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## Influence of compatibilizer type, polypropylene molecular weight and blending sequence on montmorillonite exfoliation in nanocomposites

### RAPID COMMUNICATION

**Summary** — Montmorillonite exfoliation in polymer matrix is a crucial factor for obtaining a material with improved barrier properties, reduced flammability, higher elastic modulus and tensile strength. One of the ways to obtain polypropylene based nanocomposite with montmorillonite involves an application of compatibilizers, for example maleic anhydride or acrylic acid grafted polypropylene. The effects of blending sequence, polypropylene molecular weight, and properties of a compatibilizer on exfoliation of montmorillonite were studied.

**Key words:** nanocomposites, polypropylene, montmorillonite, exfoliation, compatibilizers.

Polymer based nanocomposites with montmorillonite (MMT) are recently the subject of intense studies.

The montmorillonite is a multilayered silicate consisting of 1 nm thick layers, with galleries between them occupied by alkali cations. In the pristine state MMT is miscible with hydrophilic polymers. Exchange of those cations with cationic-organic surfactants allow to increase MMT compatibility with other less hydrophilic or even hydrophobic polymers.

Dispersion and exfoliation of MMT in a polymer matrix allows to modify the properties of the material — to enhance the barrier of gases and vapours permeation, to reduce flammability and to improve thermal stability. The presence of exfoliated montmorillonite leads also to an increase of the modulus and tensile strength. Improvement of properties is usually obtained at low nanoclay loading, not exceeding several weight per cents.

Nanocomposites with MMT based on isotactic polypropylene (*i*PP) were also obtained in the past and studied because of the industrial importance of this polymer [1]. Reference [2] reviews the routes leading to MMT nanocomposites based on isotactic polypropylene. The possibility to obtain exfoliated MMT by melt mixing of organo-modified MMT with polypropylene grafted maleic anhydride is also reported [3]. The use of maleic anhydride — modified propylene oligomers as compati-

bilizers for *i*PP/MMT system was also successfully explored [4].

The intercalation of clay multilayers by polymer chains results in broadening of galleries, while MMT exfoliation involves a complete separation of clay layers. Both effects can be studied either by high resolution microscopy like electron transmission microscopy or by X-ray wide angle diffraction due to a respectively small interlayer distances of MMT particles [5].

In the present paper we investigate the efficiency of different compatibilizers, the influence of molecular weight of polypropylene and the blending conditions on exfoliation of organo-modified montmorillonite in polypropylene based nanocomposite systems.

### EXPERIMENTAL

#### Materials

Four neat polypropylenes and three grafted polypropylenes used as compatibilizers, listed in Table 1, were used to prepare the composites. They differ in molecular weight and hence in melt flow rate (*MFR*). Among them the polish product with broader molecular weight distribution was used.

Polypropylene compatibilizers were: acrylic acid grafted polypropylene (6 wt. % of functional groups) and maleic anhydride grafted polypropylene (1 wt. % and 0.5 wt. % of functional groups). Higher concentration of maleic functional groups leads unavoidably in the case of polypropylene to higher *MFR*.

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Table 1. Characteristics of polymeric components used in nanocomposites preparation

Polypropylene code	Trade name	MFR, g/10 min (2.16 kg)	$M_w$	$M_w/M_n$	Functional groups
PPF	Malen P F401, Orlen, Poland	3.0 (230 °C)	$3.1 \cdot 10^5$	—	none
PPH	Novolen 1100H, BASF, Germany	1.8 (230 °C)	$4 \cdot 10^5$	5	none
PPL	Novolen 1100L, BASF, Germany	5 (230 °C)	$3.1 \cdot 10^5$	5	none
PPN	Novolen 1100N, BASF, Germany	11 (230 °C)	$2.5 \cdot 10^5$	5	none
PBA	Polybond 1001, Uniroyal	40 (190 °C)	—	—	acrylic acid, 6 wt. %
PB1	Polybond 3200, Uniroyal	110 (190 °C)	—	—	maleic anhydride, 1 wt. %
PB2	Polybond 3150, Uniroyal	50 (190 °C)	—	—	maleic anhydride, 0.5 wt. %

MMT used was a commercial product of Nanocor, USA, octadecylamine-modified montmorillonite Nanocor I30P, showing periodicity of 2.2 nm.

### Preparation of samples

Composites containing *i*PP, a compatibilizer and MMT were obtained by two-step blending in a Brabender internal mixer during 20 min mixing at 60 rpm. Two ways of sample preparation were used:

— Route A. *i*PP and a compatibilizer were blended prior to addition of MMT, both blending steps were conducted at 170 °C.

