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A New Elaboration Concept of Polypropylene/Unmodified Montmorillonite Nanocomposites by Reactive Extrusion Based on Direct Injection of Polypropylene Aqueous Suspensions

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Nanocomposites based on polypropylene (PP) and unmodified Montmorillonite were prepared using a novel elaboration route based on a water-assisted extrusion process. Unmodified Montmorillonite, high shear compounding together with injection of aqueous suspension and reactive processing technology were used. Different aqueous suspensions containing cationic or anionic surfactants, and a compatibilizer (PP-g-MA) were injected during extrusion to promote clay dispersion. For a comparison purpose, a commercial PP/clay masterbatch was melt mixed to PP. Structural, morphological, and rheological characterizations indicate clearly that the cationic suspensions ease the dispersion of clay platelets in the PP matrix. No full exfoliation is, however, obtained, and the system remains still less homogeneous than the nanocomposite based on the commercial masterbatch. Nevertheless, mechanical and thermal characterizations of the nanocomposites based on cationic surfactants demonstrate the efficiency to disperse clay in the polymer matrix, and the effect on the ductility compared to usual PP nanocomposites is promising.

INTRODUCTION

There is no doubt about the considerable scientific and technological interest on hybrid organic-inorganic systems. In particular, the polymer/clay nanocomposites have attracted much attention. Such hybrids, because of their very large aspect ratios, offer with a few weight percents of layered silicate clays, properties superior to the ones of neat polymers or of traditional macro/micro-composites [1].

Because the neat layered silicates show poor interactions with organic polymers, nanoscale structures are mostly obtained by dispersion of organically modified layered mineral clays [most often Montmorillonite (MMT)]. To produce organically modified MMT (“organoclays”), the inorganic cations intercalated between the silicate layers are replaced by organophilic ions such as long chain alkyl ammonium ions, which act as surfactants [2].

Nevertheless, the organic modification of MMT suffers a few drawbacks. Because of the high surface area, a large ratio modifier/clay (sometimes in the range 30%–50% by weight) is required. The organic modification is thermally rather unstable, limiting polymer processing to $T \leq 200^\circ\text{C}$. The full process remains rather expensive [3].

Compared with neat polymers, nanocomposites offer often an improvement of all mechanical performances (the rigidity is improved without sacrificing strength, elongation, or toughness) [4, 5]. Other improved properties include barrier resistance, self-extinguishing behavior, scratch/wear resistance [6, 7]. Among layered silicate nanocomposites, polypropylene (PP)-based ones show high interest because the PP is a low cost commodity polymer used in a wide range of products. Even using organoclays, PP does not wet the surface of the silicate owing to the absence of polar groups in its backbone [8–10].

TABLE 1. Physical properties of the polymer aqueous emulsion.

| Tradename | Molecular weight | | Ionic character | pH value | Solids content (%) |
|--------------|------------------|--------|-----------------|----------|--------------------|
| | M_n | M_w | | | |
| Permanol DP6 | 2050 | 8000 | Weakly cationic | 7.5–8.5 | 40 |
| Permanol KP5 | 2050 | 8000 | Cationic | 5.0–6.0 | 35 |
| Permanol 603 | 24,800 | 47,000 | Weakly cationic | 9.0–10.0 | 34 |
| Permanol 601 | 24,800 | 47,000 | Anionic | 9.5–10.5 | 32 |

Using an apolar matrix, a further compatibilization is necessary, for instance by adding a maleated PP (PP-g-MA). This allows the clay surface to be wetted by hydrogen bonding between the anhydride functions and the oxygen atoms of the silicate [4]. The interlayer spacing increases by intercalation of the PP-g-MA into the clay gallery. The result is the effective transfer of shear stress from the polymer to the clay during compounding leading to a mechanical separation (“erosion” [11]) of clay nanolayers from their aggregates (“stacks”). Moreover, PP-g-MA compatibilizer is also miscible with the bulk [12]. The molecular weight and the concentration of grafted maleic anhydride determine the amount needed to obtain the delamination of the clay [12, 13]. Generally, a 3:1 ratio of compatibilizer to clay is used [14]. Melt compounding of PP with organoclay is a generally accepted method to obtain nanocomposites [15]. Despite modification of process conditions, a full dispersion (exfoliation) is rarely achieved. Wide stacks of clays showing poor intercalation often remain in the bulk [16].

The original scope of this work was to investigate the possibility to obtain a PP nanocomposite on the basis of an extrusion process designed for polyamide nanocomposites [17]. Further research work [18] was devoted to decreasing the cost of the nanocomposites technology by avoiding the expensive chemical modification of the clay. Unmodified Montmorillonite (Na^+MMT), high shear compounding together with injection of aqueous solution, very high throughput and reactive processing technology are used. Water (or aqueous solution) is injected under pressure directly into the melt that allows clay exfoliation. To avoid premature evaporation at high temperatures, the screw design consists of high compression zones allowing pressure building-up to 100 bar. Just before the die, pressure is released and water is vaporized through an open vent port followed by a second vent equipped with a vacuum pump to eliminate residual traces.

A technique comparable with this process was already applied on PP and untreated clay added with octadecyl trimethyl ammonium chloride (OMT) and PP-g-MA in a ratio clay/PP-g-MA 6:1 [19]. The authors suggest a mechanism for the dispersion of the silicate into PP based on water swelling of the clay to form a slurry, and its dispersion in the PP under strong shear. A fast cation exchange reaction was assumed to take place between the OMT and the Na cation intercalated between silicate layers, and the hydrophilic silicate layers were stabilized in the

hydrophobic PP. Furthermore, the silicate layers stabilized by the OMT were finely dispersed by the PP-g-MA. The residence time was about 6 min.

