

THERMAL AND STRUCTURAL CHARACTERIZATION OF POLYVINYL ALCOHOL -KAOLINITE NANOCOMPOSITES

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New medical clay/polyvinyl alcohol nanocomposites of similar composition were prepared by both solution intercalation and mechanical mixing. Thermal and structural characterization of the precursors and of the composites showed that under proper parameters of mixing/milling process the composite can achieve structural properties to a large extent similar to that of the composite obtained by solution intercalation. In both cases of clay-polymer nanocomposites the clay occurs preponderantly as separated phase.

(Received August 22, 2011; accepted September 6, 2011)

Keywords: Clay-polymer nanocomposites; DTA/TGA; XRD; TEM

1. Introduction

During the last decade the properties of clays beneficial to human health received great interest although therapeutic effects of clays were used since prehistoric times [1]. Clay mineral based nanocomposites and polymer-clay nanocomposites have been proposed as very useful materials for many applications including biomaterials for tissue engineering and systems for drug delivery [2-4]. Clays are a specific class of minerals, hydrous aluminosilicates with a layered crystal structure. Because the clay particles are very small, of colloidal size, they are subjected to surface forces that influence their behavior and confer them convenient properties to be used in pharmaceuticals either as active ingredients or as excipients. They may be administered either orally as antacids, gastrointestinal protectors, antidiarrhoeaics, osmotic oral laxatives, homeostatics, direct emetics, antianemics and mineral supplements, or parenterally as antianemics and homeostatics [5]. The therapeutic activity of the clays is based on their physical and physico-chemical properties as well as on the chemical composition. The main properties which make them useful in medical applications are the structure, specific surface area and grain size distribution, that determine absorption/adsorption and cation exchange capacity. Polymer has been observed to adsorb onto clay mineral surfaces via van der Waals forces, electrostatic interactions, and hydrogen bonding interactions [6, 7].

Three different types of clay polymer nanocomposites may be obtained when a clay particle is associated with a polymer molecule in solution [8-12], wherein the clay appears as (i) separated phase, (ii) intercalated phase or (iii) exfoliated phase. In the case of phase separated structures, clay particles are simply dispersed in the system. In an intercalated structure, polymer molecules are inserted into the interlayer space of the clay, but the layers still maintain a well-defined spatial relationship to each other. In an exfoliated structure, the layers are completely separated and the individual layers are distributed throughout the system. A classical method for obtaining polymer-clay composite is the solution intercalation technique where the clay dispersions and polymer solutions are prepared separately and then mixed together. The clay-to-polymer volume ratio is defined as the proportion of clay volume with respect to polymer volume and is used to consider both clay content and polymer concentration simultaneously.

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The aim of this study was to investigate from thermal and structural point of view a new polymer-clay nanocomposite consisting of a medical clay and polyvinyl alcohol, in a first attempt to obtain clay/polymer nanocomposites for biomedical applications. The composite samples were obtained by two different synthesis routes.

2. Experimental

A medical clay pharmaceutically available as Algo clay, and polyvinyl alcohol (PVA) supplied by Acros Organics, with molecular weight from 20000 Da to 30000 Da, partially crystalline (25 %) and with 88 % hydrolyzation degree were used for the synthesis of the new composite system by both solution intercalation and mechanical mixing methods.

Clay dispersion was realized in deionized water. The mixture was placed on a magnetic stirrer and stirred for 2 hr to provide enough separation of interlayers. Polymer solution was prepared in a clay-to-polymer volume ratio 1:1 by mixing the appropriate mass of the polymer in deionized water at 70 °C. The solution was stirred for 2 hr. The two solutions were mixed together, stirred for other 2 hr and then air-dried. The obtained composite was grounded for 100 min in an agate ball mixer mill Retsch MM300 at the frequency of 30/s.

Apart from the conventional synthesis technique of solution intercalation, a new approach for obtaining a polymer-clay nanocomposite was investigated. This consists in mechanical mixing of quantities of polymer and clay for 10 hr in the agate ball mixer mill at the frequency of 30/s. The mixing/milling process provides high shear stress through mechanical energy input and this high shear stress may help the disruption of silicate layered structures and polymer to form exfoliated nanocomposites. This method is environmentally benign due to the absence of organic solvents [10].

Differential thermal and thermogravimetric analyses DTA/TGA were performed with Shimadzu DTG - 60H equipment at a 10 °C/min heating rate, from room temperature up to 700°C, in nitrogen and air dynamic atmosphere at 70 ml/min flow. The reference material was α -alumina and alumina open crucibles were used as samples and reference support. TEM analysis was carried out on a Jeol JEM 1010 microscope. X-ray diffraction analyses were made on a Shimadzu XRD - 6000 diffractometer using Ni-filtered CuK_α radiation (wavelength $\lambda = 1.5418 \text{ \AA}$) at a scanning speed of 2°/min. All measurements were taken using a generator voltage of 40 kV and a current of 30 mA.