— Route B. A compatibilizer was first blended with MMT in weight proportion of 10:3 and later added to *i*PP melt. The first blending step was conducted at 200 °C (B1) or at 170 °C (B2), while the second blending step was carried out always at 200 °C.

Composition of compatibilized systems and blending temperatures are listed in Table 2. For comparison, the

Table 2. Sample codes, compositions and blending temperature during both steps of A and B routes of samples preparations. M denotes montmorillonite

Sample code	Composition, wt. %	Blending route and temperature
PPF/PBA/M3 <sub>B1</sub>	87:10:3	B1: 200/200 °C
PPF/PB1/M3 <sub>B1</sub>	87:10:3	B1: 200/200 °C
PPF/PB1/M6 <sub>B1</sub>	74:20:6	B1: 200/200 °C
PPF/PB1/M6 <sub>A</sub>	74:20:6	A: 170/170 °C
PPF/PB1/M10 <sub>B1</sub>	57:33:10	B1: 200/200 °C
PPF/PB2/M3 <sub>B1</sub>	87:10:3	B1: 200/200 °C
PPF/PB2/M6 <sub>B1</sub>	74:20:6	B1: 200/200 °C
PPF/PB2/M10 <sub>B1</sub>	57:33:10	B1: 200/200 °C
PPF/M3	97:3	200 °C
PPF/M6	94:6	200 °C
PPF/M10	90:10	200 °C
PPN/PB1/M6 <sub>B1</sub>	74:20:6	B1: 200/200 °C
PPN/PB1/M6 <sub>B2</sub>	74:20:6	B2: 170/200 °C
PPN/PB1/M6 <sub>A</sub>	74:20:6	A: 170/170 °C
PPH/PB1/M6 <sub>B1</sub>	74:20:6	B1: 200/200 °C
PPH/PB1/M6 <sub>B2</sub>	74:20:6	B2: 170/200 °C
PPH/PB1/M6 <sub>A</sub>	74:20:6	A: 170/170 °C
PPL/PB1/M6 <sub>B1</sub>	74:20:6	B1: 200/200 °C
PPL/PB1/M6 <sub>B2</sub>	74:20:6	B2: 170/200 °C
PPL/PB1/M6 <sub>A</sub>	74:20:6	A: 170/170 °C

composites of *i*PP with MMT but without a compatibilizer were also obtained in one-pot blending procedure: both components were dry-blended and then melt mixed in a Brabender internal mixer at 200 °C.

0.5–0.8 mm thick films were obtained from chunks of blended materials by compression molding at 200 °C for 3 min followed by cooling in water.

### Methods

The composites were characterized by wide angle X-ray diffraction (WAXS) in the transmission mode and by transmission electron microscopy (TEM). WAXS system consisted of a computer controlled wide angle goniometer coupled to a sealed-tube source of  $\text{CuK}\alpha$  radiation, operating at 30 kV and 30 mA. The  $\text{CuK}\alpha$  line was filtered using electronic filtering and the usual thin Ni filter. The slit system that was used for collecting  $2\theta$  scans allowed for the collection of the diffracted beam with a divergence angle of less than 0.05 deg. MMT particles alone were also studied by WAXS for comparison.

Ultrathin sections of the films were cryo-ultramicrotomed and studied by means of transmission electron microscope (TEM) Tesla.

## RESULTS AND DISCUSSION

TEM examination (Fig. 1) showed a large amount of exfoliated montmorillonite in all compatibilized systems, although nanoclay particles with preserved multi-layered structure were also observed. Closer examination of the micrographs shows that the exfoliation process starts from the edges of montmorillonite particles and proceeds towards their centers. Such feature of exfoliation strongly suggests the importance of duration and intensity of mixing and also of interaction intensity with reactive compatibilizers.

X-ray diffractograms of MMT and selected nanocomposites are demonstrated in Fig. 2 and 3. X-ray diffractogram of MMT shows a characteristic peak at  $2\theta = 3.9$  deg, which corresponds to spacing of 2.2 nm. The peaks remained well visible for PPF/MMT compositions without compatibilizer. In X-ray diffractograms of compatibilized systems usually the decrease in the peak height and its shift towards smaller values of  $2\theta$  angle were

