JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 6, June 2008, p. 1408 - 1414

Structure and mechanical properties of nanocomposites based on polypropilene and polyethylene

I. GRECU[a], G. STRAT[a], S. GURLUI[b,d,*], V. GRECU[a], I. LIHTETCHI[c], M. STRAT[b], S. STRATULAT[d], C. PICEALCA[e]
[a] *"Gh.Asachi "Technical University of Iasi, Romania*
[b] *"Al.I.Cuza" University of Iasi, Faculty of Physics, Bdul Carol I nr 11, Iasi, 700506, Romania*
[c] *Transilvania University of Brasov, Romania*
[d] *UMF GR T Popa ,Iasi, Romania*
[e] *Laboratory of the Research Institute for Synthetic Fibres, Săvineşti, Piatra Neamţ*

Polymer clay nanocomposites are a new class of materials which show improved properties at very low loading levels of nanofiller comparing to conventional particulate composites of thermoplastic material. Polymer nanocomposites exhibit superior mechanical properties, reduced gas permeability, improved solvent resistance and enhanced conductivity over polymers. The enhanced reinforcement is a result of the much greater surface to volume ratio of these high aspect ratio fillers. The effect of clay treatment on physical and structural properties of polypropylene (PP J600) and low density polyethylene (LDPE) nanocomposite have been studied. The analysis of polypropylene and polyethylene nanocomposites was made by means of XRD, FT-IR, DSC and AFM methods.

(Received May 4, 2008; accepted June 4, 2008)

Keywords: Polypropilene, Polyethylene, Nanocomposite, XRD, FT-IR, DSC, AFM

---

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. Such compsites exhibit many levels of hierarchical structures from macroscopic to microscopic length scales. Despite such complicated structures the smallest building blocks in these materials are generally on the nanometer scale. The manufacturing of polymer nanocomposites usually consists of two stages: the compounding of a nanocomposite and the subsequent melt- forming process such as injection-moulding. 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 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 [3] and direct melt intercalation [4]. The pristine layered silicates are classified as dioctahedral or trioctahedral. 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 [5].

The replacement of inorganic exchange cations in the galleries of the native clay by cationic surfactants such as alkylammonium ions is known to help compatibles 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 [6]. In Fig. 1 the schematic presentation of montmorillonite structure is given.Since natural clay, as all natural products, suffers a lack of reliability, and therefore exhibits an experimental irreproducibility we choose to use in our research work with two types of nanoblend: i) nanoblend MB 1201 (40%

nanoclay and 60% PP J600); ii) nanoblend MB 2101 (70% nanoclay and 30% LDPE). These materials were imported from PolyOne Company, USA.

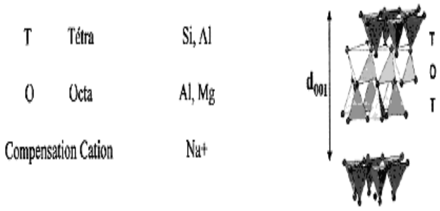


Fig. 1. Schematic presentation of montmorillonite structure.

