

**EFFECTS OF CLAY TREATMENT ON PHYSICAL AND STRUCTURAL
PROPERTIES OF POLYAMIDE NANOCOMPOSITE***

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Abstract

The effects of clay treatment on physical and structural properties of polyamide nanocomposite have been studied. In this paper the polymer layered silicates have been prepared in situ polymerization. The analysis of the polyamide nanocomposites were made by means of XRD, DSC and AFM methods.

1. Introduction

Although the terms *nanomaterial* and *nanocomposite* represent an early new and exiting field in materials science, such materials have already existed for a long time in the polymer industry and have always existed in nature. A nanocomposite is defined as a composite material with at least one of the dimensions of one of the constituents on the nanometer scale. The resulting composites exhibit a multitude of enhanced properties, both physical (for example, electrical and thermal conductivity) and mechanical, so that the material cannot easily be classified as a structural or functional composite. Polymer/layered silicate nanocomposites have drawn research attention over the last fifteen years [1]. The major reason is that, as it has been demonstrated, introducing clay into polymers at the nanoscale level one can obtain improved mechanical, thermal, flammability and other properties at low clay contents (1-10wt.%). Polymer layered silicates have been prepared in different ways: intercalation in solution [2], in situ polymerization and direct melt intercalation [3]. The pristine layered silicates are classified as dioctahedral or trioctahedral.

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In clay minerals, the smallest structural unit contains three octahedral sites. Substitutions within the layers by ions of less charge, notably Si^{4+} by Al^{3+} in tetrahedral positions and Al^{3+} or Fe^{3+} by Mg^{2+} or Fe^{2+} in octahedral positions, result in negative charges on the layers. These are normally counterbalanced by alkali or alkali earth cations situated in the interlayer space. In pristine layered silicates the interlayer cations are usually hydrated Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions but a wide range of other cations, including organic ions, can be introduced by exchange reactions [3].

The replacement of inorganic exchange cations in the galleries of the native clay by cationic surfactants such as alkylammonium ions is known to help compatibilize the surface chemistry of the clay and the hydrophobic polymer matrix. The role of alkylammonium cations in the organosilicate is to lower the surface energy of the inorganic host and improve its wetting characteristics with the polymer. Additionally, organic cations may provide various functional groups that can react with the polymer to improve adhesion or initiate polymerization of monomers to improve the strength of the interfacial bond between the silicate and the polymer [3].

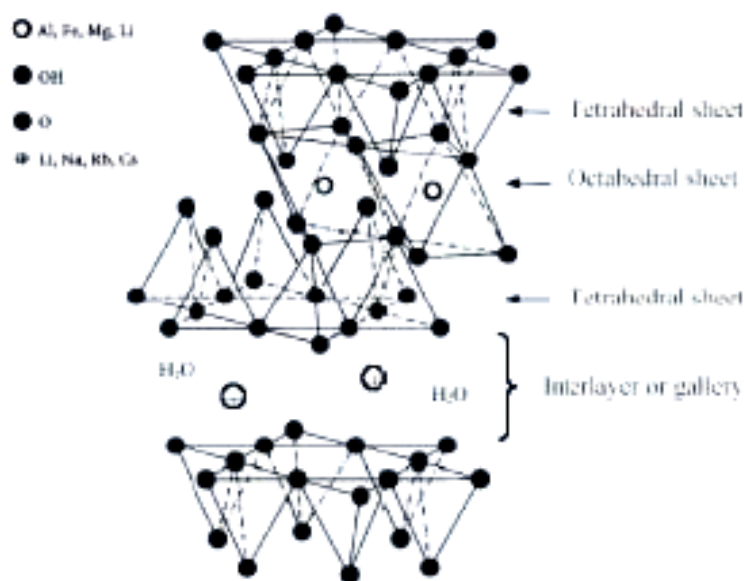


Figure 1: Structure of layered silicates

Three main types of composites (phase separated, intercalated and exfoliated or delaminated structure) may be obtained when a layered clay is associated, for example, with polyamide polymer matrix (Fig.2). These primarily depend on the method of preparation and the nature of components used (layered silicates, organic cation and polymer matrix).

