Preparation and Characterization of Cellulose/Montmorillonite Hybrid Membranes

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Abstract: The compounding of cellulose and inorganic Montmorillonite (MMT) on microscale molecular level has high potential to greatly improve the thermal stability, decay resistance and other properties of cellulose fibres. Pristine Algerian MMT was first sodium modified as Na-MMT, then organically modified as organophilic OMMT by using Octadecylamine. With OMMT and fibrous cellulose from waste cotton, cellulose/MMT composites were prepared *via* incorporation from solution process and characterized by XRD, FTIR and TGA. Dimethyl Acetamide/Lithium Chloride (DMAc/LiCl) solvent system was used for dispersing cellulose and clay. Results show that the preparation of OMMT was very successful; the X-ray diffraction results revealed that the interlayer spacing (2.17nm) for OMMT was increased compared with that (1.24nm) for Na-MMT. The composites exhibit higher thermal stability; addition of OMMT can considerably increase the decomposition temperature of cellulose matrix. An increase in thermal stability with clay content was observed by thermal analysis.

Keywords: Cellulose, montmorillonite, composite membrane, solution intercalation, thermal stability.

1. INTRODUCTION

Polymer/clay composites are a new class of materials obtained by dispersion of high quality ratio silicate particles in a polymeric matrix [1-4]. The incorporation of inorganic particles into polymer matrices has long been studied and the results show improved mechanical, thermal, and barrier polymer properties due to the presence of these dispersed particles. At the microscopic scale, the inorganic particles improve significantly both stability and properties of polymer even with a small loading. In recent years considerable research attention has been focused on these hybrid materials due to the effect of their thermal stability, their gas barrier properties, as well as their mechanical properties [5-9]. By adding just a tiny amount of clay to the polymer matrix, the composite materials exhibit significant decrease in the peak heat release rate, change in the char structure, and decrease in the mass loss rate during combustion in the cone calorimeter [10-13].

Montmorillonite clay is the layered silicate which has been widely used in polymeric matrices due to its multiscale organization. It is made of thicker platelets of some hundred nanometers long and wide. These platelets are stacked in primary particles which are themselves grouped into aggregates. In order to improve dispersion of these fillers in polymeric matrixes, organic surfactants and compatibilizers are added. The obtained product is known as "organoclay". In this context, organoclays can be readily delaminated into nanoscale platelets by the polymer molecules, leading to the formation of polymer-clay composites.

In the pristine state, layered silicates are only miscible with hydrophilic polymers, such as poly (ethylene oxide) [14], or poly (vinyl alcohol) [15]. To make layered silicates miscible with polymer matrixes, the hydrophilic silicate surface must be improved to an organophilic one, allowing possible intercalation of many engineering polymers. Generally, this can be done by ion-exchange reactions with surfactants including alkylammonium cations.

Alkylammonium cations lower the surface energy of the inorganic particles, improve the wetting characteristics of the polymer matrix and result in a larger interlayer spacing. Additionally, these cations can provide functional groups that can react with the polymer matrix, or in some cases initiate the polymerization of monomers to improve the interaction between silicate and polymer matrix [16].

Cellulose is a porous material, the microscale voids in fibres show that cellulose has inherent space to accommodate microsized materials. Due to their low density, low cost, renewability and good specific mechanical characteristics, cellulose and other raw fibers from biomass are increasingly being used as polymeric matrices [17-19]. Cellulose has a variable physical stability; therefore chemical modification of cellulose can be carried out to achieve adequate structural durability. Chemical modification can be used to vary certain properties of cellulose such as its

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hydrophilic or hydrophobic character, elasticity, and thermal resistance.

Compounding cotton cellulose and inorganic Montmorillonite (MMT) on nanoscale molecular level is very promising to greatly enhance cotton fibre fire retardancy, abrasion resistance, decay resistance, and dimensional stability [20, 21].

The present work focuses on the preparation and characterization of cellulose-clay hybrid membranes made from cotton linters fibres and modified Montmorillonite. The inorganic filler was first Namodified then the Na^+ was exchanged with ammonium cation to get organophilic clay. Thin membranes of Cotton cellulose/organoclay were thus obtained by precipitation in acetonitrile. Next, characterization of the materials: thermal analysis and structural characterization were carried out in order to better understand the behaviour of the composites.