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

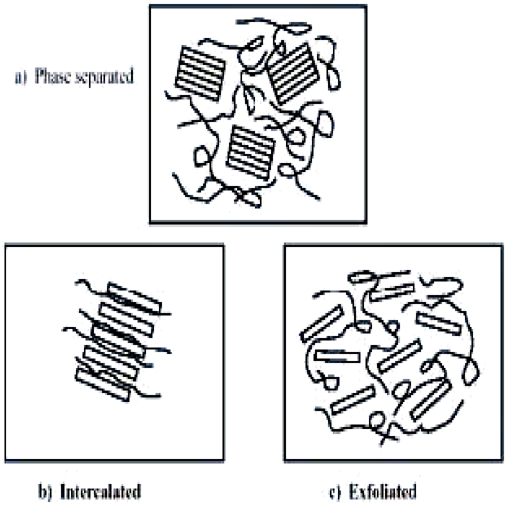


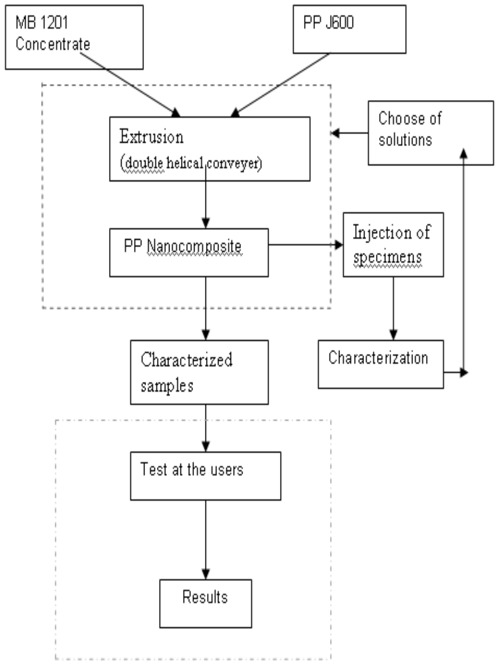
Fig. 2. Schematic representation of different polymer/silicate.

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. Nanostructure of produced composites and the interactions between atomic groups and polymer chains is demonstrated by X-ray diffraction and FT-IR spectroscopy.

2. Materials and methods

2.1. Preparation of polypropylene nanocomposites

The experiments carried out were focused on obtaining the polypropylene nanocomposite samples. In all the experiments the polypropylene (PP J600) with flow rate in melt of 9.21g/10min and nanoblend MB 1201(made by 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, while the L/D ratio ranges between 100 and 1000. Nanoblend MB 1201 was chosen for the experiments, with the following characteristics: interlayer distance (d-001) 3.5 nm, color- white, organic compound of smectite. The technological processes have different stages for the obtaining of the samples. 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 the result of the characterization of the obtained samples from the standpoint of the physical- chemical properties, the variant with ~6 % nanoclay in nanocomposite was chosen (Scheme I).



Scheme I – Experiment working stages

The concentrate was obtained on a laboratory extruder with two co-rotating helical conveyers type APV Baker, England, working at temperatures between 200- 220°C on the heating zones, using as starting material the J600 type polypropylene with fluidity index 9.21g/10min, and nanoblend MB 1201.

A polypropylene- nanoblend MB 1201 concentrate was obtained with the 50/50 mass ratio, which was later used to obtain samples of polypropylene nanocomposite on the micro- pilot installation of compounding by extrusion (*Research Institute for Synthetic Fibres-*

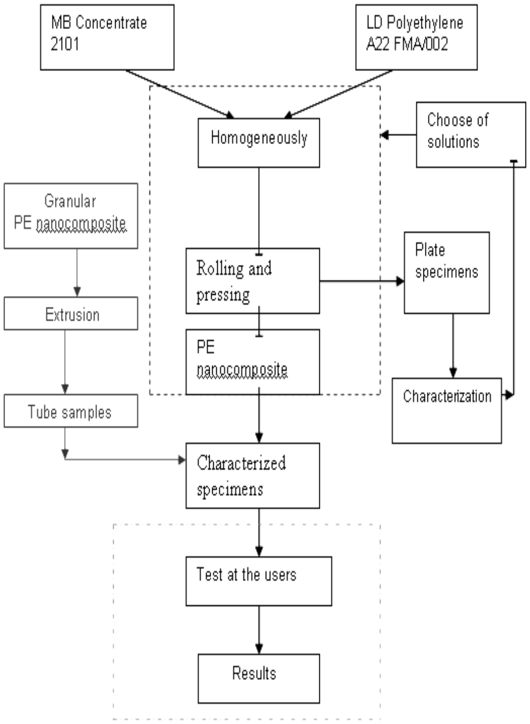
Savinesti) of a pre-established quantity, such that finally the theoretical content of nanoclay in composite was 4, and 6%. For all the experiments, the same formula was respected, as well as the same temperature zones on the extruder heating zones, namely between 200- 220°C. Even if the experimental conditions were similar, several samples of nanocomposite were obtained, with nanolin concentration between 1.5 and 7.8%. Considering the obtained data, the resulted samples were mixed on the extruder such that finally samples with nanoclay loading of 3.95 and 6.98% were produced.The target of the experiments, as well as the main purpose of the work, was to obtain polyolephyne nanocomposites with improved properties that should represent the basis of starting materials for the preparation of techno- polymers for different fields of application.In order to characterize the obtained specimens, both usual techniques for polymer characterization and techniques to determine the structure, nanomer dispersion degree, etc, were used. The flow rate on warm material (MRF) was determined on a Koka Flow Tester Shimadzu (for volume flow rate) and on an apparatus made at *Research Institute for Synthetic Fibres (RISF)*-Savinesti according to the standards for mass flow index. The flow rate is an important property for plastics processing. The dispersion of a nanomer in a polymer can change its flow properties, this involving also alterations of the processing parameters. Knowing the flow rate gives the users the necessary information for a correct processing of nanocomposites.With the view to perform the resistance tests (stretch and bending) for each of the obtained samples, specimens were injected with the injection machine IMATEX- MP- TI- 100/50, in order to choose the ones considered as having the best behavior. The resistance tests were carried out at RISF Savinesti on a dynamometer FPZ 10Heckert and a Charpy pendulum. One must specify that these tests were carried out on specimens injected on the same injection machine. In order to obtain specimens of the adequate quality, the processes occurring in the injection machine were considered, such as:

