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NOVEL POLYPROPYLENE-CLAY HYBRID MATERIALS FOR AUTOMOTIVE INDUSTRY. EFFECT OF THE COMPATIBILIZING AGENT

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Abstract: Novel polypropylene-clay (PP-clay) hybrid materials were prepared in preset ratios using an organically modified layered silicate, namely Cloisite[®] 20A, and maleic anhydride-grafted polypropylene (MA-g-PP) as compatibilizing agent. The compatibilizer was employed in order to obtain a better dispersion of the clay into the PP matrix, which was evidenced by the means of X-ray diffraction spectrometry (XRDS). The thermal stability of these new materials was assessed by thermal gravimetric analysis (TGA) and their rheological behavior was also investigated.

Keywords: PP-clay nanocomposites, compatibilizer, characterization

1. INTRODUCTION

Polymer nanocomposites, as hi-tech engineering materials, have attracted great attention due to their superior properties higher than those of conventional composites and comparable with those of metals. The effect of nanofillers on the polymer properties is different from what was predicted by classic thermodynamically studies for the reduced particle size fillers [1] and only using continuum mechanics it was possible to reveal that the properties of polymer nanocomposites are strongly dependent on the particular features of nanofiller (content, aspect ratio etc.) [2]. The automotive industry benefited of these advances (Fig. 1) since it used polymer nanocomposites to enhance the level of performance of their products (mechanical, thermal, electrical and chemical properties of various components) [3].

Polymer-clay nanocomposites are a special type of hybrid materials due to the fact that initially the filler is of micrometer dimensions, but allows nanocomposites with highly dispersed nanometric particles due to the strong interactions between the matrix and clay that occur during processing.



Fig. 1. Polymer nanocomposites in the automotive industry

This renders new materials improved properties as compared to initial polymers. As result of the good dispersion of the clay tactoids into the polymer matrix and the exfoliation of platelets, these new materials become lighter, have increased mechanical strength and scratching resistance, display flame retardancy properties, can be easily painted, and, in some cases, they can be recycled [4].

But for polymers with low polarity, such as polyolefin, the improvements are not always significant due to the very low compatibility between clays and polyolefin. Given the immiscible character of clays in relation to polyolefin, in general, and their particular layered structure, several approaches are to be considered in order to enhance the interfacial interactions between these components: (1) the use of organically modified clays to favor clays penetration among macromolecular chains [5,6]; (2) compatibilizing agents (functionalized oligomers) are employed due to their ability to form hydrogen bridges between the polymer matrix and the =O, -OH and/or -COOH groups of the silicate [6,7]; (3) appropriate processing – melt mixing was proven to be the most effective method in terms of thermoplastics; (4) combined approaches [8]. In common practice it is impossible to reach a wholly exfoliated morphology, due to various factors (*e. g.*, the secondary agglomeration of platelets as result of the electrostatic charges that can appear during processing), therefore, most of the nanocomposites have a mixed morphology where the exfoliation is preponderant as against intercalation.

Polypropylene (PP) is widely used for many applications due to its low cost, low density, high thermal stability and resistance to corrosion, and processability. The polypropylene-clays nanocomposites displayed improved mechanical and barrier properties, flame retardant characteristics [9-11] as compared to raw PP.

This study focuses on novel PP-clay nanocomposites obtained by melt compounding and using MA-g-PP as compatibilizer in order to assess its effect on some properties of these new materials.

2. EXPERIMENTAL

2.1 Materials. The polypropylene used in experiments was an isotactic polypropylene (Malen-PF 401), a product supplied by Petrochemia Plock S.A. Poland. Polymer has a melt temperature of 170°C; decomposition temperature range 250–430°C, Vicat softening point 148°C; melt flow index (2.16 kg/230°C) 2.4–3.2 g/10min; volatile matter 0.3%wt.; isotactic index 95%.

Three different types of PP-g-MA (Crompton Corporation, USA) compatibilizers having different amounts of MA in their formulation were used, as follows: Polybond 3002 (0.2wt% MA) – C1, Polybond 3150 (0.5wt% MA) – C2, and Polybond 3200 (1.0wt% MA) – C3.

The organophilically modified clay Cloisite® 20A (Southern Clay, USA), assigned in this paper as C20A, was used as received. It was modified with a dimethyl dehydrogenated tallow quaternary ammonium salt where the anion was chloride (Cl⁻). Particles size: 13µm (>90%); cationic exchange capacity: 95 meq/100 g clay; density: 1.77 g/cm³; interlayer distance 2.10 nm.