2. MATERIALS AND METHODS

2.1. Chemicals and Materials

The pristine clay mineral used in this work was the montmorillonite from Maghnia (west Algeria) purified and Na-MMT modified. The fraction with particle size smaller than 2µm was obtained after careful aqueous decantation of the natural clay. The same fraction was then used for all experiments. Its cation exchange capacity was 90meq/100g. The organic intercalation agent C18 was octadecylamine (Sigma-Aldrich) protonated by treating it with hydrochloric acid (Panreac Monplet and Esteban).

Dimethyl Acetamide (DMAc) and Lithium Chloride, Merck products, were used as received in the cellulose treatment. Acetonitrile (Sigma-Aldrich) used to precipitate the composite membranes was also used as received.

The fibrous cellulosic support used was a short fibres collected from waste cotton mill. The fibres were washed and bleached in laboratory. The nature is a Syrian Gossypium variety. Physical form: spirally white fibres, Length: 8-14mm, Conventional Moisture content: 8.5%, α-cellulose content: 88-90%, Hemicelluloses content: < 1%, Product density: 1.54g/cm^3.

2.2. Preparation of Montmorillonite Clay

Because sodium cations in MMT are easier to be substituted for organic cations, Na-MMT has higher economic value and wider application than other clays. The pristine MMT sample is Na-modified by treatment using NaCl solution (0.5M). The fraction of clay is separated by sedimentation. The Namontmorillonite collected is washed three times with distilled water and dried in oven at 80°C for 72hours and then stored.

The exchangeability of interlayer cations can be utilized to modify MMT and enhance its compatibility with polymer. An exchange of these cations for organic onium ions will lower the surface energy of clay layers, enlarge the interlayer distance to accommodate polymers, render the silicate surface organophilic, and improve the miscibility between clay and polymers. Na-MMT can generally be organically modified through two paths, i.e. dry and wet processing. Dry processing is carried out in melt modifier. Wet processing, the most widely used way, is operated in water solution of intercalation agent.

The organophilic Montmorillonite (organoclay, termed OMMT) was prepared *via* ion-exchange reaction using alkylammonium. Na-MMT (10g) was ion exchanged with C18 octadecylammonium in a 1:1 (weight ratio) ethanol-water mixture (500ml) at 80°C for 3h under stirring. The product was filtered and washed repeatedly with the ethanol-water mixture until no Cl^- was detected in the filtrate by a 0.1mol/l $AgNO_3$ solution. The OMMT final product was vacuum dried for 36h at 85°C and finally ground into powder.

2.3. Preparation of Cellulose-OMMT Clay Nanocomposites

Purpose of the association of polymer into the gallery of silicate layers is to reduce interlayer attraction and homogeneously disperse the layers in polymer matrix. On the whole, intercalation compounding includes two methods, i.e. monomer in-situ intercalation polymerization and direct polymer intercalation, which can be respectively applied in two approaches, i.e. solution intercalation and melt intercalation. We applied cellulose solution intercalation; the fibrous matrix was allowed to partially dissolve before intercalation.

2.3.1. Cellulose Partial Dissolution

Cellulose has three reactive hydroxyl groups per anhydroglucose repeating unit that form inter- and intramolecular hydrogen bonds. These bonds strongly influence the chemical reactivity and solubility of cellulose. As a result, cellulose is virtually insoluble in most common solvents, and the successful preparation of derivatives requires a special approach.

Among the various solvent systems (N-MMO, carbamation, xanthation) applied for cellulose dissolution we used the DMAc/LiCl solvent system. According to procedure of T. Heinze *et al*. [21], a known amount of dried cellulose is initially immersed in 1L of DMAc and kept at 120°C for 2h, under stirring. After the slurry had been allowed to cool to 100°C, 80g of anhydrous LiCl were added. The cellulose was softened by cooling down to room temperature under stirring overnight.

2.3.2. Incorporation of Cellulose from Solution

This is based on a solvent system in which the cellulose is melted and the silicate layers are swellable. The layered silicate is first swollen in LiCl/DMAc solvent system. When cellulose and layered silicate solutions are mixed, the polymer chains insert and displace the solvent within the interlayer of the silicate. Upon solvent removal, the enclosed structure remains, resulting in polymer layered silicate-composite. Solvent solutions were made by dissolving the appropriate amount of LiCl in DMAc at 100°C. The solvent was allowed to cool to room temperature before use. In all cases 9% LiCl/DMAc solution was the solvent used.

