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Modification of Nano-Clay and Preparation of Polylactic Acid Nanocomposite

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Nanoclays are widely used in preparation of polymer clay nanocomposites. The key to the performance of nanocomposites is the quality of dispersion of the nano-clays particles and the interfacial interaction between the matrix and the reinforced phase. Optimization of these properties requires various special and complicated treatments. Alkyl ammonium salts and alkyl amines are used as intercalates for the nano-clay preparation. Poly(lactic acid)/organo-clay nanocomposites were prepared by *in situ* polymerization technique. The samples were prepared and the effect of modifiers on the structure of polylactic acid nanocomposite samples were studied by using differential scanning calorimeter (DSC) and wide angle X-ray diffraction (XRD).

Key Words: Polylactic acid, Clay, Surfactant, *In situ* polymerization.

INTRODUCTION

Clays find wide range of applications, in various areas of science, due to their natural abundance and the propensity. Smectites are widely used clays by virtue of their high cation exchange capacity, high platelet aspect ratio and ease with which their surface can be modified[1].

Clay minerals have a crystalline structure composed of two main parts of a single four-sided and octagon is a unit. Based on the method of gathering these units together, the three main groups of the clay minerals are kaolinite, illite and montmorillonite. Building blocks of montmorillonite and illite group are very similar.

Because of an isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+} in the octahedral sheet and Si^{4+} replaced by Al^{3+} in the tetrahedral sheet), the clay layers have permanent negative charges, which are counter-balanced by exchangeable cations such as Na^+ and Ca^{2+} in the interlayer. The hydration of inorganic cations on the exchange sites causes the clay mineral surface to be hydrophilic. Ion exchange of the inorganic cations with organic cations can alter the surface properties. The intercalation of a cationic surfactant not only changes the surface properties from hydrophilic to hydrophobic but also greatly increases the basal spacing of the layers[2]. The organic modification of clay mineral leads to a decrease in surface energy making it compatible with polymers. Organically modified clay has been applied in composites and nano-scale composites[3]. Poly(lactic acid) as a biodegradable polymer has attracted great interest[4,5].

Choi *et al.*[6] reported that an exfoliated clay structure was obtained in polyacrylnitrile/silicate nanocomposites prepared by *in situ* polymerization. Exfoliation could be obtained only with *in situ* polymerization of polymer and clay[7]. Mehrabzadeh *et al.*[8,9] studied the melt preparation of high density polyethylene (HDPE)/clay, HDPE/polyamide (PA-6)/clay and HDPE/PA-66/clay nanocomposites. Their results showed that exfoliation was likely to occur, under appropriate processing condition (*e.g.*, sufficient shear force, mixing and residence time) and when suitable modification has been used[10].

In this study, we have presented the preparation of an organo-clay poly(lactic acid) nanocomposite by *in situ* polymerization. The structure of nanocomposite and thermal behaviour of the samples were measured. This organo clay nanocomposite could have tremendous potential for various applications in different fields of research and in practice.

EXPERIMENTAL

Lactic acid (LA) as a 90 wt% aqueous solution and stannous chloride ($SnCl_2\cdot 2H_2O$), benzalkonium chloride, Sodium montmorillonite clay (MMT), cloisite 30B from Southern Clay USA were used in this study. Fourier transforms infrared spectroscopy spectra were recorded on a Bomem Michelson Series-100 FTIR spectrometer from 400 to 5000 cm^{-1}. X-ray diffraction was performed at room temperature using X-ray diffractometer, Rigaku Rotaflex, in the 2θ angle range 1-10 degree, in order to determine the extent of intercalation or exfoliation in the nanocomposites. The X-ray beam was CuK_α

(λ = 0.1541 nm), radiation operated at 45 kV and 130 mA. Viscosity measurements were performed in chloroform at a temperature of 25 ºC with an Ubbelohde viscometer. Inherent viscosity was calculated based on ASTM D238. Deferential scanning calorimetry (DSC, Perkin-Elmer) was performed for the samples of nanocomposites. Scanning electron microscopy (LEO 440i) was used at high magnification to study the phase morphology of the blends. The measurement was performed under nitrogen atmosphere and the heating rate was 20 ºC/ min.