- Typological peculiarities of the olefine polymers for injection (melt viscosity, melting interval, specific heat, crystallization).
- The thermo- technological process (injection time, post-processing time, injection pressure, polymer mass temperature, mould temperature)
- Internal contractions and tensions in the injection products.

2.2 Preparation of polyethylene nanocomposites

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

A polyethylene- nanoblend MB 2101, concentrate, from PolyOne, USA, was obtained with the 50/50 mass ratio, which was later used to obtain samples of polyethylene nanocomposite on the micro- pilot installation of compounding by extrusion (*Research Institute for Synthetic Fibres*-Savinesti) of a pre-established quantity, such that finally the theoretical content of nanoclay in composite was 4, and 6%. The typological peculiarities of the polyethylene polymer for injection and the thermo- technological process (injection time, post-processing time, injection pressure, polymer mass temperature, mould temperature) were taken in consideration. The experiment working stages for polyethylene nanocomposite are given in Scheme II.



Scheme II – Experiment working stages for polyethylene nanocomposite

3. Structure

3.1 XRD analyses

Fig. 3 and Fig. 4, show the XRD spectra of the nanoblend MB 1201, PP J600 and the various PP nanocomposites compounded in a single-screw extruder configured with different temperature arrangements. The organosilicate, nanoblend MB 1201, exhibited three distinct peaks characterising its interlayer basal spacing, at 1.63, 3.82 and 8.26 ° 2θ angles. The nanocomposites spectra showed evidence of intercalation and exfoliation, indicated by the smoothening, the shifting of the second and thread, 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 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 proposed by Fornes [5] or as Kim[6] would relate, to the presence of an optimum shear stress to overcome the electrostatic force between the layered-silicate interlayer.

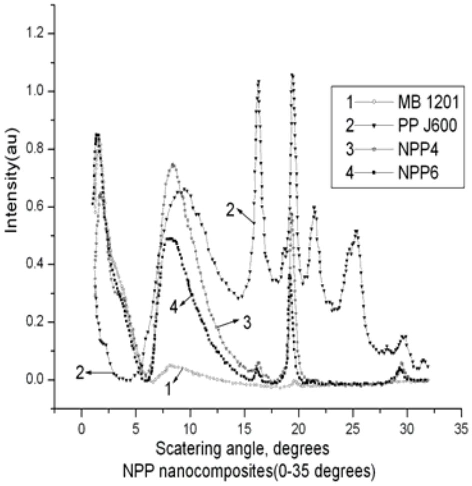


Fig. 3. XRD pattern of NPP nanocomposites.