The PP-clay nanocomposites were prepared by a two-step process. First, the compatibilizer was melt mixed with clay in a twin-screw extruder (HAAKE RHEOCORD 9000 mixer, $\Phi=19$ mm, $L/\Phi=40$, 200°C), in a preset ratio (90:10 wt%). The masterbatch samples were assigned as C1-C20A, C2-C20A and C3-C20A, respectively. In the second stage, the master-batch was melt mixed with neat PP (20:80 wt%) at 200°C. Thus, nanocomposites of PP/PP-g-MA/clay (2wt% clay) were obtained and the corresponding samples were assigned as PP-C1-C20A, PP-C2-C20A and PP-C3-C20A, respectively.

2.2 Characterization. The X-ray diffraction (XRD) measurements were run on a Bruker AD8 Advance X-ray diffractometer with Cu K α_1 radiation, with a wavelength of 1.54 Å, operated at 40 mA and 40 kV. The XRD patterns were recorded in the range 2°-40° (2 θ), at a scanning rate of 1°/min and the step interval was 0.02°. The interlayer spacing of the sample was derived from the peak position (d₀₀₁-reflection) in the XRD



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diffractograms according to the Bragg equation ($\lambda = 2d\sin\theta$).

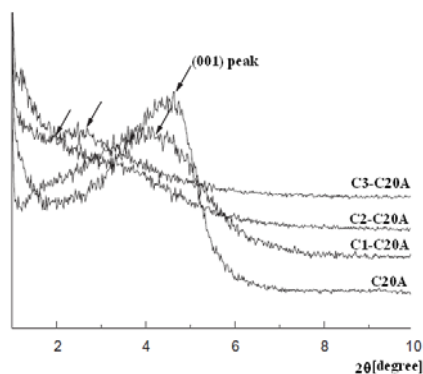
The thermal gravimetric (TG) analysis was performed on a Mettler Toledo TGA-SDTA 851 device, in air stream, with a heating speed of 10K/min, in the temperature range of 25-700°C, using samples of 4-6 mg.

The rheology study was performed on an Anton Paar rheometer equipped with CTD450, in plate-plate geometry, oscillatory mode, at a testing temperature of 200°C.

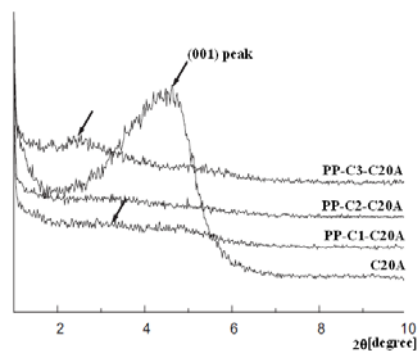
3. RESULTS AND DISCUSSION

3.1 Morphology. The changes of the interlayer distance in different polymer-clay hybrid materials can be estimated from XRD data by monitoring the position, shape and intensity of the basal reflections corresponding to the silicate layers. The intercalated morphologies are evidenced when the diffraction peak is shifted toward small angles, but the wholly exfoliated structures are confirmed when the XRD diffractograms no longer contain any diffraction peak of the clay.

In Fig. 2 are presented the XRD patterns of the master-batch samples C1,C2,C3-C20A (a) and the PP-clay nanocomposites (b), respectively.



a



b

Fig. 2. XRD diffractograms of the master-batch (a) and nanocomposites (b) samples

The organically modified clay showed a distinct peak at 4.741, indicated in both images, but for the master-batch samples (Fig. 2a) the peaks position and intensity differ. The angle lowest value was obtained for the sample that contains 0.5wt% MA (C2-C20A, 1.95), which is an indication of an highly intercalated/exfoliated morphology. But the intensity of this peak is low compared to the one corresponding to the sample C1-C20A (4.160), which contains the lowest amount of MA (0.2wt%), this peak intensity being close to the pristine clay. As for the C3-C20A sample (1.0wt% MA), the peak position is intermediary (2.50), but the intensity is close to C2-C20A. This can be explained taking into consideration the various content of MA in the structure of the compatibilizing agent: the higher the amount of MA, the higher the degree of ramification of the polymer, the better dispersion of clay tactoids and polymer-clay intercalation/exfoliation.

All nanocomposite samples (Fig. 2b) showed peaks at lower values and of very low intensity, except for the sample PP-C2-C20A where no peak appeared. This clearly indicates that the clay tactoids and platelets are better dispersed, but when C2 (0.5wt% MA) was employed in the formulation; a complete

exfoliation seemed to occur. A higher content of MA (C3, 1.0wt%) favored a secondary aggregation of clay particles, since the sample displayed a rather significant peak, although the basal distance is still greater in comparison with the neat C20A.