Sample preparation: The required amount of surfactants added to 10 g of clay sodium montmorillonite (MMT) and they were protonated in 100 mL of 1 N HCl for 1 h at room temperature with vigorous stirring. 100 mL water was added and then maintained at 80 ºC for 20 min. The solution was stirred vigorously with magnetic stirrer and 10 g clay was added slowly into the ammonium solution along with stirring. Stirring was carried out for a period of 2 h. Subsequently, the solution containing the organically modified clay was filtered through a Whatman® filter paper, washed with a hot solution of water and ethanol to remove chloride anions. The organo-clay was dried and then ground into a fine powder. Wide angle X-ray diffraction (WAXD) was performed on dried powder samples. The powder samples were pressed in a stainless steel sample holder and scanning was performed in a range of 2θ = 2-14º with a speed of 2 º/min and step size of 0.05º.

***In situ* polymerization:** The 250 mL three-neck flask and a reflux condenser was connected to vacuum system was used to *in situ* polymerization reaction. 100 g of aqueous solution of lactic acid was mixed with a 2.5 g of organo-clay. The mixture was ultrasonically treated for 0.5 h before charging into the 250 mL three-necked flask equipped with a magnetic stirrer and a reflux condenser. The mixture was dehydrated at 110 ºC under atmospheric pressure for *ca.* 2 h. The dehydration operation was continued at 130 ºC under a reduced pressure for 5 h. Then 0.46 g of $SnCl_2 \cdot 2H_2O$ (2 mol per 1 mol lactic acid) was charged into the flask and used as a catalyst. The mixture was gradually heated to 120 ºC and the pressure was reduced. The reaction was continued at 120 ºC for 7 h.

RESULTS AND DISCUSSION

Poly(lactic acid), as a biodegradable polymer is used in medical and packaging industries. *In situ* polymerization method was chosen and tin chloride catalyst used in reaction batch under vacuum conditions as catalyst. Temperature, reaction time, type and amount of catalyst affect the final product properties. In this study, the optimum temperature and polymerization time was determined.

FTIR of prepared poly(lactic acid) were provided in Fig. 1. The basic peak of polymer in FTIR spectrum indicates in 1759 and 1088 cm^{-1} related to the ester groups present in the structure of the polymer and the peaks in 1459 and 1387 cm^{-1} are related to methylene groups. Fig. 2 shows DSC of commercial poly(lactic acid) with melting temperature of *ca.* 145 ºC and glass transition temperature *ca.* 93 ºC.

Molecular mass and degree of polymerization of polymer was determined by viscosimetery. The viscosity of polymer solutions was determined and the reduced viscosity curve changes depending on concentration of polymer solution, polymer molecular mass was 11970 and the degree of polymerization was 131.

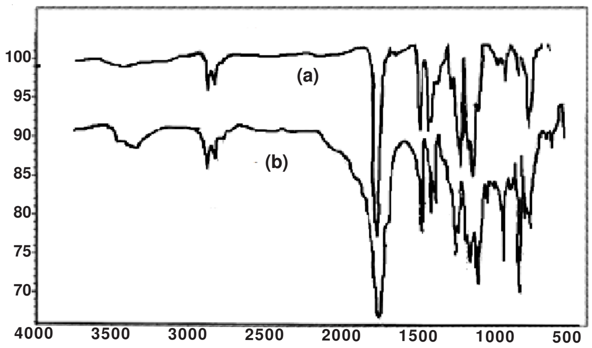

Fig. 1. FTIR of poly(lactic acid)

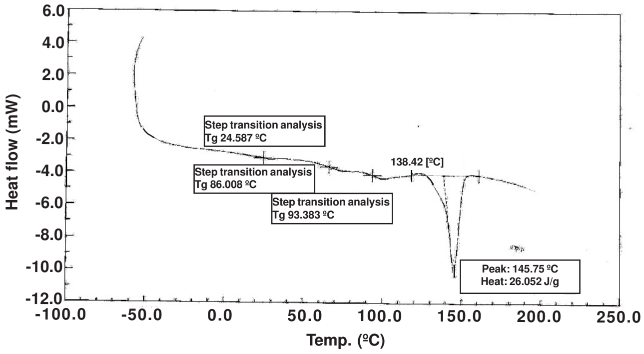

Fig. 2. DSC traces of poly(lactic acid)