Cellulose-OMMT composites were obtained by mixing the softened cellulose with OMMT in the following way. In a 500ml flask fitted with reflux system, a known amount of OMMT is allowed to swell in LiCl/DMAc solvent system for 3h at 80°C. Composites containing 0, 3, 7 and 10% w/w of Montmorillonite were then prepared by mixing cellulose slurry and swelled clay for 1h at 120°C. An amount of the mixture is pressed between two glass plates; thin membranes are thus obtained by precipitation for 1h in acetonitrile. After intensive washing with acetonitrile and distilled water, the membranes were vacuum dried at 120°C.

2.4. Characterization

- The mineralogical phase composition of natural and modified clays was determined by X-ray Fluorescence Spectrometry in a Bruker AXS SRS 3400 sequential wavelength-dispersive XRF spectrometer.
- X-ray powder diffraction (XRD) patterns of the clays and composite membranes were obtained using a Panalytical X'Pert Pro diffractometer, at 45kV and 40mA, and employing Cu*K* α filtered radiation.
- FT-IR spectra were recorded in the range 4000-400 cm^{-1} in a Nicolet Magna-IR 560 ESP infrared Fourier transform spectrometer, using the KBr pellet technique (about 1mg of sample and 300mg of KBr were used in the preparation of the pellets).
- Thermal analysis was performed on SETARAM Labsys TG-DTA 12 analyzer for thermal gravimetric analysis. All measurements were carried out from 20 to 400°C at a heating rate of 10°C/min under a nitrogen flow of $20cm_3$/min. The weight loss (TG curve) was recorded simultaneously as a function of temperature.

3. RESULTS AND DISCUSSION

3.1. Characterization of Modified Clay Minerals

Vaia *et al*. had reported that organic molecules can enter the spaces between the layers of the clay in the following ways [22, 23]: (a) cationic bonding, in which the protonated alkylammonium replaces the sodium ions in the MMT layers, (b) ion-dipole interactions, in which the polar organic molecules are related to the sodium ions in the MMT layers, and (c) dipole-dipole interactions, which include the hydrogen bonding that associates polar organic molecules with hydroxyl groups or oxygen in the clay layers. The amount of organic matter incorporated to the solids during intercalation is indicated in Table **1**, together with the whole composition of the solids determined by X-ray Fluorescence Spectrometry. Thus, because of the amounts of organic matter fixed by the solids, the amount of metallic oxides also strongly changes from

Table 1: Chemical Composition of Natural and Intercalated Clay Samples

Sample	Oxides (%)									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3	Loss on drying (%)
Pristine MMT	62.92	15.59	1.97	0.35	2.03	3.62	3.36	0.20	0.33	10.04
Na-MMT	57.22	14.76	1.89	0.29	1.92	5.99	2.99	0.18	0.07	15.04
O-MMT	57.21	14.74	2.01	0.17	1.74	0.83	3.16	0.19	0.07	18.63

one sample to others. Reduction in the quartz and oxides rate (Fe_2O_3, CaO, MgO, TiO_2 and SO_3) show that there was purification of clay. Increase in sodium oxide content shows that the montmorillonite was Namodified and Na^+ cation became the main exchangeable cation in the clay. In addition, it is remarkable that the amount of Na^+, the main exchangeable cation in the natural clay, decreases considerably in the intercalated solid, proving that the incorporation of the amine is carried out *via* cation exchange.

Figure **1** show the XRD patterns of Na-MMT (Figure **1a**) and O-MMT (Figure **1b**); we notice that the structure of clay is preserved after the organophilic modification since the two XRD patterns are similar except for the intercalation process observed. The XRD pattern of Na-montmorillonite (Figure **1a**) showed the characteristic reflections of Montmorillonite at 2θ of 6.5°, 19.8° and 28.0°. These reflections were not observed in the pattern of organo-montmorillonite (Figure **1b**); therefore, the intercalated product was presumed as organophilic montmorillonite.

The diffraction peak of Na-MMT (curve a) is at 2θ of 6.5°. According to the Bragg equation $2d\sin\theta = n\lambda$ [5], the gallery distance of Na-MMT is calculated to be 1.24nm. As for OMMT (b), the first grade diffraction peak is at 2θ of 4.07° corresponding to an increased gallery distance of 2.17nm. It is concluded that the sodium cations between MMT layers are substituted by the organic alkyl cations of an intercalation agent (octadecylamine).

