Processing of Polypropylene – Clay Hybrids

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Summary: Polypropylene compounds containing organophilic layered silicates were prepared by means of melt extrusion at 180 °C. We have studied the effect of the coupling agent on morphology development and mechanical properties. We are convinced of the importance of both the chemistry and the process conditions to elaborate nanocomposites with optimized properties.

Introduction

The introduction of tiny clay platelets in any various polymer matrices leads to a new class of materials, denoted nanocomposites. This is a basically new route for reinforcing plastics and this new class of materials is one of the most promising systems to get an attractive combination of mechanical behavior, flame retardant and improved gas barrier properties without significant loss of clarity and toughness [1-2]. As polyolefins, i.e. polypropylene (PP), polyethylene (PE) are the most widely used polymers in automotive and oil industry, they represent an important market since a few years. But the introduction and the dispersion of inorganic and hydrophilic particles in an high molecular weight-hydrophobic matrix is difficult enough [3-6]. In a first time, the clay must be made organophilic by cation exchange between sodium ions present between platelets and ammonium cations with long alkyl chains [7]. On the other side, the use of oligomers functionalized with polar groups allows to improve the compatibility between filler and polymer and helps the diffusion of PP chains between platelets [8].

To process PP/clay hybrids, we have kept the same classical tools of polymer processing by direct melt blending in a twin-screw extruder. PP nanocomposites were prepared by using different commercial coupling agents which are maleic anhydride grafted oligomers. The clay dispersion in PP matrix was analyzed at the nanometric scale by X Ray diffraction (WAXS) and by transmission electron microscopy (TEM), at the microscopic scale by rheogical measurements and at the macroscopic scale by mechanical characterization.

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Experimental Part

Material

Both organophilic clays used in this study are supplied by Süd Chemie, with the trade name Nanofil 948 and Nanofil 919. The modifying ions are dimethyl hydrogenated ditallow quaternary ammonium ions and dimethyl hydrogenated tallow-benzyl-quaternary ammonium ions respectively. The interlayer spacing increased in both cases up to 18 Å.

The used coupling agents are oligomers grafted with maleic anhydride either based on polypropylene (PPgMA) or polystyrene (SMA). The PP powder matrix, with MFI = 10g/10 min (ASTM D569-90) contains 0.1 wt.% of stabilizer (Irganox 1010). The matrix and coupling agents characteristics are reported in Table 1.

Preparation of Nanocomposite

PP powder and the organoclay (5 wt%) are melt-blended together with the coupling agent (20 wt.% of PPgMA or 5 wt.% of SMA) in a twin screw extruder (L/D = 36 with a rate 50 kg/h) at 180 °C and at 160 rpm.

The dried pellets of the nanocomposite were injection-molded into test bars for mechanical tests and WAXS tests. The temperature of the cylinder was 180°C and that of the mold was 40°C.

Table 1 : Matrix and coupling agents characteristics.

Materials	Reference	Supplier	Mw ($g.mol^{-1}$)	MA grafting ratio (wt %)
PP, homopolymer	HV001	Solvay	$2 . 10^5$	/
Maleic anhydride grafted PP, Homopolymer	Epolène E43P	Eastmann	9,100 with IP = 2.3	3
Maleic anhydride grafted PP, Copolymer	MD-353D	Fusabond	88,700 with IP = 6.5	1.4
Maleic anhydride grafted Polystyrene	SMA 1,000P	Atofina	1,500	50

Characterization

Dispersion Analysis: X-Ray wide angle diffractometry spectra (WAXS) were obtained with a Siemens D500 diffractometer with a back monochromator and a Cu anticathode. The 2Θ angles were varying between 1 and 10° at a scanning rate of 0.6°/min by step of 0.02 s in order to measure the d_{001}-spacing between platelets. TEM observations were performed on thin sections of injection-molded samples with a CM120 Philipps microscope.

Rhelogical Analysis: Rheological measurements were realized on a viscocapillary rheometer Rosand from 10 to 1000 s^{-1} at 220°C.

Mechanical Properties Analysis: The mechanical bars were stocked at 23°C during 48 h before mechanical trials to obtain the flexural modulus. Flexural tests followed ISO 179 standard.

