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Nanocomposites from Untreated Clay : A Myth ?

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Summary: Polyamide 6 and pristine montmorillonite have been melt blended in an extruder and water was injected into the melt in order to produce nanocomposites. The pristine clay was found to be exfoliated and dispersed homogenously in the nanocomposites. A mechanism explaining the formation of such nanocomposites is presented.

Keywords: extrusion; model; montmorillonite; polyamide; water injection

Introduction

In recent years, organic-inorganic nanometer composites have attracted great interest because they often exhibit unexpected properties[1]. Layered silicate clays have been successfully used as additives or reinforcing fillers to improve polymers properties[2–5]. Polymer layered silicate nanocomposites challenge traditional filled polymers. With few percent weights of layered silicate clays (montmorillonite), it is possible to reach similar properties than with higher amount of conventional filler[6,7] (talc, glass fibers, calcium carbonate). The extent of properties enhancement is related to numerous factors including clay nature, aspect ratio, synthesis of the nanocomposite, orientation in the matrix, and interaction between the nanofiller and the matrix[8–12].

Generally, inorganic material exhibits a low interaction with organic polymers, leading to a poor dispersion of the filler in the matrix. To improve this interaction, the charge balancing interlayer cations (typically sodium), present on the montmorillonite's (MMT) surface, are most often replaced by alkyl ammonium ions, enhancing the organophilicity of the layered silicate surface[13].

Among the layered silicate polymer nanocomposites, polyamide 6 (PA6) has received a high attention. Various methods from in-situ polymerization[6,14,15] to melt compounding methods[17–19] are reported for the preparation of these nanocomposites. Compounding processes have attracted a lot of attention wherein organophilic clay ion-exchanged by alkyl ammonium ions were melt compounded with nylon[13].

Publications deal with the effects of the organoclay structure on PA6 nanocomposites morphology and properties. Fornes and al.[20] showed that, in the case of PA6, a wide range of nanocomposites morphology results from altering the number of long alkyl tails attached to the nitrogen of the modifier. Platelet-platelet separation leads to dispersions ranging from ''tactoids'' or ''microcomposites'' (no separation) to ''intercalates'' (parallel increase of intergallery distance induced by molecular diffusion) to ''exfoliates'' where individual platelets are randomly dispersed. There is a balance between the amount of platelet separation, the level of exposed silicate allowed by the organic modifier and the number of unfavorable interactions between the polar nylon chain and the alkyl tail. Organoclay with one alkyl tail

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modifier seems to be an optimum combination of these effects.

Few articles deal with unmodified clay polymer nanocomposites. Intercalation of polymer into sodium montmorillonite (Na^+ MMT) seems indeed difficult and leads to micro-composite instead of nanocomposites, emphasizing the role of the organic modifier. However, Hasegawa and al.[21] reported a novel process to prepare PA6 nanocomposites, using unmodified MMT. Aqueous slurry of Na^+ MMT is melt blended with PA6 using a laboratory extruder, and the water released is evacuated by a vacuum pump. WAXS patterns and TEM micrographs clearly indicate the exfoliation of the Na^+ MMT layers and the mechanical properties of these nanocomposites appeared close to those obtained with conventional organo-modified nanocomposites. According to the authors, the exfoliation process occurs in steps: first, the water slurry is introduced in the extruder by a pump; then, the clay slurry is reduced in fine droplets' containing few Na^+ MMT platelets and the water evaporates in contact with the melt leaving the silica layers dispersed; finally, the water vapor is removed under vacuum. The advantage of this new compounding process is to reduce the costs on producing polymer layered silicate nanocomposites, by avoiding the expensive chemical modification of the montmorillonite. The authors showed the possibility to exfoliate Na^+ MMT in a polyamide matrix by the melt compounding route by adapting the process. The major drawback of this method is that huge amounts of water are pumped into the extruder to reduce the slurry viscosity.

Another melt compounding process leading to the exfoliation of Na^+ MMT in a polyamide 6 matrix is described in a patent by Korbee et al. assigned to DSM[22]. In this process, water is injected directly in the extruder melt; the natural clay is introduced with nylon 6 pellets. This idea has been also developped more recently by Yu et al.[23] As a main difference with Hasegawa's techniques, clay is not pretreated even in water before being blended in the extruder and smaller amount of water are used in this technique.

We also develop this technique in collaboration with DSM in the field of a 5th framework European research project[24]. This project aimed at decreasing the cost of the nanocomposites technology by avoiding the organo-modification step on the MMT. The major difference with the previous described technique is that in this case, the lab-extruder was set in scale-up conditions and that a combination of high shear compounding, very high throughput and reactive processing technology are used to improve the dispersion and the mechanical properties of the Na^+ MMT polyamide 6 nanocomposites.