In the present study, Kato and Korbee’s processes are “merged” [17, 19]. Aqueous suspensions of PP-g-MA (waxes and higher molecular weights) are injected into an extruder. These suspensions are stabilized by cationic surfactants comparable to the alkylammoniums used for the usual modification of MMT [20]. The interest of the process is to associate in one step the organophilic clay modifier and the compatibilizer making them immediately accessible to the polar silicate environment. Water plays the role of “reagent carrier” to the clay. After this “in situ” modification, and the elimination of water excess, the modified clay should be well distributed into the PP. For the sake of comparison, on one hand, an anionic aqueous suspension (with fatty acid salts which are the largest single type of anionic surfactant used [20]) was also used and, however, a commercial master-batch for nanocomposite adapted for PP was also studied.

In this article, this new processing method is explored and the resulting nanocomposites are analyzed. The thermal stability and the thermal behavior were first studied by thermogravimetric analysis (TGA), and by differential scanning calorimetry measurements (DSC). The phase structure of the nanocomposites and the morphology are analyzed, respectively, by X-ray diffraction (XRD) and transmission electron microscopy (TEM) combined with rheological measurements so as to evaluate the dispersion. Mechanical properties are measured by means of tensile tests. Correlation between nanocomposite properties and experimental parameters (cationic or anionic surfactants, molecular masses of PP-g-MA) were examined, and results were compared with nanocomposites made from commercial masterbatch dilution.

EXPERIMENTAL

Materials

The PP Moplen (HF500N) used in this work was provided by Basell Polyolefins, with a Melt Flow Index [MFI] of about 12 g/10 min at 230°C. The aqueous emulsions derived from maleic-anhydride-grafted PP (trade name: Permanol) were kindly supplied by Dick Peters BV Chemische Industry. Their physical properties are listed in Table 1.

TABLE 2. Composition of the extruded samples.

| Samples | PP (wt%) | Clay (wt%) | Permanol (wt% solid content) |
|---|----------|------------|------------------------------|
| Virgin PP | 100 | 0 | 0 |
| Extruded PP | 100 | 0 | 0 |
| PP/H ₂ O | 100 | 0 | 0 |
| PP/DP6 | 96.1 | 0 | 3.9 |
| PP/KP5 | 96.6 | 0 | 3.4 |
| PP/601 | 96.9 | 0 | 3.1 |
| PP/603 | 96.7 | 0 | 3.3 |
| PP/Na ⁺ MMT | 96.2 | 3.8 | 0 |
| PP/Na ⁺ MMT/H ₂ O | 96.2 | 3.8 | 0 |
| PP/Na ⁺ MMT/DP6 | 92.4 | 3.7 | 3.9 |
| PP/Na ⁺ MMT/KP5 | 92.9 | 3.7 | 3.4 |
| PP/Na ⁺ MMT/601 | 93.2 | 3.7 | 3.1 |
| PP/Na ⁺ MMT/603 | 93.0 | 3.7 | 3.3 |
| PP/PolyOne | 96.3 | 3.7 | 0 |

The clay used is a purified and untreated pristine Montmorillonite [Na⁺MMT], supplied by Southern Clay Product (Gonzales, Texas) under the trade name Cloisite Na⁺. The average powder particle size varied between 2 and 13 μm . The PP/clay master-batch nanocomposite Nanoblend Concentrate MB1001 (38%–40% by weight of Nanomer clay) was obtained from PolyOne, Belgium S.A. All materials were used as received from the manufacturers.

Nanocomposites Preparation

Melt Compounding Process. Co-rotating extruder Krupp WP ZSK25 WLE from Coperion was used to prepare nanocomposites. The screw length was 1000 mm and its L/D ratio was 40. Polymer pellets and the clay were introduced by the feeder in the melting zone of the extruder at a throughput of 20 kg/h. The screw speed was 1200 rpm. The extrusion temperature applied was 200°C from hopper to die. Such conditions yielded a residence time in the extruder of about 30 s.

Water (or aqueous suspensions) was pumped into the extruder at a rate corresponding to 13 wt % of the total throughput and was compounded with polymers and the clay in the high compression zone at barrel temperature of 200°C. The screw was designed to allow the pressure increase in this zone up to 125 bar. In such conditions, water should remain liquid at the processing temperature. The melt is then degassed in the transport zone of the screw and the water vapor is fully removed using a vacuum pump. Nanocomposites samples were obtained with a clay loading of 4% by weight. Permanol suspensions are diluted before injection in view to keep a ratio 1 between the solid content of the suspensions and the filler. The exact compositions of the extruded samples are reported in Table 2.

Injection Molding Process. Melt compounds prepared as described above are first dried for 24 hours at 70°C

under vacuum to remove traces of moisture before injection molding. The nanocomposites pellets were injection molded into standard test specimen for tensile test using a Krauss-Maffei type KM 80-160E injection molding machine. The barrel temperature ranged 205–220°C, and the mold temperature was kept at 25°C. The samples obtained are standard tensile dog-bone samples (ASTM 527).

Compression Molding. The extruded samples were melt pressed at 200°C for 30 s under 10 tons and then cooled using a cold press.