The XRD interpretations are confirmed on the FTIR spectra of the clays. The infrared spectra of modified Na-MMT (a) and O-MMT (b) are shown in Figure **2**. As depicted, the organic modification produced several new absorption peaks. The strong absorption near 2920 and 2850cm^{-1} is attributed to the stretching and contracting vibration of -CH_2- groups; the absorption near 1470cm^{-1} and 710cm^{-1} reflects the bending and rocking vibrations of -CH_2- groups. This indicates that the interaction reaction between MMT and surfactant molecules had taken place during the modifying process and that the organic groups of intercalation agents do intercalate into MMT galleries; the amount of substitution is enough large.

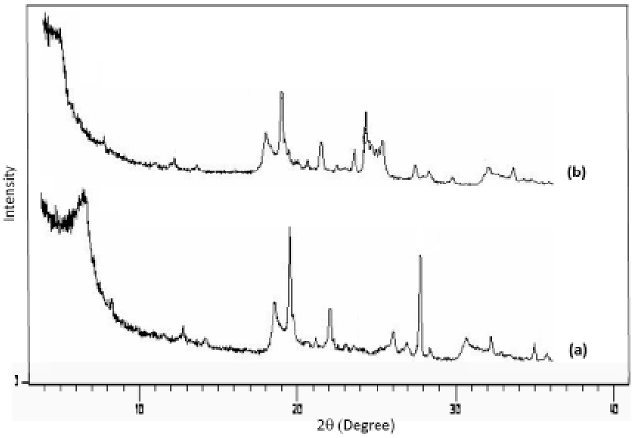

Figure 1: X-ray diffraction patterns of Na-MMT (**a**) and OMMT (**b**) clay samples.

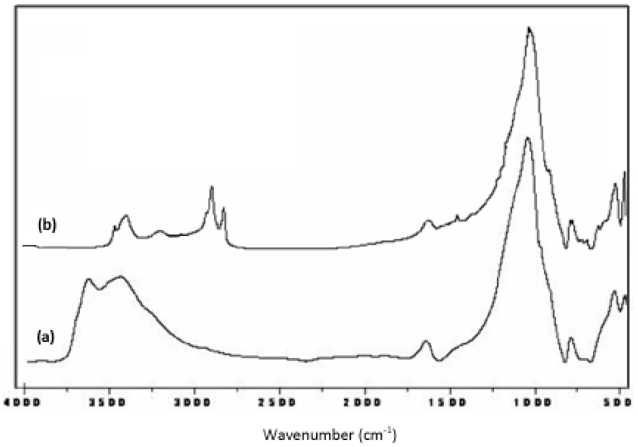

Figure 2: FTIR spectra of purified Na-MMT (**a**) and O-MMT. (**b**) Clay samples.

Compared with the IR spectra of purified Na-MMT, the absorption band at 3440cm^{-1}, corresponding to-OH stretching vibration of H_2O of MMT, weakened and shifted to the lower wave number 3428cm^{-1} (Figure **2b**). The overlaid absorption peaks in the region of about 1640cm^{-1} is attributed to -OH bending mode of adsorbed water. Compared with the IR spectra of Na-MMT, the absorption band of -OH bending vibration of H_2O of MMT (1635cm^{-1}) moved to 1642cm^{-1} (Figure **2b**). Simultaneously, the intensity of this absorption band decreases, which indicated the H_2O content reduced with the replacement of the hydrated cations by surfactant cation ions. This observation showed that the surface properties of MMT had been changed from hydrophilic to hydrophobic by modifying it with surfactant C18.

The characteristic vibration absorption at 1115cm^{-1} is due to Si-O-Si stretching vibration for layered silicates. The IR peaks at 915 and 875cm^{-1} are attributed to AlAlOH, AlFeOH and AlMgOH bending vibration [24, 25]. These vibrations have almost no obvious change before and after the organic modification.

3.2. Characterization of Cellulose-OMMT Clay Nanocomposites

Several mechanisms were proposed to describe the interaction between cellulose and the LiCl/DMAc complex; these mechanisms lead to the same observation: the complexation of Li^+ with DMAc carbonyl and formation of hydrogen bonds between Clion and cellulose -OH groups. This is due to the strong Lewis acid character of LiCl resulting from attraction between Li^+ and DMAc carbonyl, leaving the Cl^- ion to form hydrogen bonds in solution [26].