3. Results and discussions

Thermal stability of the clay/PVA composites and precursors was assessed from analysis of the DTA and TGA curves (Fig. 1). The main data are summarized in Table 1. Three endothermic events and a major exothermic one are observed in the PVA thermograms (Fig. 1a). The first event occurs in the 50-130 °C temperature range, is accompanied by a 2% weight loss and is related to the removal of the physically adsorbed water. The second event takes place at 196 °C (maximum of the peak) with no mass loss and corresponds to melting of PVA. At higher temperatures the polymer will decompose. Two decompositions processes were reported [13] for PVA, a first one at 273 °C and the second one in the range 434–561 °C accompanied by a weightloss of 42–90%. The endothermic peak with T_{max} at 310 °C is related to the first degradation step of polyvinyl alcohol, with mass loss of 73%. The second degradation process of the polymeric chains appears in 416-546 °C temperature range and is correlated with the major exothermic peak at $T_{\text{max}} = 500^\circ\text{C}$ and a mass loss of 24%, presumably via backbone fragmentation or a chain-scission reactions with H_2 elimination and carbon/hydrocarbons yield [14-16].

Table 1. DTA/TGA data for clay, and clay/PVA composite samples.

Sample	Peak I		Peak II		Peak III		Peak IV	
	T _{max} (°C)	Mass loss (%)	T _{max} (°C)	Mass loss (%)	T _{max} (°C)	Mass loss (%)	T _{max} (°C)	Mass loss (%)
ALGO	–	–	–	–	504	14.2	–	–
PVA	64	2.1	196	0	310	73	500	23.7
ALGO/PVA mechanical mixing	64	2.7	199	3.3	371	35.2	495	15.7
ALGO/PVA solution intercalation	55	3.1	199	2.1	371	30	520	21.2

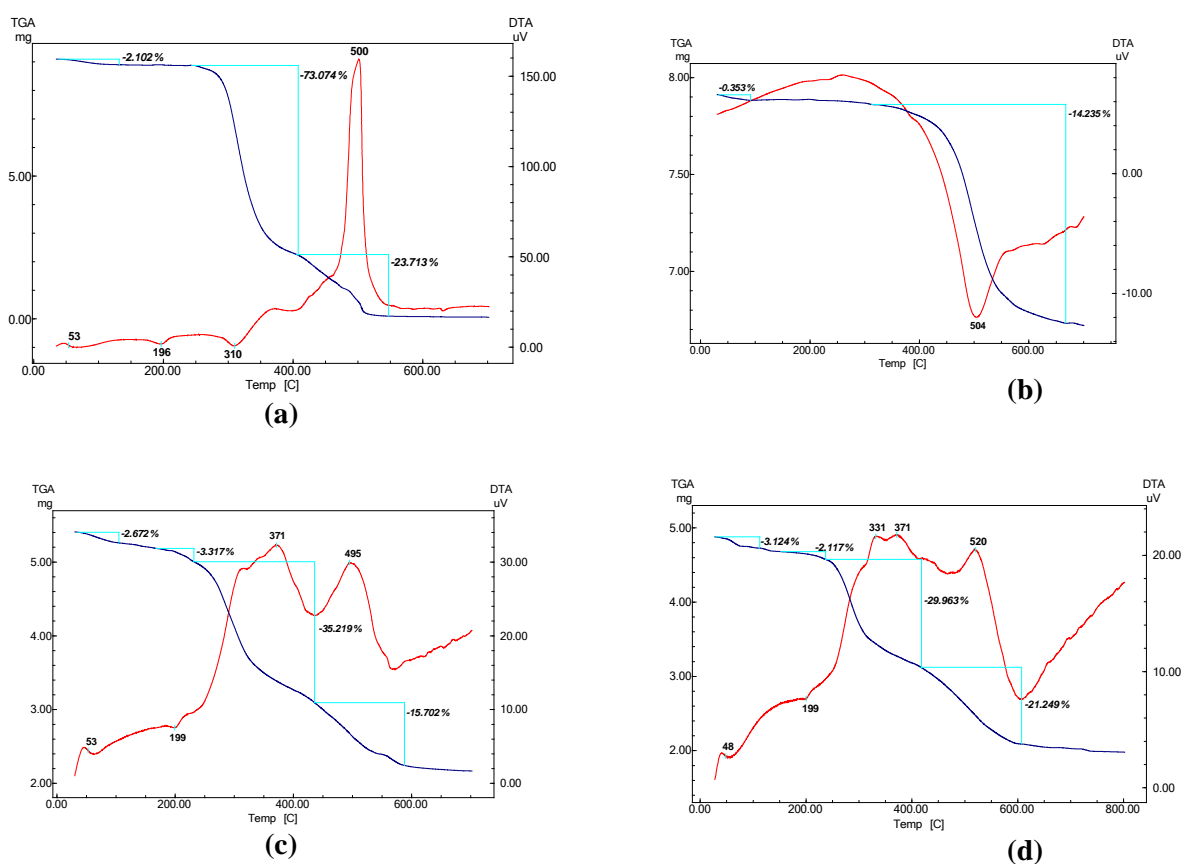


Fig. 1. DTA/TGA runs of polyvinyl alcohol (a), mineral clay (b) and the two composites obtained by mechanical mixture (c) and solution intercalation technique (d).