Fig. 5 and Fig.6, shows the XRD spectra of the nanoblend MB 2101, LDPE and the various LDPE nanocomposites compounded in a single-screw extruder configured with different temperature arrangements. The organosilicate, nanoblend MB 2101, exhibited three distinct peaks characterising its interlayer basal spacing, at 1.69, 3.55, and 8.07 º 2θ angles. The nanocomposites spectra showed evidence of intercalation and exfoliation, indicated by the smoothening and the shifting of the second and thread, 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 nanocomposite samples in Fig. 4 and Fig. 5 exhibit a depressed peak pattern without significant shift in the 2θ angles. This pattern typically suggests effective break-up of the organosilicate into thinner layered-silicate stacks by extrusion shear stress. This phenomenon may be attributed through a top-down layer by layer peeling process. The nanocomposites showed similar peaks depression observed in [5], in addition, registered a lower 2θ angle. Their second order peak was shifted from 3.97 º to below 3.42 º, which represents an interlayer expansion from 1.4 nm to greater than 2.2 nm. This type of trend would generally suggest that exfoliation of layered silicate was achieved via a combination of matrix-gallery swelling followed by spontaneous interlayer delamination by the shear stress. However, the small shift recorded for the third order peaks to a larger 2θ angle suggests that the diffusion of polymer chain into the organosilicate gallery was not effective.

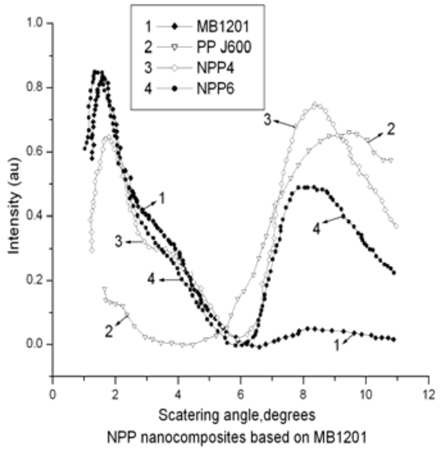


Fig. 4. XRD pattern of NPP nanocomposites (1-10 degree).

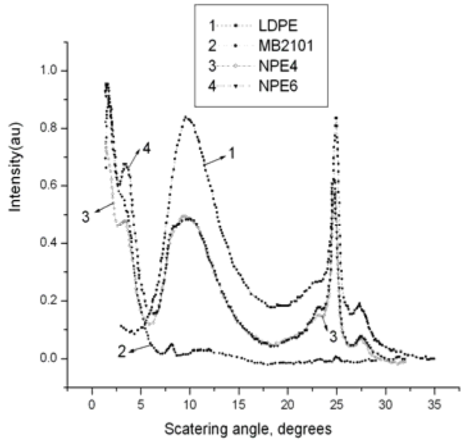


Fig. 5. XRD pattern of LDPE nanocomposites.

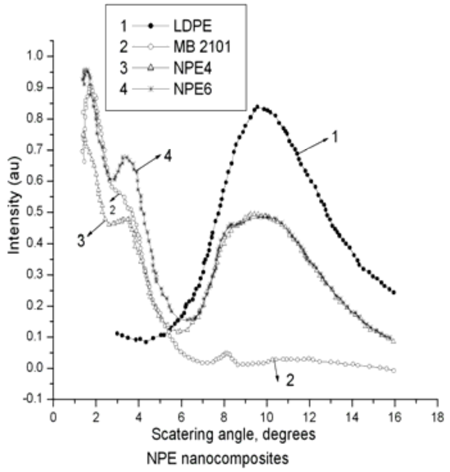


Fig. 6. XRD pattern of LDPE nanocomposites(1-16 degree).

Furthermore, the organosilicate interlayer appeared to experience some form of structural compression, resulting in smaller gallery spacing than in its pristine form. The XRD spectra would suggest highest degree of organosilicate exfoliation were the PP J600 /compatibiliser/organosilicate blends mixed using the highest extrusion temperature. The confounding aspect of this result is that a higher extrusion temperature generally dilutes the melt viscosity of polymer and thus reduces the shear strength required for the organosilicate delamination. On the contrary, a higher mixing temperature may also promote dilution between the PPthe compatibiliser matrix. This may enhance surface wetting of the layered-silicate. On this basis, the favorable exfoliation pattern exhibited by NPP may be attributed to the satisfactory mixing of the PP J600 and compatibiliser phase which promoted the wetting and diffusion of the compatibiliser into the organosilicate gallery during the first stage mixing at 215 ºC. The poor intercalation may be attributed to the low processing temperature, which was not favorable for diffusion of polymer chain into the organosilicate interlayer. Therefore, layered-silicates in this group were exfoliated primarily through a physical shearing rather than a thermodynamic process.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 orients along the flow direction.