Results and Discussion

Morphology and dispersion analysis

Figure 1 shows X ray diffraction spectra of PP/PPgMA-20/948-5. We observe that the peak, d_{001}, significant of spacing between clay platelets is shifted towards lower angles. The spacing between platelets is increased from 2.0 to 3.6 nm after nanocomposite process. With the PPgMA homopolymer, an intercalated nanocomposite structure at 3.6 nm is formed. On the other side, when the PPgMA copolymer is used, clay platelets are better dispersed. We don't obtain longer the periodicity of X-ray peaks significant of an intercalated structure but we tend to an exfoliated structure. The higher molecular weight of the copolymer helps the chains diffusion and the clay dispersion. Figure 2 shows the X-ray diffraction spectrum realized on nanocomposites based on SMA as coupling agent. The effect of the clay surface treatment is clearly put into evidence from X-ray measurements. An exfoliated nanostructure is only obtained when silicate platelets are modified with benzyl ammonium ions because these ions have a good compatibility with the aromatic groups present on polystyrene chains of coupling agent.

It is interesting to observe the nanocomposite morphology. By TEM, we have obtained two distinct morphologies as reported in Figure 3 and 4. With PPgMA coupling agent, the morphology is very different and the nanofiller is rather well-dispersed. At a micrometric scale, we can see a homogenous structure : isolated platelet and stack of clay in all the matrix. At a smaller scale, we can see agglomerates of 3-4 platelets and isolated platelet but homogeneity is still present. On the other side, the introduction of SMA leads to a nodular morphology because SMA encapsulates the clay platelets and the miscibility with PP matrix is not sufficient. As a result, by using SMA as coupling agent, we have obtained a PP matrix filled with SMA nodules themselves filled with clay. With PPgMA coupling agent, we have obtained a PP nanocomposite with well dispersed clay. We can hope to get an attractive combination of mechanical behavior, flame retardantancy and improved gas barrier properties with this material.

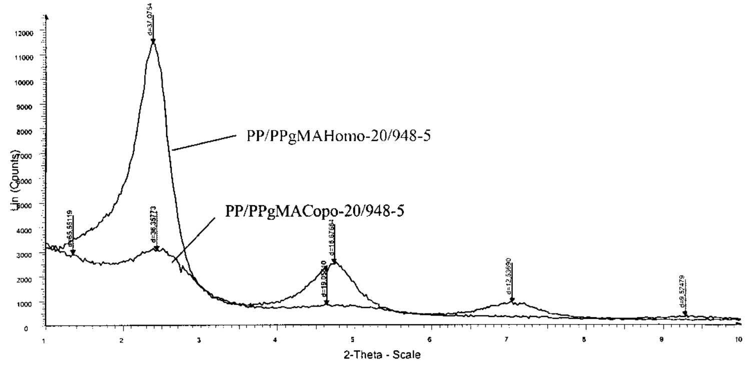

Figure 1 : WAXS analysis on PP/PPgMA-20/948-5 nanocomposite

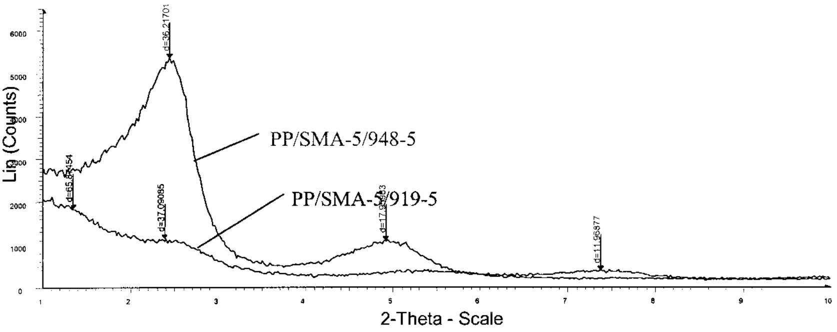

Figure 2 : WAXS analysis on PP/SMA-5/clay nanocomposite

Rheological analysis

The rheological tool can be very sensitive to characterize the nanocomposite microstructure. Capillary rheometer measurements reported in Figure 5 show a different behavior in the field of low shear rates. For well-dispersed nanocomposites (PP/PPgMA copo20/948-5), the viscosity is higher than one determined on intercalated nanocomposites (PP/PPgMAhomo20/948-5). The high aspect ratio of silicates when the platelets are well separated leads to an viscosity increase at lower shear rates whereas the platelets are oriented in the flow at higher shear rates and the viscosity decreases. Viscosity measurements are directly linked to clay dispersion in the matrix.

