Properties of plasticized cellulose acetate/clay nano-biocomposites

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Abstract

Green nanocomposites films were elaborated from cellulose acetate (CA) powder, eco-friendly triethyl citrate (TEC) plasticizer and three types of nonofillers, namely, natural montmorillonite (Na-MMT) and organo-modified with gelatin (Ge-MMT) or chitosan (Cs-MMT), using solvent casting method. The effects of plasticizer and clay type on morphology and thermal properties of these bio-based nanomaterials were investigated. The clay dispersion in the films was analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). In all case, intercalated/exfoliated partially structures, with small clay tactoïds remaining, were suggested in absence of TEC. The Plasticized nanocomposites exhibited mainly intercalated structure with preferential plasticizer intercalation in presence of Na-MMT and Cs-MMT. However, mostly exfoliated structure was proposed with Ge-MMT, due to favorable interactions between this bio-modifier and the CA.
An improvement in thermal stability of CA matrix with the addition of clay was also observed by means of thermogravimetric analysis (TGA), as evidenced by the shift of their onset degradation temperatures toward higher values.

Key words: Nano-biocomposite, cellulose acetate, clay, plasticizer, exfoliation.

1. Introduction

Nowadays, excessive levels of plastic waste have caused the concern of scientific community to develop eco-friendly materials. Polymers from renewable resources are an innovative alternative to petroleum-based polymers and fits with a real sustainable development approach.

In this context, nano-biocomposites, based on bipolymer as matrix and layered silicate as nanofiller, represent an emerging group of hybrid materials with often improved properties of the bio-matrix (mechanical, thermal, barrier…), at low filler levels [1-3]. The key to this performance lies in the ability to exfoliate and disperse silicate platelets within the polymer matrix.

Cellulose acetate (CA) is a thermoplastic derived from cellulose that is the most abundant polysaccharide in the earth. Owing to its biodegradability, excellent optical clarity and stiffness, CA has been widely used in diverse areas, such as filters, membranes, packing films, adhesives, coatings for paper and plastic products, textile fibers and drug delivery systems [4-6]. Thus, CA can be considered a good candidate for the preparation of nanocomposites that is promising pathway to develop of plastic devices and more impermeable packing films and coatings.

To enhance the intercalation/exfoliation process, a chemical modification of the clay surface, with the aim to match the polymer matrix polarity, is often carried out. Alkyl ammoniums salts are the most common cationic intercalants used in the preparation of commercial organoclays. However, these materials are mostly toxic and thus not suitable for bio-applications [7]. So, in the present report, biological macromolecules intercalants, namely gelatin (Ge) and chitosane (Cs)

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were selected to organo-modified MMT layers with negative surface charges. Gelatin, a typical polyelectrolyte protein, is a denatured derivative of collagen with plenty of NH_2 and COOH groups, which can intercalate into MMT galleries at different pH values [8-10].

Chitosan is a copolymer of N-acetyl-glucosamine and N-glucosamine units. Its Amine groups in acidic solution convert to a cationic form $-NH_3^+$ which is necessary for the cation exchange reaction between clay and intercalant. Hence, Ge- and Cs-intercalant clays were used as nanofillers, with the aim to prepare entirely green plastic CA-based nanocomposites for various applications. We have first prepared and characterized Ge- and Cs-modified MMT. We then used them to prepared CA-based nano-hybrids in presence and absence of triethyl citrate plasticizer. The morphology and properties of the obtained materials with 5 wt % of clay were studied using XRD, TEM and TGA analyses and compared to CA/Na-MMT nanocomposites counterparts.

On the basis of our knowledge, this work has not been reported in the literature so far.

