

Structure and Mechanical Properties of Nanocomposites Based on Polypropylene - Clay Hybrids

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The effect of clay-hybrids treatment on physical and structural properties of polypropylene (PP J600) nanocomposite has been studied. The experiments carried out were focused on obtaining the polypropylene nanocomposite samples. In all the experiments the polypropylene with flow rate in melt of 9.21g/10min and nanoblend MB1201 were used. The structure analysis of polypropylene nanocomposites was made by means of XRD and FT-IR methods. XRD analysis shows that for nanocomposite based on polypropylene, the exfoliation of organo-bentonites takes place. The results shows a high improvement in the mechanic properties of the NPP4 with 5% and NPP4 with 15% glass fiber nanocomposite compared to the NPP4 nanocomposite.

Keywords: nanocomposite, structure; diffraction, absorption, mechanical properties

Polymer clay nanocomposites form a new class of materials which shows improved properties at very low loading levels of nanofiller in comparison to conventional composites of thermoplastic material. Polymer nanocomposites exhibit superior mechanical properties, reduced gas permeability, improved solvent resistance and enhanced conductivity over polymers. The analysis of polypropylene nanocomposites was made by means of XRD and FT-IR methods.

Although the terms *nanomaterial* and *nanocomposite* are defined within a new materials science field, such materials have already existed in the polymer industry and in nature. A nanocomposite is defined as a composite material with at least one of the dimensions of the constituents on the nanometer scale. Despite such complicated structure the smallest building block in these materials is generally on the nanometer scale [1].

The manufacturing of polymer nanocomposites usually consists of two stages: the compounding of a nanocomposite and the subsequent melt-forming process such as injection-molding. A primary concern is the achievement of a polymer nanocomposite containing homogeneously distributed and well-dispersed nanoparticles. The dispersion of nanoparticles especially depends on a magnitude of processing parameters, e.g. shear rate and processing temperature, as well as on the selection of appropriate materials. 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.%).

Materials

Preparation of samples

The pure layered silicates are classified as dioctahedral or trioctahedral. In clay minerals, the smallest structural unit contains three octahedral sites. Substitution within the layers by ions of smaller 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, results in negative charges on the

layers. These are normally counterbalanced by alkali or alkali earth cations situated in the interlayer space. In pure 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 [2].

Polymer layered silicates have been prepared in different ways: intercalation in solution [3], in situ polymerization [4] and direct melt intercalation [5].

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 [6]. Natural clay, as all natural products, suffers from lack of reliability, and therefore exhibits an experimental irreproducibility. Because of this, we use in our research work one type of nanoblend:

i) nanoblend MB 1201 (40% nanoclay and 60% PP J600) - imported from PolyOne Company, USA.

The majority of the papers use chemical or mechanical approaches to reach exfoliation (i. e. delamination and dispersion of individual clay lamellae inside the polymeric matrix).

High shear stresses are required to destroy the clay galleries and to exfoliate the clay lamellae.

An initial intercalated structure is needed to allow polymeric chains to penetrate the galleries and to exert local stresses that would exfoliate the structure under mechanical shearing.

Three main types of composites (phase separated, intercalated and exfoliated or delaminated structure) may be obtained when layered clay is associated, for example, with polypropylene matrix (fig.1).

These primarily depend on the method of preparation and the nature of components used (layered silicates, organic cations and polymer matrix).

The experiments carried out were focused on obtaining the polypropylene nanocomposite samples. In all the experiments the (PP J600) polypropylene with flow rate in melt of 9.21g/10min and nanoblend MB 1201 (made by