Although good results are obtained with this technique, no details are reported so far concerning the exfoliation mechanism. This paper deals with fundamental understanding of the process and the driving forces leading to the exfoliation/intercalation of the Na^+ MMT in a polyamide 6 matrix using this water injection extrusion process.

Experimental

Materials

The polyamide 6 (Akulon K122) was supplied by DSM, Geleen (The Netherlands). This PA6 is an extrusion grade polymer with a low viscosity. Two different types of clay have been used. A purified pristine MMT (p-MMT) was purchased from Southern Clay Product under the trade name Cloisite Na^+. The average powder particle size is about 8 μm. To compare the results obtained using this technique with conventional method, Nanofil 784, a long chain carboxylic acid modified MMT (o-MMT) purchased from Süd Chemie, has been used. The average particle size is 3 μm.

Melt Compounding

Co-rotating extruder ZSK25 WLE from Coperion was used to prepare nanocomposites. The screw length was 1000 mm and L/D ratio was 40. Figure 1 shows schematic

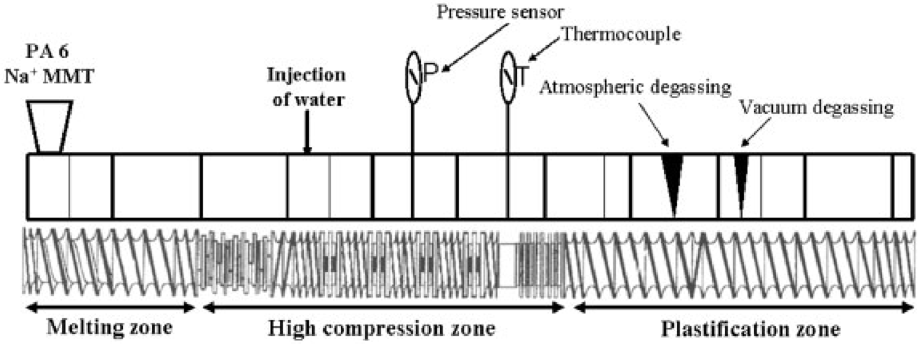

Figure 1.
Extruder and screw configuration used to produce Na^+ MMT/polyamide 6 nanocomposites with the water injection system.

figure depicting the compounding process for preparing the nanocomposites using the water injection system. PA6 pellets and the clay are introduced by the feeder in the melting zone of the extruder at throughputs varying between 10 and 50 kg/h. The screw speed varies from 200 to 1200 rpm. The water is pumped into the extruder from 0 to 20%wt of the total throughput and is compounded with the PA6 and the clay in the high compression zone at barrel temperature of 240 °C. The screw is designed to increase the pressure in this zone up to 125 bars in order to avoid water evaporation at the processing temperature. The water is eventually degassed in the transport zone of the screw and the evapoaration is completed using a vacuum pump. The residence time in the extruder varies from 17 s to 60 s depending on the processing conditions.

Samples prepared with the organo-modified clay were compounded without injection of water and with a conventional mixing screw design.

Wide Angle X-Ray Scattering (WAXS)

WAXS measurements were performed with a θ–2θ goniometer (D5000 from Siëmens, radius of goniometer = 30 cm) using as X-ray source a copper rotating anode (Cu Kα, $\lambda = 1.5418$ Å). Photons are selected by a graphite secondary monochromator, and counted by scintillation counter. To avoid orientation effects, extruded pellets are ground to fine powder prior to analysis.

Transmission Electron Microscopy (TEM)

Specimens of the produced nanocomposites were taken from the extruded pellets, perpendicular to the extruded rods. Prior to cutting the extruded pellets were put in a 4%wt. solution of phosphotungstic acid at 60 °C for 2 hours. Ultrathin sections were cut at ambient temperature with a Leica Reichert FCS microtome and collected on a 300 mesh copper grid. They were examined with a Leo 922 TEM instrument.

Thermo Gravimetric Analyser (TGA)

Thermal stabilities of samples and MMT powder were evaluated on a Mettler Toledo TGA/SDTA851^e instrument from 25 to 550 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Samples weighted about 2–3 mg and were stabilized at 25 °C 10 min before measurement.

Differential Scanning Calorimetry (DSC)

Thermal properties of samples were evaluated on a Mettler Toledo DSC821^e instrument. First heating was conducted from 25 to 250 °C at a rate of 10 °C/min. Pellets were melted at 250 °C for 2 min then cooled down at same rate and the second heating follows the same conditions as the first heating. Special high pressure crucibles ME-511404404 A from Mettler Toledo were used.

