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Biocomposites Based on Cellulose Acetate and 12-Aminolauric Acid Modified Montmorillonite

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Abstract. Polymer-clay composites films based on cellulose acetate (CA) and 12-aminolauric acid-modified montmorillonite (AMMT) were prepared by solution intercalation method with clay loadings 1, 5, 10, 15 to 20%wt. Cellulose acetate is a good material resource due to its green qualities and ease with which it is processed, and using this material in combination with naturally derived material, montmorillonite, is a good means tune and improve the materials properties. To achieve compatabilization between the polymer and the clay, 12-aminolauric acid (12-ALA) was ionically exchanged with the Na⁺-counter ions of the clay, producing an organically modified clay. The 12-ALA modifier is also an attractive resource due to its biocompatibility and relative abundance. The composites were characterized based on their chemical properties by Fourier Transform Infrared (FTIR), thermal properties by Differential Scanning Calorimetry (DSC), morphological characteristics by Scanning Electron Microscopy (SEM). X-ray diffraction (XRD) analyses revealed the presence of polymer intercalated and/or completely exfoliated silicate structures within the composites.

1. Introduction

The improvements in the functional properties of natural and semi-synthetic polymers have been made by reinforcement of the polymer matrix with layered silicates [1], [2]. Polymer-layered silicate (PLS) nanocomposites, where high aspect ratio silicate platelets of clay are dispersed in the polymer matrix. The formation of nanocomposites result to the improvement of the physical properties of these materials including increased mechanical strength, chemical resistance, gas barrier performance and flame retardancy when compared to the pure polymer or conventional composites [3]. Polymer nanocomposites with various clays have been extensively investigated due to their cost effectiveness and potential applications in different fields, including the structural, electronics, aerospace, and biomedical industries, and for use in sensors [4]. In the present study, the Na⁺-Montmorillonite (Na⁺-MMT) clay was used as a reinforcing material of the cellulose matrix. The attractiveness of MMT to be applied in many industries are due it its naturally abundant, nontoxic, chemically and thermally stable. It has been the most commonly employed layered silicate clay mineral in polymer composites and has been shown to improve the barrier and mechanical properties [5]. Also, cellulose acetate (CA) [6] is another material that is used in many applications because of their excellent processability. MMTs that are intercalated with fatty acid-derived surfactants was also used in the present study to promote the interxmixing between CA and MMT. Fatty acid based organo-modifier is an underutilized resource but offers many advantages in producing a polymer miscible nano-filler. The natural abundance, numerous, biocompatibility and thermal stability are some of the desirable characteristic of the fatty acid based modifiers [7]. The present study investigated the viability of preparing a CA based nanocomposites with different organo-clay loadings with different morphology, thermal stability,



microstructures and tensile properties. To the knowledge of the author, this is the first study that utilized a fatty acid-modified clay as a filler of a cellulose acetate based nanocomposite.

2. Methodology

2.1. Intercalation of 12-ALA in Na^+ -MMT

The 12-ALA modified MMT was synthesized based on Na^+ -MMT (Nanofill 116, Southern Clay Products, Inc., Gonzales, Texas USA) and 12-ALA (Trade Tokyo Chemical Industry, Japan) by a simple cation exchange reaction. Briefly, twenty-five (25) grams of Na^+ -MMT was dispersed to 1000 mL of deionized water at 90 °C. The dispersion was stirred for approximately 1 hour. Independently, an appropriate amount of 12-ALA (2.0 x CEC of Na^+ -MMT) was introduced in a 150 mL of pre-heated deionized water (90 °C) with a pH of 1.5. The 12-ALA solution was slowly added to the Na^+ -MMT slurry and was stirred for 2 hours at 90 °C. The intercalated MMTs were harvested in the mixture by centrifugation at 2000 rpm, washed 10 times with deionized water and vacuum dried at 90 °C for 24 hours.

2.2. Synthesis of Cellulose Acetate Composites

Pristine cellulose acetate (average $M_n \sim 30,000$ by GPC, Sigma-Aldrich) was purchased from Sigma-Aldrich and cellulose acetate composites consists of varying amounts of AMMT (0, 1, 5, 10, 15, and 20 wt.%) were prepared by means of solution intercalation method using tetrahydrofuran (THF) as solvent. The sample code assigned for the composite for example is CA-1AMMT which stands for the cellulose acetate with 1 wt % AMMT, and so on. Pristine CA serves as the control. Basically, 1.5 g of cellulose acetate along with the corresponding weight of AMMT were dissolved in 20 ml of THF under vigorous stirring for 1 hour at room temperature. Solvent casting method was used to prepare the polymer-clay composite films. The solution was placed on petri dish and air dried overnight.