From thermodynamics, a negative variation in free energy (ΔG) is required for the intercalation process between clay and cellulose. As for constant temperature, there is the equation $\Delta G=\Delta H-T\Delta S$, in which ΔH is dependent on the affinity between polymer molecules and OMMT; ΔS is related to the constrained states of solution polymer. The driving force for direct polymer intercalation from solution is the entropy gained by desorption of solvent molecules [27]. So the solvation of interlayer cations and replaced solvent exiting from gallery particle produce an increase in entropy, i.e. $\Delta S > 0$ induce $\Delta G < 0$.

The incorporation of organic molecules, with the subsequent change from the natural organophobic clay to the organophilic one, allows a better interaction of the inorganic filler with cellulose. In the current work we perform cellulose dispersion from solution; cellulosic composite membranes containing 0, 3, 7 and 10wt % O-MMT clay were thus prepared.

3.2.1. XRD Analysis

For XRD analysis, we used the same apparatus as in the clay characterization but the procedure is different. We carried out a small angles analysis, scanning interval was $2.01° < 2\theta < 14.98°$. Samples of $1cm^2$ of area and 0.1mm thickness are cut out on the prepared plates. In order to ensure a maximum flatness of the sample, cut out surface is never exposed to x-ray beam. Three composites membranes with 3, 7 and 10wt % clay were analyzed by XRD; the patterns of cellulose and composites are presented in Figure **3**.

After association between cellulose and clay, a typical diffraction peak of MMT appears at 6.95° in the composite patterns. The intensity of this peak decreases and even disappears with decreasing of the amount of clay to cellulose, showing that the formation of compexe structure in Cellulose/MMT composites.

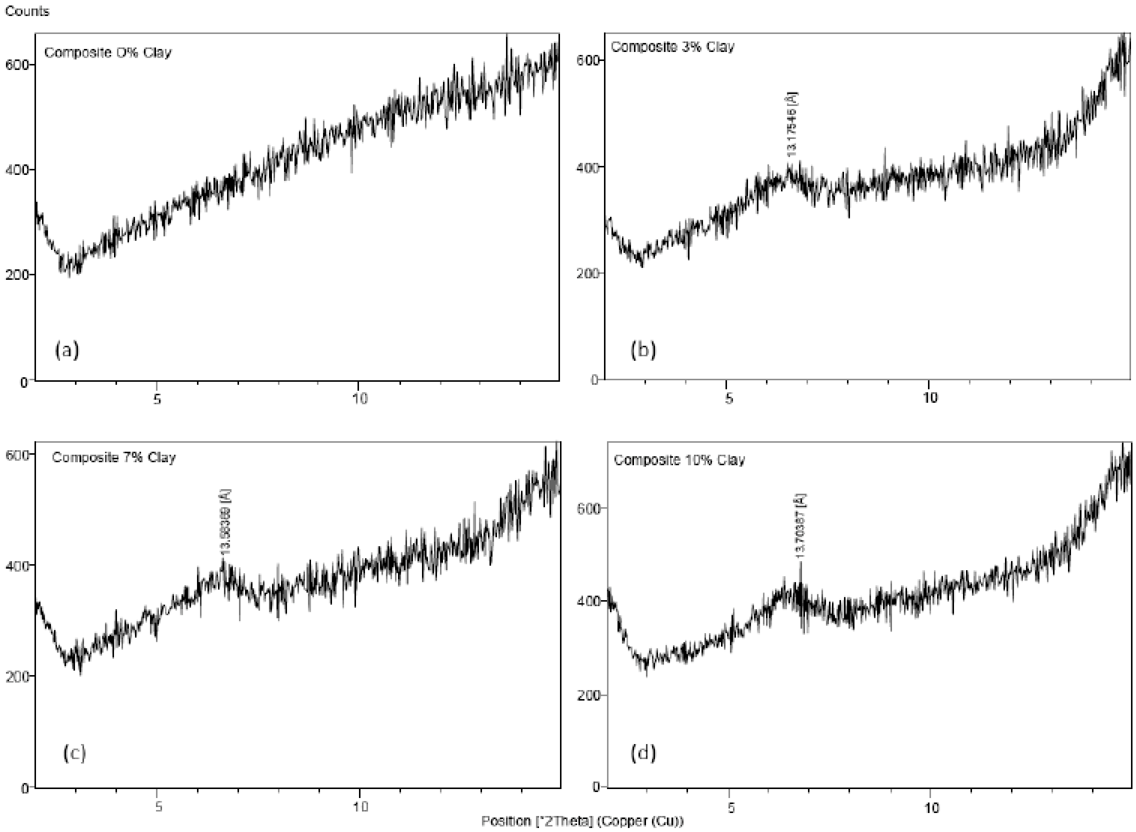

Figure 3: X-ray diffraction patterns of Cellulose-OMMT composite membranes. Clay content: (**a**) 0%; (**b**) 3%; (**c**) 7% and (**d**) 10%.