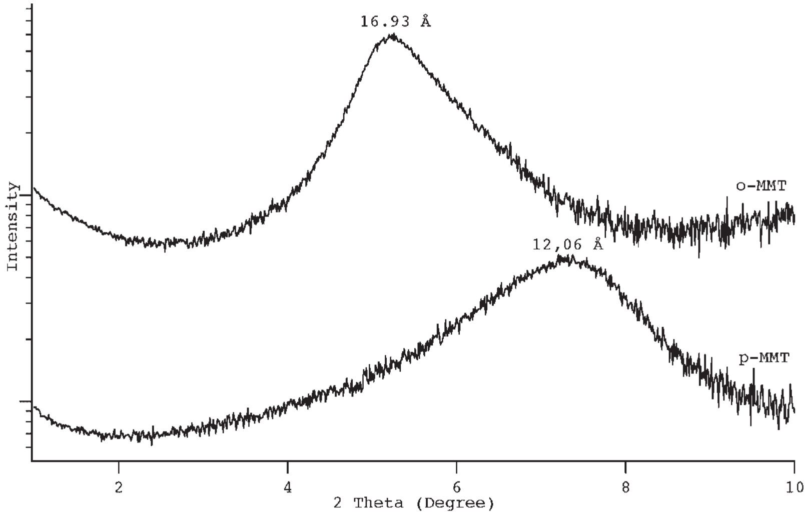

Figure 2.
WAXS patterns of the pristine clay (p-MMT) and the organo-modified clay nanofil 748 (o-MMT).

Result and Discussion

Morphology

Figure 2 shows the WAXS patterns of pristine (p-MMT) and organo-modified clay (o-MMT). They show diffraction peak at $2\theta = 7.33^\circ$ and $2\theta = 5.22^\circ$, respectively, corresponding to basal spacing $d_{001} = 12.06$ Å and $d_{001} = 16.93$ Å. Completely dried p-MMT usually exhibits a diffraction peak around $d_{001} = 9.7$ Å, the difference with the observed d-spacing is due to the absorption of one monolayer of water molecules within the gallery to balance ambient humidity. The o-MMT has an increased basal spacing compared to the p-MMT. The organic surfactant increased the gallery interdistance and reduced the electrostatic attraction between adjacent platelets providing the possibility to the polymer chain to diffuse between the layers during processing. The o-MMT does not exhibit lower angle diffraction peak meaning that the o-MMT is fully intercalated.

Figure 3 shows WAXS patterns of PA6 nanocomposites extruded with p-MMT and o-MMT. The samples extruded without water are compounded with conventional screw and the one extruded with 5% wt. of water is compounded with the water injection system and the special screw design. When organo-clay is melt blended with PA6 in the extruder, a broad and very weak diffraction peak appears around $d_{001} = 19.38$ Å. The presence of this peak represents the small part of o-MMT that does not completely exfoliate during the processing. The d-spacing being higher than the o-MMT itself indicates that the non exfoliated part of the o-MMT is at least intercalated. This means that, due to the high initial d-spacing of the o-MMT and the weakness of the electrostatic interaction between the platelets, PA6 chains can diffuse in the gallery. When the pristine clay is blended to PA6 without water, a large peak can been observed around $2\theta = 5.59^\circ$, meaning a d-spacing of 15.08 Å. This means when no water is added during processing, polyamide chains are able to diffuse between the silicate layers because of the polar interaction between the PA6 chain and the silicate surface. The very large diffraction peak around this value can be attributed to a very wide distribution of the intergallery spacing is the nanocomposite. When water is injected during the extrusion, the WAXS pattern of this nanocomposite is very similar to the pattern of the nanocomposites prepared with the

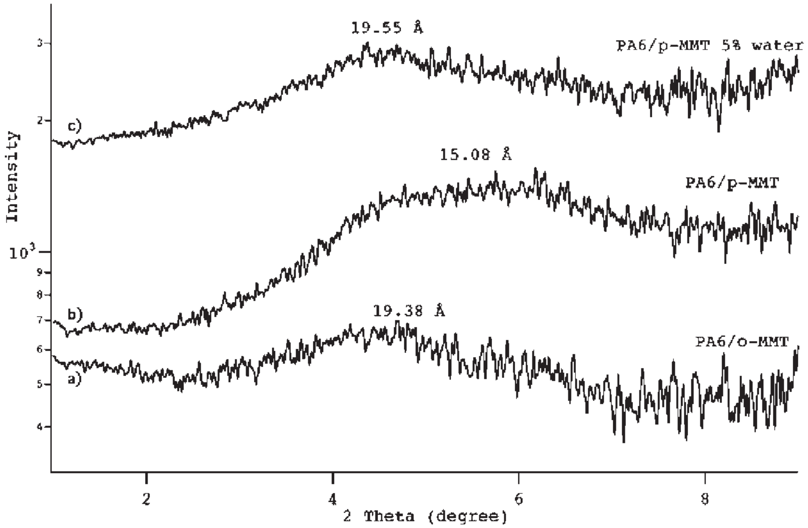

Figure 3.
WAXS patterns of polyamide 6 nanocomposites prepared by extrusion and with a) organo-modified clay (nanofil 748); b) pristine clay; c) pristine clay with 5%wt. water injected during processing.

organo-modified clay. The basal spacing is 19.55 Å. The addition of water displaces the diffraction peak from $2\theta = 5.59^\circ$ to $2\theta = 4.52^\circ$ and reduces it's intensity. This implies that a higher extend of exfoliation can be reached when water is added during extrusion.