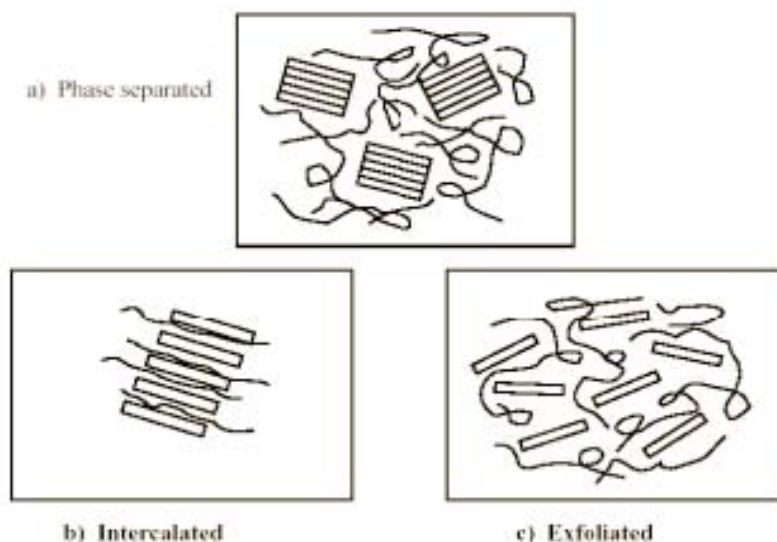


Figure 2: Schematic representation of different polymer/silicate

In this paper the polymer layered silicates have been prepared by in situ polymerization. This fact allows in the greater degree to realize their useful qualities and to carry out the directed influence on processes of structure formation and improvement of the operational characteristics of polymeric composites.

It is explained to that the quaternary ammonium salts particles brake electronic process basically at the expense by creation of adsorption potential by the positively charged atom of nitrogen, and the polymer, alongside with it, brakes process and at the expense of blocking a surface of polymeric structure. Nanostructure of produced composites and the interactions between atomic groups and polymer chains is demonstrated by X-ray diffraction and AFM methods.

2. Materials and methods

The preparation of polymer-clay composites has been conducted in two steps. Melt blended composites were prepared using an ED-2.2 disk-screw extruder at a constant rotating speed of 30 rpm and at temperature $200 \pm 5^\circ\text{C}$. Prior to each melt processing step, the samples based on polyamide were dried in a vacuum oven for 10 h at 80°C .

Extruded composites were injection molded into standard specimens using a Kuasy 25-32 injection molding machine at optimal temperature ranges. The same procedure was used to prepare the pure polymers.

Wide-angle X-ray scattering (WAXS) profiles of the samples were collected in the reflection mode using a DRON-2.0 diffractometer. Cobalt-filtered radiation (radiation wavelength $\lambda = 1.7889 \text{ \AA}$) was produced by an IRIS-M7 generator at an operating voltage of

25 kV and a current of 20 mA. The scattering intensities were measured using a scintillation detector scanning in 0.2° steps over the range of angles of 10 to 60°. The diffraction curves obtained were normalized for the intensity of the primary beam and the scattering volume by the usual technique.

2.1. Mechanical properties of polymer – organo-nanoline composites

The mechanical properties of all the composites were examined. For pure PA the tensile strength is 31 MPa and Sharpy impact 3, 2 kJ/m². With the incorporation of 3 wt.% organo-nanoline, the tensile strength increased to 64 MPa (which is 100 % higher than that of the pure PA) and, surprisingly, the Sharpy impact also increased to 6, 08 kJ/m² (which is ~ 100 % higher than that of the pure PA). As summarized in Table 1, there was a clear tendency that both mechanical properties (tensile strength and Sharpy impact) improve with increasing organo-nanoline content in PA composites. The decrease for 5 wt % seems consistent with the reduced exfoliation beyond 3 wt %.

This deterioration of the mechanical properties can be attributed to the aggregation of the organo-nanoline nanolayers. Summarizing, we observed a strong relationship between morphology and mechanical behavior of the investigated polymer-organo-nanoline composites.

Table I. Mechanical Properties

Nanocomposite	Properties	Nanolin DK4 (3%) P ₁	Nanolin DK4 (6%) P ₂
Polyamid 6	Tensile strength (MPa)	64,16	54,84
	Tensile strength at break (MPa)	71,92	72,46
	Sharpy impact (kJ/m ²)	6,08	8,64
	Elasticity Modules Strength (Mpa)	1440,79	1504,62
	Elasticity Modules at Flexion (Mpa)	2218,79	2245,82

2. 2. Effect of injection molding on nanoclay dispersion.