3.2 Thermal stability. The thermal stability of hybrid materials is a key element in their processing, as well as applications. Therefore, it is necessary to study the thermal behavior and degradation mechanisms of polymer-clay nanocomposites, given the specific influence of the clay which acts as a thermal insulator: it reduces the diffusion of volatiles out of the matrix and renders the corresponding hybrids thermal and mass barrier properties [9].

In Fig. 3 are represented the curves corresponding to the pure PP and nanocomposites samples as obtained from the thermal gravimetric analysis (TGA).

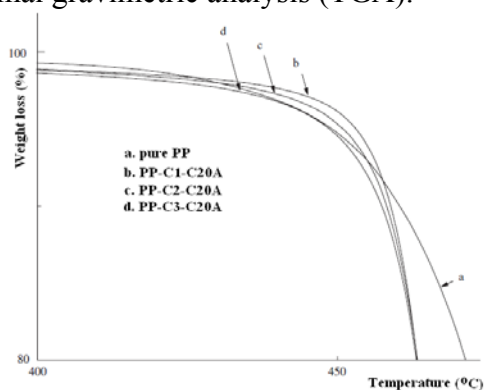


Fig. 3. TGA curves of nanocomposites samples as compared to neat PP

The first observation was the increase of the onset of degradation for all nanocomposites as compared to neat PP, which confirms the role of clay as thermal insulator and is consistent with literature data previously reported [6,13]. The weight losses of PP and its nanocomposites measured up to 250°C were found to be very small and correspond to the loss of water and some volatiles.

Assessing the influence of the compatibilizer on the thermal stability of hybrids, it is noticeable that the higher amount of MA has a negative effect on the samples thermal stability. The branching, that occurs subsequently to grafting, contributes to the clay dispersion, but, at the same time, it favors the thermal degradation of small chains and

promotes the decomposition. Moreover, the thermal degradation of the organic modifier from the structure of the compatibilizers can be added to this phenomenon.

3.3 Rheology. The rheological properties of polymer-clay nanocomposites are related to their distortion or deformation. The rheological properties can be an indication of melt-processing behavior in certain procedures (e. g., injection molding). Since the rheological characteristics of particulate suspensions are sensitive to the structure, particle size, shape, and surface features of the dispersed phase, the rheology studies potentially offer the means to assess the dispersion of nanocomposites in the molten state [14].

The shear viscosity of the considered nanocomposites samples as a function of the shear rate, at 200°C, as shown in Fig. 4.

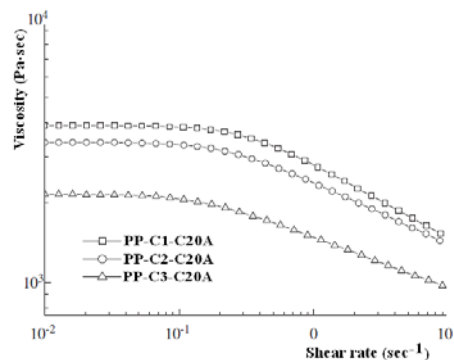


Fig. 4. The rheology data for the nanocomposites samples

It is noteworthy the significant decrease in shear viscosity, as a general trend for all studied nanocomposites. Considering the content of MA in compatibilizers as a criterion, it was concluded that a higher amount of MA entails a pronounced decrease in shear viscosity, as illustrated for sample PP-C3-C20A. Given the lower molecular weight of PP-g-MA compared to the neat PP, its shear viscosity is correspondingly lower. Thus, it enhances the general effect by adding a supplementary shear-thinning behavior [6]. Furthermore, some thermal and oxidative degradation secondary reactions may occur during melt processing which are also contributing to the overall effect.

Still, this specific behavior is a result of the preferential orientation of the clay tactoids and



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platelets as well, effect enhanced by the presence of the compatibilizing agents.

4. CONCLUSIONS

Novel (PP-clay) hybrid materials were prepared using an organically modified layered silicate, namely Cloisite[®] 20A, and various compatibilizers (MA-g-PP with different content of MA) in order to investigate the effect of compatibilization on some properties of the nanocomposites.

The morphology study confirmed the improved dispersion of the clay into the PP matrix and the exfoliation of the clay platelets in the case of PP-C2-C20A (0.5 wt% MA). The higher amount of MA was proven to have negative effect on the thermal stability of the nanocomposites due to certain degradation processes, such as thermal and oxidative reactions, or secondary aggregation of the clay platelets. Nevertheless, the rheology study evidenced that PP-clay nanocomposites are allowed to simultaneously achieve higher moduli and improved processability if their formulation includes compatibilizing agents. Further investigation will aim to optimize the PP: compatibilizer: clay ratio, in relation to processing parameters.

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