of CNTs in diminishing the strong intra-molecular attraction between the cellulose chains. Thus, it reduced the tensile strength of the prepared nanocomposites by weakening the hydrogen bonds among cellulose chains.

Keywords: nanocomposites, cellulose, carbon nanotube, surfactant, properties, mechanism

INTRODUCTION

Cellulose is one of the most naturally abundant biopolymers. Cellulose derivatives have been used for coatings, laminates, optical films and pharmaceuticals.[1] Due to its biocompatibility and biodegradability, cellulose has been utilized in many new application fields. One of these is the field of sensors and actuators, where cellulose paper is used as a smart material.[2] For many industrial applications, a uniform and stable dispersion of particulate matter plays an important role. This requirement is critical when submicron- or nanometer-sized particles are involved. In such ranges, surface chemistry controls the dispersion state of the particles within the final product. It is extremely important to learn how to manipulate the surface properties in order to achieve a product with the desired properties.

A surfactant's property of accumulation on surfaces or interfaces has been widely utilized to promote stable dispersions of solids in different media.[3-7] Those amphiphilic molecules, *i.e.*, compounds having both polar and apolar groups, adsorb at the interface between immiscible bulk phases, such as oil and water, air and water or particles and solution, and act to reduce the surface tension. The distinct structural feature of a surfactant originates from its "duality": the hydrophilic region of the molecule or the polar head group, and the hydrophobic region or the tail group that usually consists of one or a few hydrocarbon chains. Surfactants are classified according to the charge of their head groups, thus cationic, anionic, nonionic or zwitterionic surfactants are known.

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Two important features that characterize surfactants, namely adsorption at the interface and self-accumulation into supramolecular structures, are advantageously used in processing stable colloidal dispersions. The adsorption of surfactants onto inorganic and organic surfaces usually depends on the chemical characteristics of particles, surfactant molecules and solvent. Thus, the driving force for the adsorption of ionic surfactants onto charged surfaces is the Coulombic attraction, which is formed, for example, between the surfactant's positively charged head group and the negatively charged solid surface. The mechanism by which nonionic surfactants adsorb onto a hydrophobic surface is based on a strong hydrophobic attraction between the solid surface and the surfactant's hydrophobic tail. Once the adsorption of surfactant molecules on particle surfaces is established, self-organization of the surfactant into micelles (aggregative structures of surfactants) is expected to occur above a critical micelle concentration (CMC).[8]

As an effective nanoscale reinforcement, carbon nanotubes (CNTs) have attracted great interest in the field of conducting polymer nanocomposites.[9,10] These nanocomposites should possess good mechanical properties, excellent electrical and thermal conductivities, which are considered useful attributes for many applications in the electronics industry.[11-13] However, the high aspect ratio and the flexibilities of CNTs,[14]along with the van der Waals forces between them, cause CNTs to be severely entangled in close packing upon synthesis.[15]Furthermore, the chemically inert nature of CNTs leads to poor dispersibility and weak interfacial interactions with a polymer matrix.

Various methods have been developed in recent years to efficiently disperse individual CNTs in a polymer matrix. Direct mixing of the CNTs and the polymer, with[16] or without[17] the help of a solvent, has proven to be efficient and appears to be the easiest and least laborious way to achieve this goal. On the other hand, the dispersion of the nanotubes in a polymer matrix is often rather inhomogeneous, even sometimes with formation of millimeter-scale inhomogeneities. However, the existence of a certain amount of agglomerates can be a key factor in considerably lowering the value of the percolation threshold and increasing the conductivity.[18-21] Modifying either the nanofiller surface itself or the polymer matrix by functionalization improves the quality of the interface between two components of the nanocomposite by enhancing the interfacial interactions, but this approach has some drawbacks. In one possible case, the interaction of the filler with the polymer is realized by covalent binding, and in another case, by means of π–π stacking. Both approaches lead to disturbances of the π-electrons delocalization of the CNTs surfaces, which results in a significant deterioration of its electrical properties. Another main approach to incorporate a nanofiller into a polymer matrix is based on the use of a third component, *i.e.*, a surfactant.