Nanocomposite Characterization

Thermogravimetric Analysis. Thermogravimetry was performed using a Mettler Toledo TGA/SDTA 851e to follow the thermal stability (on heating) of the two kinds of samples: in one hand, the dried residue of the commercial suspensions and, however, of the nanocomposites. Drying of the suspension was performed under vacuum at room temperature during 48 h. About 10 mg of dried suspension sample was loaded into a platinum pan and placed on the microbalance. An isotherm at 200°C during 20 min under oxygen and another one under nitrogen were carried out on the dried Permanol suspensions. For the nanocomposites, the loaded (about 10 mg) thimbles were heated in air (100 ml/min) at 10°C/min, and the relative weight of the sample was recorded in the temperature range of 25°C–600°C.

Size Exclusion Chromatography. Samples with aqueous suspensions are analyzed for their molecular weight distribution by size exclusion chromatography (polystyrene calibration). About 5 mg of polymer is dissolved in 5 ml of trichlorobenzene at 160°C during 60 min. The chromatographic system was an Alliance GPCV 2000 from Waters with three Styragel columns (HT 6E, HT 6E, and HT 2, respectively) coupled to a refractive index meter (DRI). The columns were kept at 145°C. Trichlorobenzene stabilized with Irganox 1010 was used as eluent, and its flow rate set to 1 ml/min. The molecular weight distribution was analyzed using Waters Millennium 32 version 4.00.

X-ray diffraction. The interlayer spacing of the dispersed layered-silicates in the various nanocomposites were recorded using Siemens D5000 diffractometer with nickel-filtered CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The angle range is between 1° and 10°. Analysis was performed on the surface of the compression molded specimens.

Transmission Electron Microscopy. Nanoclay dispersion, intercalation, and exfoliation in nanocomposites samples were examined by means of TEM. Specimens of the nanocomposites produced were cut perpendicularly to the axes of the extruded pellets. Ultrathin sections of

approximately 95 nm in thickness were cut at ambient temperature with a Reichert Microtome and collected on a 300 mesh copper grid. They were examined with a LEO 922 transmission electron microscope operating at 200 kV.

Rheological Measurements. Shear rheology on compression molded samples is performed on an ARES rheometer from Rheometric Scientific. Cone-plan geometry is used with a diameter of 25 mm set at a gap of 0.46 mm. All the measurements are carried out under nitrogen atmosphere at 180°C and at a strain rate of 10%. The complex viscosity (η^*) and storage modulus (G') are measured over an angular frequency range of 100–0.1 rad/s.

Differential Scanning Calorimetry. The investigation of thermal behavior was carried out on a Perkin Elmer DSC7 operating in standard DSC mode on about 10 mg samples in nitrogen atmosphere. The temperature and heat of melting were calibrated with indium and tin standards. The sample was first heated at a heating rate of 10°C/min from 35°C to 200°C. After annealing at this temperature for 5 min to eliminate thermal history effects, the sample was cooled and reheated under the same conditions.

Mechanical Characterization. Tensile tests are performed at room temperature using Lloyd LR50K tensile machine according to ISO 527-1. Reported values are averages obtained from a minimum of five tests. The Young moduli are recorded at cross-head speed of 1 mm/min. The elongation at break and tensile strength are recorded at cross-head speed of 25 mm/min.

RESULTS AND DISCUSSION

The production of nanocomposites based on polyolefins and layered silicates is complex. It requires an intercalation of polymer in between the silicate layers. This intercalation is governed by the diffusion phenomenon of the polymer into the gallery and is achieved by a combination of shear and residence time into the extruder [21]. However, the process conditions must be carefully selected to avoid a certain extent of degradation. Indeed, it is well known that a degradation reaction of the matrix and of the filler would affect the quality of the desired nanocomposite. Both PP chain scission and degradation of the surfactant used to organo-modify the clays can occur. Paradoxically, high extrusion rates are recommended to increase shearing stresses to break down the clay aggregates (stacks) and finally to promote silicate clay exfoliation [22]. However, the latter is dependent on the diffusion of the polymer matrix, thus on process duration. The intercalation is usually improved when a longer residence time is adopted [23].

The process conditions are selected in view to minimize the components degradation of the nanocomposites

TABLE 3. Molecular weights distribution of the extruded samples and virgin matrix.

| Samples | Molecular weights (Daltons) | | |
|---------------------|-----------------------------|----------|-----------|
| | M_n | M_w | M_w/M_n |
| PP pellets | 55,057 | 2,46,033 | 4.47 |
| PP extruded | 44,435 | 1,41,288 | 3.18 |
| PP/H ₂ O | 55,304 | 2,32,060 | 4.20 |
| PP/DP6 | 50,641 | 2,20,273 | 4.35 |
| PP/KP5 | 47,698 | 2,05,749 | 4.31 |
| PP/603 | 57,032 | 2,33,773 | 4.10 |
| PP/601 | 51,363 | 2,16,929 | 4.22 |

while keeping shear as high as possible. Whatever the suspension studied, the isothermal TGA analysis under oxygen or nitrogen show a weight loss lower than 2% after 20 min at 200°C. The suspension constituents (e.g. PP-g-MA) could be considered thus thermally stable enough for the selected process conditions.

Moreover, the full process including aqueous suspension injection must be inert toward the matrix. Results of molecular weights distribution are summarized in Table 3. A slight decrease of the molecular weight can only be noticed for PP extruded as such without any injection. But almost no decrease is observed for any other sample. There is thus no evidence of PP degradation even in the presence of the different suspensions. Moreover, water seems to protect PP matrix against thermal degradation during the process. Similar results were previously reported, and it was suggested that water may act as a lubricant [24, 25].

The efficiency of clays in reinforcing the polymer matrix is primarily determined by the degree of its dispersion in the matrix. Highest mechanical reinforcements are obtained on full exfoliation of clays. This latter is linked to the diffusion of the polymeric chains into the spaces between the clay galleries in view to surpass their cohesive forces by the hydrodynamic separation forces applied by the matrix in the molten state.