WAXS is an useful tool to study the d-spacing in nanocomposites but it does not constitute a stand alone technique to study their morphology. Literature reports that the nanoscale dispersion of the clay in the polymer is best revealed by TEM, especially when mixed morphologies are present.

Figure 4 presents TEM micrograph of the polyamide 6/organo-clay nanocomposite prepared by extrusion. At low magnification (Fig. 4a), the MMT is finely dispersed in the matrix and no tactoid could be observed. At higher magnification (Fig. 4b), single platelets and very small stacks of two or three intercalated platelets of the o-MMT are uniformly dispersed in the PA6 matrix indicating that the clay is very well exfoliated. On the contrary, the nanocomposites made with the pristine clay without water shows large p-MMT intercalated structure (Fig. 5). Figure 5b shows the typical size of these intercalated structures, they range from few to hundred nanometers. It can be observed also that these structures are not tactoids because they are intercalated. When water is injected with the appropriate screw design, the size and the number of the intercalated structures are reduced (Fig. 6). The p-MMT with the aid of water exhibits a rather fine dispersion of the platelets (Fig. 6b) and most of the intercalated structures are divided in layers of silicate dispersed in the matrix. When Figure 5b and 6a are compared, it seems obvious that the injection of water during processing has a great impact on the level of exfoliation that can be achieved. Even if some small intercalated structures are still observable (Fig. 6a), TEM pictures confirm that nanocomposites made from pristine clay and using the injection of water exhibit similar morphology as compared to conventional nanocomposites made with organo-modified MMT.

Description of the Model

Although, it is possible to produce exfoliated polyamide 6 nanocomposites using pristine clay and water injection system

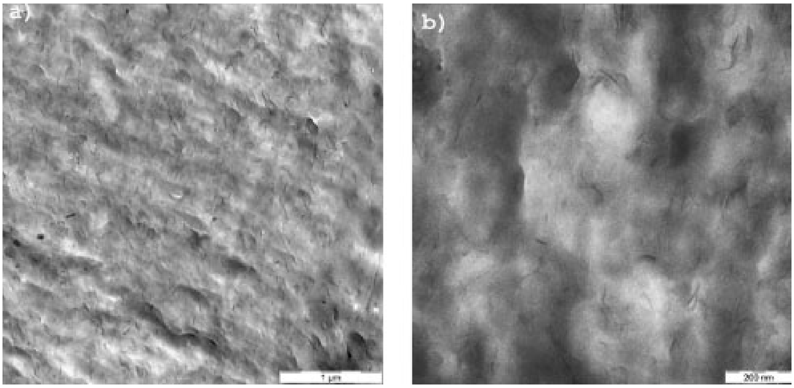

Figure 4.
TEM micrograph of PA6/o-MMT nanocomposites prepared by extrusion at 200 rpm and 10 kg/h: a) 5000 ×; b) 16000 ×.

during extrusion, no convincing model describing the mechanism of formation are reported. The model described by Hasegawa et al.[21] is not suitable for this technique because clay is pre-exfoliated in the water slurry before being blended with the molten polyamide. In this section, a model describing a route to exfoliation / intercalation of the p-MMT in a polyamide 6 by extrusion and a water injection system is described. A schematic description of the model is shown in Figure 7.

During processing, water is injected in the molten polymer at high pressure and high temperature. Water plays two roles.

On one hand, the addition of water modifies the fluidity and the polarity of the polyamide. Indeed, at the processing conditions of temperature and pressure water is completely miscible with the polyamide. It forms a one phase system of high polarity and lower viscosity. Figure 8 is a high pressure thermogram of neat PA6 and PA6 with the addition of 20% of water at 80 bars. Neat PA6 exhibits a melting peak at 220 °C and while upon water addition, the melting peak shifts down to 157 °C. This large cryoscopic effect witnesses a water polyamide miscibility as also observed by Wevers et al[25]. SEC measurements were

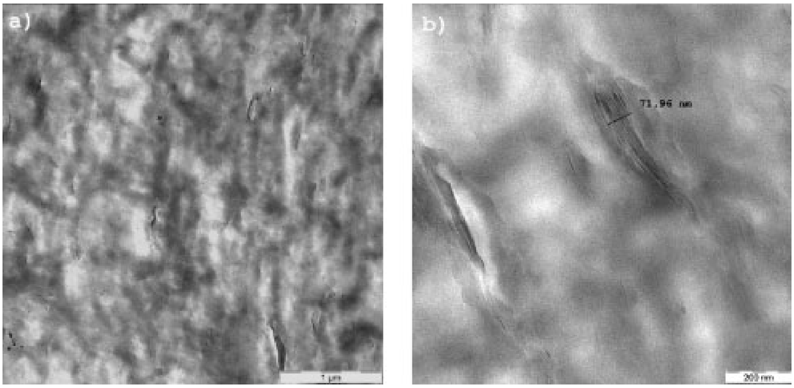

Figure 5.
TEM micrograph of PA6/p-MMT nanocomposites prepared by extrusion at 200 rpm and 10 kg/h without the injection of water: a) 5000 ×; b) 16000 ×.