Very recently, Lee[22] and Sun[23] reported the preparation carbon nanotube/cellulose papers by dip-coating and vacuum filtration methods, respectively, in the presence of anionic surfactant.

In this work, we prepared cellulose/CNT nanocomposite papers containing different amounts of CNTs. An anionic surfactant, sodium dodecyl sulfate, (SDS) was used for CNT dispersion. Bleached Kraft pulp was dispersed in water. Cationic surfactant, cetyltrimethyl ammonium bromide (CTAB), used as fixer, was then added to the pulp and mixed with the CNT dispersion. The CNT-pulp was then transformed into cellulose/CNT paper using a common papermaking process. Structural, electrical and mechanical properties of the prepared nanocomposites were studied by scanning electron microscopy (SEM) and using a Keithly microprobe (current-voltage measurement system). Also, the effect of CNT amounts was studied on different properties, such as tensile strength, tear and burst indices of nanocomposites.

EXPERIMENTAL

Cellulose/CNT nanocomposite preparation

Multi-walled carbon nanotubes (MWCNTs) were provided by Neutrino Corporation (Iran). The average diameter of the CNTs was 10-20 nm, and the length was 0.5-2 µm. An anionic surfactant, sodium dodecyl sulfate (SDS) (Merck, 8.22050) was used to disperse CNTs. Bleached kraft pulp was dispersed in water. Cationic surfactant, cetyltrimethyl ammonium bromide (CTAB), (Merck, 1.02342) used as a fixer, was then added to the pulp and mixed with the CNT dispersion. The CNT-pulp was then transformed into cellulose/CNT paper using a common papermaking process. We prepared five samples with different CNT contents of 1, 2, 3, 5 and 7 wt%. Table 1 shows the amounts of CNTs, SDS and CTAB that we used for preparing the nanocomposites. For example, we prepared the nanocomposite containing 1% CNTs as follows: 0.05 g CNTs and 0.1 g SDS were added to 100 mL distilled water and stirred in an ultrasonic bath for 1h at 25 ºC (suspension A). An amount of 5 g of pulp and 0.126 g CTAB were added to 250 mL distilled water and mechanically stirred for 1h at 25 ºC (suspension B). Then, suspension A was added to suspension B and stirred for 1h at 25 ºC. The obtained sample (black color CNT-pulp) was then filtered and washed with distilled water. The CNT-pulp was then transformed into cellulose/CNT paper using a common papermaking process. The prepared cellulose/CNT nanocomposites are labeled as NKP(a), where N: nanocomposite, KP: Kraft pulp and (a) is the nominal weight percentage of CNTs in the final solid. We used TAPPI standard method (T 205 sp-02) for the papermaking process.

Characterization

Electric conductivity was measured by a microprobe (IV Measurment Keithley 2361). The voltage was increased from -100 to +100 V to check the linearity of current-voltage characteristics. Structural, electrical and mechanical properties of the prepared nanocomposites were studied scanning electron microscopy (FESEM), and using a Keithly microprobe (current-voltage measurement system). Also, the effect of CNT amounts was studied on different properties, such as tensile strength, tear and burst indices of nanocomposites.