The XRD spectra of solid nanocomposites are shown in Fig. 3.

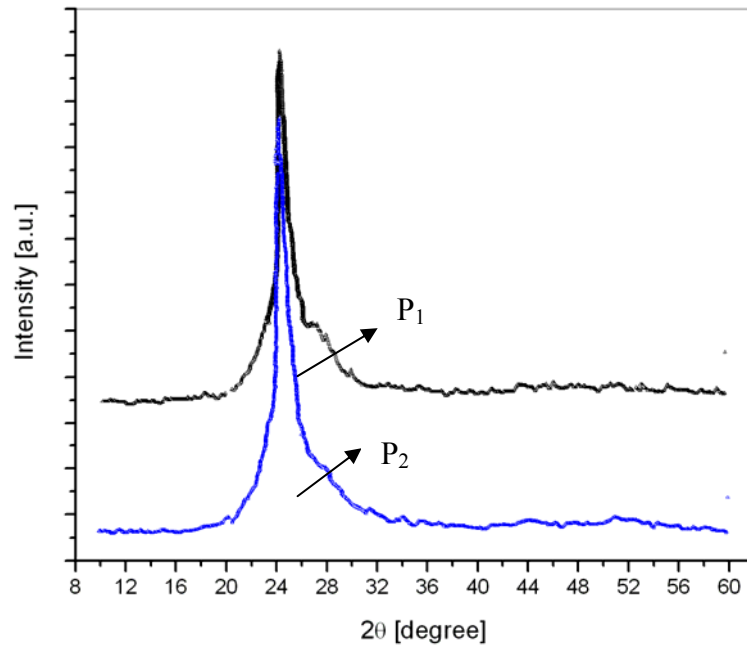


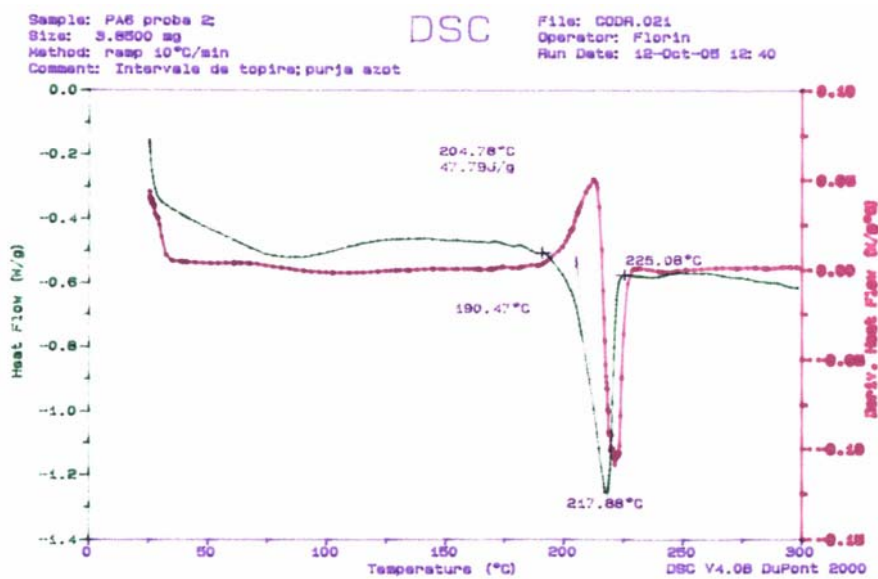
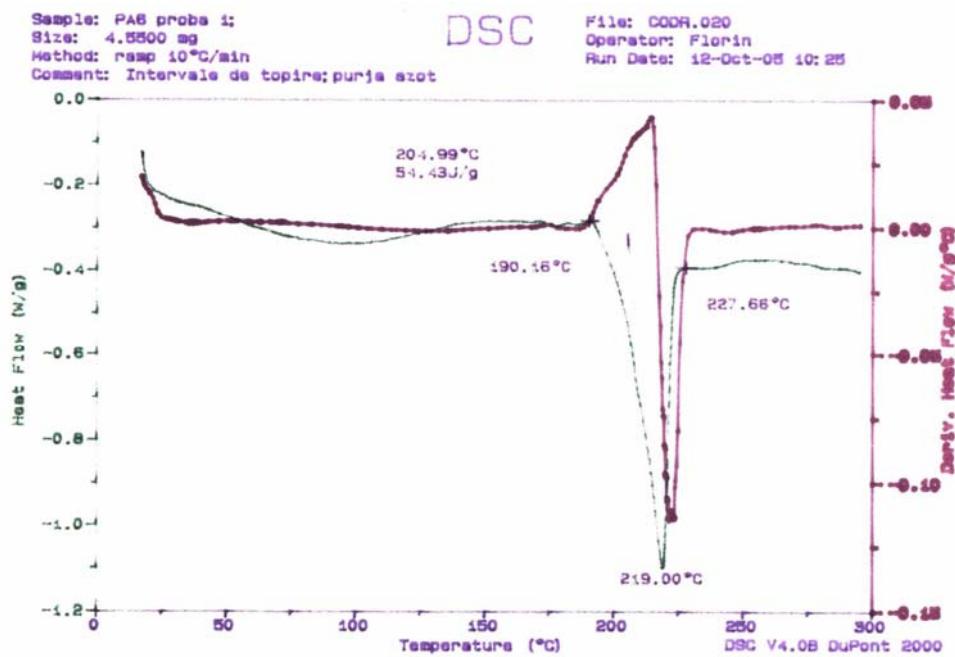
Fig.3. XRD pattern for P₁ and P₂ nanocomposite