Poly(lactic acid) nanocomposites were prepared by adding nano-clay cloisite 30 B. We added 2.5 % wt of nano-clay to polymer batch. Using ultrasound increase the efficiency of intercalation of organo-clay to polymer. Prepared nano-composite is characterized by DSC (Fig. 3) and crystallography spectroscopy XRD (Fig. 4). DSC thermal analysis indicated that the glass transition temperature increased to about 109 ºC[11,12] and melting temperature is *ca.* 145 ºC the same as commercial one. The degradation temperature of nanocomposite was *ca.* 168 ºC. Crystallography analysis of the nanocomposite shows the presence of nano-clay in polymer matrix[13-15].

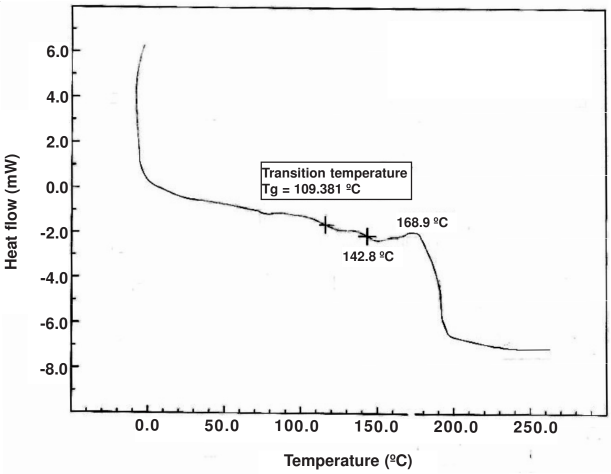

Fig. 3. DSC trace of prepared composite

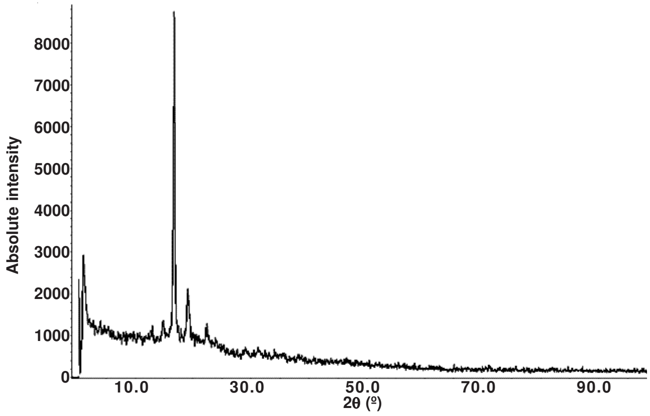

Fig. 4. XRD of prepared composite

Thermal analysis in nano-composite spectrum shows that the crystallization at low temperature is suggested due to presence of the endothermic peak. The presence of montmorillonite nanoparticles in crystal growth rate was effective. Therefore, crystal growth rate increased. Thermal degradation temperature of nano-composite approximately is equal to the amount of poly(lactic acid). But the presence and absence of montemontmorillonite in thermal degradation is shown.

Cation exchange capacity by titration with ammonium acetate method is determined by the amount of cations in the montmorillonite. Cation typically sodium or calcium montmorillonite which is combined with positive ions by correcting ion exchange reaction is displaced. Cation exchange capacity (CEC) value for the montmorillonite was 90 meq/100 g clay.

Two types of modifiers *viz.*, benzalkonium chloride (surfactants with benzene rings) and estearyl ammonium chloride (surfactant chain) were used because both types of compounds are non-pollutant compounds.

Crystallographic data can be determined the structure of amorphous and crystalline composition of clay. Crystallographic data of montmorillonite with benzalkonium chloride modifier (Fig. 5) and crystallographic data of montmoriollonite with stearyl ammonium chloride modifiers (Fig. 6) and their nanocomposite with poly(lactic acid) (Figs. 7 and 8) showed.

Comparison of structural information of crystallography showed that the crystal surfaces of both materials are comparable. The only major difference between them is the angle of the signal in the presence of modifiers.