3.2 FT IR analyses

FT IR spectra of the studied nanocomposites have been obtained by means of Varian EXCALIBUR 3100 spectrophotometer, using single reflection ATR technique.Analyze of the FT IR spectra (Fig. 7-9) permit us to make the next underlines. For NPP nanocomposite, in spectral range 2800-3000 $\mathrm{cm^{-1}}$, appear a change of the position and intensity of the ν-CH symmetric band (2950 $\mathrm{cm^{-1}}$).The δ-CH band (1460 $\mathrm{cm^{-1}}$) have a higher intensity for NPP nanocomposite then for PP J600.The band from 1260 $\mathrm{cm^{-1}}$ have a lower intensity for the NPP6 nanocomposite. In spectral range 950 – 1150 $\mathrm{cm^{-1}}$ appear two bands with the maximum at 1077 $\mathrm{cm^{-1}}$ and 1044 $\mathrm{cm^{-1}}$. The intensities of these bands increase when the concentration of the nanoblend is higher. In LDPE nanocomposites (Fig. 10, Fig. 11) , the same bands, have the maximum at 1074 $\mathrm{cm^{-1}}$ and 1040 $\mathrm{cm^{-1}}$, respectively. The shifts, (~ 4 $\mathrm{cm^{-1}}$), appear because of influence of medium.

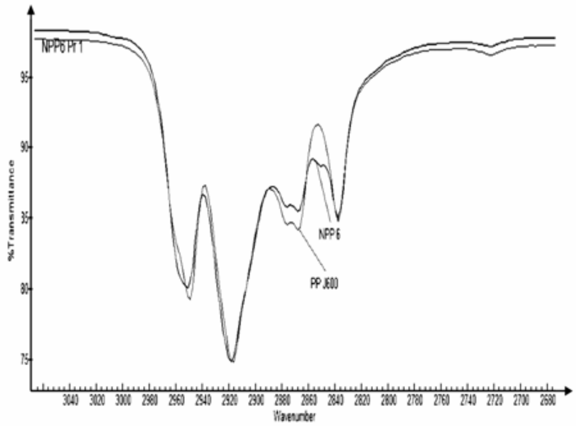


Fig. 7. FT IR spectra of polypropylene PP J600 and NPP6 nanocomposite in spectral range 3000-2700 cm^{-1}.

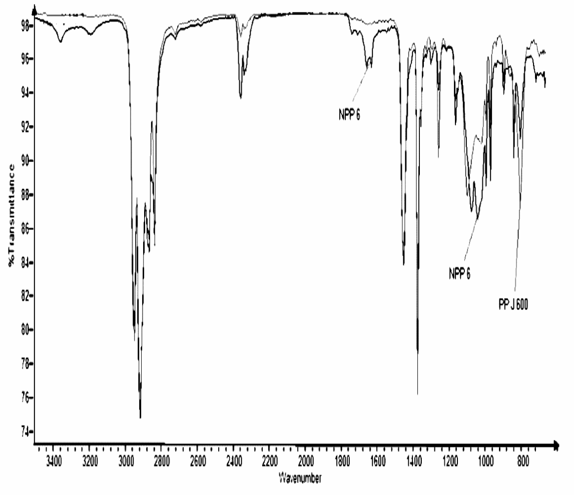


Fig. 8. FT IR spectra of polypropylene PP J600 and NPP6 nanocomposite.

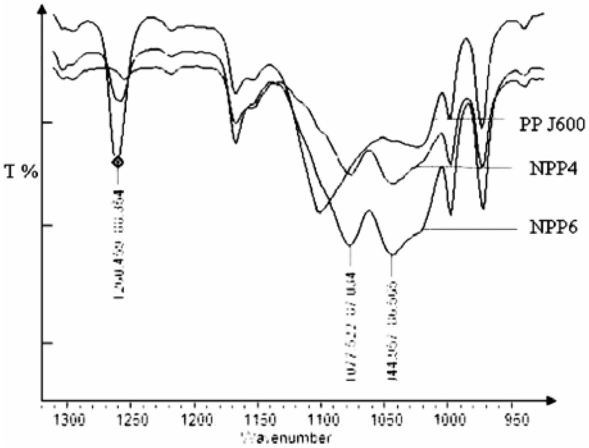


Fig. 9. FT IR spectra of polypropylene PP J600 and NPP4, NPP6 nanocomposites.