Exfoliation is always preceded by intercalation which results from the diffusion of polymer chains in the inter-gallery spaces of the clay. By injection of Permanol suspensions, it is aimed in one step, to ease the diffusion of PP-g-MA between the silicate platelets, to separate them and to stabilize their dispersion in the PP matrix.

The Fig. 1 depicts the X-ray diffraction patterns of the various nanocomposite samples compared with the pristine clay itself (Na⁺MMT). A shift in the clay peak indicates the increase of the intergallery space assigned to the formation of an intercalated structure, whereas disappearance of the peak indicates a potentially exfoliated structure.

The basal reflection, characteristic peak of the pure pristine clay ($2\theta = 7.8^\circ$; $d_{001} = 1.1$ nm, see sample Cloisite Na⁺) is included in the diffraction pattern. The clay characteristic peak of PP/Na⁺MMT/H₂O does not shift demonstrating that injection of water alone does not

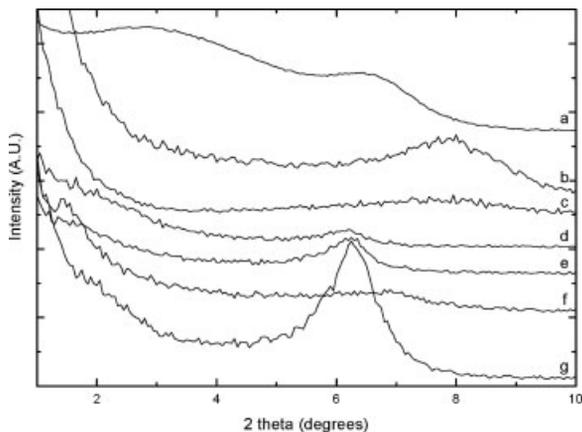


FIG. 1. XRD patterns of PP/PolyOne (a), Na⁺MMT (b), PP/Na⁺MMT/H₂O (c), PP/Na⁺MMT/KP5 (d), PP/Na⁺MMT/DP6 (e), PP/Na⁺MMT/601 (f), and PP/Na⁺MMT/603 (g).

(permanently) increase enough the intergallery space to ease intercalation when there is no polar group onto the neat polymer. As a result of the injected Permanol suspension melt-mixing process, for PP/Na⁺MMT/Permanol systems, the basal peak of the clay shifts to lower angles ($2\theta = 6.2^\circ$; $d_{001} = 1.39$ nm), which is attributed to intercalation. Considering the limited increase of the basal spacing, one can consider that only alkylammonium surfactant is intercalated. The clay characteristic peak of sample with 601 (PP/Na⁺MMT/601) shifts less than other Permanol systems ($2\theta = 6.7^\circ$; $d_{001} = 1.29$ nm). Permanol 601 contains anionic surfactant whereas others have cationic ones that could act like alkylammonium in organo-modified clay. Two characteristic peaks are present for PolyOne masterbatch based nanocomposite ($2\theta = 2.7$ and 6.3° ; $d_{001} = 3.19$ and 1.37 nm). However, the basal reflection peak for the organomodified clay used in the PolyOne masterbatch is unknown.

Another approach of the clay dispersion was performed by TEM. The PP/Na⁺MMT and PP/Na⁺MMT/H₂O injected composites samples present large clay aggregates even visible under naked eye and were thus discarded from TEM examination. As expected, the layered structure exhibiting narrow intergallery space is very difficult to break into small stacks even under severe process conditions because of the strong interaction between platelets.

The injection of 601 anionic suspension shows clay clusters with a well-aligned densely compacted structure, thus confirming the X-ray results that indicate poor intercalation for this nanocomposite. No indication of exfoliation can be observed.

The dispersion of Na⁺MMT in the PP matrix using cationic Permanol suspensions exhibits, whatever the type of PP-g-MA suspension (weakly cationic: DP6 and 603; cationic: KP5) and the molecular weight of the PP-g-MA (low M_w : DP6 and KP5; high M_w : 603), multilayer stacks with partially exfoliated structure in spite of the presence of a few large stacks. At higher magnification, it is very interesting to observe a very loose layer structure, which

is quite different from the well-ordered layer structure of the stacks. The disappearance of the ordered structure of the clay should be the result of an improved interaction between the bare clay surface and the surfactant and/or the compatibilizer. Figure 2a shows TEM micrographs at low (Fig. 2a) and high magnification (Fig. 2b and c) for PP/Na⁺MMT/KP5 composite. The light gray area corresponds to the PP matrix and the darker lines are attributed to the silicate layers. The TEM micrographs at high magnification exhibit a mixed distribution of individual platelets and of tactoids comparable to one observed for the micrographs of the PP/PolyOne nanocomposite (Fig. 2d–f). At low magnification (Fig. 2d), the distribution of the clay tactoids in PP/PolyOne is, however, more uniform than for samples with cationic suspensions.

Nevertheless, these observations confirm that with the aid of Permanol suspensions, the clay aggregates have been broken down into smaller stacks. As confirmed by X-ray diffraction analysis some intercalation occurs and even exfoliation can be thought to occur to a certain extent. In the absence of Permanol suspension, the clay aggregates seem only sheared off and broken down into rather large stacks.

Moreover, using these compatibilizers, a diffusion process is also promoted in addition to shear effect. As seen in Fig. 3, the clay layers are peeling off from one end, indicating the diffusion of polymer macromolecules into the clay galleries by such a mechanism as proposed by Cho and Paul [26]. This phenomenon is observed only for the nanocomposites containing compatibilizers, proving that they have better compatibility with the clay nanoplatelets than the pure PP matrix [27].