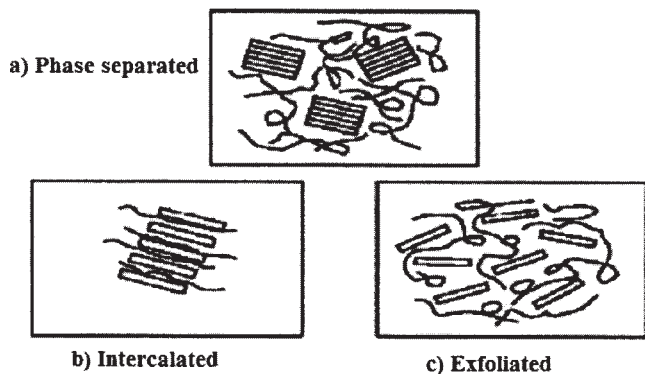


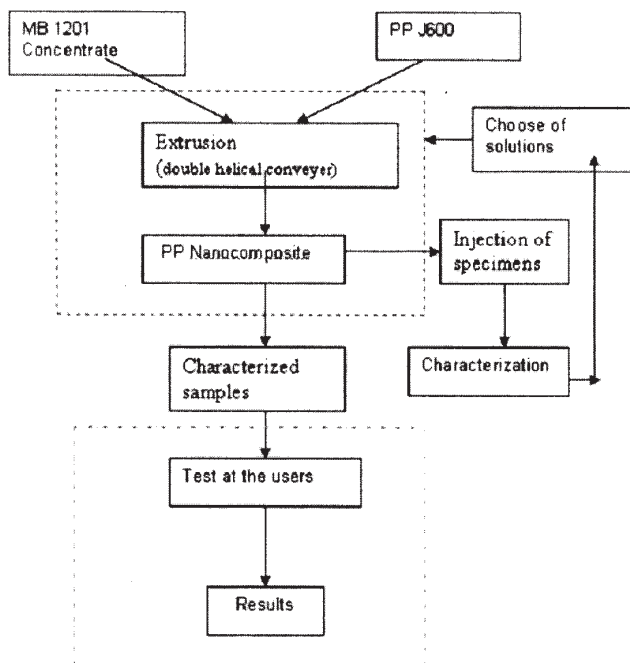
Fig. 1. Schematic representation of the composite types

PolyOne, USA) (40% nanoclay and 60% PP J600) were used. The dimensions of nanoblend MB 1201 nanoclay usually range between 1- 100 nm. It can be completely dispersed, the average size of the dispersed layers being around 25 nm.

Nanoblend MB 1201 was chosen for the experiments, with the following characteristics: interlayer distance is (d-001) 3.5 nm, white color, the organic compound is smectite.

The technological processes for the obtaining the samples have different stages. Here we have marked the segments of experiments which were repeated for different percentage mixtures of concentrate and polypropylene necessary to obtain the samples with final nanoclay contents of 4 and 6%, respectively.

We have worked according to this pattern and, as a result, the variant with 4 and 6% nanoclay in nanocomposite was chosen (scheme 1).



Scheme 1. Experiment working stages for NPP nanocomposite

Structure

1. XRD Analyze

Figures 2-4 show the XRD spectra of the nanoblend MB 1201, PP J600 and the various PP nanocomposites (NPP) compounded in a single-screw extruder configured with different temperature arrangements.

The organosilicate, nanoblend MB 1201, exhibited three distinct peaks characterizing its interlayer basal spacing, at 1.63, 3.82 and 8.26 ° 2 θ angles (fig.2).

The nanocomposites spectra show evidence of intercalation and exfoliation, indicated by the smoothing and the shifting of the second and third, order organosilicate reflections. In addition, intercalation of the organosilicate galleries by polymer matrix can be witnessed by the shift to lower 2θ angles of the second and third order organosilicate peaks. The shift of the diffraction patterns can be explained by means of the molecular interactions that take place in the nanocomposite. Molecular self-assembly is directed through noncovalent interactions (e.g., hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, and electrostatic effects) [7-8].

The variation in pattern observed for the various nanocomposites spectra would corroborate the influence of temperature configuration on the structural development of layered-silicate during the extrusion process would relate, to the presence of an optimum shear stress to overcome the electrostatic force between the layered-silicate interlayer [2, 6].