The DTA and TGA runs of the mineral clay (Fig. 1b) shows that the major thermal event occurs in 350-700 °C interval where the dehydroxylation of the silicate layers takes place. The polymer-clay composites exhibit a distinct behavior from both PVA and clay at temperatures above 200 °C as indicated in the DTA signals (Figs. 1c and 1d). The weak endothermic peak at 199 °C is related to the polymer melting process, while the about 3% mass loss along with the small shifting of the onset melting temperature towards higher temperatures, could be a consequence of the restricted segmental mobility of the polymer chains due to their attachment to the clay layers. Therefore the melting is accompanied by the releasing of polymer-clay links and

the removal of the related ions or gaseous by-products. The degradation of the polymer takes place in two steps of mass loss accompanied by two exothermic events with peaks maximum temperature at 371 °C and 497 °C, and 520 °C for solution obtained composite (Fig. 1d). The first decomposition stage occurs on a broader temperature range (230-430 °C) with an exothermic process unlike in the PVA, possibly due to the discharge of certain –OH or acetate groups. The second decomposition stage is extended on a larger temperature interval too, the exothermic peak overlays on the dehydroxylation process of the clay interlayers and present a much smaller intensity that in the PVA case. The silicate layers may act as a barrier for both the incoming gas and also the gaseous by-products, that on the one hand increases the degradation onset temperature and on the other hand widens the degradation process. The total mass loss of 51% in the decomposition stages unlike a major (97%) mass loss in pure PVA indicate a better thermal stability of both ALGO/PVA materials and the attainment of different composite structures.

The state of dispersion and exfoliation of clay nanoparticles are usually tested using X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses [10, 17]. The intercalated or exfoliated structure of clay nanocomposites is most commonly identified based on XRD data concerning the position, shape, and intensity of the basal reflections from silicate layers. In an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix is revealed by the disappearance of the clay diffraction peaks due to crystallographic order loss. On the other hand, for intercalated nanocomposites, the finite layer expansion associated with the polymer intercalation results in the appearance of a new basal reflection corresponding to the larger gallery height.

The ALGO clay diffractogram (Fig. 2) indicates a major crystalline phase of kaolinite [JCPDS card no. 29-1488], that is an aluminosilicate mineral, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, with a layered structure built up from silicon tetrahedra sheets crosslinked through oxygen atoms by other sheet of aluminum octahedra. The (001) reflection of kaolinite at $2\theta = 12.42^\circ$ indicate a basal d spacing of 7.11 Å. A minor phase of gibbsite, $\text{Al}(\text{OH})_3$, and quartz, SiO_2 , were identified by smaller intensity peaks. The maximum intensity peak at $2\theta = 18.42^\circ$ corresponds to (002) plane reflexion of gibbsite, and that at $2\theta = 26.76^\circ$ corresponds to the (011) plane reflexion of quartz.

The occurrence of the diffraction peak at $2\theta = 20.15^\circ$ in PVA diffractogram is due to the (101) plane reflection of crystalline PVA, with a d spacing of 4.40 Å. This XRD pattern indicates a typical semicrystalline structure.

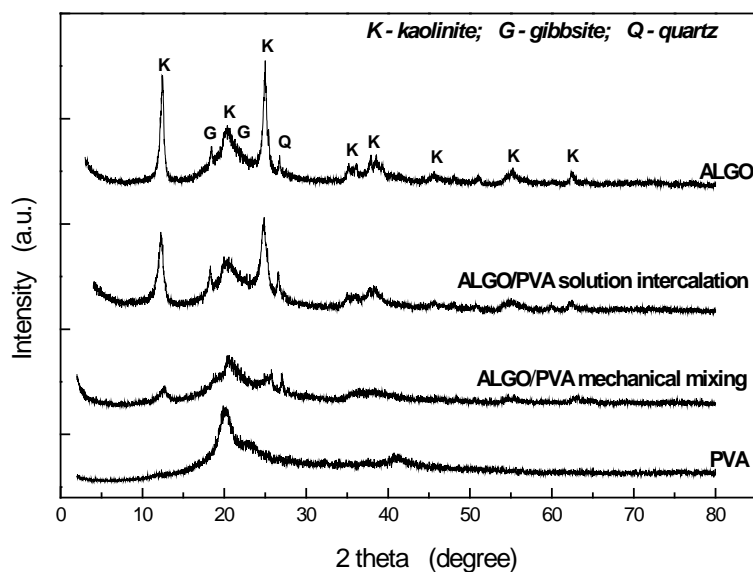


Fig. 2. XRD patterns of ALGO clay, PVA, and ALGO/PVA composites obtained by solution intercalation, and by mechanical mixing.

