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Biodegradable poly(lactic acid)/kaolin clay nanocomposites prepared by melt mixture

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Abstract

Biodegradable polymer nanocomposites of poly (lactic acid) (PLA) and several organically modified kaolin, namely, Kaolin raw (K08), kaolin APTES (KS) and kaolin CTAB (KC) were prepared by melt compounding using a Brabender mono-screw extruder.

An exfoliated morphology was observed using both X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) for the combination of PLA with kaolin raw, with kaolin CTAB (the kaolin modified with a quaternary ammonium salt) and with kaolin APTES (the kaolin modified with 3-aminopropyltriethoxysilane).

Further studies were carried out to compare the properties of the nanocomposites with those of the neat PLA. Thermal stability of the nanocomposites was studied using thermogravimetric analysis (TGA).

Keywords: Biodegradable; Polylactic acid; Kaolin; Nanocomposite; Melt mixture.

1. Introduction

Poly (lactic acid), PLA, has received much attention for applications in biodegradable materials [1-3]. The polymeris produced from renewable resources, has excellent properties comparable to many petroleum-based plastics, and is readily biodegradable. Consequently, it has been proposed as a renewable and degradable plastic for use in service ware, grocery bags, waste-composting bags, films, and controlled release materials for pesticides and herbicides [4-7].

There are many types of philo-silicates: kaolinite, montmorillonite, hectorite, saponite, synthetic mica, etc [8, 9].The kaolin has sandwich-type structures with one octahedral Al sheet and one tetrahedral Si sheets, the so called philo-silicate [10].

Intensive mixing involves mixing the layered silicate with the polymer matrix in the molten state. Under these conditions and, if the layer surfaces have enough compatibility with the chosen polymer, the polymer can crawl into the interlayer spacing and form either an intercalated exfoliated nanocomposite [11]. Nanocomposites are a class of composites derived from ultrafine inorganic particles with sizes in the order of nanometers that are homogeneously dispersed in a polymer matrix. Because of their nanometer sizes, nanocomposites possess properties that are superior to those of conventional composites because of the interfacial adhesion being maximized. Recently, nano-scale composites of polymers with clays or organoclays have been studied extensively [12-17].

2. Materials and Methods

2.1. Materials

Poly (lactic acid) was supplied by Scopus S.A (Merignac, France) is in the form of spherical granules 3 to 4 mm in diameter. It is used without any special treatment, and was used as a matrix.

The kaolin used was collected from a naturaldeposit located in Tabelbala in BecharProvince,

Algeria. The average surface area and CEC (cation exchange capacity) of kaolin, which were measured using methylene blue technique, were 10.60 m2/g and 8.01 meq/100 g, respectively

The reagents used in this study were all extrapure analytical grades.

✓ 3-aminopropyltriethoxysilane (APTES) used for APTES-kaolin (KS) was purchased from Sigma-Aldrich. Its chemical formula is ($C_9H_{23}NO_3Si$); it is a

liquid product at 98% of purity with molecular weight of 221.37 g/mole.

- ✓ Cetyltrimethylammonium bromide (CTAB) used for CTAB-kaolin (KC) preparation was of analytical grade and was purchased from Aldrich Chemical. Its chemical formula is $(C_{16}H_{33})N(CH_3)_3Br$ with molecular weight of 363.9 g/mol.

2.2. Modification of kaolin (KC and KS)

20 g of natural Kaolin (K) dried at 105ºC wasdispersed into 300 mL toluene by ultrasound for 15 min. Then, 20 mL of APTES was added dropwise during vigorous stirring. The dispersion was refluxed at 100ºC for 24 h [18]. The modified kaolin was centrifuged and washed with toluene, followed by volume mixture between ethanol and distilled water (75/25 v%), respectively. The product was dried at 105ºC and sieved. This composite material Kaolin/APTES is named (KS). The sketch in Fig. 1 shows the structure of products and the grafting process with different types of interaction between the surface of the clay and APTES a) hydrogen bonding, b) proton transfer and c) an amine in the high position.

For CTAB-kaolin (KC) preparation, 10 g sample of the dried K08 was added to 200 mL of distilled watercontaining 0.3 g of CTAB. The suspension was then shaken, at 70˚C, for 24 h. The treated clay was then washed by shaking with 250 mL of water. The washing process was repeated several times until the washings were free from bromide ions as indicated by $AgNO_3$. The organokaolin was at last separated from water by centrifigation, dried at 80˚C and gently ground with a mortar and pestle to break up aggregate particles [19].