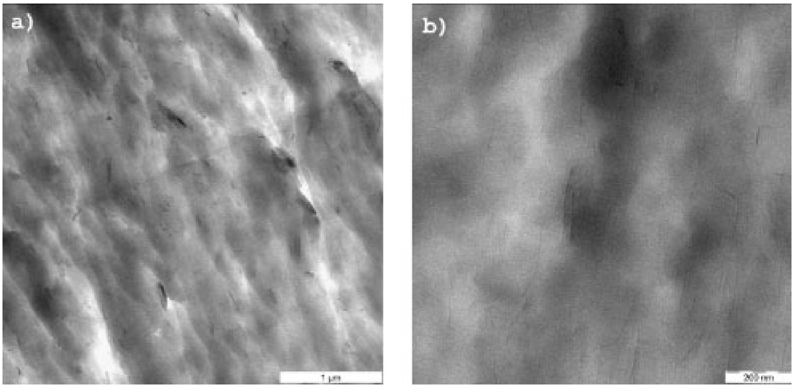

Figure 6.
TEM micrograph of PA6/p-MMT nanocomposites prepared by extrusion at 200 rpm and 10 kg/h without 5%wt. water injected during processing: a) 5000 ×; b) 16000 ×.

also undertaken showing surprisingly that no significant molecular mass decrease was observed.

On the other hand, water diffuses between the silicate layers and is adsorbed on the surface. The intergallery distances increases because water swells the p-MMT. When montmorillonite is in contact with water or water vapour, the water molecules diffuse between the platelets and increase the interlayer distance. The hydration of the exchangeable cations is the first step of the interlayer adsorption of the water. X-ray studies show that water organizes itself in plane molecular layer on the silicate surface. Grim[26] already showed under increasing water relative pressure the existence of one to four successive water layers in the interlayer. Those layers correspond to d-spacing of 12.6, 15.6, 18.6 and 21.4 Å.

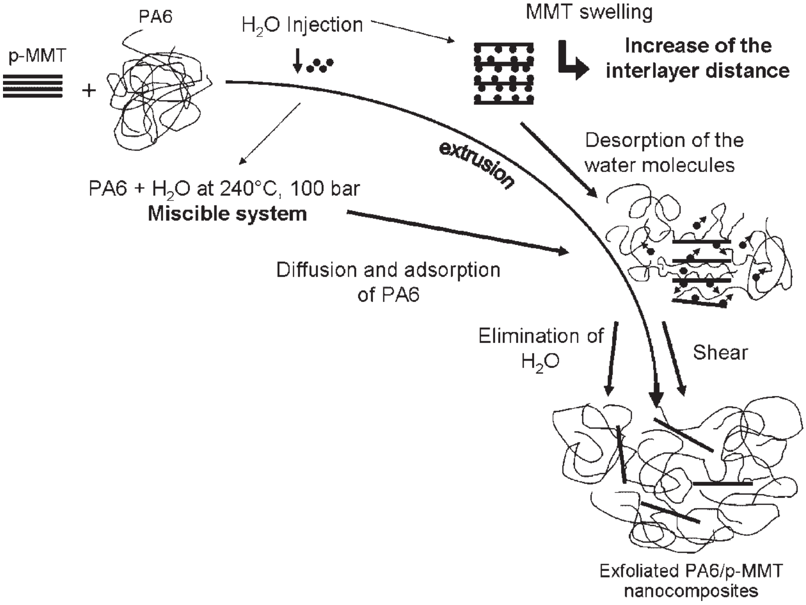

Figure 7.
Schematic description of the dispersion of the p-MMT in a polyamide 6 matrix during extrusion with the water injection system.