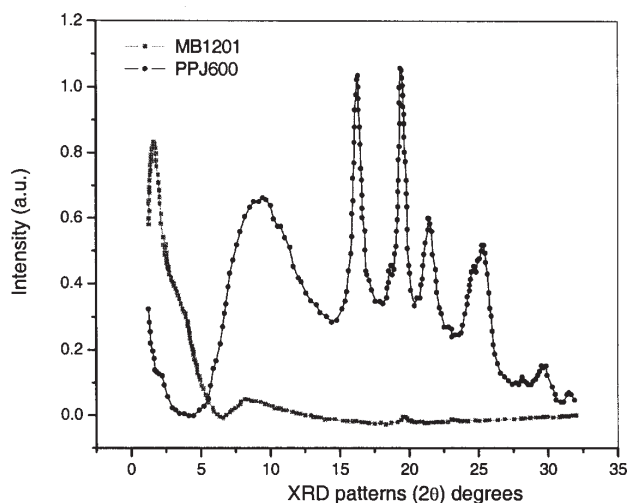


Fig. 2. XRD patterns of PPJ600 and MB 1201 nanoclay

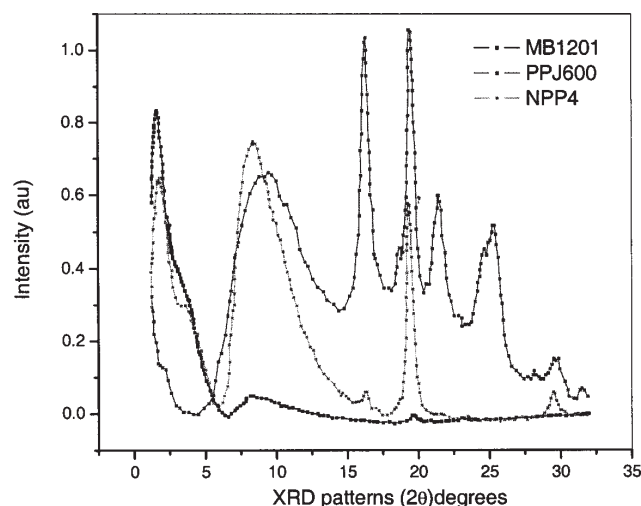


Fig. 3. XRD patterns of NPP4, PPJ600 and MB 1201 nanoclay

The influence of glass fibres

Figure 5 and figure 6 show the XRD spectra of the nanoblend MB 1201 (PP J600 with 40% clay), polypropylene with density J600 (PPJ600), polypropylene nanocomposites with 4% clay (NPP4) and NPP4 nanocomposites with 5% and 15% glass fiber in composition. The second diffraction peak of the NPP4 nanocomposites is shifted from 3.97 degree to below 3.42 degree corresponding to an interlayer