2.3. Preparation of PLA/Kaolin raw and PLA/Kaolin modified nanocomposites

The main function of the extruder is to convey, melt and pressurize the material introduced into the hopper so that it can cross the die. The maximum temperatures were maintained between 175 and 220 ° C. The speed of rotation of the screw is fixed at 63 turns / minute and the mass used of the clay / polymer or modified clay / polymer mixture is 6 g / 14 g. Let the mixture cool, crushed and sieved to obtain particles of 80 μm.

2.4 Scanning Electron Microscopy (SEM)

Morphology of the kaolin raw and nanocomposites were evaluated by scanning electron microscopy (SEM). The SEM study was carried out using Hitachi S-4800 equipped with energy dispersive spectrometry for chemical analysis (EDS) and operating at 15 kV acceleration voltages.
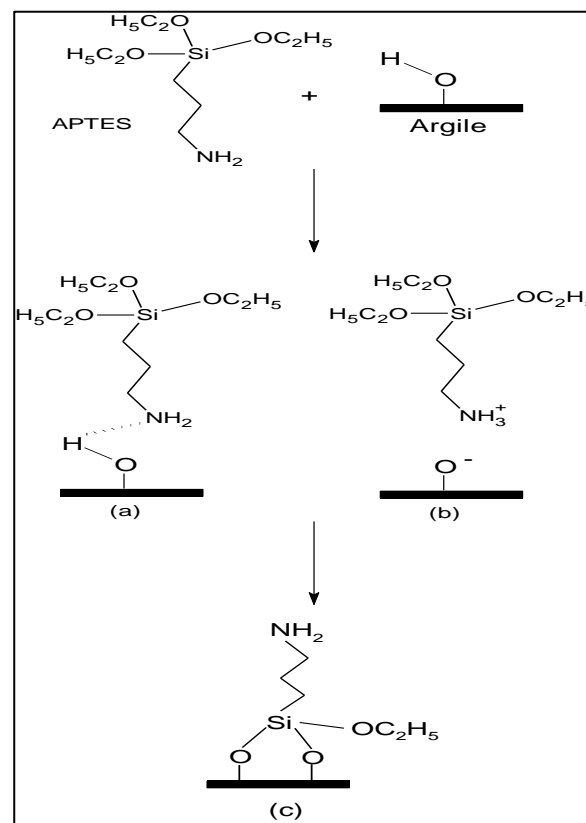

Figure 1. Modification of natural clay surface with APTES

2.5. X-Ray Diffraction (DRX)

Crystal structures of kaolin rawand the nanocomposites were investigated with an X-ray diffraction (XRD) technique with a diffractometer (Phillips-1730, PAN analytical). The X-ray diffractometer using Cu Kα radiation (λ=1.54Å).

2.6. Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier Transform Infrared (FT-IR) spectroscopy is used to identify functional groups of organic or inorganic compound. FTIR analysis was conducted using the BX Perkin Elmer-FTIR Spectrometer. The samples were grounded with KBr powder. The powdered mixture was then filled into a press where a thin and transparent pellet was made. The pellets were placed into the sample holder for scanning.

2.7. Thermogravimetric analysis (TGA)

TG-DTA thermograms were plotted using the multi-module 92 - 10 Setaramanalyser operating from room

temperature up to 1000°C in a Al₂O₃ crucible, at 10°C/mn heating rate.

3. Results and Discussion

3.1. Scanning Electron Microscope (SEM) Analysis

Figures 2 show SEM images obtained from the lateral surface of the nanocomposites.
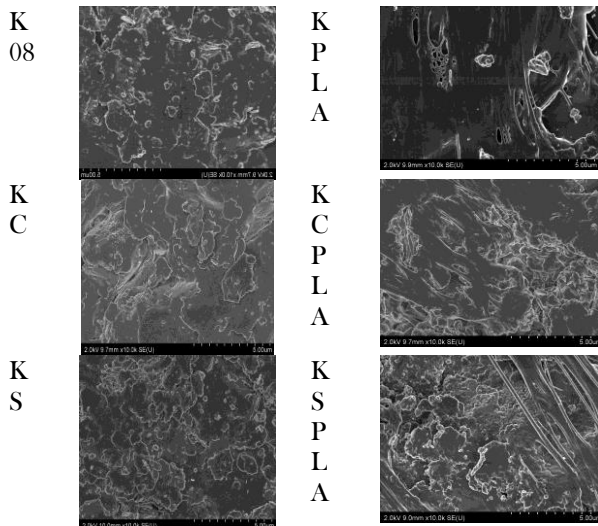

Figure 2. SEM images of Kaolin raw (K08), Kaoli modified by CTAB (KC), Kaolin modified by APTES (Ks) and Nanocomposites (KPLA, KCPLA and KSPLA) prepared by melt blending methods.