RESULTS AND DISCUSSION

SEM analysis

The cellulose fibers had negative charges on their surfaces when dispersed in water. This is due to the carboxyl groups that were generated during the papermaking processes, such as cooking or bleaching.[24] Chemicals are usually fixed to cellulose fibers during paper manufacturing using this electrical charge. When an anionic surfactant is used to disperse the CNTs, the surfaces of the CNTs also have negative charges. Therefore, a cationic fixer can be applied to fix the CNTs to the cellulose surfaces. Figures 1 and 2 present FESEM micrographs of the prepared nanocomposites (with two magnifications: 30 and 5 KX). Figure 1 (Mag. = 5 KX, 200 nm) reveals the interconnected network established by individual CNTs. Carbon nanotubes can be found on the surfaces of the cellulose fibers connected to each other. The CNTs easily aggregate due to their van der Waals force, so it is important to prevent them from self-agglomerating before bonding with the cellulose. With a loading of 3 and 5 wt% of CNTs, larger diameters are observed, which suggests that the MWCNTs were wrapped in or covered by a cellulose layer, indicating good adhesion between the CNTs and the cellulose. In contrast, with a CNT loading of 7 wt% (NKP(7)), severe aggregation of CNTs and poor interfacial adhesion between CNTs and cellulose are remarked. This could result in the slipping of CNTs and failure to transfer the load from the cellulose matrix to the CNTs, with a consequently significantly reduced reinforcement capability of the CNTs.[21]

Electrical and mechanical properties of cellulose/CNT nanocomposites

The properties of each composite material are shown in Table 2. The cellulose/CNT composites show electric conductivities. This is attributed to the high aspect ratio of CNTs, which make a network as many conduction paths are effectively formed. It is necessary to optimize the fabrication method for different CNT dispersions.[25] The tensile, bursting and tearing strengths of the composites are also shown in Table 2.

The tensile, bursting and tearing strengths of the composites decreased when the added amount of CNTs was increased. However, as described above, CNTs can improve the electric conductivity even when added in small amounts because they form a network structure in the material. Due to this, they interfere with the hydrogen bonding of the cellulose fibers less than other carbon materials do, resulting in highly strong material.

Table 1
Nominal amounts of CNTs and surfactants

Sample	CNT (g)	SDS(g)	CTAB(g)
NKP(1)	0.05	0.1	0.126
NKP(2)	0.10	0.2	0.250
NKP(3)	0.15	0.3	0.379
NKP(5)	0.2	0.5	0.632
NKP(7)	0.25	0.7	0.885

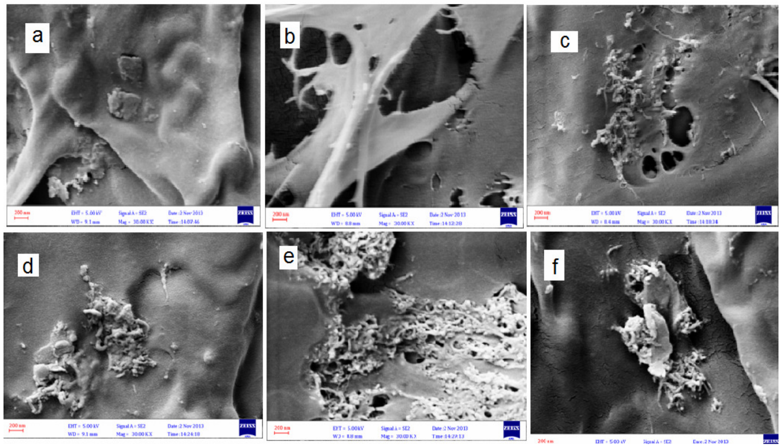

Figure 1: FESEM micrographs of a) NKP(0), b) NKP(1), c) NKP(2), d) NKP(3), e) NKP(5) and f) NKP(7) (Mag. = 30 KX, 200 nm)