The diffractograms of the ALGO/PVA composites present similar diffraction lines, with very small shifts in their position and intensity. The basal d spacing characteristic to kaolinite from $2\theta = 12.42^\circ$ is decreased in the diffraction pattern of the mechanically mixed composite ($d = 7.03 \text{ \AA}$, $2\theta = 12.58^\circ$) while in composite obtained by solution intercalation method a slight increase of this parameter is obtained ($d = 7.23 \text{ \AA}$, $2\theta = 12.22^\circ$). Although the differences are not sufficiently large to sustain an exfoliated microstructure, these results indicate that the microstructure of the composite obtained by mechanical mixing is of phase separated type, and the composite obtained by solution intercalation appears to be of intercalated type, based on the increase of the basal spacing. The basal d spacings and the crystallites dimensions of the kaolinite phase, calculated using Scherrer formula, are summarized in Table 2.

Table 2. Characteristic parameters for kaolinite phase in clay, and clay/PVA composite samples.

Sample	Most intense peak 2θ (degree)	Basal d spacing (\AA)	Crystallite dimension (nm)
ALGO	12.42	7.11	35.56
ALGO/PVA mechanical mixing	12.58	7.03	14.64
ALGO/PVA solution intercalation	12.22	7.23	16.56

The analysis TEM images (Fig. 3) allows a qualitative understanding of the nanostructure, spatial distribution and dispersion of the nanoparticles within the polymer matrix. The TEM micrographs of the clay (Fig. 3a) shows well-defined pseudohexagonal crystals characteristic to kaolinite structure. A less crystalline structure with white thin intercalations representing the polymer (Fig. 3b) is observed for the composite obtained by mechanical mixture.

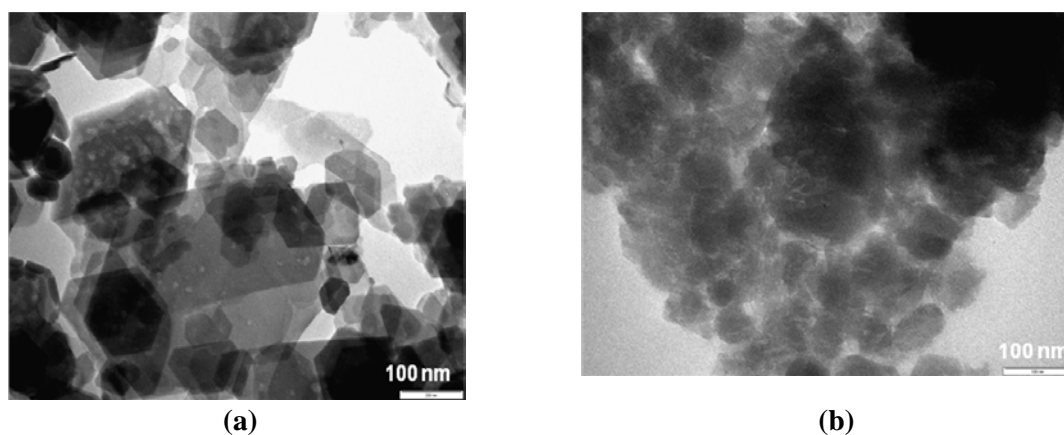


Fig. 3. TEM image of ALGO clay (a) and ALGO/PVA mechanically mixed composite (b).

The structure and properties of the clay based nanocomposites can be modified by changing both the synthesis method and the content of the components [18]. At the same time, the properties of the clay component strongly depend on the applied heat treatment [19, 20], that offers new possibilities to adjust the properties of clay nanocomposites. In this respect the selection of proper heat treatment parameters demands to know the structure and thermal behavior of the pristine samples.

4. Conclusions

Medical clay / polyvinyl alcohol composites of similar composition were prepared by both solution intercalation and mechanical mixing. DTA/TGA analysis points out a better thermal stability of the clay/polymer composites compared to the precursor polymer, as well as similar thermal behavior of the two composites, and implicitly a structural resemblance of the composite obtained by mixing/milling process under described conditions, and the composite prepared by solution intercalation. X-ray diffraction recordings and TEM images suggest a phase separated microstructure of both composites with a slight tendency of intercalation in the sample prepared by solution intercalation technique.

Acknowledgements

This research was accomplished in the framework of PNII Idei PCCE-248/2008 project granted by the Romanian National University Research Council – CNCSIS Romania.

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