Indeed, the raw and modified clays are randomly dispersed within the PLA polymer matrix showing a crumpled structure which is generally connected to the thinnest thickness of the nanosheets.The images of nanocomposite materials show that the layers of raw and modified kaolin are completely exfoliated and well dispersed. This indicated that the crude and modified kaolin can be dispersed / distributed within the polymer matrix via the melt mixing process.

3.2. X-ray Diffraction (XRD) Analysis

The important parameter to achieve the best performance of polymer/clay composites, if clay does not produce defects, is the clay dispersion. X-ray diffractometry was used in order to identify intercalated structures. The intercalation of the polymer chains usually increases the interlayer spacing, leading to a shift in the diffraction peak towards lower angle values. The XRD results for the unmodified and modified kaolin are shown in the Fig.3. The measured d-spacing of kaolin raw is 14.8 Å. After cation exchange with CTAB, the d-spacing is

fixed at 14.9 Å and after fixed the APTES, the d-spacing is 19.5 Å. Kaolin is clearly affected by coating with APTES, as observed by the change in the peak corresponding to (001) reflection to low angles (5.96° in (K) to 4.63° in (KS)).
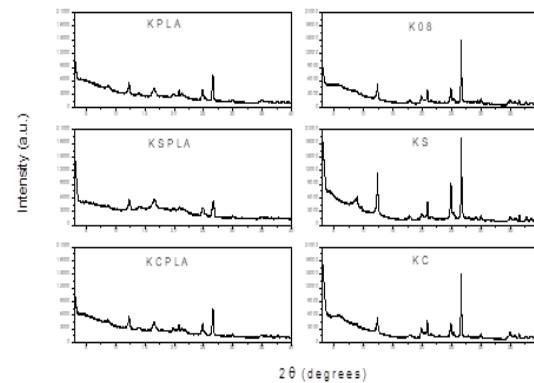

Figure 3. XRD of Kaolin raw (K08), Kaoli modified by CTAB (KC), Kaolin modified by APTES (Ks) and Nanocomposites (KPLA, KCPLA and KSPLA) prepared by melt blending methods.

It has been reported that the coupling agents can be attached to clays by chemical bonding, adsorption and coating to form a monomolecular layer or oligomer film on the clay mineral surface [20].
Fig. 1 shows no peak for PLA/ Kaolin raw and Kaolin modifieds nanocomposites, suggesting exfoliation of kaolin layers in PLA matrix.

3.3. FTIR Analysis

FTIR spectroscopy was used to characterize the interfacial interaction between the modified PLA/K08, PLA/KC and PLA/KS by melt-blending technique (Figure 4).

From the infrared spectra that we have obtained experimentally, it is a question of identifying each peak and confirming the real nature of the polymer analyzed. According to the different chemical groups present in the PLA polyesters, the infrared spectra of the nanocomposites will be divided into four regions shown in Fig. 4.

➢ Between 1090 - 1210 cm⁻¹ there are absorption bands which shoulder each other and which confirm the presence of the ester function -C-O-.

➢ The –C-H present in the form of a mixture of symmetrical and asymmetrical deformation vibrations materialize by the appearance of pronounced absorption bands in the area 1350 - 1472 cm⁻¹

➢ The carboxylic group -C = O can be identified by an intense absorption band present between 1750 and 1773 cm⁻¹

➢ The absorption bands between 2872 and 2950 cm⁻¹ are attributable to –C-H of the methyl groups.

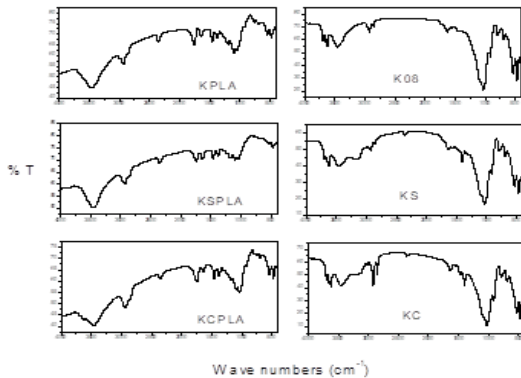The positions and intensities of the absorption bands correspond to the different groups constituting the PLA.

Figure 4. FTIR spectra of Kaolin raw (K08), Kaoli modified by CTAB (KC), Kaolin modified by APTES (Ks) and Nanocomposites (KPLA, KCPLA and KSPLA) prepared by melt blending methods.