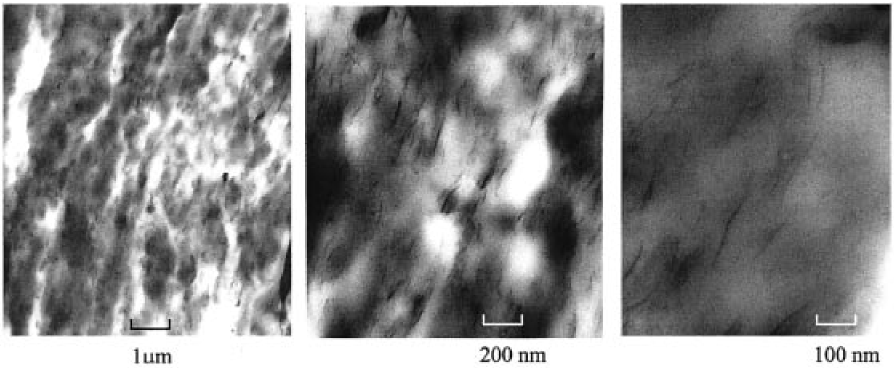

Figure 3 : TEM images on PP /PPgMA-20/948-5 at different scales

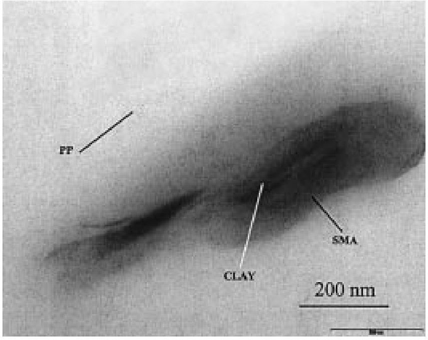

Figure 4 : TEM images on PP /SMA-5/919-5

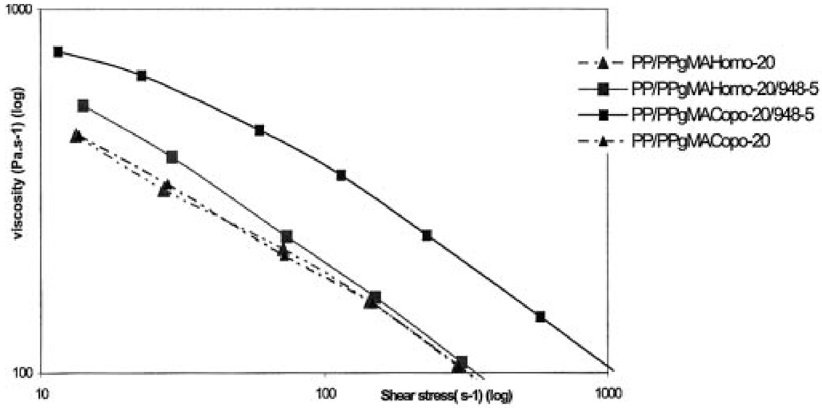

Figure 5 : Evolution of viscosity as a function of shear stress on a PP/PPgMA-20/948-5

Mechanical analysis

Macroscopic properties evolve with the materials nanostructure as shown in Figure 6. With 5% of organophilic clay and 20% of copolymer PPgMA as coupling agent, we have got an increase of 40 % for flexural modulus. The better mechanical properties are obtained for the nanocomposite which shows the best exfoliated nanostructure.

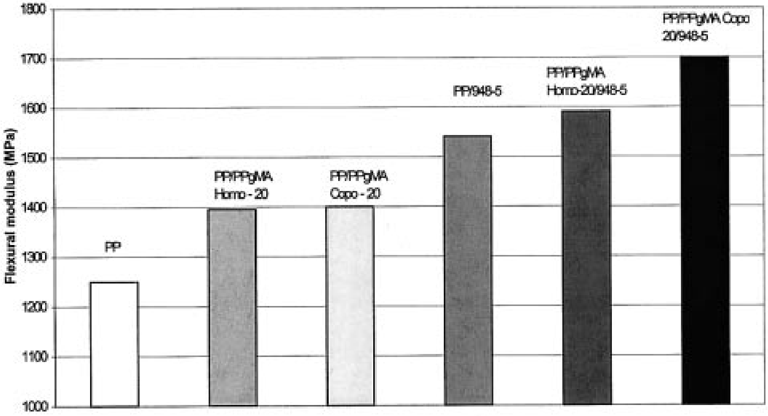

Figure 6 : Evolution of flexural modulus

Conclusion

In this work, we have prepared nanocomposites based on PP matrix by melt extrusion. Maleic anhydride grafted PP copolymer is the coupling agent which gives the better results. Its high molecular weight, its wide molecular weight distribution coupled with the relatively high grafting ratio can explain the better dispersion of clay. The short grafted chains can enter in the interlayer gallery, attracting longer chains which can transfer shear stress from matrix to layer. We get an increase of mechanical properties, but further works are in progress to characterize macroscopic properties such as barrier, flame retardant properties.

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