2. Materials and Method

2.1. Materials

Cellulose acetate (39.8 wt % acetyl content, Mn 30000 g/mol and DS 2.45) of pure powder free from additives was supplied by Sigma-Aldrich. Gelatin (Type B, extracted from bovine skin, isoelectric point (IEP): 5.05) was purchased from (Merck Darmstadt). Chitosan, from Sigma-Aldrich, has 75% degree of deacetylation and medium weight. triethyl citrate plasticizer (99 % purity) was provided by SAFC Inc. The montmorillonite, originates from Maghnia bentonite, was kindly supplied by ENOF Chemical Research Company of Algeria. The Na^+-montmorillonite (Na-MMT) was homoionized and its cation exchange capacity (CEC) was 86.16 meq /100g [11].

2.2. Sample preparation

2.2.1 Preparation of organo-modified montmorillonite

The organo-modification of Na-MMT with gelatin or chitosan, was prepared according to the following procedure: 1g of Ge was soaked in 50 ml of deionized water and heated at 70 °C to obtain a homogeneous solution, followed by addition of 0.5M HCl aqueous solution to adjust the pH value to 4 (before the isolectric point, IEP). In the other hand, Cs solution was prepared by dissolving 1 g of Cs in 150 mL of 1% (v/v) acetic acid aqueous solution, and then the pH was adjusted to 4.9 using a 0,5 N NaOH aqueous solution. Subsequently, Ge and Cs solutions were added separately dropwise to a 2 wt % ultrasonically pretreated Na-MMT aqueous suspensions followed by vigorous mechanical stirring at 70 and 60 °C for further 2 h and 4h to obtain Ge- and Cs-intercalated MMT, respectively. Finally, the products were harvested by centrifuge, washed with hot distilled water, centrifuged again and then dried at 60 °C in a vacuum oven for 12 h.

2.2.2 Synthesis of CA/clay nano-biocomposites

CA-based nano-biocomposites were prepared in presence of 5 wt % of different clays by solution method according to procedure reported elsewhere [12]. Clay was dispersed in acetic acid/water solvent mixture, stirred at room temperature for 24 h and then treated by sonication during 30 min. The suspension clay was added slowly to CA solution with and without 20 wt% of TEC plasticizer. The mixture was stirred mechanically for another two days, then ultrasonically treated for 15 min. Films were obtained by casting pouring the hot suspension into rectangular glass moulds and evaporating it at room temperature and in an oven under air at 80 °C until constant weight was reached.

2.3. Characterization

XRD analyses of Na-MMT, organoclays and their CA-based nanocomposites were recorded on a Bruker D8 advance diffractometer using CuKα radiation (40 kV, $\lambda = 1.54$ A^0) under 0.01°/s scan rate. The basal spacing (d_{001}) of the silicate layer was calculated using the well known Bragg's equation ($n\lambda = 2d \sin\theta$), where θ is the diffraction angle and λ is the wavelength.

TEM observation was operated on a transmission electron microscope a JEM-2000EX equipped at an acceleration voltage of 120 Kv.

TGA analysis was performed on Q500 analyzer, at heating rate of 10 ºC/min, under nitrogen air.

3. Results

All nano-biocomposites were prepared with the combination of mechanical and ultrasonic mixing modes that represented the best dispersion degree of silicate layers due to contribution of both dispersive and distributive mixing mechanisms.

3.1. XRD analysis of clays and CA nano-biocomposites

Figures 1-3 display XRD patterns of pristine Na-MMT, Ge-MMT and Cs-MMT together with the virgin CA and their plasticized and unplasticized nano-hybrids.