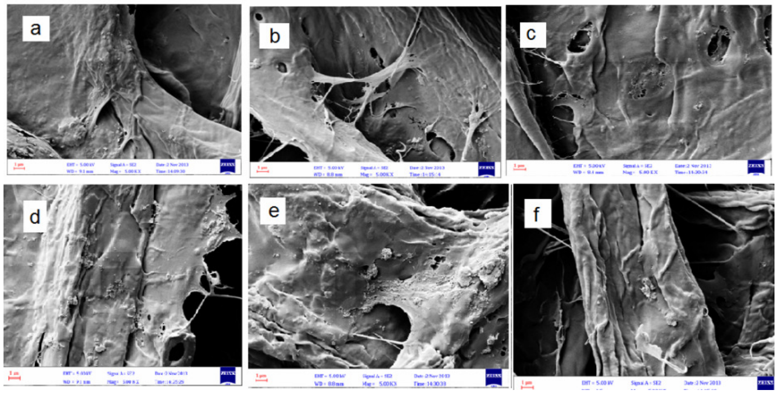

Figure 2: FESEM micrographs of a) NKP(0), b) NKP(1), c) NKP(2), d) NKP(3), e) NKP(5) and f) NKP(7) (Mag. = 5 KX, 1µm)

Table 2
Properties of cellulose/CNTs nanocomposite papers

Sample	Basis weight (g/m^2)	Electrical resistivity (Ω)	Electrical conductivity (S/m)	Tensile strength (N/m)	Bursting strength (kPa)	Tearing strength (mN)
NKP(0)	63	2.0×10^{10}	5.0×10^{-11}	24.35	129	162
NKP(1)	61	2.0×10^{10}	5.0×10^{-11}	20.5	107	162
NKP(2)	62	1.0×10^{10}	10×10^{-11}	19.22	98	146
NKP(3)	64	9.0×10^{9}	11×10^{-11}	18.26	80	146
NKP(5)	63	1.0×10^{8}	1.0×10^{-8}	14.74	68	106
NKP(7)	62	2.0×10^{6}	5.0×10^{-7}	13.18	60	81

The bursting strength of paper or paperboard is a composite strength property that is affected by various other properties of the sheet, principally tensile strength and stretch. Generally, bursting strength depends upon the kind, proportion, and amount of fibers present in the sheet, their method of preparation, their degree of beating and refining, upon sheet formation, and the use of additives.[26] Also, tearing resistance is primarily a property of the inner structure of the sheet, but surface treatment sometimes affects the values to a marked degree. In this work, surface modification of the cellulose network and CNTs by cationic and anionic surfactants, respectively, can change the bursting and tearing strength of the prepared composites.

Also, as our literature survey showed, we can discuss about the plasticizing effect of a surfactant by tensile strength results of the prepared nanocomposites. Sapuan *et al.* studied the effect of different plasticizer types and concentrations on the tensile strength of SPS films.[27] The presence of a plasticizer in a low concentration led to a high tensile strength value of different plasticized films. The possible reason for the high tensile strength at low plasticizer concentration is the domination of strong hydrogen bonds produced by starch–starch intermolecular interaction over starch–plasticizer attraction. However, the addition of plasticizers in concentrations from 15% to 45% caused significant reduction in the tensile strength of the films, regardless of the plasticizer type. The decrease in the tensile strength of starch and cellulose based films as the plasticizer concentration increased was reported by numerous authors.[28-30] This phenomenon can be explained by the role of a plasticizer in diminishing the strong intra-molecular attraction between the starch chains and promoting the formation of hydrogen bonds between plasticizer and starch molecules. Thus, it reduces the tensile strength of SPS plasticized films by weakening the hydrogen bonds between starch chains.[25]

In the case of our work, we observed a reduction in the tensile strength of the prepared nanocomposites (Table 2), which may lead to the conclusion that the surfactant concentration was too high, and it could reduce the strong intra-molecular attraction between the cellulose chains, promoting the formation of hydrogen bonds between surfactant and cellulose molecules. Also, Imai *et al.*[23] studied the tensile strengths of CNT/cellulose nanocomposites containing different amounts of CNTs. They observed that when the CNT content was low, the tensile strength of the CNT/cellulose composite was almost the same as that of plain paper. Inter-fiber bonding of cellulose consists in hydrogen bonding, and adding much carbon or fibers without hydroxyl groups to the pulp inhibits the interaction between cellulose fibers. The tensile strength decreased when the added amount of carbon material was increased. However, as described above, CNTs can improve the electric conductivity even when added in small amounts because they form a network structure in the material. Due to this, they interfere with the hydrogen bonding of the cellulose fibers less than other carbon materials do, resulting in highly strong material. From the above data, we can prove the presence of CNTs and surfactant, as the interaction between cellulose chains was weakened and the tensile strength of the nanocomposites was reduced.

