Macromol. Symp. **2005**, *228,* 147-154

Preparation of Isotactic Polypropylene/Organoclay Nanocomposites by Solution Mixing Methodology: Structure and Properties Relationships

Maurizio Avella, Simona Cosco, Maria Emanuela Errico*

Institute of Chemistry and Technology of Polymers (ICTP)-CNR, Via Campi Flegrei, 34 c/o Comprensorio Olivetti, 80078 Pozzuoli (NA), Italy
E-mail: mave@irtemp.na.cnr.it

Summary: Isotactic Polypropylene (iPP) based nanocomposites filled with organo-clay nanoparticles were prepared and the relationships between their structure and properties were investigated.
Modified C_{16}-C_{18} smectite clay nanoparticles were used in order to promote matrix/filler compatibilization and to improve interfacial adhesion. X-Ray analysis performed on the nanocomposites demonstrated that at low organo-clay content (1 and 3% by weight) a nanostructure has been obtained, while in presence of 5% by weight of organoclay cluster regions have been formed. Mechanical tests showed that the elastic modulus increases of about 20% compared to the neat polymeric matrix value when 1 and 3% of nanofiller is added.

Keywords: nanocomposites; organoclay; polypropylene; properties; WAXS

Introduction

Recently, as a result of developments in nanotechniques, there has been a growing interest in the field of polymer-based nanocomposites.[1-6] Polymer-based nanocomposites are defined by the particle size of a dispersed inorganic filler in a polymeric matrix having at least one dimension in the nanometer range. Such inorganic/organic hybrid systems have attracted great interest both from scientific and industrial point of view because they can confer strong improvements to the final material performances with respect to those normally obtained by using conventional synthesis methodologies (production of new polymers) or by blends and composites preparation (microcomposites).[7-11] These unexpected properties can be obtained owing to the enormous interfacial adhesion region characteristic of the nanoparticles. Then the nanocomposite properties are strongly influenced by the nature of the interface, hence a strong polymeric matrix/nanofiller interface allows having unusual properties.[12]

The most popular polymer nanocomposites are hybrid based on organic polymers and inorganic layered natural silicates (i.e., smectite-clays such as montmorillonite, mica,

DOI: 10.1002/masy.200551013

hectorite and saponite).[13-15] The layers in the clay minerals consist of silicate platelets typically 1 nm thick and about 1000 nm across the face, more than a thousand times thinner than the finest talc reinforcements in use today. In the natural state, strong interlayer interactions hold the platelets together in stacks, but chemical treatments can reduce the interactions, swelling the clay to produce "smectite" additives. One of the most used chemical method to swell clay interlayer and to render its surface more hydrophobic and so available to the polymer is based on ionic exchange reactions of the sodium interlayer cations with "onium" cations bearing long alkyl chains.[16-18] As long as the alkylated surface of the silicate layers is compatible with the polymer, the polymer chains can crawl into the interlayer space and form either an intercalated or an exfoliated nanocomposite. Critical to the enhanced properties of nanocomposites is the subsequent exfoliation process in which the individual layers are peeled apart and then dispersed throughout the polymeric matrix. The greater degree of exfoliation, the thinner particles and the greater surface area available to interact with the host polymer produce improved performance.

In the present paper results about iPP based nanocomposites filled with organo-clay nanoparticles are reported. Nanocomposites based on polypropylene matrix constitute a major challenge for industry since they represent the route to substantially increase the mechanical and physical properties of one of the most widely used thermoplastic commodity. In particular an organo-modified clay has been used as nanofiller since the polarity of neat clay does not match well with polyolefins. Nanocomposites containing 1, 3 and 5% by weight of organoclay have been prepared by solution methodology. The dispersion of the silicates layers in the iPP matrix has been evaluated by using X-Ray diffraction analysis and scanning electron microscopy. Mechanical properties have been tested and correlated to the nanocomposites structure.

Experimental

Preparation of iPP based nanocomposites

In a cylindrical flanged flask equipped with inlets for refrigeration, mechanical stirring and nitrogen, iPP has been dissolved in o-dichlorobenzene at 180°C. In a tube, modified organoclay (1, 3 and 5% by weight of iPP) has been dissolved in o-dichlorobenzene by using an ultrasonic bath operating at 100 rev min^{-1} and 80°C .Then the iPP and organoclay solutions have been mixed. The mixing has been carried out at 140°C for 1 h under vigorous stirring. The product has been separated by cold precipitation in ethanol and the solvent removed in a separation funnel. Finally the material has been dried in oven under vacuum overnight. Successively neat iPP and iPP-based nanocomposites have been compression-molded in a heated press at 210°C for 3 minutes, without any applied pressure. After a pressure of 100 bar has been applied for 2 minutes, then the press platelets, containing coils for fluids, have been rapidly cooled to the room temperature by cold water. Films of 150-200 μm thickness have been obtained.