According to the results of XRD and FTIR, it can be concluded that almost all cellulose are inserted into MMT interlayer with destroying the clay crystalline structure.

3.2.2. FTIR Analysis

FTIR spectra of cellulose membranes are shown in Figure **4**. It can be found that the band of the composites at 3440cm^{-1} is successively increased, which suggests that the vibration band in cellulose (OH stretching) overlap with the bands of MMT (-OH stretching of H_2O).

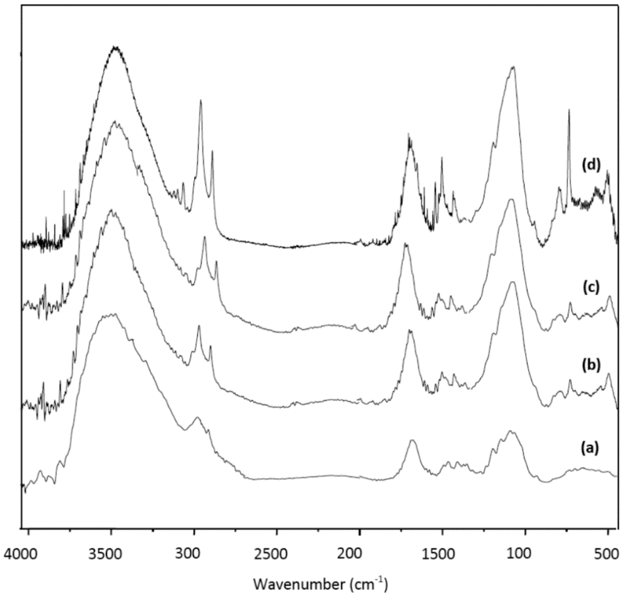

Figure 4: FTIR spectra of cellulose-OMMT composite membranes. Clay content: (**a**) 0%; (**b**) 3%; (**c**) 7% and (**d**) 10%.

The bands attributed to the intercalated organoclay, C-H stretching on methyl (2920cm^{-1}) and methylene (2880cm^{-1}) groups, are observed in the composites spectra, and the intensity of the both absorption bands increased with increasing the clay amount to cellulose. In addition, the bands attributed to the associated cellulose, C-H bending on methyl (1440cm^{-1}) and methylene (1380cm^{-1}) groups are also observed in the spectra of the composites. Compared with the spectra of Figure **2**, the absorption peaks attributed to the -OH bending mode of adsorbed water moved to the region of 1660cm^{-1}.

The characteristic peak at 1115cm^{-1} is due to the out-of plane Si-O stretching mode of Montmorillonite. The peaks at 915 and 875cm^{-1} could be attributed to AlAlOH, AlFeOH and AlMgOH bending vibrations, respectively. The intensity of these three absorption bands also increased with increasing the molar ratio of clay to cellulose.

3.2.3. Thermal Analysis

Thermal stability of polymers in many applications is of critical importance. Thus it is particularly significant to analyse the thermal degradation of cellulose and cellulose/clay composite. The mechanisms by which composite formation can improve the thermal stability of polymers have been of interest for some time. The first suggestion of a mechanism is due to Gilman and Kashiwagi [28], who suggested that the composite structure collapses during combustion and this forms a carbonaceous silicate structure on the surface which can act as a barrier to mass transport and can also insulate the polymer from the heat source. The growth of layered silicates on the burning/gasifying sample surface is the result of the decomposition of the polymer matrix by pyrolysis [29].

Thermogravimetric analysis provides a method for the determination of mass change in the material as a function of time and temperature, this technique reflect reactions which occur at the molecular level of the materials. Figure **5** shows the TG scans of the of cellulose composite membranes. From the TGA curves a similar degradation process is observed for all samples. However for samples of 0, 3 and 7% clay loading degradation occurs in two steps (first at 100-120°C, second at 250°C) whereas the degradation process of the last composite (10% clay content) occurs in only one stage (at 270°C). A mass loss at low temperatures due to water desorption is first observed for primary samples, then cellulose decomposition occurs at about 250°C. With degradation process in one step the ultimate sample has a higher thermal stability.