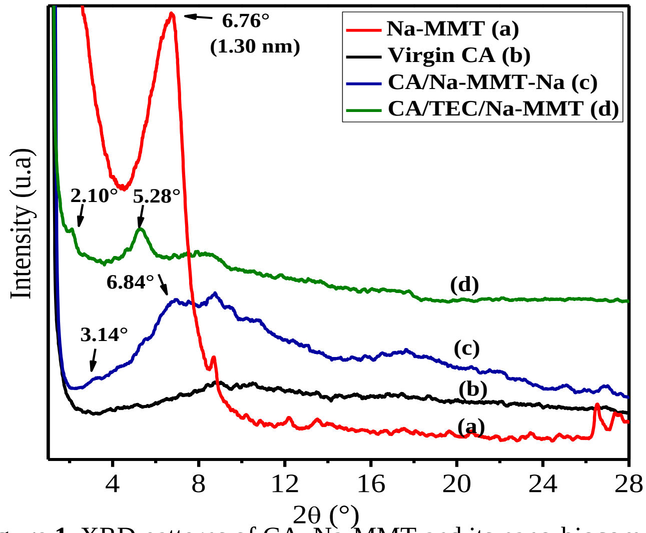

Figure 1. XRD patterns of CA, Na-MMT and its nano-biocomposites

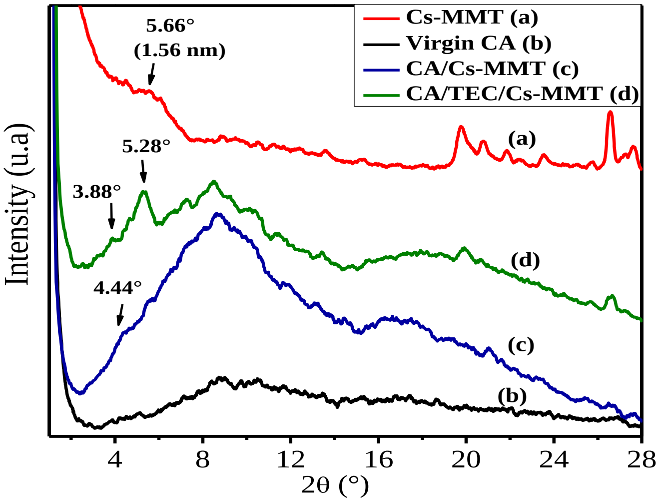

Figure 2. XRD patterns of CA, Cs-MMT and its nano-biocomposites

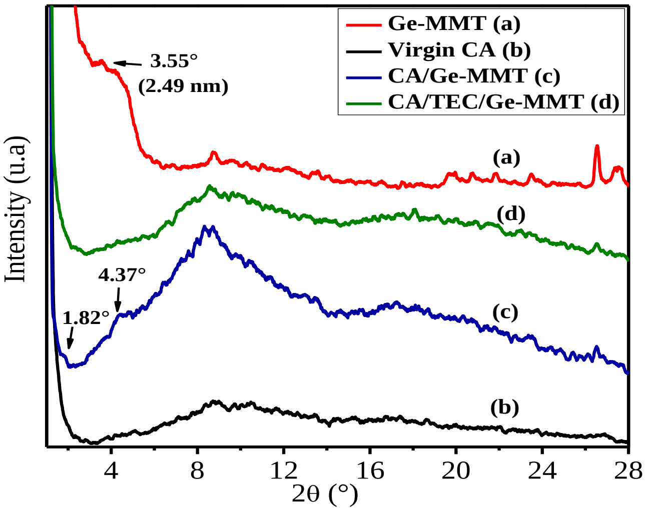

Figure 3. XRD patterns of CA, Ge-MMT and its nano-biocomposites

From figure1, Na-MMT exhibits a single sharp diffraction peak at 2θ = 6.76° corresponding to d-spacing (d_{001}) of 1.30 nm. After the organo-modification reactions with Ge and Cs, (figures 2,3), this peak becomes relatively broad and shifts to lower angle at 3.55° for Ge-MMT and 5.66° for Cs-MMT corresponding to d-spacing of 2.49 and 1.56 nm, respectively.
Besides, CA curve shows no diffraction peak in the study 2θ range. In absence of plasticizer, all nanocomposites exhibit very weak diffraction peak at lower angle compared to the diffraction peak of original clay, regardless the clay type. Another lower intensity peak is clearly observed for CA/Na-MMT nano-hybrid, which almost directly corresponds to the initial MMT interlayer spacing before incorporation into the CA matrix.

The impact of plasticizer on clay intercalation/exfoliation process is also analyzed in this study.
In figure1, AC/TEC/Na-MMT composite exhibit a diffraction peak located at 5.28° and another one of lower intensity at 2.10° corresponding to d_{001} values of 1.67 nm and 4.20 nm, respectively.

