Structure and physical properties of cellulose triacetate/ nanoclay nanocomposites

Tariq R Sobahi[1], Magdy Y Abdelaal[1, 2], Mohamed Abdel Salam*[, 1]

[1]Chemistry Department, Faculty of Science, King Abdulaziz University, PO Box 80203, Jeddah 21589 Saudi Arabia
[2]Chemistry Department, Faculty of Science, Mansoura University, 35516 Mansoura, Egypt
E-mail: masalam16@hotmail.com

The nanoclay has been used to modify cellulose triacetate by forming nanocomposites of different composition. The nanoclay and cellulose triacetate as well as the resulting nanocomposites were identified using Scanning Electron Microscopy (SEM). The mechanical and thermal properties of different nanocomposites are also investigated. It was generally observed that the addition of the nanoclay to cellulose triacetate increased the thermal conductivity, tensile strength and Young's modulus by 415, 81 and 93%, respectively, on adding only 5% of the nanoclay to cellulose triacetate.

Keywords: Nanoclay, Cellulose triacetate, Nanocomposites, Thermal properties, Mechanical properties

The need for new types of materials attracted much attention because the existing materials either are not enough for the usage and applications of the mankind, or more advanced materials with new properties are needed. Hence, most of the research scientists focused till now to explore the material science in order to synthesize new advanced materials with exceptional and distinguished properties compared with the existing ones. The research scientists focus on development of new materials or modification of the existing materials and mixing them to improve their properties. Nanotechnology and nanomaterials are playing a crucial role in the modification of the existing materials with extraordinary properties. Nanoclays are new attractive nanomaterials which are showing extraordinary properties. Nanoclays are mineral silicates ordered as layered nanoparticles which are organized into several classes based on chemical composition and morphology. Kaolinite, bentonite, halloysite, hectorite and montmorillonite are representative examples for nanoclays. Organoclays are modified nanoclays with organic materials which attracted much attention as a class of hybrid organic-inorganic nanomaterials with potential uses in polymer nanocomposites for different applications such as flame retardant[1], Electrical and electrochemical properties improver[2,3] and promising in water remediation[4]. In this research proposal, different nanocomposites of cellulose triacetate (CTA), with different nanoclays have been prepared and characterized by using scanning electron microscope and thermal analysis. The different physical and mechanical properties of the produced nanoclay/CTA nanocomposites have been investigated.

Experimental Section

Materials

Cellulose triacetate with acetyl content of 43-45 wt% was supplied by ACROS ORGANICS CO; the M.W. was ~ 970 g/mol. Chloroform was used as a polymer solvent. Two types of nanoclay, namely halloysite and bentonite, were purchased from Sigma-Aldrich. Halloysite is a naturally occurring aluminosilicate nanotubes with average dimensions of 15 μm which are chemically similar to kaoline. Both halloysite and bentonite were modified by tetraethylammonium chloride and hexadecyltributyl phosphonium bromide salts and all of the materials required for the modification were obtained from the Sigma–Aldrich Co. All chemicals were used as received without further purification.

Chemical modifications of the clay

Ion exchange reactions between the nanoclay and the two different surfactants were used to modify the nanoclays. A salt solution was heated at 50–80°C for one h and a hot aqueous suspension of the clay (5 g/400 mL) was added. The mixture was stirred for 4 h at 70°C. The cation exchanged silicates were filtered off and subsequently washed with hot ethanol/water mixture until negative silver nitrate test indicating the absence of halide anions. The obtained materials were

dried at room temperature, ground, and further dried overnight at 70-80°C under vacuum.

Synthesis of cellulose triacetate/organoclay nanocomposites

Solution dispersion method was used to prepare the nanocomposite membranes in presence of chloroform as a solvent. Cellulose triacetate was dissolved in a suitable amount of chloroform (25 mL) under constant stirring at room temperature for 3 h followed by sonication for 10 min for homogeneous mixing of the components. Then, 5 wt% of an organoclay was also dissolved in a small amount of chloroform (5 mL) and was sonicated in a water bath until a clear homogenous suspension was obtained. The desired CTA/organoclay composites were obtained by mixing both solutions and stirring the solution for 15 min. The resulting solution was poured into a glass blade (mold); evaporation of CH_3Cl yielded homogenous films (25 μm thick). Components of cellulose triacetate/organoclay nanocomposite membranes are summarized in Table 1.

