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iPP Based Nanocomposites Filled with Calcium Carbonate Nanoparticles: Structure/Properties Relationships

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Summary: Isotactic polypropylene (iPP) based nanocomposites filled with calcium carbonate nanoparticles ($CaCO_3$) were prepared by melt mixing and structure-properties relationships of the nanomaterials were studied. Elongated $CaCO_3$ nanopowders coated with two different coating agents, polypropylene-maleic anhydride graft copolymer (iPP-g-MA) and fatty acids (FA), were tested as nanoreinforced phases. The influence of surface treatment of the nanoparticles on the polymer/nanofillers interfacial adhesion and on the final materials properties was investigated. Morphological analysis showed that the selected coating agents induce different iPP/nanofiller adhesion degrees. Young's modulus increases as a function of the nanoparticles content and the coating agent nature. Finally, all the prepared nanocomposites showed a significant improvement of iPP barrier properties either to oxygen or to carbon dioxide.

Keywords: barrier; interfaces; mechanical properties; nanocomposites

Introduction

Isotactic polypropylene (iPP) films hold a prominent position in the food packaging sector, due to their transparency, brilliance, low specific weight and high chemical inertness.[1] Unfortunately polypropylene, like other polyolefins, has a high gas permeability, which results in a poor protection of the packaged food.[2]

Nowadays, 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.[3–8] The enhanced properties are presumably due to the synergistic effects of nanoscale structure and interaction of fillers with polymers. The size and nanostructure of the dispersed phase significantly influence the properties of polymer based nanocomposites.[9–14]

The key factors for the preparation of enhanced performance nanomaterials are to obtain a fine and a homogeneous dispersion of the nanopowders and to promote a strong interface adhesion between matrix and nanofillers. Nevertheless the nanoparticles have a strong tendency to agglomerate giving rise to clusters formation due to their high adsorption surface energies and to a different polarity with respect to that of common polymers. Modification of the nanoparticles surface by using organic coating agent represents an effective route in the attempt to improve the nanophase dispersion into polymeric matrix. These surface modifiers mediate nanoparticles interactions by effectively lowering the interfacial free energy, moreover the organic surface modifiers impart hydrophobic

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features to the nanoparticles improving filler/matrix compatibility.

In this paper results about iPP based nanocomposites filled with innovative modified calcium carbonate nanoparticles ($CaCO_3$) are reported.

Experimental

Materials

Isotactic polypropylene (iPP), Moplen X30S (Mn $= 4.69 \times 104$ g/mol, Mw $= 3.5 \times 105$ g/mol and Mz $= 2.06 \times 106$ g/mol), was kindly supplied by Basell Polyolefins (Ferrara-Italy). Calcium carbonate ($CaCO_3$) nanoparticles were kindly supplied by Solvay Advanced Functional Minerals (Giraud-France). Elongated $CaCO_3$ nanoparticles coated with two different coupling agents, fatty acids (FA) and polypropylene-maleic anhydride graft copolymer (iPP-g-MA), were tested as nanoreinforced phase, coded as EC-FA and EC-PPMA respectively. Average nanoparticles dimensions are about 250 nm in length and 50 nm in thickness.

Preparation of iPP Based Nanocomposites

iPP/$CaCO_3$ nanocomposites were obtained by mixing the components in a Brabender-like apparatus (Rheocord EC of HAAKE Inc., New Jersey, USA) at 200 °C and 32 rpm for 10 min. The mixing ratios of iPP/$CaCO_3$ (wt/wt) were: 100/0, 99/1, 97/3.

Plain iPP and iPP/$CaCO_3$ nanocomposites were compression-molded in a heated press at 200 °C for 2 min without any applied pressure. After this period, a pressure of 100 bar was applied for 3 min, then the press platelets, containing coils for fluids, were rapidly cooled to room temperature by cold water. Finally, the pressure was released and the mold removed from the plates.

Morphological Analysis

The surface analysis was performed by using a scanning electron microscope (SEM), Cambridge Stereoscan microscope model 440, on nanoparticles powders and on cryogenically fractured surfaces of the nanocomposites. Before the observation, samples were metalled with a gold layer.

Mechanical Analysis

Tensile tests were performed on dumb-bell specimens (4 mm wide and 15 mm long) by using an Instron machine (model 5564) at room temperature and a cross-head speed of 10 mm/min. Young Modulus (E) was calculated from these curves in accordance to the ASTM D256 standard (average 10 samples tested).