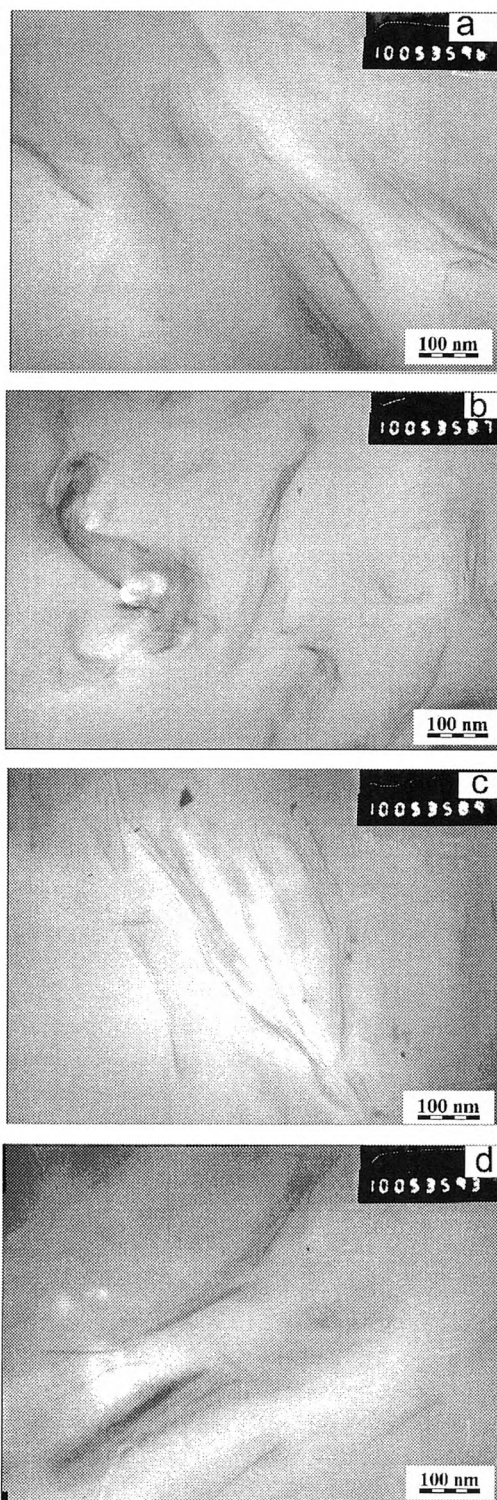


Fig. 1. TEM micrographs of compatibilized polypropylene based nanocomposites with MMT: a) PPH/PB1/M6<sub>B1</sub>, b) PPH/PB1/M6<sub>A</sub>, c) PPN/PB1/M6<sub>A</sub>, d) PPL/PB1/M6<sub>A</sub>. Codes of samples as in Table 2

observed due to exfoliation and broadening of the inter-platelet distance resulting from intercalation by compatibilizer and polypropylene chains. As it is seen from Fig. 2 and 3 these effects depend, however, on the nanocomposite preparation route and on composition.

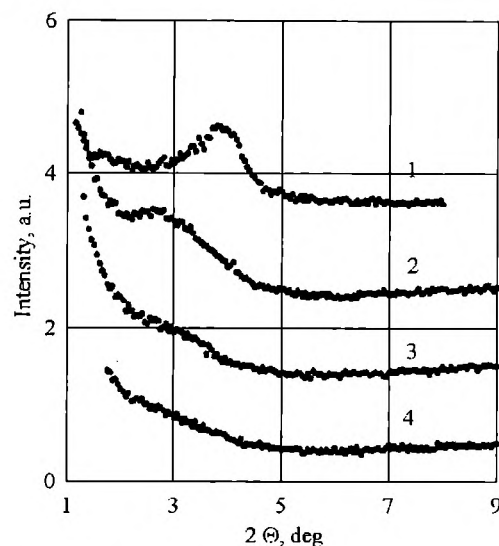


Fig. 2. X-ray diffractograms of MMT and compatibilized polypropylene based nanocomposites with 3 wt. % of MMT (preparation — route B1): 1 — MMT, 2 — PPF/PBA/M3<sub>B1</sub>, 3 — PPF/PB1/M3<sub>B1</sub>, 4 — PPF/PB2/M3<sub>B1</sub>. Codes of samples as in Table 2