For the AC/TEC/Cs-MMT composite, figure2, only single diffraction peak appeared, in the same region observed for Na-MMT, at 5.31° indicating expansion of d_{001} to 1.66 nm.
However, the diffractogram of CA/TEC/Ge-MMT, figure 3, displays no diffraction peaks in the 2θ range of 1.5°- 8°. All these XRD data are collected in Table 1, given in discussion section.

3.2. TEM analysis of CA-based nano-biocomposites

Information concerning the dispersion of the silicate layers in the matrix and the shape of the resulting hybrid nanocomposites were not conclusively provided by XRD analysis. Thus TEM images are used to complement the limitation of XRD curves.
Figure 4 illustrates typical TEM micrographs of the nanocomposites CA/Ge-MMT, CA/TEC/Na-MMT and CA/TEC/Ge-MMT.

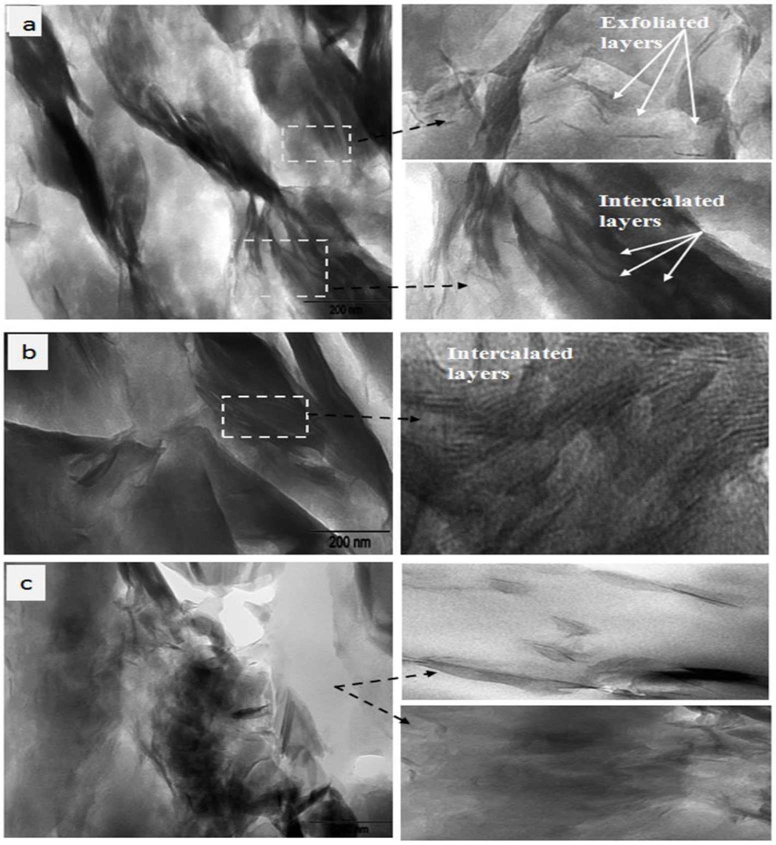

Figure 4. TEM images of (a) CA/Ge-MMT, (b) CA/TEC/Na-MMT and (c) CA/TEC/Ge-MMT nano-biocomposites

3.3. Thermal analysis of CA nano-biocomposites

Thermal analysis was performed in order to study the effects of clay and plasticizer on the thermal stability of cellulose acetate.TGA and respective D(TG) curves of virgin CA and its nano-hybrids prepared without and with TEC are depicted in figures 5 and 6, respectively.

From figure 5, it can be seen that the weight losses, within the temperature range of 30-600 °C, of all the nano-biocomposites prepared without TEC occur in single main decomposition step that is attributed to the degradation of CA chains.