X Ray diffraction analysis.

Wide angle X-Ray (WAXS) spectra have been recorded measured using a Philips powder diffractometer (PW 1050 model) operated at the CuKα wavelength of 1.542 Å. Measurements of the diffracted intensities were made in the angular range of 2-40° (2θ), at room temperature and at a scanning rate 1°/min.

Calorimetric measurements

The glass transition temperature (T_g) of the samples was measured with a differential scanning calorimeter Mettler DSC-30. Each sample was heated from 30 to 190°C at a scanning rate of 20°C/min, kept at this temperature for 5 min, then quenched to -50°C and then re-heated to 190°C at 20°C/min. The T_g was taken as the temperature corresponding to the maximum of the peak obtained by the first order derivate trace of the DSC thermoanalytical curve.

Morphological analysis by scanning electron microscopy (SEM)

Morphological analysis of the compression-molded samples has been conducted with a SEM Philips XL 20 series microscope. Small pieces of the compression molded samples have been kept in liquid nitrogen for 5 minutes and fractured. Before the electron microscopy observation, the surface has been coated whit a thin layer of Au/Pd alloy, with a SEM coating device (SEM Coating Unit E5150-Polaron Equipment Ltd.).

Mechanical tests

An Instron machine (model 5564) has been used to perform at room temperature and a cross-head speed of 10 mm/min tensile tests. Young Modulus (E) has been calculated in accordance to the ASTM (D256) standard.

Results and Discussion

iPP based nanocomposites filled with organo clay nanoparticles have been prepared and their structure and properties have been analyzed.

In order to prevent face-to face stacking in agglomerated tactoids of smectic layers and to improve the compatibility between hydrophilic clay and hydrophobic iPP, a modified organoclay has been used. In particular the hydrated cations Na^+ have been exchanged with stearyl ammonium ions, obtaining an organoclay characterized by long alkylic chains (clay-N NC_{16}- C_{18}).

The replacement of inorganic cations by organic onium ions on the gallery surfaces of smectic clays not only serves to match the clay surface polarity with the polarity of the polymer, but it could also promote the enlargement of the clay galleries.

Nanocomposites have been prepared by solution methodology. This preparation strategy has been selected in order to promote the intercalation of the iPP matrix into interlayer galleries due to a lowering of the polymer viscosity.

The structure of iPP/clay nanocomposites has been successively investigated by X-Ray diffraction analysis and by scanning electronic microscopy (SEM).

The X-Ray diffraction (XRD) is the most common technique used to probe polymer/clay nanocomposite structure because it can detect the periodically stacked clay layers to which a particular nanocomposites structure is associated.

Figure 1 shows X-ray diffraction profiles of C_{16}-Mt (fig. 1A), of neat iPP (fig. 1B) and iPP based nanocomposites (fig. 1C-1E).

The organoclay pattern has shown a peak at ~3° (2θ) corresponding to a 29,5 Å interlayer distance, d_{001}. To this d-spacing value is associated to a paraffin monolayer arrangement of alkyl ammonium ions.[19]

As far as the nanocomposites containing 1% and 3% by weight of clay (fig 1C-1D) are concerned, the films patterns are characterized by the presence of crystalline iPP diffraction peaks while the organo-clay diffraction peak ($2\theta= 3°$) disappears. This result demonstrates that an exfoliated/delaminated structure is obtained for both systems. In fact the disappearance of the organo-clay peak is correlated to the polypropylene molecules insertion into the silicate galleries that destroys the periodical layered structure of the clay.

On the contrary, the pattern of the nanocomposite film containing 5% of clay is also characterized by the presence of the C_{16}-Mt diffraction peak. Then, as it can be observable