Instrumentation

The obtained nanocomposites were investigated by FT-IR spectroscopy in the region from 4,000 to 400 cm^{-1} using a JASCO model FT-IR 310 spectrophotometer. The thermal properties were investigated using a Shimadzu Thermal Analyzer. Polymer samples of approximately 10 mg were heated from 0 to 900°C with a scan rate of 10.0°C/min in an air atmosphere. Scanning electron microscopy (SEM) images were collected using a Quanta 600 FEG with a 20 kV voltage. The surfaces were sputter-coated with gold with a Bal-tec SCD 050 metallizer to make the surface conductive. According to an ASTM D882-02 standard, an Instron Model 5567 tensile strength measuring machine was used at room temperature with a crosshead speed of 50 $mm.min^{-1}$ to determine the tensile strength of the samples. CTA nanocomposite specimens were cut in the bone dog shape with the dimensions illustrated in Fig. 1.

Results and Discussion

The present work focuses on the preparation and characterization of CTA-based organoclay nanocomposites ($CTAH_{1-3}$, $CTAB_{1-3}$) *via* solution casting. Before the preparation, halloysite and bentonite were chemically modified by ammonium and phosphonium quaternary salts. Different compositions of CTA and organoclay were used to study the nanoclays impact on the morphology, thermal, and mechanical properties. The desired

products showed good antibacterial activities against both Gram-negative and Gram positive bacteria. Pure CTA, $CTAH_{1-3}$, and $CTAB_{1-3}$ were characterized with different methods including FT-IR, SEM & TEM, thermal analysis, and mechanical properties.

Spectroscopic characterization of CTA nanocomposite

FT-IR was used to examine the extent of the interaction between clay and the polymer matrix. The common features of organoclays were clearly observed from the FT-IR spectra Fig. 2. FT-IR results showed
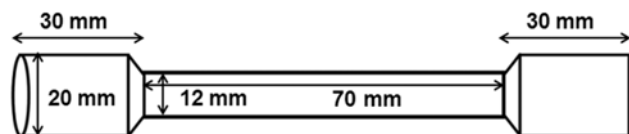

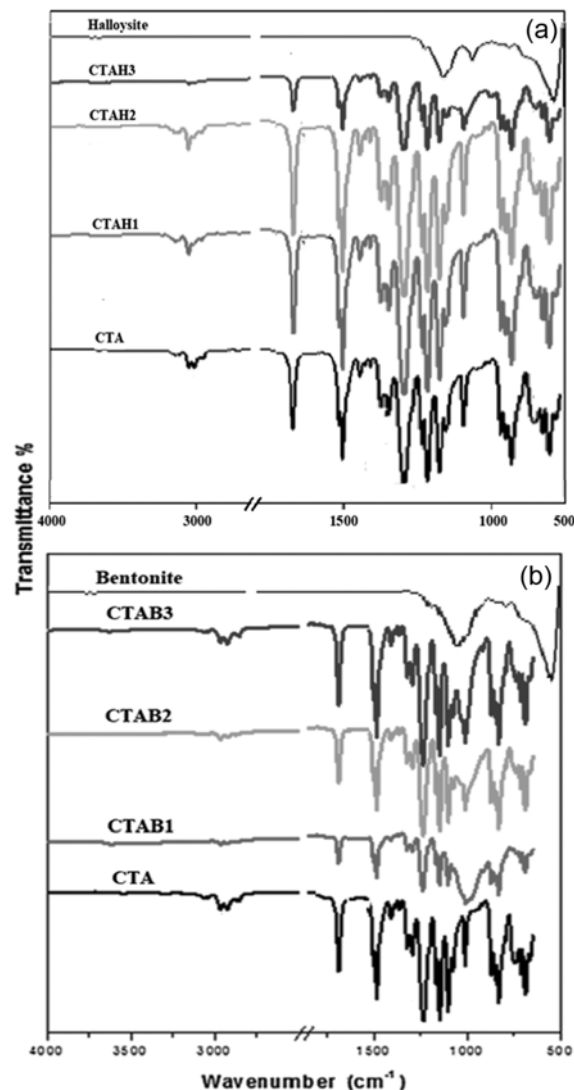Fig. 1 — Mechanical testing specimen with dimensions.