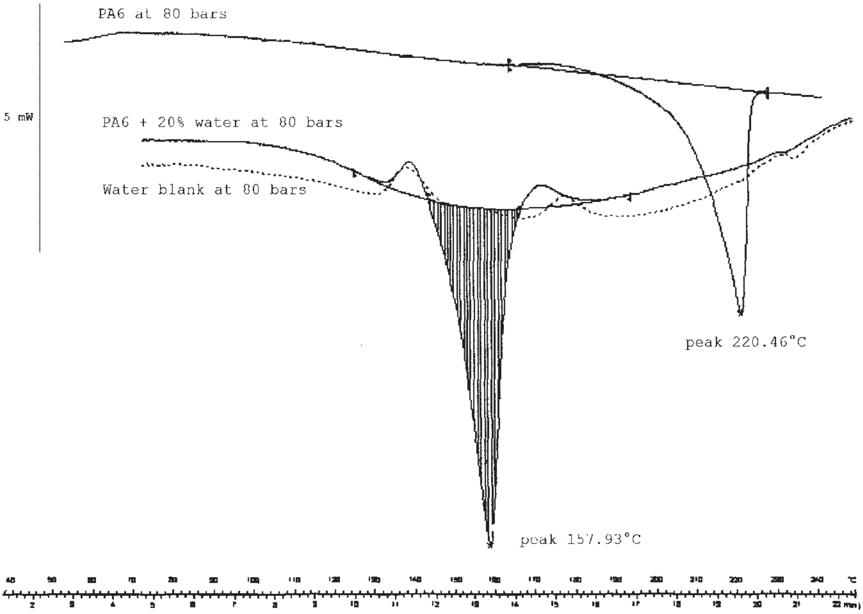

Figure 8.

High pressure DSC thermogram of polyamide 6 and polyamide 6 with water. The dot line represents the thermogram of water at 80 bars.

When more than one molecular layer of water is adsorbed, the d-spacing of the hydrated MMT are in the same range of distance than the d-spacing of organo-modified clay.

The combination of these two effects creates the ideals conditions for the diffusion and adsorption of PA6 chains onto p-MMT surface. Indeed, PA6 chains can diffuse between the platelets because d-spacing becomes large enough. This is enhanced by the miscibility of the polyamide with the injected water.

The polyamide chains increase their ability to be adsorbed onto the p-MMT surface. Thus, while diffusing between the silicate layers, polyamide chains are adsorbed on the surface and they desorbed the water molecule previously adsorbed. The water excess is removed through the atmospheric and vacuum degassing sections.

It is well known that the γ crystalline structure of polyamide 6 is significantly enhanced by the addition of organo-modified clay[6,11,27–31]. It is also the case for the PA6/p-MMT nanocomposites made with the water injection system (Figure 9). The γ crystalline peak around 21,5° in WAXS pattern clearly indicates that the γ phase is promoted in the nanocomposites. This means that the polyamide chains are in intimate contact with the MMT surface. This is a first indication of the adsorption of the polyamide chain on the silicate surface. A more detailed article dealing with the γ nucleation of PA6/p-MMT nanocomposites will be published in a near future.

A second indication was looked for by solvent extraction. For this purpose, hexafluoro isopropanol (HFIP) wich is a well know solvent for polyamide 6 was used. After washing extruded PA6/p-MMT nanocomposites in this solvent, p-MMT was separated by centrifugation at 40000 rpm during 60 min at ambient temperature. This operation was repeated three times in order to remove all the polyamide from the clay. Figure 10 represent the TGA curves of this extracted p-MMT and of a neat pristine MMT. A large peak around 380 °C in the derivative TGA curve of extracted p-MMT clearly shows that PA6 layers remains adsorbed on the silicate surface, even after extraction. The total mass loss for this

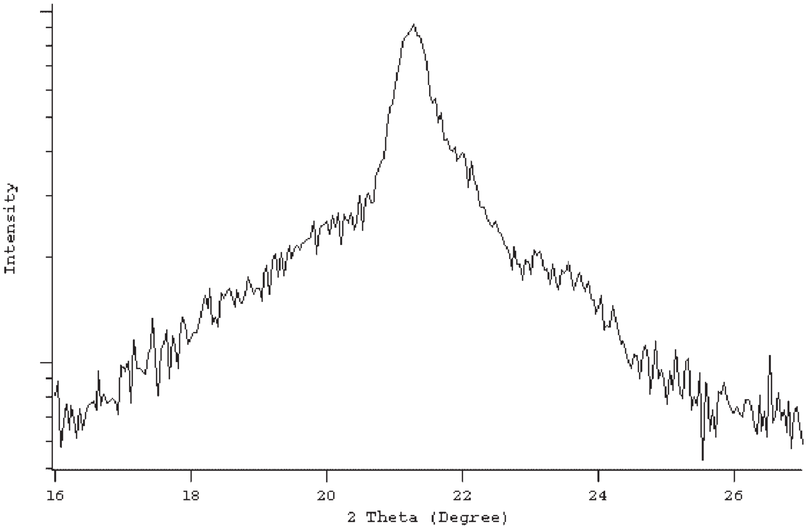

Figure 9.
WAXS pattern of the PA6/p-MMT prepared by extrusion with the water injection system.

sample is 15%wt. The peak below 100 °C for the neat p-MMT represents the mass loss of the naturally adsorbed water. In the case of the extracted p-MMT, this peak is also present but at a much lower extent, due to the surface coverage by PA6.