Permeability Tests

Permeability tests were performed in a gas-membrane-gas instrument based on measurement of the downstream pressure increase at a constant upstream side-driving pressure. The apparatus and experimental procedures were similar to those reported elsewhere.[15,16] In each experiment, sufficient time was allowed to ensure attainment of steady-state permeation. The measurements were carried out at a pressure of 1 atm and at a temperature of 30 °C. The permeability was computed from the slope of the linear, steady-state part of the curve representing the permeated gas volume as a function of time. The gas diffusivity was calculated from the 'time lag' determined from the intercept of the steady-state permeability curve on the abscissa.

Results and Discussion

In literature [1,2] it can be found that modified nanofillers compatible with polypropylene, as for instance $CaCO_3$, can be well dispersed and improve the tensile and impact properties as well as the scratch resistance, but not the barrier properties. The absence of any significant enhancement in the barrier properties was attributed to the spherical shape and low specific surface of the used nanofillers (<30 m^2/g). In this research innovative $CaCO_3$ nanoparticles characterized by a very big specific surface (>200 m^2/g) and by elongated particle shape (high aspect ratio) were tested. This particular shape aims to merge the advantages of the well-assessed $CaCO_3$ know-how together with the properties enhancement attainable, for instance, by addition of nanotubes and clay platelets. In fact, in this way it should be possible to simulate the nano-clay behaviour, that reduces gas permeability of polymers according to a tortuous path model, in which the platelets obstruct the passage of gases and other permeants through the polymeric matrix. In order to promote iPP/$CaCO_3$ interfacial adhesion and fine nanoparticles dispersion, key issues for extending properties and performances of the nanomaterials, elongated nanoparticles coated with polypropylene-maleic anhydride graft copolymer (iPP-g-MA) and fatty acids (FA) were tested as nanoreinforcement phase.

The preparation of iPP-based nanocomposites was performed by melt mixing and structure-properties relationships were studied with particular attention to the influence of the surface modifiers nature on the polymer/nanofillers interaction and consequently on the final materials properties.

The dispersion of the nanoparticles into iPP and the polymer/$CaCO_3$ interfacial adhesion were investigated by morphological analysis (SEM) performed on the fractured surfaces of the compression molded samples.

In Figures 1–2 SEM micrographs of the nanocomposites containing the highest amount of EC-FA and EC-PPMA nanoparticles (3% wt/wt) are reported as examples of the obtained nanocomposites morphology. In both the cases, the nanoparticles appeared completely covered by the iPP phase and no voids were evidenced due to an applied mechanical stress. At the same time, different morphologies were reached as a function of the surface modifiers nature. EC-PPMA nanoparticles were homogeneously and finely dispersed into polymeric matrix while in the case of EC-FA partial agglomeration phenomena were evident. In fact, as it is possible to observe from Figure 1, some nanoparticles aggregates of about 500–700 nm in dimension are also noted together with discrete nanofillers. These morphological observations permitted to assess that the presence of iPP-g-MA coating agents on the nanoparticles surface was responsible for a stronger polymer/EC-PPMA adhesion with respect to that achieved by using EC-FA nano-reinforcement. This result could be ascribed to the nature of the coating agents able to promote different polymer/nanoparticles surface modifiers interactions.

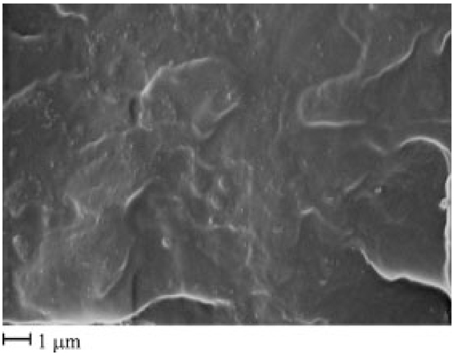

Figure 1.
SEM micrograph of SEM micrograph of iPP based nanocomposites filled with 3% (wt/wt) of EC-FA.

In particular, unless the presence of fatty acids on the nanoparticles reduced the polarity of the fillers improving their compatibility with the matrix, the nanoparticles surface modifiers – nanoparticles

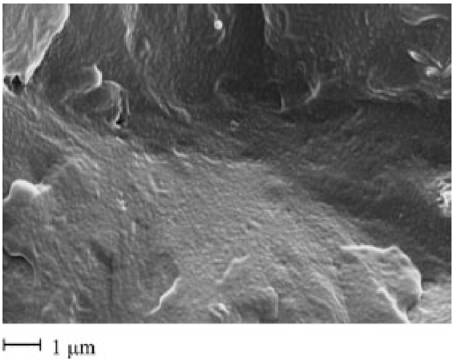

Figure 2.
SEM micrograph of SEM micrograph of iPP based nanocomposites filled with 3% (wt/wt) of EC-PPMA.

surface modifiers were still the predominant interactions thus inducing partial clustering phenomena. On the other hand, in the case of EC-PPMA the strong interfacial adhesion can be explained by taking into account that physical interactions between polymer chains and surface modifiers molecules via entanglements occurred due to their similar chemical nature.