From figure 6, obviously the plasticized matrix and its nanocomposites exhibit a similar three-stage thermal degradation. The first step is below 220 °C and the second one is located in 220-300 °C range. These two steps are ascribed to the mass losses of moisture adsorbed by samples together with the TEC plasticizer used, which is free or associated by hydrogen bandings with different species, namely the CA chains, the hydroxyl of clay and the adsorbed water. The third stage above 300 °C represents substantial mass loss due to the main CA chains degradation.

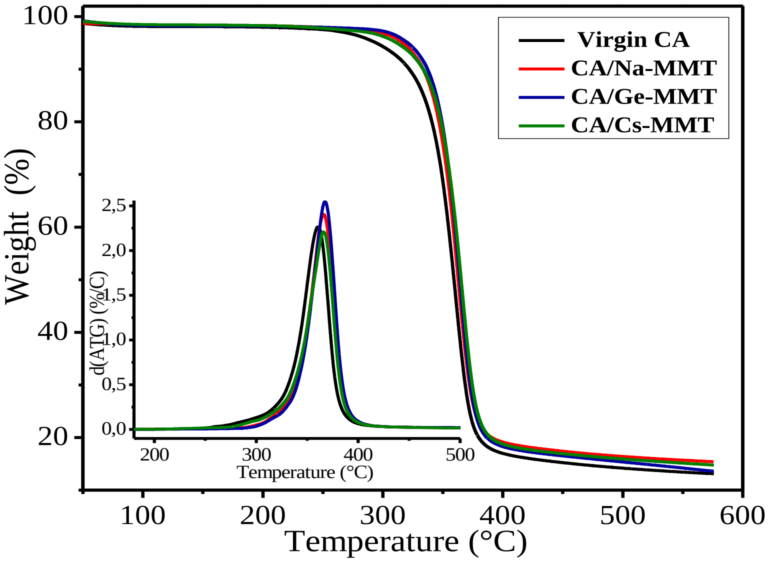

Figure 5. TGA and D(TG) curves of CA and its CA/clay nano-biocomposites

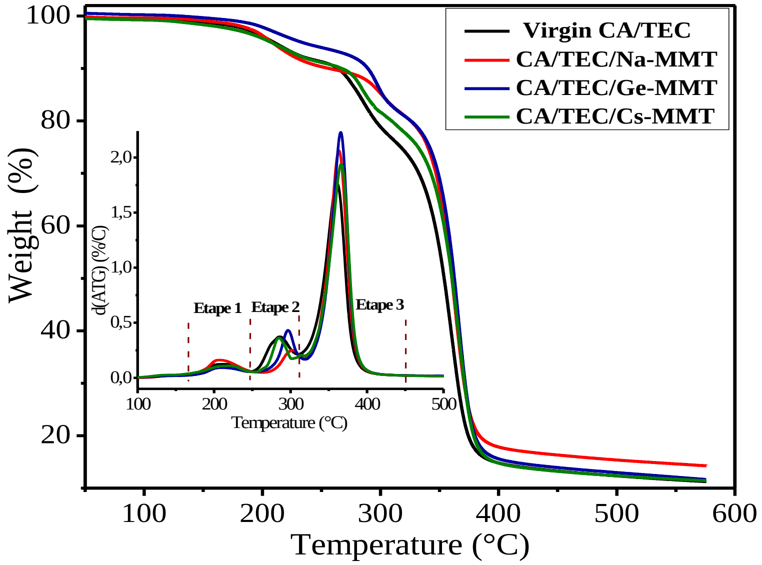

Figure 6. TGA and D(TG) curves of CA and its CA/TEC/clay nano-biocomposites

4. Discussion

4.1 Evidence of MMT organomodification

In the case of Ge-MMT and Cs-MMT, the acidified chains cations intercalate into the interlayer space of clay and replace the sodium cations through cationic exchange reactions. That would result in enlarging of the gallery spacing and hence a shift in the peak position towards a lower angles in the XRD pattern. Based on Zheng et al. studies [8-10], the ionized states of gelatin vary with different pHs of media. The charge changes as below:

$$\mathrm{NH_3^+{-}Ge{-}COOH} \xleftarrow[\mathrm{pH<IEP}]{\mathrm{H^+}} \mathrm{NH_3^+{-}Ge{-}COO^-} \xrightarrow[\mathrm{pH>IEP}]{\mathrm{OH^-}} \mathrm{NH_2{-}Ge{-}COO^-} + \mathrm{H_2O}$$

Therefore, in acidic media at pH < IEP, gelatin chains with more $-NH_3^+$ can bind with the negative sites onto MMT sheets and intercalate into MMT interlayers.