Up to now it has been demonstrated that the PA6 chains are adsorbed on the PA6 surface, even after extraction, but to demonstrate that polyamide chains are adsorbed on the clays surface between the platelets and does not cover stacks of non-intercalated platelets, WAXS analysis has been performed to evaluate the d-spacing of the extracted p-MMT (Figure 11). A very broad peak centered

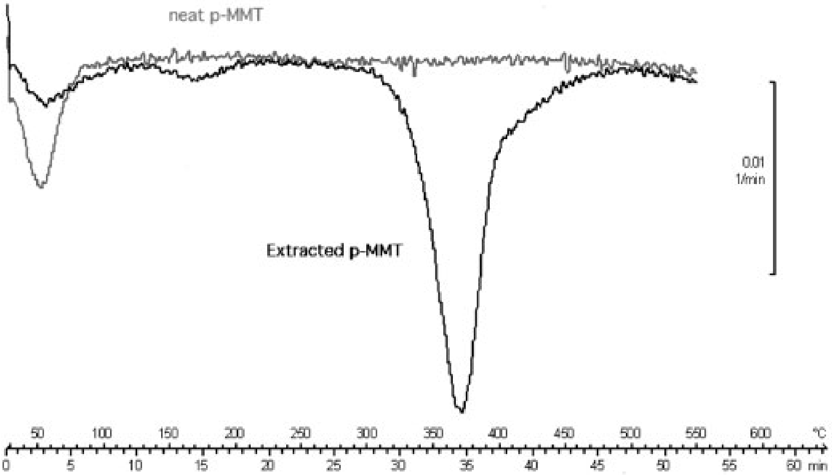

Figure 10.
TGA pattern of the extracted p-MMT from PA6/p-MMT nanocomposites (in black) and from neat pristine MMT (in grey). The coordinate correspond to the percentage mass loss per 1 °C increase in temperature.

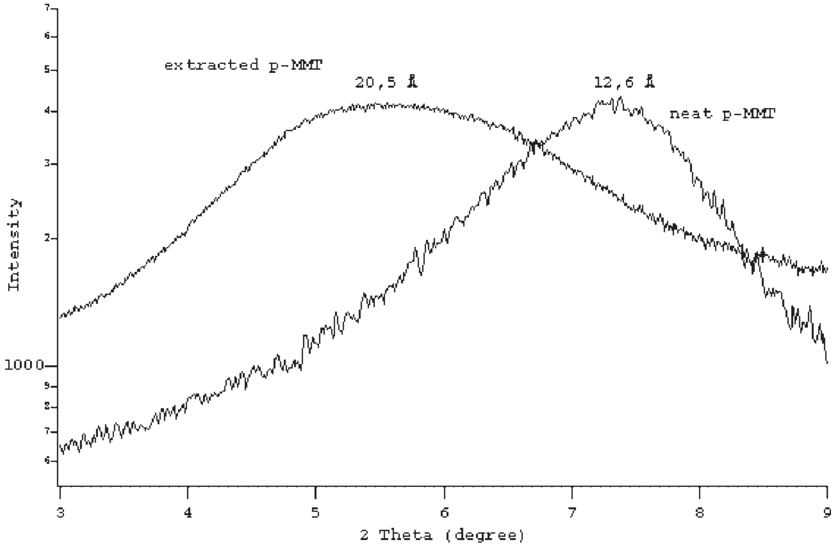

Figure 11.
WAXS pattern of the extracted p-MMT from a PA6/p-MMT nanocomposite and the neat p-MMT.

around 5.5° corresponding to a d-spacing of 20.5Å can be observed. This d-spacing being higher that the one of neat p-MMT (12.6Å), it indicates that the adsorption of the polyamides chains on the clays surface occurs between the clay platelets.

p-MMT platelets are thus coated with polyamide chains and this increase the interlayer spacing, decreases the electrostatic attraction of the platelets and improves the compatibility of the clay with the matrix. As a matter of fact, this is an in-situ organo-modification of the p-MMT. The problem of the dispersion and exfoliation of this p-MMT coated with polyamide chains is thus comparable to the dispersion of organo-modified clay in a PA6 matrix as already been discussed by Cho and Paul[18]: to achieve the dispersion and the exfoliation of this in-situ organo-modified clay, the combination of an appropriate shear and a long enough residence time are required. In this paper, this modelling is described step by step, but in real time conditions, within the extruder, everything happens simultaneously.

A paper dealing with the influence of the processing conditions (rpm, throughput, amount of water injected…) on the morphology of the ternary PA6/water/p-MMT system and the mechanical properties of the resulting nanocomposite will be submitted in a near future.

One can say that these nanocomposites exhibits mechanical properties similar to nanocomposites prepared with o-MMT.

Conclusion

Polyamide 6/pristine montmorillonite nanocomposites were prepared by extrusion with a water injection system. Nanocomposites exhibits exfoliated structure similar to nanocomposites prepared with organo-modified clay.