Mechanical Properties

In Figure 3 Young's modulus (E) values of iPP/EC-FA and iPP/EC-PPMA nanocomposites as a function of the nanoparticles content are shown. The addition of EC-FA and EC-PPMA nanoparticles was responsible for a significant increase of the nanocomposites Young's Modulus that reached up to 30% more than that of neat iPP. This increase is a function of the nanoparticles content and the coating agent nature.

In fact a comparison between the E values of nanocomposites with the same amount of calcium carbonate, but with different surface modifiers showed that the EC-PPMA nanoparticles gave rise to a more pronounced increase of the modulus with respect to that obtained with EC-FA nanofillers. Generally speaking, the improvement of mechanical parameters are strictly correlated to the polymer/filler interfacial adhesion due to the fact that an applied mechanical stress can be transferred from the polymeric matrix to the nanoparticles through the interphase. This justifies the more significant improvements recorded by addition of EC-PPMA where strong polymer chains/surface modifiers molecules interactions occurred, in agreement with the result obtained by morphological analysis.

Barrier Properties

The addition of inorganic fillers into polymer affects the gases diffusion mechanism through the material due to different permeability properties of the matrix and the foreign particles.[17–19] The permeability of a multiphase material (Pc) can be described by the following relationship:[4]

$$Pc = Pm(1 - \phi)/\tau$$

$$\tau = 1 + (L/2W)\phi$$

where Pm is the neat matrix permeability, ϕ the filler volume fraction, τ is the tortuosity

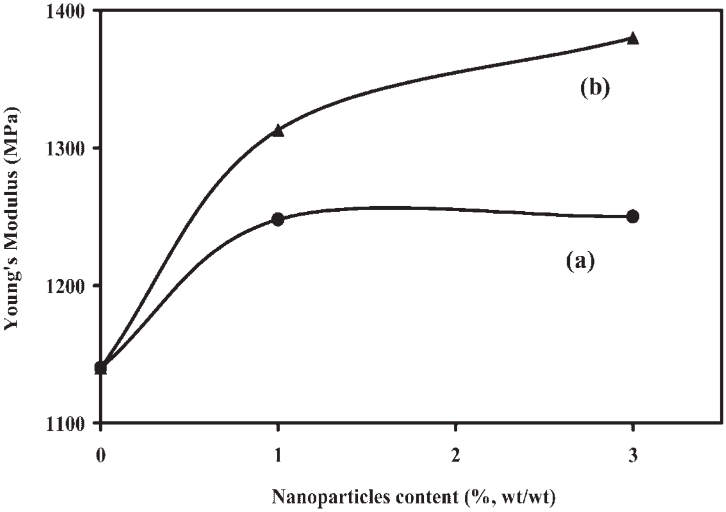

Figure 3.
Young's Modulus of iPP and iPP based nanocomposites filled with: a) EC-FA nanoparticles; b) EC-PPMA nanoparticles.

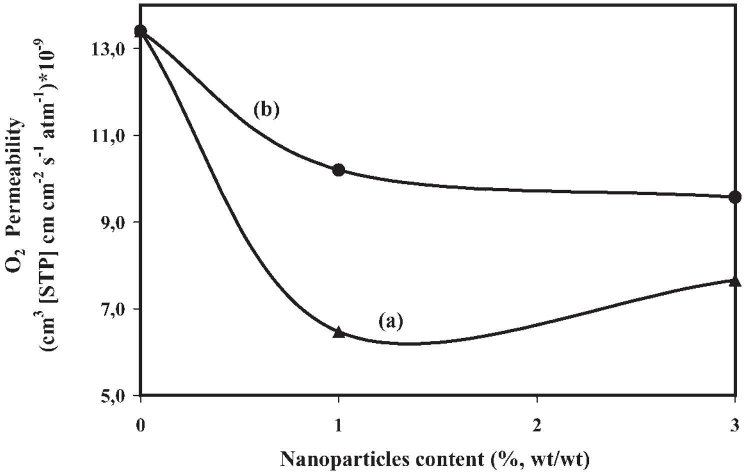

Figure 4.
Oxygen permeability of iPP and iPP based nanocomposites filled with: a) EC-FA nanoparticles; b) EC-PPMA nanoparticles.

factor, and L and W denote the length and the thickness of the fillers, respectively.

This phenomenon is particularly stressed when a filler of nanometric size is dispersed into polymeric matrix because of the high specific surface of the nanoparticles responsible for wide contact area between the polymer and the nanofillers.