Comparison between the spectrums of the X-ray diffraction of the clay and poly(lactic acid) nano-composite, found that the characteristic peak of the clay in poly(lactic acid) nanocomposite is shifted to lower 2θ that means the nanocomposite has intercalated structure. With increasing distance between the layers allows for better penetration represents strength materials are provided. Crystallography range direct evidence of a layer of polymer chains to silica by the gallery shows. It is believed that the presence of montmorillonite as strengthener in increasing the crystallization level.

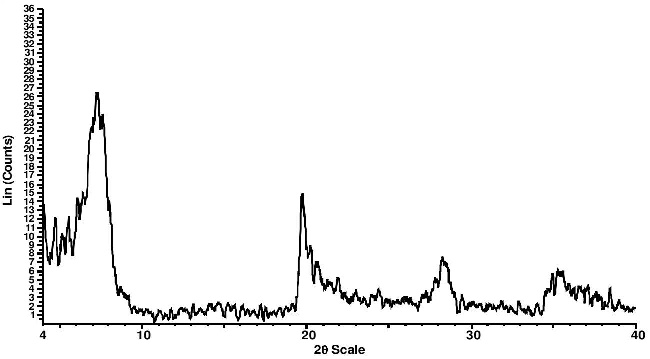

Fig. 5. Crystallographic data of montmorillonite with benz alkonium chloride modifier

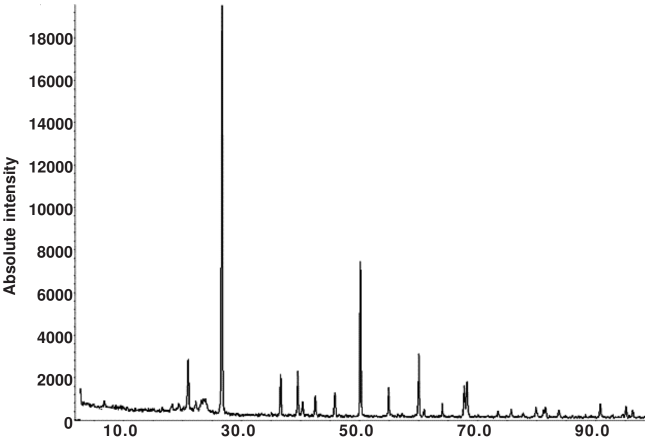

Fig. 6. Crystallographic data of mont moriollonite with stearyl ammonium chloride modifiers

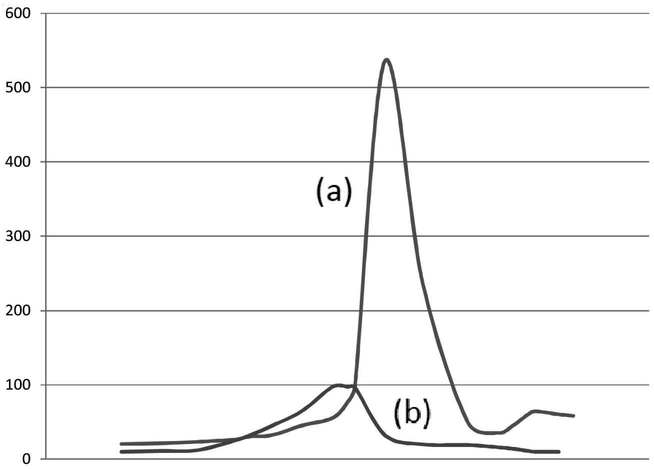

Fig. 7. Comparison of crystallography data between Organo clay and nanocomposite (a) clay sample, (b) organoclay