Even if WAXS combined with TEM observations give some indications of the dispersion, the conclusions from these results have to be confirmed. Indeed, the TEM due to the scale of the observations does not provide representative view of the material at the macroscopic scale. WAXS measurements only give indication of intercalation but not on exfoliation. In this way, rheology seems to be a well adapted characterization method to obtain a quantitative evaluation of the clay dispersion in the molten state. Indeed, the rheological properties of the melt are sensitive to the structure, particle size, shape, and surface properties of the dispersed phase, and thus to the dispersion.

Figure 4 shows the evolution of the complex viscosity η^* of the virgin PP, extruded PP and PP blended with the different Permanol suspensions. The severe extrusion conditions with a high shear clearly induce a degradation of the PP matrix highlighted by the difference between the viscosities of virgin PP and extruded PP. In the same extrusion conditions, the injection of water allows to control the degradation. Indeed, the viscosity of PP/H₂O is quite similar as one of the virgin PP, only a slight decrease is visible. Such an effect of water injection was already reported [24] and could be ascribed to the lubricant effect of water. Injection of water suspensions induces the same effect as shown for PP/H₂O sample.

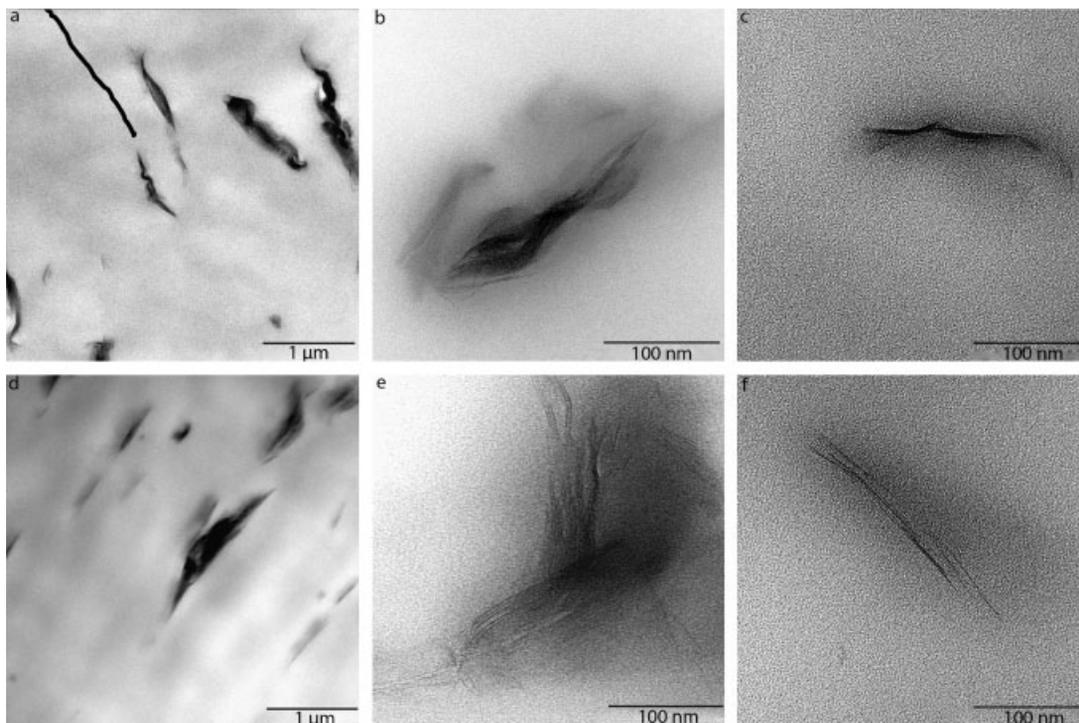


FIG. 2. TEM micrographs of PP nanocomposites: PP/Na⁺MMT/KP5 (a in low magnification and b, c in high magnification) and PP/PolyOne (d in low magnification and e, f in high magnification).

Presence of water in the suspensions degradation is also limited. However, a decrease of the viscosity for all the frequencies is observed compared to PP extruded with water injection only.

The presence in the suspensions of PP-g-MA induces a decrease of the viscosity which may be assigned to a plasticization effect of the low molecular weight compatibilizer [28].

The Fig. 5 gathers the evolution of the storage modulus (G') of the different extruded nanocomposites with

injection of water and of aqueous suspensions. These curves are compared to PP extruded in the same conditions without water. The storage modulus of PP is clearly lower than the one of the nanocomposites. The increase of G' for the nanocomposites is induced by the presence of the rigid and highly anisotropic clay nanoplatelets, but the injection of water also induced an increase of G' by controlling the degradation during extrusion. Finally, a limited increase of the nanocomposites storage moduli is obtained, indicating that the optimal dispersion of the clay

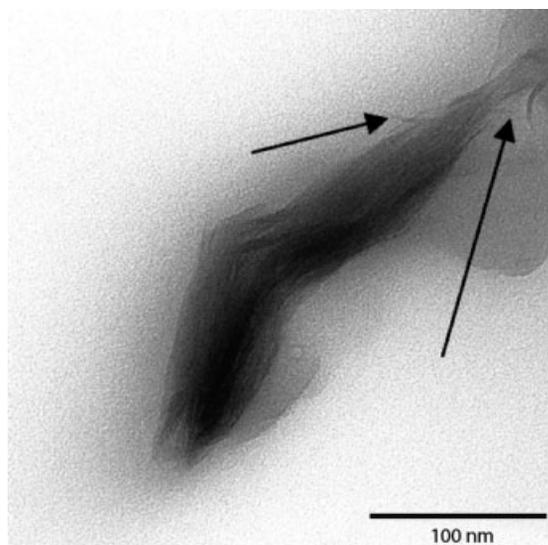


FIG. 3. TEM micrograph of the PP/Na⁺MMT/KP5 nanocomposite.