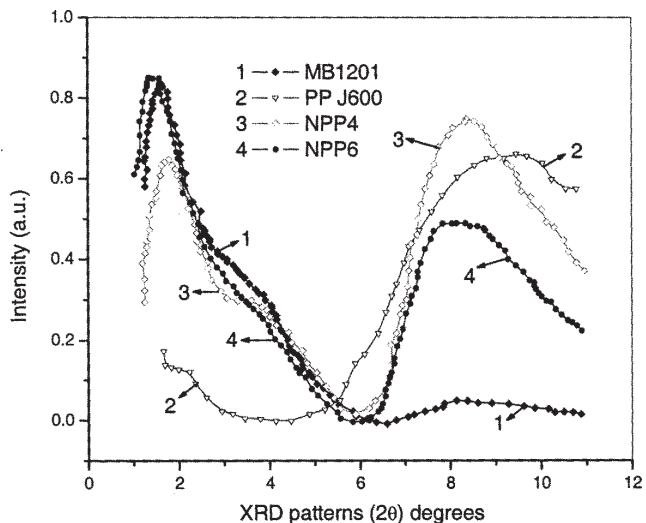


Fig. 4. XRD pattern of NPP nanocomposites

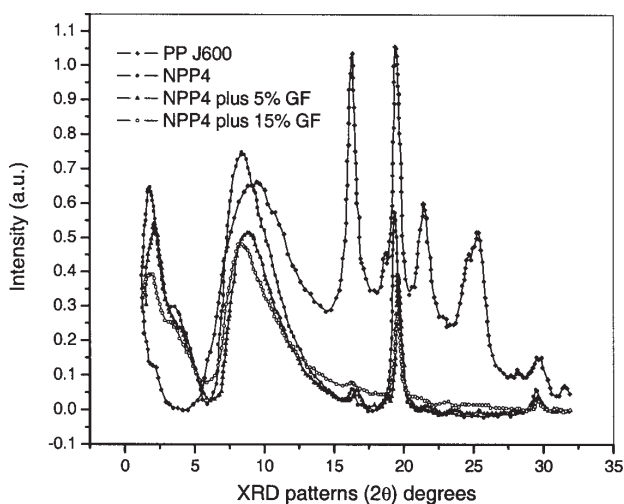


Fig. 5. XRD pattern for NPP4 with 5% and 15% clay hybrids nanocomposites

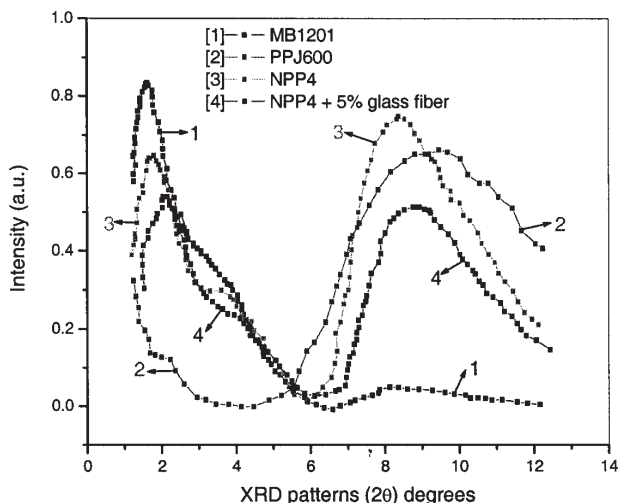


Fig. 6. XRD pattern for NPP4 with 5% clay hybrids nanocomposites expansion from 1.4 nm to greater than 2.2 nm. Figure 5 and 6 show the smaller shifts for nanocomposites containing 5% or 15% glass fiber.

FT-IR analyses

FT IR spectra of the studied nanocomposites have been obtained with a Varian EXCALIBUR 3100 spectrophotometer, using single reflection ATR technique. Analysis of

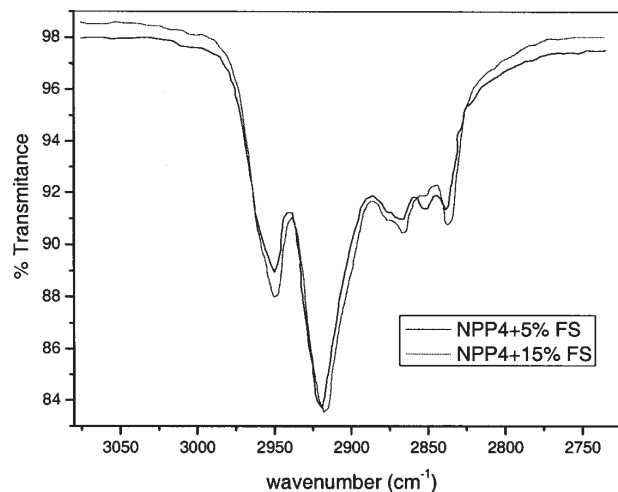


Fig. 7. FT-IR spectra of NPP4 clay hybrids in the range 2750-3000 cm^{-1}

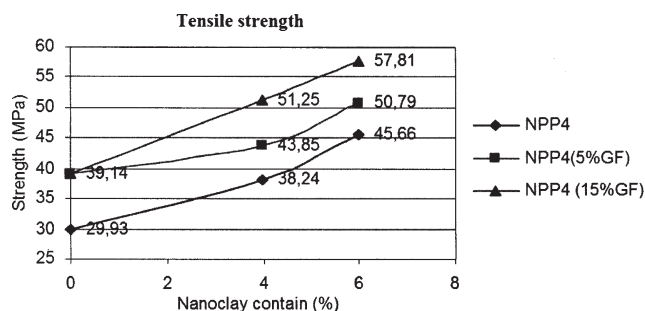


Fig. 8. Tensile strength vs. nanoclay content of NPP4, NPP4 (5%GF) and NPP4 (15%GF)