In Figures 4–5 oxygen and carbon dioxide permeability coefficient values are plotted as a function of the nanoparticles amount and the coating agent nature. For both the systems a decrease of permeability, either to oxygen or to carbon dioxide, was observed with increasing the nanoparticles content. This result can be easily explained by considering the parameters influencing the permeability coefficient, as described in the above reported relationships. In fact, the elongated shape of the nanoparticles contributed to the permeability decrease by increasing the tortuosity factor (τ), and their high specific surface area (>200 m^2/g) was responsible for a large volume fraction (ϕ).

Moreover, as it can be observed from the figures, the nature of coating agent seems to influence the extent of the iPP barrier properties improvement; EC-FA nanoparticles induced a higher decrease of oxygen and carbon dioxide permeability with respect to that obtained by the addition of EC-PPMA nanofillers. This result could be justified by considering that different interactions between the two coating agents (FA and PP-g-MA) and either oxygen or carbon dioxide occurred. Although the C-PPMA nanoparticles were better dispersed into matrix and a stronger adhesion C-PMMA/iPP was reached, the nature of the coating agent is similar to that of the neat polymeric matrix such as their permeability properties to oxygen and carbon dioxide. As a result no additional interactions between the tested gases and the surface modifier occurred, thus suggesting that the barrier properties were influenced only by the high volume fraction occupied by the elongated nanoparticles.

As far as EC-FA nanofillers, the unsaturated groups on the fatty acids chains can be considered as potential sites of interactions with both oxygen and carbon dioxide molecules, thus inducing the additional effect of hindering and slowing the diffusion of the gases through the nanocomposite. The drastic extent of the permeability decrease as a function of the coating agent nature can be explained only by considering the high surface area of the nanoparticles, coated by a monolayer of FA molecules, responsible for a very wide interfacial

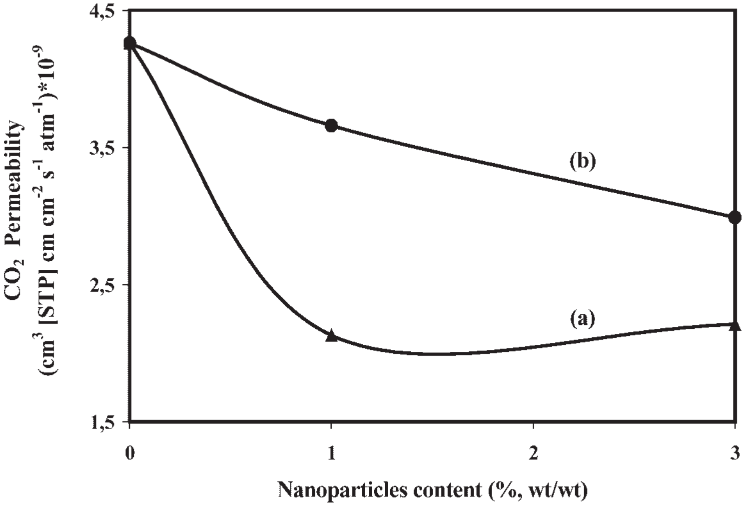

Figure 5.
Carbon dioxide permeability of iPP and iPP based nanocomposites filled with: a) EC-FA nanoparticles; b) EC-PPMA nanoparticles.

region and a very large occupied volume fraction. This well explains the additional maximized effect on the permeability due to the small amount of fatty acids molecules covering the nanoparticles surface.

Conclusions

High performance iPP based nanocomposites filled with innovative calcium carbonate nanoparticles and characterized by enhanced mechanical and barrier properties were prepared. Elongated calcium carbonate nanoparticles coated with fatty acids (EC-FA) and polypropylene-maleic anhydride graft copolymer (EC-PPMA) were used as iPP nanoreinforcements. The above discussed results can be summarized as follows:

- EC-FA nanoparticles appear quite welded to the iPP matrix and both a great number of very small discrete particles and clustering areas can be observed;
- EC-PPMA nanoparticles are homogeneously and finely dispersed into iPP matrix. The discrete nanofillers are completely covered by the iPP phase;
- The Young's modulus of the iPP based nanocomposites increases in presence of nanoreinforcements; the EC-PPMA nanoparticles induce higher increase of the modulus than that obtained with EC-FA nanofillers;
- Elongated $CaCO_3$ significantly reduces the iPP permeability either to oxygen or carbon dioxide as a function of nanoparticles amount; the EC-FA nanofillers are responsible for higher barrier properties improvements than those obtained by the addition of EC-PPMA due to the different interactions between the surface modifiers and the tested gasses.

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