For chitosan, it is well establish that in acidic diluted medium its protonated chains, rich in NH_3^+ groups, exhibit an extended structure that facilitates its intercalation into MMT layers [13].

4.2 Morphological study on CA nanocomposites

XRD analyses were performed in order to investigate the dispersion of clay within the matrix. The obtained XRD data are shown in Table 1.

Table 1. Diffraction peaks and d-spacing's of the clay and its corresponding nano-biocomposite.

Samples	2θ (°)	d_{001} (nm)
Na-MMT	6.76	1.30
CA/Na-MMT	6.84 3.14	1.29 2.81
CA/TEC/Na-MMT	5.28 2.10	1.67 4.20
Cs-MMT	5.66	1.56
CA/Cs-MMT	4.43	1.99 ....
CA/TEC/Cs-MMT	5.31 3.88	1.66 2.27
Ge-MMT	3.55	2.49
CA/Ge-MMT	4.37 1.82	2.02 4.84
CA/TEC/Ge-MMT	.....	.....

From XRD patterns of unplasticized CA nanocomposites, it can concluded that the movement of the basal reflection of original clay to lower angle indicates the formation of an intercalated nanostructure, while it's broadening and intensity decrease is most likely due to the presence of intercalated/partially exfoliated structure. The coexistence of small clay tactoïds remaining is also confirmed, where low clay platelets agglomerates in presence of both organo-modified MMT compared to unmodified MMT that led to a more aggregated structure.

This result gives evidence that the modification of MMT surface polarity by bio-intercalants has not only induced a better CA matrix/nanofiller interface affinity, but has increased the d-spacing, which also facilitate the polymer chains intercalation and enhance the intercalation/exfoliation process. Hence, the nanocomposite formation may be mainly controlled by hydrogen interactions between CA (carbonyl, hydroxyl) and bio-modified clay groups (hydroxyl, carboxyl and amine).

Besides, TEC plasticizer is another factor that influences the properties of CA/clay nano-hybrids.

For nano-hybrids CA/TEC/Na-MMT, the presence of the two diffraction peaks in the low angle region reveals that this material is mainly intercalated and that both the plasticizer and the CA chains entered into the silicate layers forming mainly intercalated structures, without reaching complete exfoliation.

However, plasticizer and CA molecules can compete to intercalate into the clay. The interaction between plasticizer and MMT tends to be more favourable because of the smaller molecular size of plasticizer, which is suitable for the expansion of the basal spacing of MMT in nanocomposite. So, intercalation of TEC into MMT interlayer spacing results in an ordered structure with a characteristic diffraction peak at 2θ ca. 5°, while the intercalation of CA is more difficult and only few CA chains have been incorporated into the clay layers.

This competitive intercalation process of the plasticizer could also be due to strong hydrogen interactions between its hydroxyl and carbonyl groups and the hydroxyl groups of MMT [14,15].

These results clearly highlight a disruption of the clay intercalation/exfoliation process induced by the addition of plasticizer that inhibits the exfoliation of clays layers within the CA matrix.

To overcome the limitation of plasticizer preferential intercalation, we have focused our attention on the organo-modification of the clay surface by the use of Ge and Cs as organo-modifiers.

Morphological analysis performs on CA/TEC/Cs-MMT nanocomposites provide strong evidence that the clay nanolayer formed an intercalated structure with preferential plasticizer intercalation but not complete exfoliation.