Fig. 2 — FT-IR spectra of a) pure CTA, $CTAH_{1-3}$ & pristine halloysite, and b) pure CTA, $CTAB_{1-3}$ and pristine bentonite

the appearance of characteristic absorption bands at 3,600 and 1,039 cm^{-1} due to the –OH stretching of water and Si–O stretching, respectively, and Al–OH at 918 cm^{-1} (Ref. 5, 6). Furthermore, the characteristic vibration bands of pure CTA were confirmed and assigned at 1,180 cm^{-1}, 1,530 cm^{-1} (C-O-C stretching), 1,730 cm^{-1} (asymmetric sulfone linkage), $3,000 \approx 3,100$ cm[-1] (aromatic CH stretching), and 2,900 cm^{-1} (aliphatic CH_3 stretching)[7]. All the peaks observed for CTA nanocomposites remained the same as those for pure CTA. These results also showed that there were no major chemical or structural changes in the CTA

Table 1 — Components of pure CTA, $CTAH_{1–3}$, and $CTAB_{1–3}$

Sample	Clay type	Modifier type
CTA	No clay	No modifier
$CTAH_1$	Halloysite	No modifier
$CTAH_2$		Tetraethylammonium chloride
$CTAH_3$		Hexadecyltributylphosphonium bromide
$CTAB_1$	Bentonite	No modifier
$CTAB_2$		Tetraethylammonium chloride
$CTAB_3$		Hexadecyltributylphosphonium bromide

nanocomposites due to the presence of organoclay[8]. In all the nanocomposite membranes, the band related to acetyl unit methyl group C–H stretching diminished, suggesting that this part of the CTA molecule displayed restricted movement in the nanocomposite structures due to the clay contents, which restricted CTA chain vibration[9]. All the bands had high intensities; however, $CTAH_3$ had low intensities, indicating the good interfacial adhesion between CTA and the organoclay. These results revealed that the phosphonium surfactant's long alkyl chains were more easily and deeply diffused into the halloysite interlayer than with the bentonites which contained obstructive water molecules[5,10]. Moreover, no regular behavior was present in relation to the intensities of the CTA bands and the type of clay[11].

Microscopic characterization of CTA nanocomposite

SEM imaging was performed to ascertain the dispersion of the clays in the CTA matrix. Figure 3(a) shows that the homogenous surface of pure CTA is smooth. The addition of the modified clay ($CTAH_2$ &
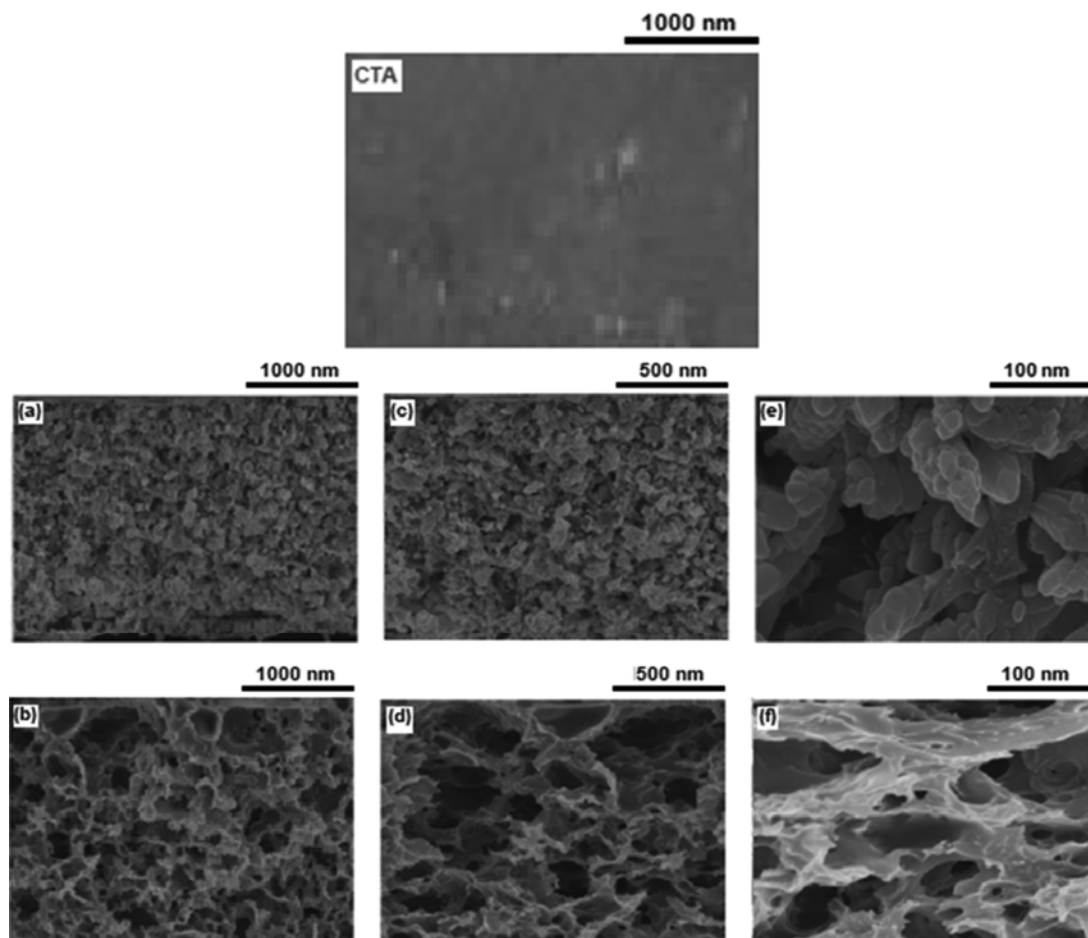