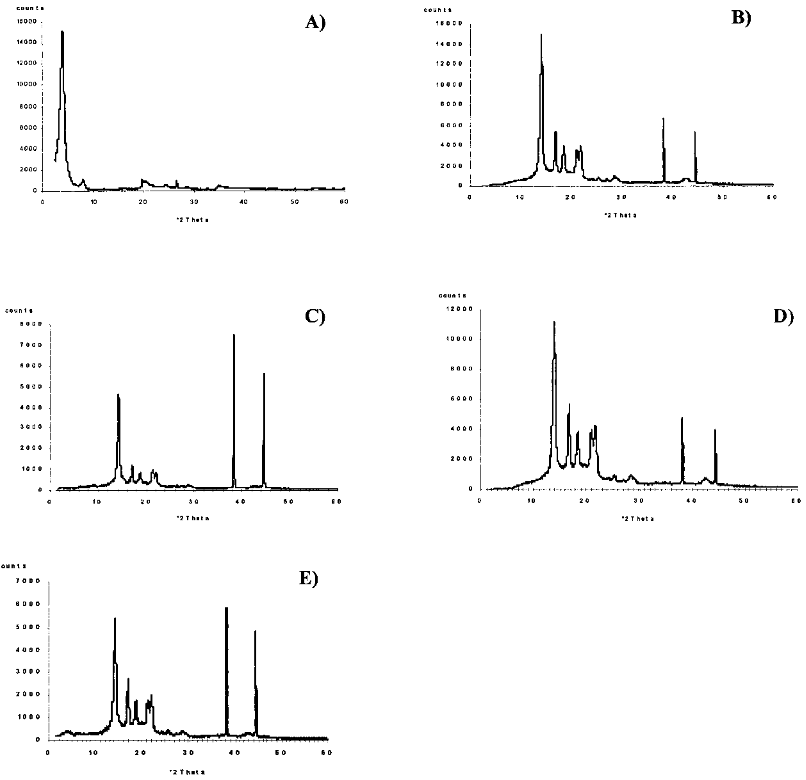
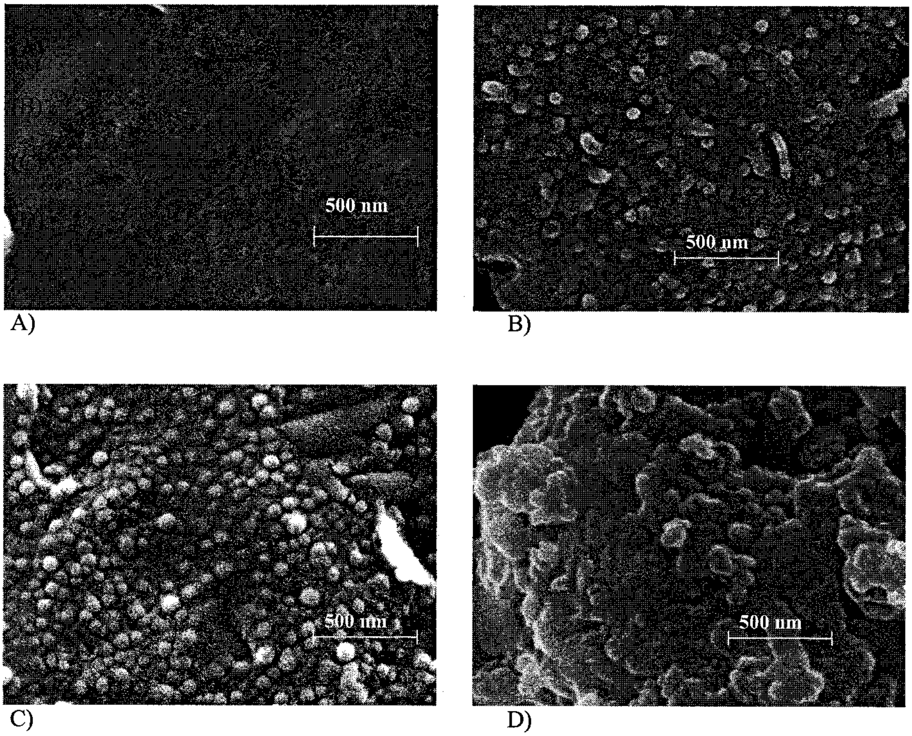


Figure 1. X-Ray diffraction patterns of *A)* pristine organoclay, *B)* iPP neat, *C)* iPP/clay (1%), *D)* iPP/clay (3%), *E)* iPP/clay (5%).

the position of this plane peak (001) is partially shifted at higher angles 2θ = 4° (d-spacing = 22,1 Å) (fig. 1E). This decrease of the interlayer spacing is probably correlated to a clay layers collapse which leads an “immiscible” system.

From the analysis of X-Ray diffraction patterns it can be deduced that the nanocomposites preparation methodology by solution mixing is a good approach to obtain exfoliated structures at low clay content (1 and 3%).

The nanophase dispersion into iPP matrix has been also investigated by scanning electronic microscopy performed on the fractured surfaces of the nanocomposites (fig. 2).



A) B) C) D)

Figure 2 SEM micrographs of fractured surfaces: A) neat iPP, B) iPP/clay (1%), C) iPP/clay (3%), D) iPP/clay (5%).

As it can be observed from the figs 2, the nanophase appears quite welded to the polymeric matrix for all the systems. Then, a fine and homogeneous organoclay dispersion can be observed for the nanocomposites containing 1% and 3% of fillers, (2B, 2C).