2.3. Instrumentation

The characteristic functional groups of the samples were determined by Diffuse Reflectance Fourier-Transform Infrared Spectroscopic (DR-FTIR) analyses using a Shimadzu IR Prestige 21 Fourier-Transform infrared spectrophotometer (FTIR). The samples were scanned from 4000 to 600 cm^{-1} . Phase transformations and melting transitions were determined by Differential Scanning Calorimetry (DSC) using a TA Instruments DSC Q10. The analysis was performed at a heating rate of 10 °C/min in N_2 gas with temperature range from 30 to 300 °C. The melting temperature (T_m) was acquired in the thermograms. Morphological changes of the clay material, pristine and organo-modified clay were observed by using a Hitachi S-3400N Scanning Electron Microscope at an accelerating voltage of 10kV. To determine the intercalation, molecular structure, and conformation of 12-ALA in the clay in its silicate layers, and the formation of intercalated polymer-clay composite films, samples were subjected to x-ray diffraction analyses with a Shimadzu XRD-700 x-ray diffractometer (XRD) with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40kV and 30 mA in the 2θ range of 3-90 ° with a scan rate of 2 °/min. Values of interplanar (d) spacing were calculated according to Bragg's equation.

3. Results and Discussion

Polymer-clay composites of cellulose acetate and 12-aminolauric acid-modified clay was developed by solution intercalation method. Initially, the organo-modified clay was synthesized via cation exchange between the Na^+ ion of MMT and 12-ALA. The Na^+ ions of the clay material was determined to be exchanged with 100% x CEC surfactant by thermogravimetric analysis. The modification of the clay material with cationic surfactant result to the significant changes in their physical and chemical properties such as: hydrophobicity, basal spacing, textural properties and surface morphology and even biocompatibility.

3.1. Fourier-Transform Infrared (FTIR) Spectroscopic Analyses

The functional groups and possible molecular interaction between CA and AMMT were evaluated by FTIR. The FTIR spectra of pristine CA and samples of CA with varying amounts of AMMT are

shown in Figure 3.1. For CA, the band at 2944 cm^{-1} represents the aliphatic of C-H group. The band at 1751 cm^{-1} is attributed to the stretching vibration of C=O bond and a band at 1370 cm^{-1} shows O-H group. The characteristic bands around 1433.56 cm^{-1} represent the bending vibration of CH_2 , 1238 cm^{-1} assigned stretching vibration of the C-O group and the band at 902 cm^{-1} corresponding to the out-of-plane C-H bend. In addition, the main characteristic bands of CA are slightly shifted, which may be due to weak polymer-clay interaction or overlapping characteristic bands of CA and AMMT. It should be noted that no peak is observed to indicate the presence of a chemical bond between AMMT and CA chains. CA-AMMT composites are considered as effective biosorbents due to their high content of amino acid and hydroxyl functional groups, which show significant adsorption potential for the removal of various aquatic pollutants.

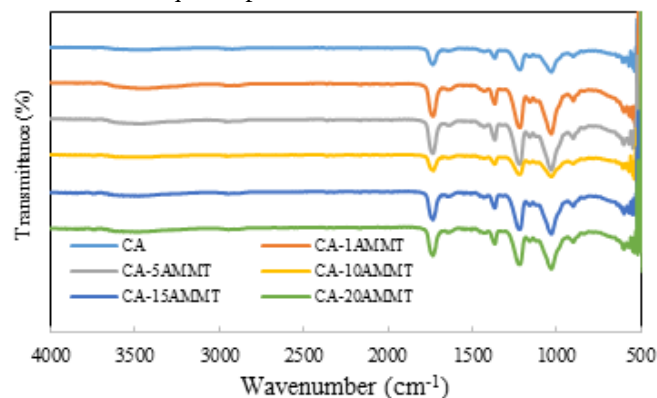


Figure.1. FTIR spectra of CA and its grafted forms

3.2. Thermal Analyses of Cellulose Acetate/ Organo-clay Composites

The melting behaviors of free 12-ALA and the clay-bound surfactant were probed by DSC and is shown in Figure 3.2. The 12-ALA surfactant in free form exhibited a sharp melting peak at 189°C which indicates that the melting confined alkylamine. Additionally, the T_m of the surfactant in AMMT was lower than that of the pristine 12-ALA as shown in Figure 3.2 and 3.3. The order of the alkyl amine in the silicate sheets is affected by the combination of the electrostatic attraction and repulsion between alkyl chains silicate sheets and carboxylic acid groups. It has been pointed out earlier that the amino fatty acid may be ionically bound to the silicate sheets of the clay or attracted to the metal ion via ion-dipole interaction.