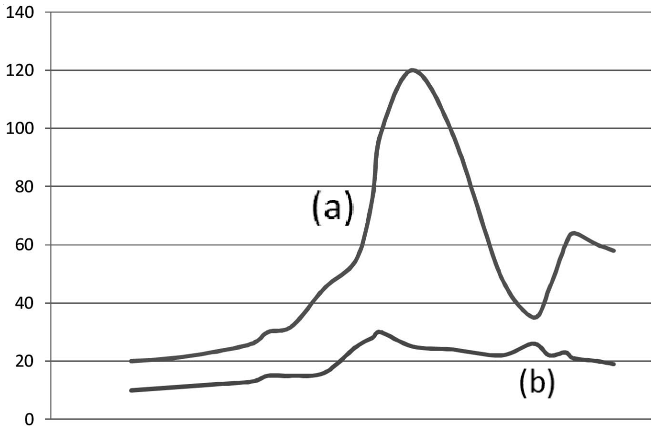

Fig. 8. Comparison of crystallography data between Organo clay and nanocomposite (a) clay sample, (b) organoclay

Fig. 6 showed the crystallization data of montmorillonite with stearyl modifier. This combination has been a long alkyl chain, thus the preventing effects on its behaviour is effective. Benzalkonium modifier compound structure is less perturbed space are created. It is noted that the nano-composite peak corresponding shift towards smaller angles has found that represents the space between the layers is increased.

Scanning electron microscopy was used to obtain micrographs of the PLA/OMMT blends at a magnification of 2000x. These reveal details of the phase structure with the dispersed rubber phase appearing as dark features against a lighter poly(lactic acid) continuous phase as shown in Figs. 9 and 10. In the images, it is observed partially exfoliated layers which are randomly distributed in the poly(lactic acid) matrix.

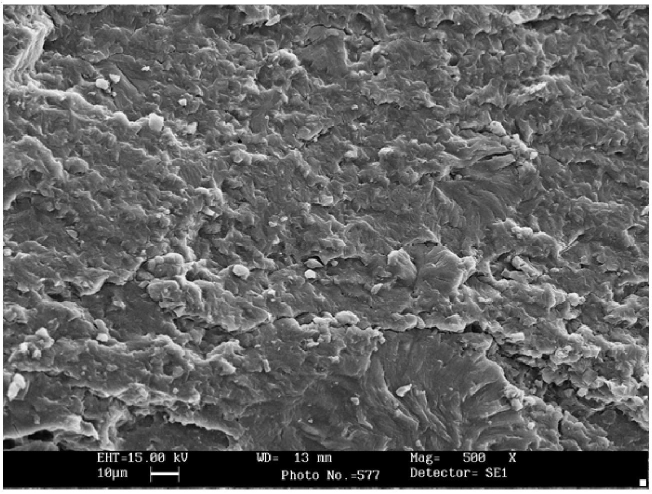

Fig. 9. SEM micrograph of PLA/OMMT

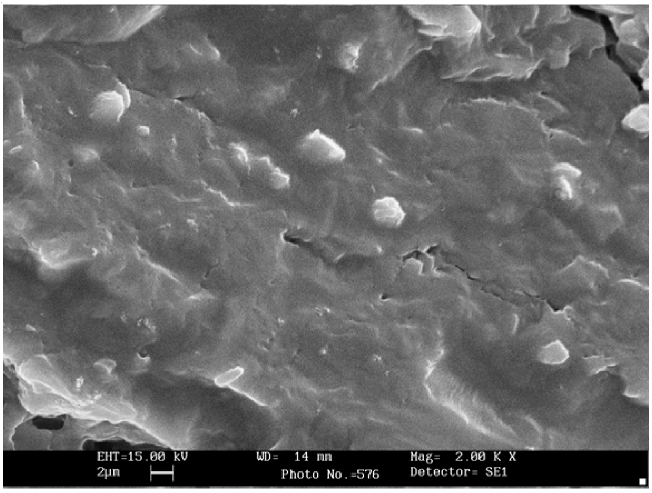

Fig. 10. SEM micrograph of PLA/OMMT

It is thus suggested that the organoclays prepared in this study can be used to prepare nanocomposites with poly(lactic acid) in order to render good level of dispersion and improved mechanical properties. Our efforts to examine the mechanical properties and permeability are under way.

Conclusion

Clay has been successfully modified using surfactants. The crystallographic results show intercalation of the organic cations between the clay mineral layers. *In situ* polymerization of lactic acid in the presence of organo clay was used to prepare poly(lactic acid)/clay nanocomposites. During the process, chain growth occurred in the poly(lactic acid) matrix. Our efforts to examine the mechanical properties and permeability are under way.

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