Our proposed mechanism

The dispersion of carbon nanotubes in the cellulose matrix plays an important role in the nanocomposite's performance. To optimize the papermaking process for cellulose/CNT composites and the quality of the resultant paper, it is important to improve the interaction between the pulp fibers and paper chemicals used in the process. The main interaction between these chemicals is ion binding; whether or not these chemicals bond with the pulp fibers depends on the charge of the pulp suspension. Pulp fibers have negative charges because they generate carboxyl groups during the papermaking processes, such as cooking or bleaching. When an anionic surfactant is used to disperse CNTs, CNT surfaces also have negative charges. Therefore, a cationic fixer can be applied to fix the CNTs to the pulp. CNTs are known to make strong aggregates due to van der Waals force. Therefore, it is important to prevent dispersed CNTs from self-agglomeration before they bond with cellulose fibers. For this purpose, a cationic fixer is mixed with cellulose fibers, so that it adsorbs on the cellulose surfaces before the CNT water dispersion is added. Fixers have three adsorption states on surfaces: train, tail and loop (Fig. 3).[31] The train segments are the parts that contact the surface, and the loop and tail segments diffuse in solvents. When a CNT anionic dispersant is added to the cellulose-fixer mixture, the loops and tails of the fixer adsorb on the CNT surfaces and create cross-linkage between the cellulose fibers and CNTs; the bonding of CNTs to cellulose fibers were facilitated.[23] Figure 4 illustrates our proposed mechanism for interaction between the MWCNTs, cellulose, cationic surfactant (CTAB) and anionic surfactant (SDS) in our prepared nanocomposites.

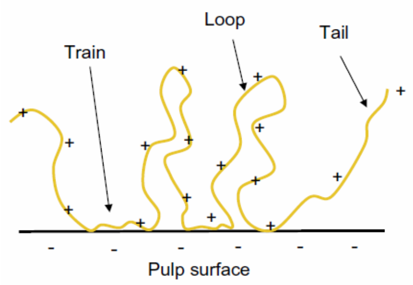

Figure 3: Adsorbed state of surfactant on solid surfaces in water dispersion[31]

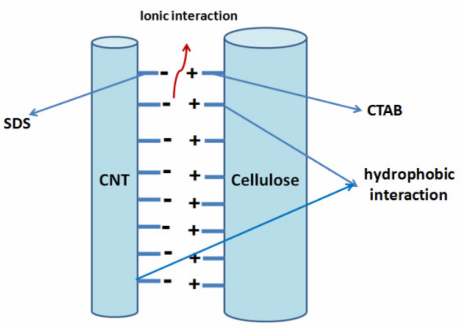

Figure 4: Our proposed mechanism for interaction between MWCNTs and cellulose after surface modification by surfactants

CONCLUSION

We fabricated cellulose/CNTs nanocomposite materials containing different amounts of CNTs, using a papermaking process. This goal was achieved by dispersing CNTs into individual tubes, followed by transferring these tubes onto the surfaces of cellulose fibers. We used an anionic surfactant (SDS) for CNT dispersion and a cationic surfactant (CTAB) as a fixer. The electrical conductivity of the prepared nanocomposites was increased by increasing the CNT amounts. The tensile, bursting and tearing strengths of the nanocomposites decreased when the added amount of CNTs was increased. Inter-fiber bonding of cellulose is hydrogen bonding, and adding a high amount of CNTs without hydroxyl groups to the pulp inhibits the interaction among cellulose fibers. The tensile strength decreased when the added amount of carbon material was increased.

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