The peak at the smaller 2θ angle reflects the larger platelet spacing of the intercalated nanoclay. The larger spacing means the greater delaminating effect of molding process. Depending on the molding conditions, better delamination and exfoliation can be achieved. The peaks for nanocomposite also decrease in height and get broader as delamination increases. This implies that the intercalated nanoclay preferentially orient along the flow direction.

2. 3. Thermal behavior of polyamide nanocomposites

On the thermal graphs of PA6 and PA6 nanocomposites, the strong endothermic peak around 219.4°C during the heating process is usually associated with the α form due to its high thermal stability, while the peak at 212.4°C is due to the γ form. Fig. 4(a) and 4(b) shows the melting curves of nanocomposite P1 under different molding conditions. By changing the molding conditions, the different ratio of the relative peak heights at about 212.4°C and 219.4°C, which corresponds to the different portion of α . and γ forms, can be obtained. For most molded parts, the deviation from the baseline at the starting and ending points of melting

curves can be clearly seen, which indicates the crystalline transformation occurring during the heating.



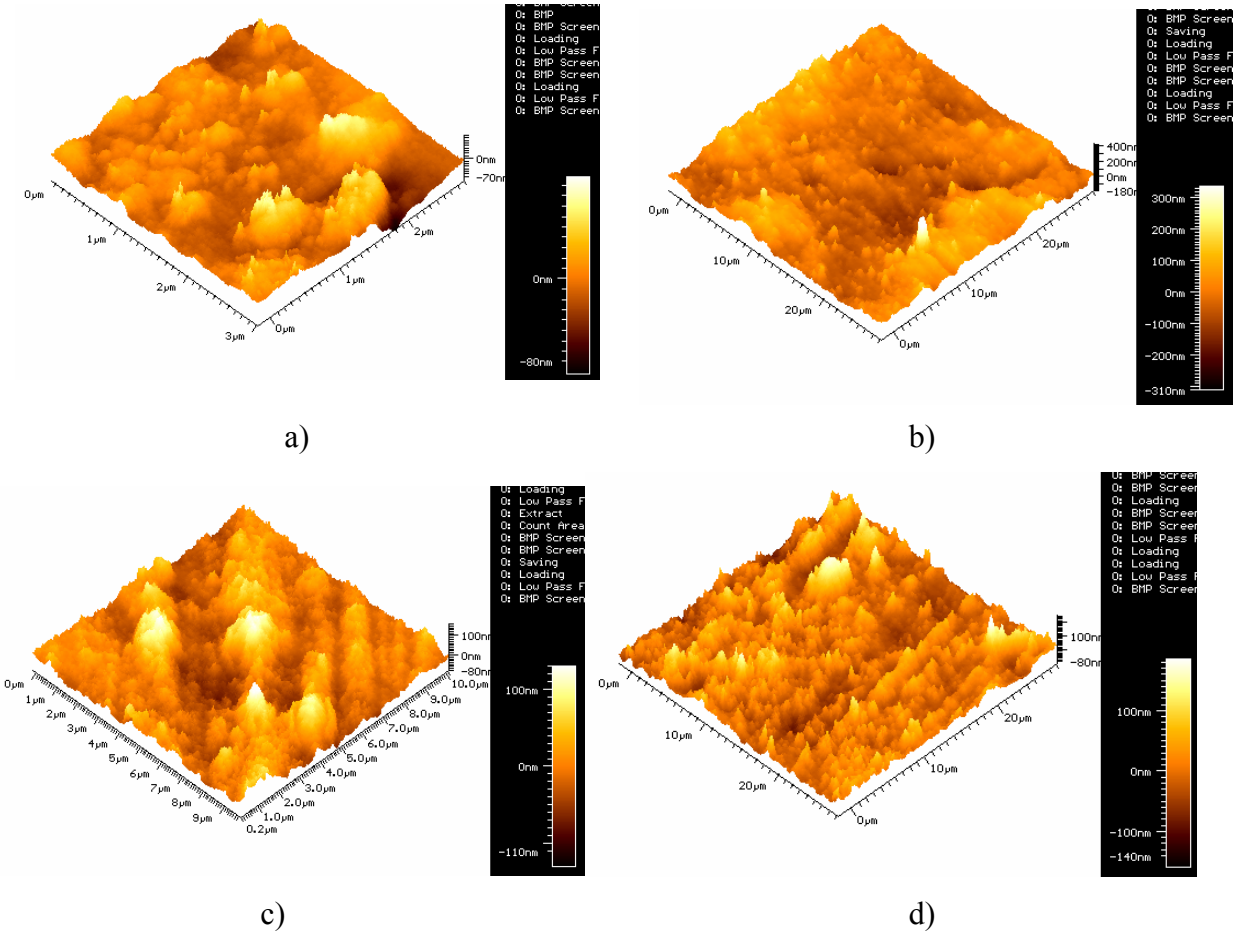
Figs.4. DSC for P₁ and P₂ nanocomposites