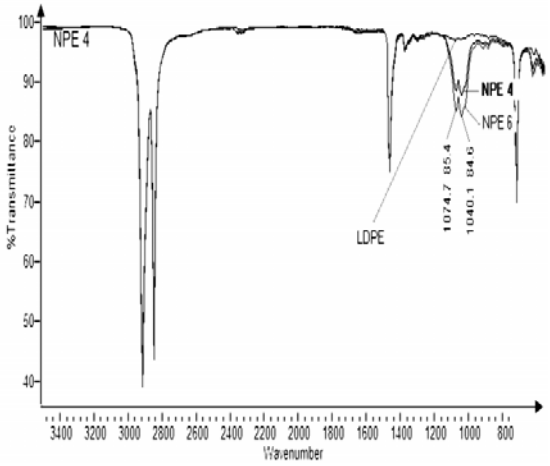


Fig. 10. FT IR spectra of LDPE and NPE4, NPE6 nanocomposite in spectral range 3500-600 cm^{-1}.

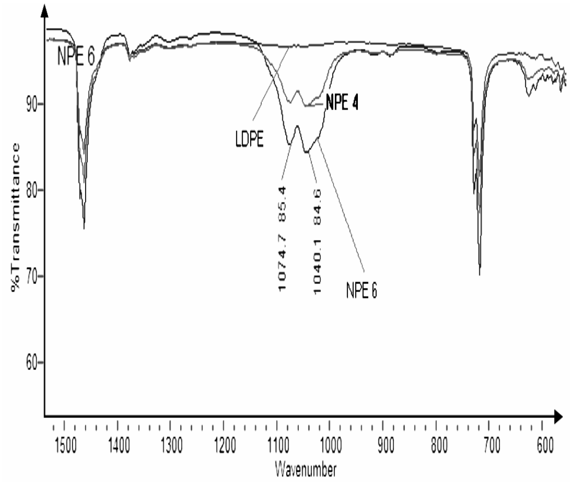


Fig. 11. FT IR spectra of LDPE and NPE4, NPE6 nanocomposite in spectral range 1500-600 cm^{-1}.

4. Mechanical properties

The resistance tests for the obtained samples have been done on injected samples (on an IMATEX – MP – TI – 100/50 injection machine), and on samples cut from the plate (for nanoPE). The resistance tests have been done at ICEFS SA Savinesti on a FPZ 10Heckert dynamometer and a Charpy pendulum MOLDOPLAST SA Iasi on a traction machine TIRATES 2200, a FP2-10 dynamometer and a Charpy PSW pendulum. For obtaining quality injected samples we took into account the processes taking place in the injection machine:

- typological peculiarities of the polyolephinic polymers for the injection (melt viscosity, melting time, specific heat, crystallization);
- thermotehnological process (injection time, postpressing time, injection pressure, injection speed, polymer mass temperature, matrix temperature);
- internal tensions and contractions in the injection products.

Table 1a,b. Mechanical properties of NP nanocomposites vs. PP J600.

Sample	Content of nanoclay wt %	Tensile strength (MPa)	Elongation at break (%)
PPJ600	0	29.93	9.82
NPP4	3.99	38,24	9,31
NPP6	5.98	45,66	8,95
Increase % (NPP4)		21.73	- 5.47
Increase % (NPP6)		34.45	- 9.72

Sample	Elasticity Modules Strength (MPa)	Elasticity Modules at flexion (MPa)	Soc Charpy (KJ/m^2)
PPJ600	1877.41	1568.66	5.51
NPP4	2955,73	2471,65	5,41
NPP6	3511,4	2917,31	5,22
Increase % (NPP4)	36.48	36.53	- 1.8
Increase % (NPP6)	46.53	46.23	- 5.5

From the resulting data one can see a high improvement in the mechanic properties compared to the natural polypropilene. The mechanic tests for polypropilene and for the polypropilenic nanocomposite show an increase of traction and bending module which trigger a better thermal stability and a reduction of the contraction during the injection.