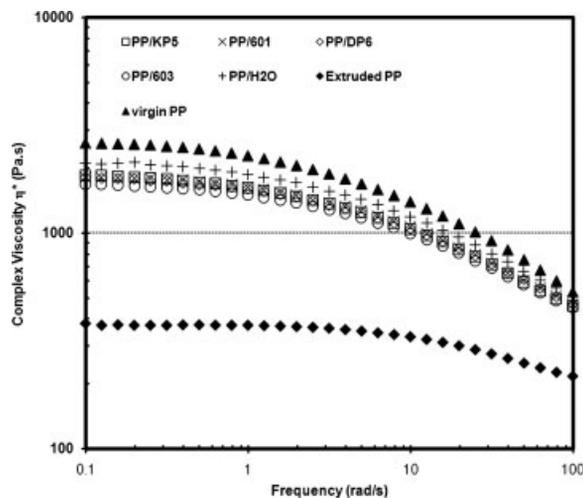


FIG. 4. Complex viscosities η^* of the virgin PP, extruded PP, PP/KP5, PP/DP6, PP/601, and PP/603.

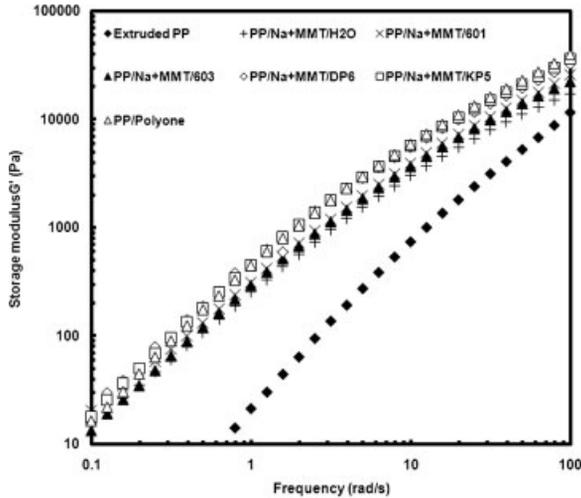


FIG. 5. Storage modulus G' of the extruded PP, PP/Na⁺MMT, PP/Na⁺MMT/H₂O, PP/Na⁺MMT/KP5, PP/Na⁺MMT/DP6, PP/Na⁺MMT/601, PP/Na⁺MMT/603, and PP/PolyOne.

platelets does not occur even with the help of Permanol suspensions. The nanocomposite obtained with injection of water only exhibits the lower storage modulus indicating that Permanol suspensions support the dispersion of clay platelets. Nevertheless, the efficiency of the suspensions is demonstrated by the comparison with PP/PolyOne nanocomposite. The results suggest that the dispersion of the clay (based on the value of G') in this case is comparable to the one of nanocomposites obtained with injection of aqueous suspensions, for all that PP of the PP/PolyOne does not degrade during the extrusion process.

The TGA results in Table 4 present for the extruded nanocomposites, the temperatures at which 5, 10, and 50% weight loss occur. These values are compared to the ones obtained without Na⁺MMT. The initial decomposition temperature (T_i , temperature at 5% weight loss) obtained reflects the thermal stability. The temperature at 10% weight loss is considered as the onset (T_o) of the degradation, and the temperature at which 50% degradation occurs, the midpoint of the degradation (T_m) [29].

T_i , T_o for PP with and without Na⁺MMT are similar, when T_m is increased by adding Na⁺MMT. The injection of water simultaneously with Na⁺MMT addition increases these three values. The protecting mechanism of water is not clearly established. A higher quantity of water could remain trapped by the clay and postpones the thermal degradation of this nanocomposite. The thermal decomposition of the different PP nanocomposites obtained with the injection of aqueous Permanol suspensions will be compared to this latter nanocomposite (PP/Na⁺MMT/H₂O), thus considered as a reference.

Whatever the nature of the Permanol suspension used, T_i , T_o , and T_m are clearly shifted to temperatures higher to the ones of the reference. This increase is higher for cationic suspensions than for the anionic one. The nanocomposite obtained using 603 (PP-g-MA with a high M_w)

exhibits the highest thermal stability and is quite similar compared to the one of PP/PolyOne nanocomposite. Furthermore, it can be noticed that adding Permanol suspensions without Na⁺MMT lowered T_i , T_o , and T_m . Finally, the synergy of Permanol suspension in combination with Na⁺MMT is necessary to obtain a positive effect on the thermal stability of the nanocomposites.

One of the major interests on nanocomposites is the specific mechanical properties of these materials. Indeed, improving the mechanical properties without increasing the weight is still an issue in industry. The polymer clay nanocomposites represent a promising route to solve this problem by increasing the strength and stiffness of the polymers even for low clay content. However, the improvement of the mechanical properties is intimately correlated to the dispersion of clay platelets. The best properties are obtained in case of exfoliated nanocomposites.