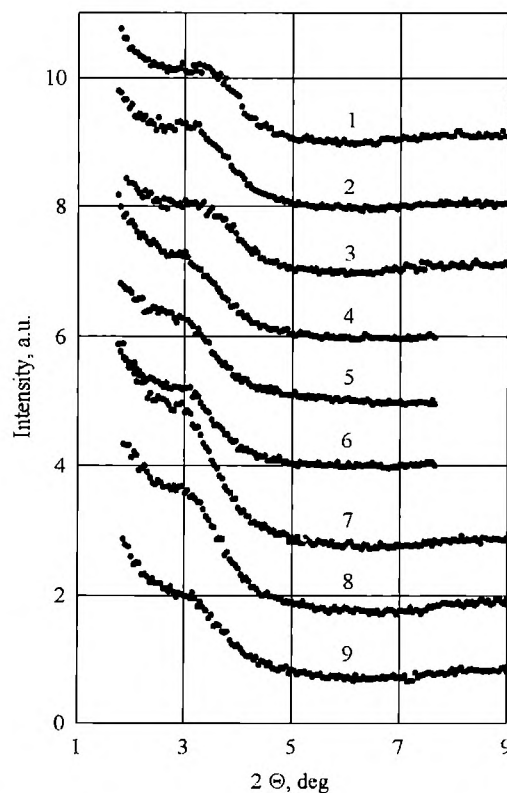


Fig. 3. X-ray diffractograms of compatibilized polypropylene based nanocomposites with 6 wt. % of MMT prepared using routes A and B and PB1 compatibilizer: 1 — PPN/PB1/M6<sub>A</sub>, 2 — PPL/PB1/M6<sub>A</sub>, 3 — PPH/PB1/M6<sub>A</sub>, 4 — PPN/PB1/M6<sub>B2</sub>, 5 — PPL/PB1/M6<sub>B2</sub>, 6 — PPH/PB1/M6<sub>B2</sub>, 7 — PPN/PB1/M6<sub>B1</sub>, 8 — PPL/PB1/M6<sub>B1</sub>, 9 — PPH/PB1/M6<sub>B1</sub>. Codes of samples as in Table 2

PB2 was found to be the most effective compatibilizer leading to most efficient exfoliation while PBA was the worst among the compatibilizers used in this work, as it is illustrated in Fig. 2.

As it is seen in Fig. 3 the isotactic polypropylene molecular weight has no significant influence on the exfoliation and intercalation of MMT when the composites were obtained by blending first polypropylene with a compatibilizer at 170 °C and then with MMT (route A). Apparently the dilution of polypropylenes with low viscous compatibilizers significantly reduces the differences between the polypropylenes by lowering their MFR.

Route B2, by preparation of a masterbatch of a compatibilizer and MMT at 170 °C and then blending with polypropylene at 200 °C appears to be more effective than the route A in MMT exfoliation, as it is seen from Fig. 3. Also here the molecular weight of polypropylene plays little role in exfoliation and intercalation of MMT. This observation indicates that the most intensive exfoliation and intercalation takes place during preparation of a masterbatch of MMT with compatibilizer. Subsequent blending of the masterbatch with polypropylenes is not much effective in further exfoliation and intercalation of MMT. This is the reason of low influence of the molecular weight of polypropylenes on the exfoliation and intercalation of MMT.

The increase in the temperature of the masterbatch preparation to 200 °C led to similarly efficient exfoliation in the case of higher molecular weight of polypropylene *i.e.* when the masterbatch was added to PPH type of polypropylene (route B). However, in the case of PPN and PPL polypropylenes, the exfoliation was less efficient than in the case when the masterbatch was prepared at 170 °C. It appears that high molecular weight of polypropylene enhances to some extent the penetration of polymeric component into galleries and the separation of MMT platelets during the melt blending of the masterbatch and polypropylene.

The results obtained for PPL and PPF are essentially similar because they show similar MFR.

Polypropylene molecular weight affected also the position of peak related to MMT interplatelet distance, which is best visible for nanocomposites prepared according to the route B1, 200 °C/200 °C. The peak shift towards smaller  $2\theta$  value increases with the decrease in polypropylene molecular weight indicating the broadening of the distance between clay platelets due to more efficient intercalation by polypropylene chains. Usually,

the increase in MMT content resulted in less efficient exfoliation — larger fraction of non-exfoliated clay particles remained.

## CONCLUSIONS

The results obtained indicate that the sequence of blending plays a crucial role in montmorillonite exfoliation in these three component systems — polypropylene, montmorillonite and a compatibilizer. The best results were obtained by preparation of compatibilizer/MMT masterbatch followed by melt blending with a neat polypropylene. Acrylic acid grafted polypropylene was found significantly less effective than maleic anhydride grafted polypropylenes. However, better results were obtained when using a compatibilizer with smaller content of maleic anhydride grafted but showing higher viscosity. This observation points out that not only the amount of reactive groups is important, but also the viscosity during mixing, which influences the transmission of shear. For higher viscosity the shear is transmitted to particles more efficiently. The influence of the temperature of the masterbatch preparation also indicates the positive effect of higher viscosity during blending process on MMT exfoliation. If the masterbatch is prepared at higher temperature, *i.e.* at lower viscosity of a compatibilizer, then the molecular weight of polypropylene used as a matrix should be as high as possible to enhance MMT exfoliation.

## ACKNOWLEDGMENT

This work was partially supported by the State Committee for Scientific Research (Poland), Technical University of Lodz and Centre of Molecular and Macromolecular Studies, PAS, under grant PBZ 13/T08/99.

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Received 18 VII 2003.