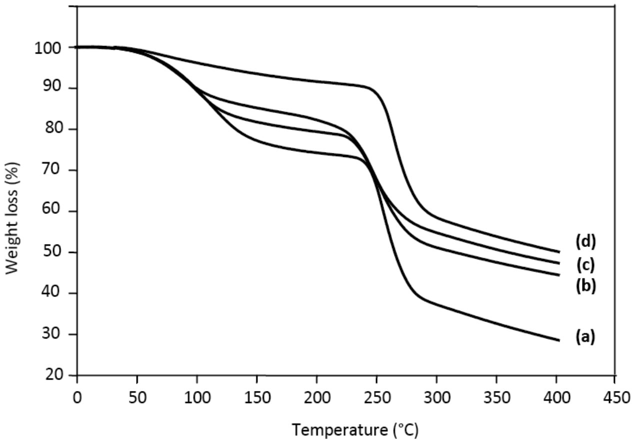

Figure 5: TG scans of cellulose-OMMT nanocomposite membranes: Clay content: (**a**) 0%; (**b**) 3%; (**c**) 7% and (**d**) 10%.

For cellulose and in accordance with the literature it has been established that there is no degradation

Table 2: TGA Data of Cellulose-OMMT Composite Membranes

Sample	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Residue at 400°C (%)
Cellulose/OMMT (0 wt %)	100	265	28
Cellulose/OMMT 3 wt %	100	315	39
Cellulose/OMMT 7 wt %	100	359	44
Cellulose/OMMT 10 wt %	245	400	46

taking place until 200°C, above this temperature thermal stability is gradually decreasing and decomposition occurs at 250°C, which corresponds to the beginning of the thermal degradation (Td). The main mass loss is produced in the 250-320°C temperature range (>50%) as a consequence of the cellulose combustion process. Finally, from 350°C the mass loss continues but with a low gradient. The onset temperature of the degradation (TGA) is higher for the cellulose/OMMT composites and it increases with clay content (for 10% clay loading this temperature is increased by about 20°C). An increase in thermal stability with the clay content is observed, with a maximum obtained for a loading of 10wt% clay.

From TGA curves, we analysed the degradation process of all samples starting from three characteristic temperatures T_{10}, T_{50} and residue at 400°C: T_{10} refers to temperature at which the loss mass of the materials is 10%; whereas, T_{50} refers to the temperature at which the remained mass of the materials is 50%. Table **2** shows T_{10}, T_{50} and residue at 400°C of cellulose and cellulose/OMMT composites. Thus the degradation process is slowed down by clay addition and the residues have drastically increased; however the interval of cellulose degradation remains in the same limits for all samples (233-283°C).

CONCLUSION

In this work, Cellulose/OMMT composites have been prepared by complexation from solution processing and their thermal stability has been investigated. Algerian montmorillonite has been successfully modified using octadecylamine, the clay surface was significantly modified by the surfactant coverage and it became hydrophobic. The XRD results show intercalation of the organic cations between the clay mineral layers and good agreement is found with theoretically calculated results of basal spacing for ideal cation exchange. FTIR spectra demonstrate that CH_2 stretching (2950-2800cm^{-1}), scissoring (1470cm^{-1}), and rocking (740-710cm^{-1}) modes are diagnostic for the conformation of intercalated surfactants within the gallery. Key factors for cellulose association from solution were: first, an increase of the *d*-spacing of clay gallery; second, partial dissolution of fibrous matrix. The compounding process includes solvent molecules entering gallery, polymer linking and solvent volatilization. The incorporation of organic molecules, with the subsequent change from the Na- MMT clay to O-MMT, allows a better interaction between the inorganic filler and cellulose.

Association of MMT can considerably increase the decomposition temperature of cellulose matrix and reduce the combustion. An increase in thermal stability with clay content is observed by TGA. The clay acts as a heat barrier, which enhances the overall thermal stability of the cellulose/MMT hybrids, as well as helps in the formation of char after thermal decomposition. In the early stages of thermal decomposition, the clay would shift the decomposition to higher temperature.

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