A model describing the mechanism of formation of these nanocomposites has also been presented. The injection of water enhanced the polarity and the fluidty of the polyamide chains and increased the interlayer spacing of the p-MMT. The polyamide chains are able to diffuse between the platelets and are adsorbed on the silicate surface. This coating of the clay contributes to enhance the clay compatibility with the matrix, to reduce the electrostatic interaction between the platelets and as a matter of fact constitutes an in situ organo-modification of the p-MMT. The problem of the dispersion and exfoliation of this p-MMT coated with polyamide chains is thus now comparable to the dispersion of organo-modified clay in a PA6 matrix.

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[1] E.P. Giannelis, *Adv. Mater.* **1996**, *8*, 29.
[2] E.P. Giannelis, *Appl. Organomet Chem* **1998**, *12*, 675.
[3] P.C. LeBaron, Z. Wang, T.J. Pinnavaia, *Appl. Clay Sci.* **1999**, *15*, 11.
[4] T.J. Pinnavaia, G.W. Beal, ''Polymer-Clay Nanocomposites'', Wiley, New York, 2000.
[5] L.A. Utraki, ''Clay-Containing Polymeric Nanocomposites'', Rapra Technology, Shawbury, 2004.
[6] Y. Kojima, A. Usuki, M. Kawasumi, Y. Fukushima, A. Okada, T. Kurauchi, O. Kamigaito, *J. Mater. Res.* **1993**, *8*, 1185.
[7] Y. Kojima, A. Usuki, M. Kawasumi, Y. Fukushima, A. Okada, T. Kurauchi, O. Kamigaito, *J. Appl. Polym. Sci.* **1993**, *49*, 1259.
[8] M. Alexandre, P. Dubois, *Mater. Sci. Eng. Rep. A* **2000**, *28*, 1.
[9] S. Sinha Ray, M. Okamoto, *Prog. Polym. Sci.* **2003**, *28*, 1539.
[10] M.A. van Es, ''Polymer Clay Nanocomposites : The importance of particle dimensions'', Ph. D. Dissertation, T.U. Delft, The Netherlands, 2001.
[11] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi, O. Kamigaito, K. Kaji, *J. Polym. Sci. Part B: Polym. Phys.* **1994**, *32*, 625.
[12] K. Varlot, E. Reynaud, M.H. Kloppfer, G. Vigier, J. Varlet, *J. Polym. Sci. Part B : Polym. Phys.* **2001**, *39*, 1360.
[13] T. Fornes, P. Yoon, D. Hunter, H. Keskkula, D. Paul, *Polymer* **2002**, *43*, 5915.
[14] A. Okada, M. Kawasumi, T. Karauchi, O. Kamigaito, *Polym. Prep.* **1987**, *28*, 447.
[15] A. Usuki, M. Kawazumi, Y. Kojima, Y. Fukushima, *J. Mater. Res.* **1993**, *8*, 1174.
[17] L. Liu, Z. Qi, X. Zhu, *J. Appl. Polym. Sci.* **1999**, *71*, 1133.
[18] J. Cho, D. Paul, *Polymer* **2001**, *42*, 1083.
[19] H. Dennis, D. Hunter, D. Chang, S. Kim, J. White, J. Cho, D. Paul, *Polymer* **2001**, *42*, 9513.
[20] T. Fornes, D. Hunter, D. Paul, *Macromolecules* **2004**, *37*, 1793.
[21] N. Hasegawa, H. Okamoto, M. Kato, A. Usuki, N. Sato, *Polymer* **2003**, *44*, 2933.
[22] WO99/29 767 (1999), DSM, invs: R. Korbee and A. Van Geneen.
[23] Z.Z. Yu, G.H. Hu, J. Varlet, A. Dasari, Y.W. Mai, *J. Polym. Sci. Part B: Polym. Phys.* **2005**, *43*, 1100.
[24] Melt Made Polymer Nanocomposites, G5RD-2000-00348.
[25] M. Wevers, V. Mathot, T. Pijpers, G. Groenincks, 8th European Symposium on Polymer Blends and Eurofillers 2005, May 9–12, 2005, Bruges, Belgium.
[26] R. E. Grim, ''Clay Mineralogy'', 2nd ed., McGraw-Hill, New York, 1968.
[27] L. Liu, Q. Z.N., X. Zhu, *J. Appl. Polym. Sci.* **1999**, *71*, 1133.
[28] D. VanderHart, A. Asano, J. Gilman, *Chem. Mater.* **2001**, *13*, 3781.
[29] D. VanderHart, A. Asano, J. Gilman, *Chem. Mater.* **2001**, *13*, 3796.
[30] D. Lincoln, R. Vaia, Z. Wang, B. Hsiao, *Polymer* **2001**, *42*, 1621.
[31] P. Maiti and M. Okamoto, *Macromol. Mater. Engng.* **2003**, *288*, 440.