In general, for establishing the processing conditions, the technopolymer users can use only the information given by the mechanical properties.

In the following, the obtained results for the polyethilenic nanocomposites are given. The experiments have been done on low density polyethilene (LDPE) for injection and for extrusion. At ICEFS the experiments have been done on LDPE for injection (for extrusion LDPE only nanocomposite grains have been obtained) whereas at Moldoplast Iasi extrusion experiments on LDPE have been done.

The values for the injection LDPE are given in Table 2.

One can see an improvement of the mechanic properties in the polyethilenic nanocomposites.

Concerning the polyethilenic nanocomposite with polyethylene injection matrix, after the mechanic tests, we have obtained on samples cut from plates values and pressed for polyethilene and nanocomposite with 6% nanoclay mean values for the traction elasticity module of 199.05MPa PE and 263.55MPa NPE6, respectively, which means an increase of 24.47 while the resistance and elongation values remain approximately the same.

Table 2. Mechanical properties of NPE nanocomposites vs. LDPE.

Sample	Content of nanoclay wt %	Tensile strength, (MPa)	Elongation at break (%)
LDPE	0	10,88	158,0
NPE4	4	13,52	152,6
NPE6	6	17,86	140,32
Increase % (NPE4)		19,53	- 3,54
Increase % (NPE6)		39,08	- 12,6
Sample	Elasticity Modules Strength (MPa)	Elasticity Modules at flexion (MPa)	Soc Charpy (KJ/m^2)
LDPE	114,79	147,3	Without strength
NPE4	138,91	169,61	
NPE6	147,27	196,35	
Increase % (NPE4)	17,36	13,15	Without strength
Increase % (NPE6)	22,05	24,98	

7. Conclusions

The preparation of nanocomposites by extrusion of linear polymers with organoclay depends on the level of polymer's polarity. As a result, the mechanical properties were improved (Table 1 and Table 2). As summarized in Table 1, there was a clear tendency that mechanical properties improve with increasing organo-nanoline content in PP J600 composites.

XRD analyze shows that for nanocomposite based on polypropylene and polyethilene takes place the exfoliation of organo-bentonites during preparation of composites.

The favorable exfoliation pattern exhibited by NPP may be attributed to the satisfactory mixing of the PP J600 and compatibiliser phase which promoted the wetting and diffusion of the compatibiliser into the organosilicate gallery during the first stage mixing at 215 ºC.

References

[1] M. Bousmina, Proceeding of PPS-21, 16-19 June 2005, Leipzig, Germany.

[2] V. I. Ovcharov, M. V. Burmistr, K. M. Sukhyy, V.V, Shilov, Yu.P. Gomza , V.G. Ovcharenko , I.V. Sukha, V.I. Tomilo, L.A. Sokolova, Proceeding of PPS-21, 16-19 June, 2005, Leipzig, Germany.

[3] C. Y. Lew, I. Moore, G. M. McNally, W. R. Murphy, K. Abe, S. Yanai, K. Y. Tshai, Proceeding of PPS-21, 16-19 June, 2005, Leipzig, Germany.

[4] Mingjun Yuan, Lih-Sheng Turng, Proceeding of PPS-21, 16-19 June, 2005, Leipzig, Germany.

[5] T. D. Fornes, P. J. Yoon, H. Keskkula, D. R. Paul, Nylon 6 Nanocomposites: The Effect of Matrix Molecular Weight, Polym., 42, pp. 9929-9940 (2001).

[6] S. W. Kim, W. H. Jo, M. S. Lee, M. B. Ko, J. Y. Jho, Effects of Shear on Melt Exfoliation of Clay in Preparation of Nylon 6/Organoclay Nanocomposites, Polym. J., **34**, 103-111 (2002).

[7] K. Varlot, E. Reynaud, M. H. Kloppfer, G. Vigier, Varlet J. J Polym Sci. Polym Phys 2001; 39(12): 1360-1370.

[8] C. R. Tseng, Wu SC, Wu JJ, F. C. Chang., J Appl Polym Sci; 86(10): 2492-2501 (2002).

---

[*] Corresponding address: sgurlui@uaic.ro