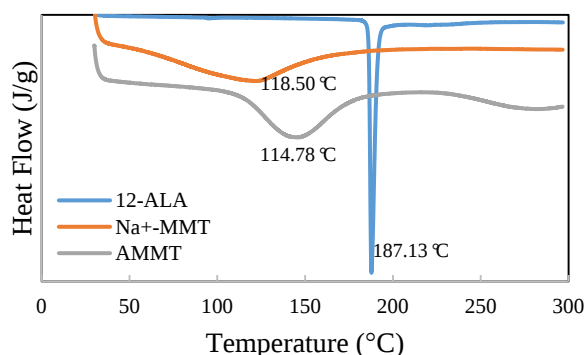


Figure.2. DSC thermogram of 12-ALA, Na^+ -MMT and AMMT.

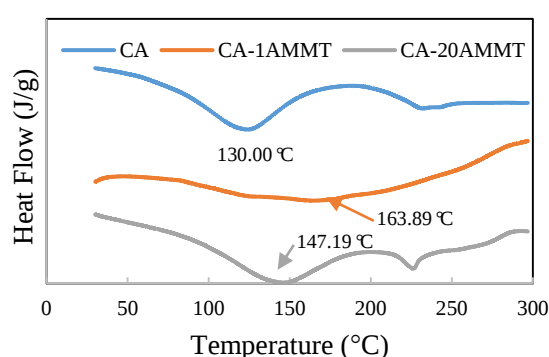


Figure.3. DSC thermogram of CA, CA-1AMMT AND CA-20AMMT.

The thermal transition of CA and the polymer-clay composites were probed by DSC as shown in Figure 3.3. The thermogram of CA exhibited a sharp endothermic transition at 130°C which is attributed to the phase transition of the polymer from solid to liquid. The polymer melting temperatures in the composite were found to vary with clay loading. It can be observed that CA with AMMT composites exhibited higher T_m . This might be attributed to the overall reduction in crystallite

size with increasing organo-modified clay loading. The size of these microstructures also affects polymer melting temperature. The broadening of the melting endotherm might suggest the reduction of the polymer crystallites where the clay silicate layers acts as physical barriers during the crystallization process.

3.3. Morphological Analysis of Polymer-Clay Composites

SEM was employed to examine the morphological properties of 12-ALA, unmodified Na^+ -MMT, 12-ALA-intercalated MMT (200CEC-AMMT), pure CA, and the CA-AMMT composite films. Their electron micrographs are depicted in Figure 3.4. It can be observed that the unmodified MMT was smooth and non-agglomerated (Figure 3.4b).

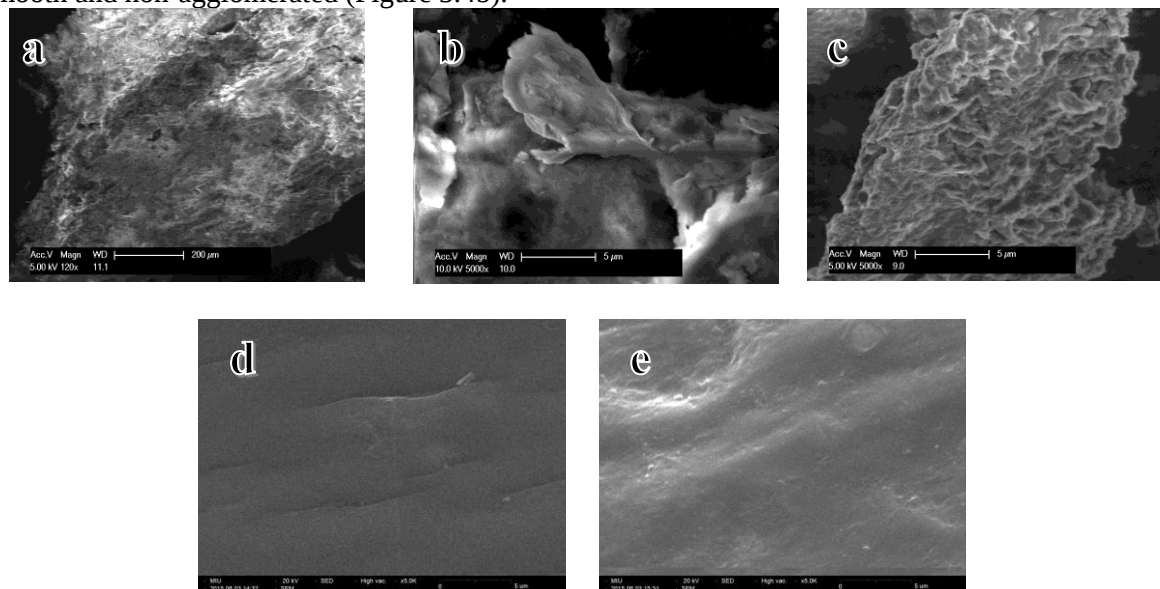


Figure.4. Scanning Electron Micrographs of (a) 12-ALA, (b) Na^+ -MMT, (c) AMMT, (d) CA-AMMT and (e) CA-20AMMT at 3,500X.