Comparing the XRD results with the DSC results, it seems paradoxical that the single α peak of the nanocomposite in the XRD spectra is split into two peaks for both α and γ forms in the DSC thermographs. Such imperfect structures will reorganize and transform into more perfect structures at the appropriate heating rate when the diffusion of the polymer species is improved during heating. [3]. The strong effect of some chain fraction reorganizing that

causes the lamellae to thicken can be expected. Therefore, the DSC peak at 212.4 °C is caused not only by the γ form but also by the thickening effect. The small γ form crystals melt so fast that they cannot keep up with the heating rates, hence their melting peak combines with that of the α form and the position of the peak appears at a higher temperature.

3. AFM Analyse

The measurements were performed using a home made atomic force microscope operating in the tapping mode. A commercial standard silicon cantilever NSC16 having a force constant of 17.5 Nm⁻¹, 210 kHz resonance frequency and tips with radius of 10 nm was used. The images consist of 256 × 256 samples over an area of 30 μm × 30 μm and 3x3μm. The analysis of the AFM images of the P₁ nanocomposite (see Table I) shows the presence of many spherical or oval particles with diameters of ~ 100nm. The AFM image of 3X3 μm, Fig. 5a, shows that, apart from these particles, there are smaller agglomerated particles (clusters). Consequently, we can say that, at the surface of the nanocomposite there are spherical structures (monomers, agglomerations, etc.).



Figs.5. AFM Images for P₁ and P₂ nanocomposites.

The analysis of the AFM images of the P₂ composite (see Table I) shows some chains or additions quite long and wide. In addition, on the surface of these chains, there are other particles, grains, obtained by polymerization in the presence of DK4 nanolin particles (see the image 30x30 μm, Fig. 5d). We can also see the small rugosity of the nanocomposite surface. Comparing the two nanocomposite samples, we observe that in sample P₁ there are high, numerous peaks, while in sample P₂ we have 100-150 nm high chains (see the image 10x10μm, Fig. 5c). On these chains we can see also, particles of 10 nanometers high, but these are less numerous than in P₁.

4. Conclusions

1. As summarized in Table 1, there was a clear tendency that mechanical properties improve with increasing organo-nanoline content in PA composites.
2. On the thermal graphs of PA6 and PA6 nanocomposites, the strong endothermic peak around 219.4 °C during the heating process is usually associated with the α cristalinity form due to its high thermal stability.
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References

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