Due to the presence of PP-g-MA of lower molecular weight than PP, a plasticization effect occurs as observed from the rheological measurements, and might affect the mechanical properties of the nanocomposites. To evaluate this effect, the mechanical properties of PP extruded with injection of 4% wt of the aqueous suspensions alone (a similar content as for the nanocomposites) were evaluated and are gathered in Fig. 6. A plasticization effect could explain again the decrease of the Young moduli compared to neat PP observed for all the samples containing the Permanol suspensions. No significant effect of the suspensions is noted on the yield stress. Concerning the elongation at break, a slight increase is evidenced compared to neat PP. Due to the severe extrusion conditions (high shear) degradation of PP may occur during extrusion. As discussed earlier, the injection of water suspensions limit this degradation leading to increase the elongation at break. Clay is often considered as nucleating agent and may influences also to some extent the mechanical properties of PP [30, 31]. So as to eliminate any potential influence, the thermal behavior was measured by DSC for the different nanocomposites. No significant effect is noted.

TABLE 4. The TGA results of used PP formulations.

| Samples | $T-5\%$ (°C) | $T-10\%$ (°C) | $T-50\%$ (°C) |
|---|-----------------|------------------|------------------|
| PP | 254 | 265 | 300 |
| PP/Na ⁺ MMT | 256 | 268 | 319 |
| PP/Na ⁺ MMT/H ₂ O (reference) | 266 | 283 | 344 |
| PP/Na ⁺ MMT/DP6 | 274 | 291 | 352 |
| PP/DP6 | 250 | 264 | 315 |
| PP/Na ⁺ MMT/KP5 | 275 | 294 | 359 |
| PP/KP5 | 256 | 272 | 333 |
| PP/Na ⁺ MMT/603 | 281 | 300 | 365 |
| PP/603 | 256 | 270 | 321 |
| PP/Na ⁺ MMT/601 | 271 | 288 | 349 |
| PP/601 | 260 | 277 | 339 |
| PP/PolyOne | 273 | 297 | 377 |

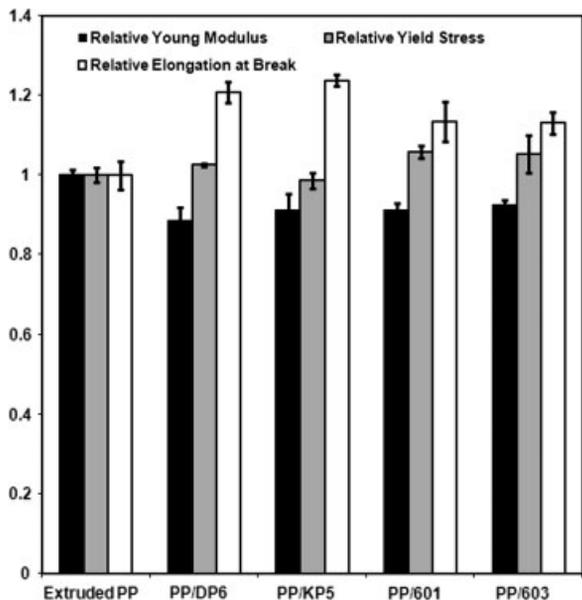


FIG. 6. Relative Young modulus, yield stress and elongation at break of extruded PP, PP/KP5, PP/DP6, PP/601, and PP/603.

Mechanical properties of the different nanocomposites have been evaluated, and the results are shown in Fig. 7 that gathered relative Young modulus, relative yield stress, and relative elongation at break of the nanocomposites. It is most commonly found that the mechanical properties of polymer nanocomposites, especially the modulus, are increased and depend to a great extent on filler dispersion and interfacial interaction. Good dispersion of the clay platelets signifies an increase of the interface between the polymer and the nanofiller, and, thus, the extent of influence of the clay platelets on the polymer chains. Indeed, increasing the interface increases the volume of polymer chains influenced by the rigid clay platelets leading to increase the Young modulus of the nanocomposites. The improvement of clay dispersion induces also an increase of the average aspect ratio of the nanofillers in the polymer matrix and as a consequence Young modulus is improved. As already reported [32], the higher the aspect ratio of clay platelets the higher the Young modulus can be expected.

Results point out a slight increase in Young's modulus values of all the nanocomposites compared to the neat PP. The weakest increase is attributed to PP/Na⁺MMT/601 nanocomposite. The 601 is referenced as an aqueous suspension with an anionic character. It can be assumed that the interactions between the negatively charged clay platelets and the anionic surfactant are unfavorable and may promote aggregation of clay platelets leading to a limited increase of the Young's modulus even lower than PP/Na⁺MMT/H₂O nanocomposite for which no favorable interactions exist between apolar PP and highly hydrophilic clay. Concerning the nanocomposites based on DP6, KP5, and 603, the Young's moduli are slightly improved probably due to the cationic character of the

water suspensions. In these cases, the swelling of the clay platelets by the water molecules and cationic surfactants, supported by the XRD results, must improve the dispersion and ease the intercalation of the polymer chains due to the good interactions between the cationic surfactant and the negatively charged clay platelets. No big difference in Young's modulus can be noted between the different nanocomposites based on cationic suspensions. Nevertheless, the Young's moduli of these nanocomposites are lower compared to the nanocomposite obtained from the commercial PolyOne PP/clay masterbatch. However, considering the plasticization that occurs due to the presence of PP-*g*-MA in the water suspension, the relative value (compared to neat PP and not PP/Permanol) might be underestimated.