Fig. 3 — SEM images for CTA, (a,c, e) $CTAH_2$ at different magnifications and (b,d,f) $CTAB_2$ at different magnifications

CTAB$_2$) is spread randomly and homogeneously on the whole surface, Fig. 3(a) and (b). Moreover, the clay particles are closer to each other and display poor interfacial adhesion between CTA and platelets due to their incompatibility. Figure 3(c), (d) and their magnifications in Fig. 3(e), (f) which shows that the spaces between the modified clay particles (CTAH$_2$ & CTAB$_2$) are increased due to the presence of alkyl groups. Moreover, the images of (CTAH$_2$, & CTAB$_2$) indicated that the top surfaces of the clay particles are pale due to increase in the hydrophobicity property and the good compatibility between the CTA and organoclay layers[12]. Moreover, the clay layers are separated in the continuous polymer matrix by an average distance that depends on modified clay loading. It is worth to mention that the morphology of the unmodified nanoclays, namely halloysite and bentonite, are shown in Fig. 4(a), (b), respectively for their TEM images.

Mechanical characterization of CTA nanocomposite

The mechanical properties of the organoclay reinforced the CTA nanocomposites (CTAH$_{1-3}$ & CTAB$_{1-3}$). The neat CTA matrices were evaluated by tensile studies that included examining the tensile strain at break and the modulus of elasticity in tension. Polymers have a basic elasticity; the addition of nanoparticles made the elastic polymers more brittle due to pinning at the clay interaction sites, as the deforming forces are then transferred to the nanoclay. The tensile strain at break is considered an essential measure of ductility and is related to the clay type. As evident from the test results reported in Table 2 and Fig. 5, pure CTA showed a percentage tensile strain at break of 25.16%, which decreased with the addition of clay. The tensile strain at break of the nanocomposite types (CTAH$_{1-3}$) was 8.20, 5.88, and 10.05%, respectively. Also, the tensile strain at break of the nanocomposites types (CTAB$_{1-3}$) showed a large decrease in the tensile strength at break 3.66, 2.79, and 2.85%, respectively. Generally, the presence

of clay in nanocomposites makes them more brittle, causing a decrease in the tensile strain at break. In contrast, at 5 wt% clay loading discontinuity in the form of bonding is present because of the poor adherence by the layered silicate to the polymer and the stress transfer at the clay/CTA interface becomes ineffective[11,12]. Moreover, comparison of both types of cellulose triacetate nanocomposites showed that CTAH$_{1-3}$ displayed higher tensile strength at break than CTAB$_{1-3}$. This decrease in CTAB$_{1-3}$ nanocomposites could be explained by the presence of obstructive water molecules that weaken the interfacial adhesion between the CTA chains and