3.4. Thermogravimetric Analysis (TGA)

Figure 5 shows the thermogravimetric curves for nanocomposites based on raw and modified Kaolin.
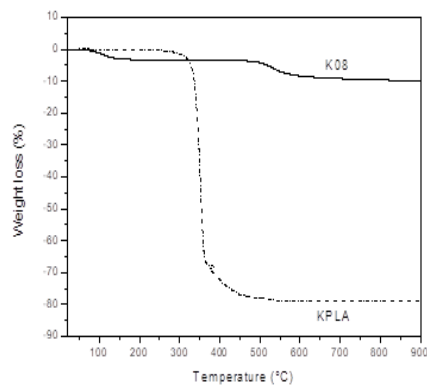

Figure 5(a). TG analysis of Kaolin raw (K08) and Nanocomposites (KPLA) prepared by melt blending methods.
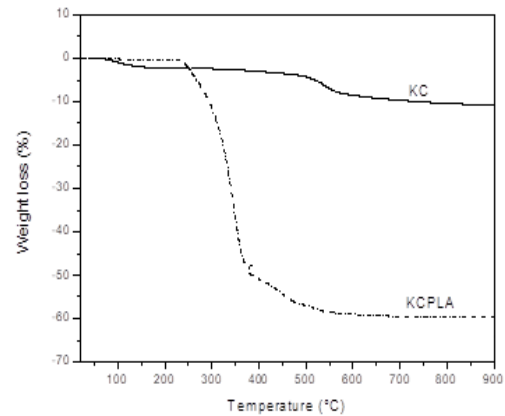

Figure 5(b). TG analysis of Kaolin modified by CTAB (KC) and Nanocomposites (KCPLA) prepared by melt blending methods.
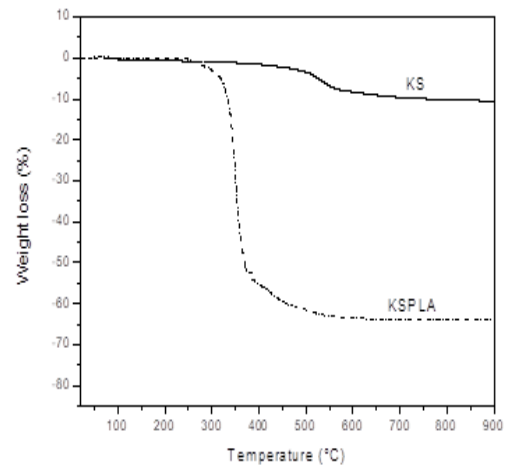

Figure 5(c). TG analysis of Kaolin modified by APTES (Ks) and Nanocomposites (KSPLA) prepared by melt blending methods.

Thermal degradation occurs over a temperature range of between 300 and 550 °C approximately. The samples begin to degrade at the same temperature. This degradation is then faster. The addition of crude or modified clays shifts the degradation temperature from 290 °C for the PLA polymer to around 364 °C for nanocomposites. This result is in agreement with those mentioned in similar research work or the authors generally observe an increase in the degradation temperature of nanocomposites due to good polymer / clay interactions or the clay platelets slow down the diffusion of the degradation products [21, 22].
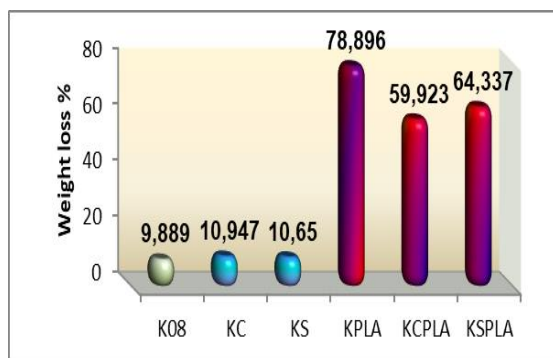
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Figure 6. Percentage of mass loss of materials prepared by the melt mixture

4. Conclusion

In this work, the PLA/Kaolin raw and PLA/Kaolin modifieds by CTAB and APTES nanocomposites were prepared as an exfoliated structure by melt blending method.

Fourier transform infrared (FTIR), X-ray diffraction (DRX), scanning electron microscopy (SEM) and thermogravimetric technique (TGA) were used to confirm the complete exfoliation of raw and modified kaolin by PLA polymers in the melt.

The dispersion / distribution of these nanolayers throughout the matrix volume require chain and nanofiller movements, on a large scale. These movements are generated by the imposed shear and heat during the production of the nanocomposite by the melt mixture. The most interesting technique is to melt nanocomposites. It has many advantages: the simplicity of implementation and the absence of organic solvents.

Acknowledgments

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