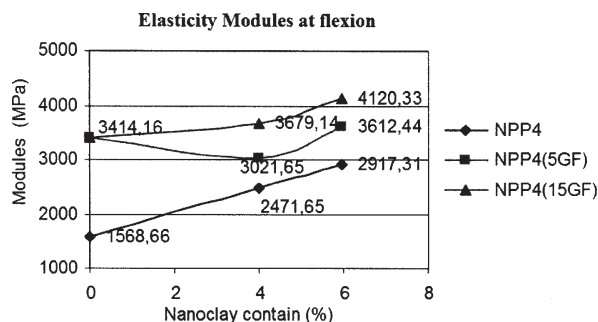


Fig. 9. Elasticity of modules of flexion vs. nanoclay content of NPP4, NPP4 (5%GF) and NPP4 (15%GF)

the FT IR spectra (fig.7) shows a change of the position and intensity of the v-CH symmetric band (2950 cm^{-1}) for NPP4 nanocomposite in spectral range $2800-3000 \text{ cm}^{-1}$. The intensity band of the NPP4 with 15% glass fiber nanocomposite is higher than the intensity band of the NPP4 with 5% glass fiber nanocomposite. The intensity of molecular interaction for NPP4 with 5% glass fiber nanocomposite is much smaller than in the case of NPP4 with 15% glass fiber nanocomposite. This result is in agreement with the results based on XRD method.

Mechanical Properties

The resistance tests for the obtained samples have been done on injected samples (on an IMATEX-MP-TI -100/50 injection machine). The resistance tests have been done at ICEFS SA Savinesti on a FPZ 10Heckert dynamometer and MOLDOPLAST SA Iasi on a traction machine TIRATES 2200 and a FP2-10 dynamometer. The processes taking place in the injection machine were taken into account for obtaining high quality samples:

- typological peculiarities of the polypropylene polymers for the injection (melt viscosity, melting time, specific heat, crystallization);
- thermotechnological process (injection time, post-pressing time, injection pressure, injection speed, polymer mass temperature, matrix temperature);
- internal tensions and contractions in the injection products. The data (fig.8, fig.9) show a high improvement in the mechanic properties of the NPP4 with 5% and NPP4 with 15% glass fiber nanocomposite compared to the NPP4 nanocomposite. The data (fig.10) also show, that in case of elongation of break we have obtained much smaller values for NPP4 with 5% and NPP4 with 15% glass fiber nanocomposite compared to the NPP4 nanocomposite.

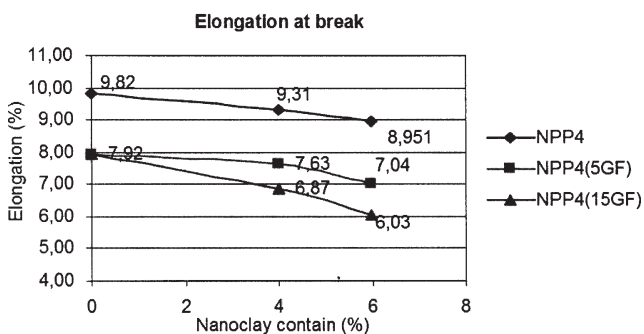


Fig. 10. Elongation at break vs. nanoclay contain of the NPP4, NPP4 (5%GF) and NPP4 (15%GF)

Conclusions

The preparation of nanocomposites by extrusion of linear polymers with organoclay depends on the level of polymer polarity. As a result, the mechanical properties were improved with increasing organo-nanoline content in PP J600 composites.

XRD analysis show that for nanocomposite based on polypropylene, the exfoliation of organo-bentonites takes place.

Data in figure 8 and 9 show a high improvement in the mechanical properties of the NPP4 with 5% and NPP4 with 15% glass fiber nanocomposite compared to the NPP4 nanocomposite.

The resulting data in figure 10 show also, that in case of elongation of break we have obtained much smaller values for NPP4 with 5% and NPP4 with 15% glass fiber nanocomposite compared to the NPP4 nanocomposite.

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