As far as the system having the highest nanoclay content, larger domains due to agglomeration phenomena can be evidenced (fig. 2D), in agreement with the results of the X-ray diffraction analysis.

In table 1 the tensile properties of iPP/clay nanocomposites are reported. The Young Modulus of iPP has increases by about 30% with the addition of only 1-3 wt% of organoclay. In the case of nanocomposites containing the 5 wt% of nanoreinforcement, the

Young Modulus value slightly decreases with respect to the value obtained for iPP filled with lower clay content due to the agglomeration phenomena.

The improvements of tensile modulus obtained suggest that the performance of nanocomposites is related to the degree of delamination of the clay in the polymeric matrix that increases the interaction between the clay layers and polymer. In fact in presence of a strong interaction between the two phases the external load will be transferred from the polymer matrix to the reinforcement through the interface and the mechanical properties of the material increase. Then, this strong interface is responsible to a restricted mobility of the polymer chains. This is in agreement with the increase of glass transition temperature (Tg) found in the iPP-based nanocomposites, whose values are also reported in table 1. These data show that the presence of nanoparticles shifts the Tg to higher values with respect to the homopolymer. This result is justified by the homogeneity of dispersion of the nanofillers into iPP, as revealed by SEM analysis, and by large interfacial area of the nanoparticles, as the strong interconnection between the two phases reduces iPP chains mobility. It can be also underlined that these values increase as a function of the amount of nanoparticles, although in the case of high nanoparticles content this increase is limited probably because of the above discussed agglomeration phenomena.

Table 1. Variation of Young Modulus and of glass transition temperature in function of nanoparticles amount.

Organoclay %	E (MPa)	Tg (°C)
0	1140	-8
1	1520	-4
3	1585	-4
5	1391	-3

Conclusions

iPP based nanocomposites filled with organo-clay have been prepared by solution methodology. This preparation strategy has allowed to prepare nanomaterials characterized by a stable and exfoliated structure at lower organo clay content (1 and 3% by weight) while in the case of iPP containing 5% of organoclay a partially collapsed structure has been obtained. The variation of iPP physical paramenters (Tg, Young Modulus) due to the presence and the amount of organo clay are strictly correlated to the morphology of the nanomaterials.

[1] D.W. McCarthy, J.E. Mark, D.W. Schaefer, *J. Polym. Sci. Part B: Polym Phys* **1998,** *36*, 1167.
[2] D.W. McCarthy, J.E. Mark, S.J. Clarson, D.W. Schaefer, *J. Polym. Sci. Part B: Polym Phys* **1998,** *36*, 1191.
[3] C.-C. Sun, J.E. Mark, *Polymer* **1989,** *30*, 104.
[4] C.J.T. Landry, B.K. Coltrain, M R. Landry, J.J. Fitzgerald, V.K. Long, *Macromolecules* **1993,** *26,* 3702.
[5] J. Jose-Yacaman, L. Rendon, J.Arenas, M.C.S. Puche, *Science* **1996,** *273*, 223.
[6] E.P. Giannellis, *Adv. Mater.* **1996,** *8*, 29.
[7] G.D. Stucky, J.E. MacDougall, *Science* **1990,** *247,* 669.
[8] V. Kresin, V *Phys. Rep.* **1992,** *220*, 1.
[9] X. Cao, Y. Koltypin, R. Prozorov, G. Katabi, A. Gedanken, *J. Mater. Chem* **1997,** *7*, 2447.
[10] M. Avella, M.E. Errico, E. Martuscelli, *Nanoletters* **2001**, *1*, 213
[11] M.L. Di Lorenzo, M.E. Errico, M. Avella, *J. Mater. Sci.* **2002**, *37*, 2351
[12] C. Sanchez, F. Ribot, *New J. Chem.* **1994,** *18*, 1007
[13] A. Okada, A. Usuki, *Mater. Sci. Eng.* **1995**, *C3*, 109.
[14] M. Ogawa, K. Kuroda, K. Kuroda, *Bull. Chem. Soc. Jpn* **1995**, *70*, 2532.
[15] M. Alexandre, Ph. Dubois, *Materials Science and Engineering* **2000**, *28*, 1.
[16] J.W. Jordan, *J. Phys. Colloid Chem.* **1949**, *53*, 294.
[17] A. Weiss, *Angew. Chem. Internat. Edit.* **1963**, *2*, 134.
[18] Y.Fukushima , S. Inagaki, *J. Inclusion Phenom.* **1987**, *5*, 473.
[19] P. C. LeBaron, Z. Wang, T. J. Pinnavia in: *"Applied Clay Science"*, G. Lagaly, T.J. Pinnavia, Eds., Elsevier Science B. V., 1999, p. 11