Interestingly, a significant change in geometry and morphology for the organo-modified clays were observed. The AMMT clay (Figure 3.4c) exhibited massive and highly aggregated flakes that exhibit rough surface and edges. The unmodified MMT, initially, exhibits curved plates which then transform into flat flakes depending on the surfactant loading. The transformation of the clays plates is heavily affected by the molecular interaction with the surfactant head group and tail group to the silicate sheet and the interaction of the surfactant tail group with another surfactant tail group. The micrographs of CA-20AMMT composite films (Figure 3.4d and e) presented a more rugged structure on the surface, in which agglomeration clay indicates good adhesion at the polymer-clay interface.

3.4. Microstructural Analysis of Polymer-Clay Composites

X-ray diffraction analysis revealed the presence of intercalated surfactants within the clay's aluminosilicate galleries. The XRD patterns of Na^+ -MMT and its organo-modified forms are shown in Figure 3.6. It was observed that with 12-ALA loading in the clay, there is a shift of the (001) peak to a lower 2θ position indicating that there is an increase in d_{001} -spacing. The 2θ position was found to be at 4.85° when the 12-ALA was loaded to the unmodified clay. The AMMT used in the study is a pseudotrilayered structure, the calculated d_{001} -spacings should be 1.75 nm. However, the d_{001} -spacing observed varies with that of calculated, and so it can be deduced that the 12-ALA does not accurately/precisely adopt the mentioned conformation. These d_{001} -spacing deviations can be accounted to the fact that the molecular dynamic calculation assumed that the methylene (CH_2) in the hydrocarbon chain of 12-ALA adopts an all-anti conformation, discounting the presence of methylenes in gauche/disordered conformation and coexistence of 12-ALA isomers in same clay system. Initially, Na^+ -MMT exhibited a narrow and sharp diffraction peak of the 001 position; then, at

12-ALA loading, the 001 diffraction peaks became sharper and more intense which suggests the formation of more ordered intercalated surfactant. The pristine CA and CA-20AMMT composite films were also subjected to X-ray diffraction. The diffraction peak of AMMT might be masked by the diffraction peaks of the polymer. The diffraction planes attribute to cellulose acetate were (101), (002), and (10 $\bar{1}$), found at 21, 25, 29 °, respectively. The 001 diffraction plane of AMMT was not observed for the CA-20AMMT which may indicate that the former is exfoliated in the polymer matrix.

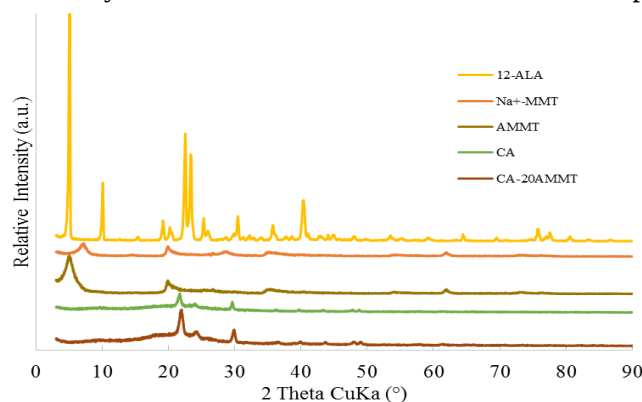


Figure5. X-ray diffractograms 12-ALA, Na⁺-MMT, AMMT, CA and CA-20AMMT.

4. Conclusion

Polymer-clay composite (CA-AMMT) films, with varying loads of 12-ALA-modified montmorillonite (AMMT) as the organo-modified clay, were successfully prepared by solution casting method. The organo-modified clay was successfully synthesized by a simple cation exchange in which the Na⁺ counter ions of the clay are exchanged with the protonated 12-ALA. The formation of composites was assessed by X-ray Diffraction. XRD analyses showed a broadening/disappearance of diffraction peak of the AMMT, indicating the presence of intercalated and exfoliated layers of AMMT. Due to the controlled swelling of the material, the polymer-clay composites may be used as food packaging, gas barrier and wound dressing material. Another potential use of the polymer-clay composites is in controlled drug delivery and tissue engineering applications.

5. References

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