The yield stress, which is the stress that can undergo the material before plastic flow, gives a supplementary evaluation of the material strength and is greatly influenced by the interactions between the polymer and the fillers. As shown in Fig. 7, an increase in yield stress values is also observed for all the nanocomposites except for the PP/Na⁺MMT/601. This last result confirms the imperfect dispersion of the clay platelets probably dispersed as micrometer sized aggregates that act as stress concentrators easing the plastic deformation, thus decreasing the yield stress. It's interesting to notice that the yield stress of the PP/Na⁺MMT/H₂O nanocomposite is higher than for neat PP. It indicates that the size of the clay aggregates is limited and demonstrates that the injection of water is already efficient for apolar PP to break the large clay aggregates and disperse clay tactoids even if intercalation/exfoliation is not possible due to the unfavorable interaction. The yield stress values of PP/Na⁺MMT/KP5

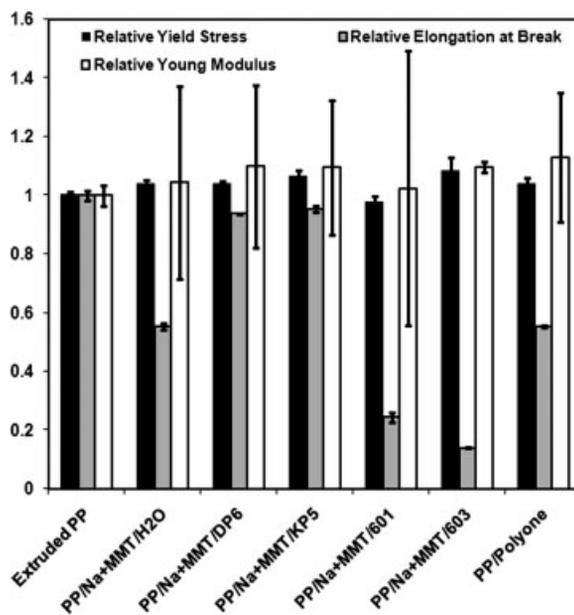


FIG. 7. Relative Young modulus, yield stress, and elongation at break of extruded PP, PP/Na⁺MMT/H₂O, PP/Na⁺MMT/KP5, PP/Na⁺MMT/DP6, PP/Na⁺MMT/601, PP/Na⁺MMT/603.

and PP/Na⁺MMT/DP6 nanocomposites are higher than neat PP, this result is attributed to the cationic character of both KP5 and DP6. Indeed, due to the negative charge of the clay platelets, favorable interactions are developed between the nanofiller and the cationic surfactant may lead to a better interfacial cohesion which would increase the yield stress. PP/Na⁺MMT/603 leads to the highest increase, in addition to the ionic character, this may be related to the high molecular weight of the 603 compatibilizer.

In summary, the nanocomposites based on untreated clays and cationic aqueous suspensions show improved yield stress results even in comparison with the one based on industrial masterbatch PP/PolyOne. This should result from an interesting improvement of interfacial adhesion.

Elongation at break results (Fig. 7) show a better ductility for PP/Na⁺MMT/KP5 and PP/Na⁺MMT/DP6 nanocomposites. Ultimate properties for these two polymer/clay formulation are almost at the level as neat PP and definitely above the one of the nanocomposite based on the commercial masterbatch. This is again an interesting result because the general tendency of mineral fillers is to decrease the ductility of the polymer. The reason for maintaining ductility could be attributed, as already discussed for the yield stress values, to favorable interactions between the clay and the matrix, and also to the absence or the small number of clay agglomerates in the bulk. In contrary, the elongation at break of PP/Na⁺MMT/601 and PP/Na⁺MMT/603 are very low compared to the neat PP. The reasons for that are not obvious because the elongation behavior evaluated for PP/601 and PP/603 formulations without clay are similar to the one of extruded PP, eliminating an effect of the water suspensions. Besides, if for PP/Na⁺MMT/601, the low elongation could be attributed to the presence of aggregates, it could not be the case for PP/Na⁺MMT/603 because as already demonstrated the clay platelets are well distributed. Finally, the nanocomposites based on cationic aqueous suspensions present a really interesting ductility, which could be attributed to the good interfacial adhesion and confirm that this new elaboration route seems to be hopeful.

CONCLUSION

New nanocomposites based on the aqueous suspensions, containing cationic surfactants and a PP-g-MA compatibilizer, and untreated clay were obtained using direct suspension injection in the molten PP. This route allows operating a simultaneous in-situ organo-modification and compatibilization of the clay platelets and PP matrix. The characterization of the nanocomposites obtained via this method presents dispersion of clay tactoids without the presence of large clay aggregates. As shown by the XRD analysis, a slight intercalation was obtained. The morphological characterization performed by TEM demonstrates that these suspensions promote to a certain extent the diffusion of PP chains and clay platelets

peeling off. At a macroscopic scale, the rheological results confirm the homogeneous dispersion of clay tactoids comparable to the dispersion obtained by using the commercial PP/clay masterbatch. However, the full exfoliation is not obtained for nanocomposites based on cationic aqueous suspensions. The thermal stability of these nanocomposites is clearly evidenced thanks to a synergistic effect of the cationic aqueous suspensions and the unmodified MMT. Due to the perfectible dispersion of the clay, the improvement of the strength and stiffness of the obtained nanocomposites is limited, but the ductility of the nanocomposites based on the low molecular weight PP-g-MA cationic or weakly cationic (KP5 and DP6) is really interesting and clearly indicates the favorable interaction developed due to the presence of cationic surfactants combined with the compatibilizer.

Finally, the original method developed in the frame of this work seems to be really promising. Indeed, the suspensions clearly help the dispersion of the clay platelets combined with the development of good interfacial properties. The method has to be optimized to take full advantage of the interest of this in-situ compatibilization. This work paves the route toward a novel elaboration of nanocomposites using native clay.

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