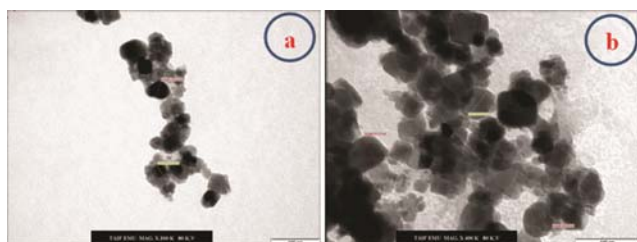Fig. 5 — Mechanical properties of the different types of CTA nancomposites

Fig. 4 — TEM images of unmodified (a) halloysite (b) bentonite nanoparticles

Table 2 — Modulus of elasticity in tension and tensile strain at break of pure CTA, CTAH$_{1-3}$, and CTAB$_{1-3}$ nanocomposite membranes

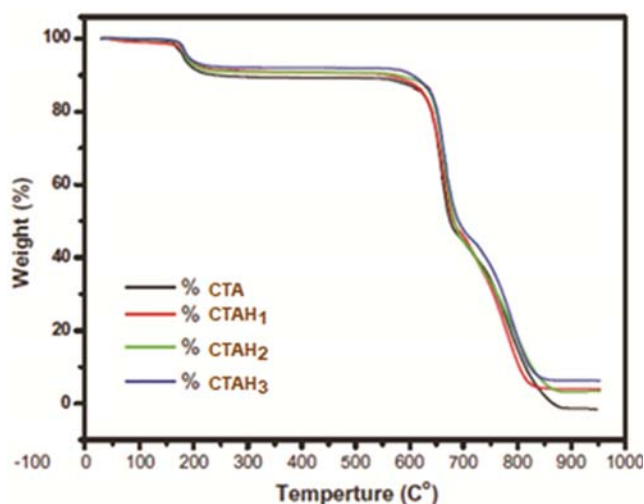| Sample	Modulus of elasticity (MPa)	Elongation at break (%)
CTA	68.33 ± 2.8	25.16 ± 0.25
CTAH$_1$	62.28 ± 2.6	8.20 ± 0.16
CTAH$_2$	43.93 ± 2.0	5.88 ± 0.16
CTAH$_3$	46.15 ± 2.4	10.05 ± 0.36
CTAB$_1$	48.59 ± 2.6	3.66 ± 0.20
CTAB$_2$	35.28 ± 2.1	2.79 ± 0.12
CTAB$_3$	37.91 ± 2.0	2.85 ± 0.16

Fig. 6 — TGA thermograms of pure CTA, CTAH$_1$, CTAH$_2$, CTAH$_3$ membranes and pristine halloysite

silicate layers. CTAH$_3$ had the highest value among the nanocomposite membranes.

This enhancement is due to the excellent clay matrix interfacial adhesion and its morphology, predominantly intercalated morphology. Pure CTA exhibited an optimum modulus of elasticity in tension of 68.33 MPa, which decreased significantly in the nanocomposite films and is primarily attributed to the presence of silicate layers, which imparted brittleness to the membranes. This phenomenon is probably due to the lack of proper dispersion by the nanocomposite membranes in CTA and the less favorable interaction between the clay and CTA matrix[13].

Thermal characterization of CTA nanocomposite

Figure 6 shows the thermal characterization of CTA nanocomposites represented by their TGA bahaviour. This figure shows that the incorporation of the nanoclays improved slightly the thermal stability of CTA up to 600°C after which the polymer matrices are broken down drastically until the temperature reaches close to 900°C. This behavior reflects the suitability of the investigated CTA nanocomposites for different applications involving thermal treatment up to 600°C only.

Conclusion

The results showed that modified nanoclays were great candidates for the modification of the cellulose

triacetate (CTA) through the formation of nanocomposites as the nanoclays worked as reinforcing material. Different modified nanoclays were mixed with CTA and the obtained CTA/clay nanocomposites were characterized with scanning electron microscopy. The results revealed the great homogeneity of the composites and the dispersion of the nanoclays within the CTA matrix. The thermal and mechanical properties of the CTA/Nanoclay naocomposites were studied and it was found that the change in the thermal conductivity was significant. Also, that the addition of the nanoclay enhances the tensile strength of CTA as well as the other mechanical properties. Further increase in the nanoclay content is accompanied by little decrease in the thermal conductivity and mechanical properties of the CTA/nanoclay nanocomposites due to the difficulty in dispersion of nanoclay in nanocomposites.

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