However, in the case of CA/TEC/Ge-MMT, the loss of the d_{001} peak of Ge-MMT is attributed to the good clay dispersion state. This indicates that CA intercalated into layers of modified-MMT and disordered clay tactoids then leading to mostly exfoliated nanostructure.

The gelatin chains play a role of bridge between MMT surface and CA chains through hydrogen bonding. This result highlights the interesting role of the organic treatment of MMT layers by gelatin, resulting to highly Ge-MMT/matrix affinity that diminishes the impact of the plasticizer on the process of intercalation/exfoliation.

In agreement with XRD observations, TEM micrographs (Fig. 4a) of CA/Ge-MMT confirm the formation of mixed intercalated/exfoliated nanocomposite structures, as evidenced by the presence of some intercalated layered stacks of relatively small thickness randomly dispersed within CA matrix coexisting with of disorderly exfoliated platelets. Some agglomerations of platelets are also observed.

As expected, the CA/TEC/Na-MMT images (Fig. 4b) show mainly intercalated clay layers, most likely by preferential TEC plasticizer intercalation, coexisting with some clay agglomerates.

However, in CA/TEC/Ge-MMT nanocomposite images (Fig. 4c), the clay platelets are well dispersed throughout the CA matrix so that an exfoliated structure is predominantly obtained. Some agglomerations internally disordered of layers are also observed.

According to all results, we conclude that the addition of plasticizer to the formulation CA/clay can inhibit intercalation of the MMT layers by CA chains or even prevent their exfoliation.

Therefore, a good dispersion of layers clay in CA matrix would be achieved by first preparing the nanocomposite in suspension solution, to promote attractive interactions between CA and clay groups, followed by plasticization.

4.3 Thermal stability evaluation of CA nanocomposites

The onset degradation temperature Td_{onset} is a key parameter since it determines the maximum processing temperature which can be applied without thermally damage the material. So, it is a criterion to evaluate the stability of polymers.

From TGA curves in figure 5 of CA/clay nanocomposites, it can be seen that addition of clay increase the Td_{onset} of CA matrix from 265 °C, indicating an improvement in thermal stability of cellulosic films. The clay modified by gelatin represented better thermal resistance in comparison with Na-MMT and Cs-MMT owing to favorable interactions between gelatin and CA chains.

The highest Td_{onset} value of 304 °C, reached in presence of 5 wt % Ge-MMT, is about 39 °C greater than that of virgin CA. Besides, the maximal degradation temperature Td_{max} of the matrix is slightly affected by the added clay, while the char obtained at 575 °C is increased.

The increase in thermal resistance is mainly attributed to tortuous pathway of the diffusion induced by the clay dispersion, which delays the diffusion of the combustion gas to the material surface and the escape of volatile degradation products [16,17].

Regardless clay type, it can also be seen (figure 6) that the incorporation of TEC has not affected the main thermal degradation of the matrix and its CA/clay nano-hydrids.

Conclusions

Two organo-modified MMT based on gelatin and chitosan were prepared. Then, cellulose acetate nanocomposites were elaborated using these organoclays and natural MMT as nanofillers, with and without TEC eco-friendly plasticizer.

From XRD patterns together with TEM images, it was suggested in absence of TEC plasticizer, the formation mixed intercalated/exfoliated structures with small clay agglomerates remaining.

Morphological study on the plasticized nano-hybrids revealed mostly intercalated/aggregated structures, with preferential TEC intercalation, in presence of Na-MMT and Cs-MMT, coexisting with some fraction of exfoliated silicate sheets in the case of the Cs-modified clay. This trend was related to the hydrogen bonding established between TEC and MMT platelets, which disturb the MMT exfoliation process. Better clay dispersion was obtained for CA/TEC/Ge-MMT nano-hybrid by the presence of mostly exfoliated structure, with small clay tactoïds remaining.

Thermal stabilities of CA/clay nano-hybrids were greatly enhanced compared to virgin matrix, as evidenced by an increase in their onset degradation temperatures, being the highest with Ge-MMT. This improvement was related to clay heat barrier effect.

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