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Polymer nanocomposites with layered silicates

Summary — The topics of current research in the field of polymer nanocomposites with layered silicates are addressed. The factors influencing the efficiency of the clay exfoliation in a polymer during melt processing are summarized, namely type of a machine used, mixing conditions and molecular characteristics of polymers utilized, including that of polymeric compatibilizers. New methods leading to the clay exfoliation in a polymer matrix are described. Application of exfoliation promoter allows to eliminate the necessity to compatibilize organo-modified clay with hydrophobic polymer matrix. Shear induced crystallization of polyolefin based nanocomposites is also addressed; even weak shearing induces alignment of clay platelets, results in polymer chains orientation and enhances the nucleation of crystallization.

Key words: nanocomposites, montmorillonite, exfoliation, crystalization, polyolefines.

NANOKOMPOZYTY POLIMEROWE Z WARSTWOWYMI KRZEMIANAMI

Streszczenie — Omówiono zagadnienia będące przedmiotem aktualnych badań w dziedzinie nanokompozytów polimerowych z warstwowymi krzemianami. Przedstawiono czynniki wpływające na intensywność rozwarstwiania glinki w polimerze podczas przetwarzania w stanie stopionym, mianowicie rodzaj stosowanego urządzenia, warunki mieszania oraz charakterystykę molekularną stosowanych polimerów, w tym polimerowych kompatybilizatorów. Ponadto, opisano nowe metody rozwarstwiania glinki w polimerowej matrycy. Zastosowanie środka wspomagającego rozwarstwienie pozwala wyeliminować konieczność kompatybilizacji modyfikowanej organicznie glinki z hydrofobową matrycą polimerową. Omówiono również indukowaną odkształceniem ścinającym krystalizację nanokompozytów z matrycą poliolefinową. W takich układach nawet niewielkie i powolne odkształcanie prowadzi do orientacji płytek glinki oraz powoduje orientację łańcuchów polimeru i nasila zarodkowanie krystalizacji.

Słowa kluczowe: nanokompozyty, montmorylonit, eksfoliacja, krystalizacja, poliolefiny.

Polymer-layered silicate nanocomposites are relatively new materials, offering reinforcement, improved barrier properties, reduced flammability [1], increased dimensional stability, elevated heat deflection temperature (HDT) and also increased melt viscosity. The important advantage is that the enhancement of material performance is achieved at low content of nano-clay, usually being at the level of few percents. That is because the specific surface of exfoliated montmorillonite (MMT) is about 800 m^2/g [2]. However, it is clear, that in order to improve the properties clay particles have to undergo efficient exfoliation in a polymer matrix [3, 4].

MMT is usually organo-modified (o-MMT) to improve compatibility with a polymer [2, 5]. In the case of polyolefins, maleic anhydride grafted polypropylene or polyethylene, are used to improve further the compatibility between the matrix and the organo-modified clay [6, 7]. Compatibilizer as a third component of the system is added in the amount exceeding few times of that of clay, and may influence the structure and properties of a nanocomposite.

Current subjects of research include an improvement of known routes to exfoliate clay particles and also a development of new procedures to exfoliate the clay. Dispersed in a crystallizable matrix, clay particles and/or exfoliated platelets influence the crystallization. Recent studies [8] have demonstrated that a shear accelerates strongly the overall crystallization kinetics in polyolefin based nanocomposites by enhancement of nucleation.

In this paper we will address the factors influencing exfoliation level on the clay during melt mixing. Also, a new approach leading to exfoliation of the clay in polymers will be described, that involves application of an exfoliation promoter instead of a compatibilizer. New findings concerning shear induced crystallization of polypropylene will be also discussed.

FACTORS AFFECTING EXFOLIATION OF THE CLAY

Frequently used method of production of nanocomposites is melt-mixing [9]. In ref. [10, 11] it was shown that in the case nanocomposites of isotactic polypropylene (iPP) and o-MMT ("Nanomer I30P", modified with octadecyl amine, produced by Nanocor, USA) compatibilized with maleic anhydride grafted iPP (PP-*g*-MA), a two step procedure consisting of preparation of a compatibilizer/clay masterbatch and then diluting the masterbatch with iPP led to good results. However, higher viscosity of the components resulting from their higher molecular weight allowed to achieve more efficient exfoliation of the clay due to higher shear forces during melt processing. PP-*g*-MA with the content of maleic groups of 0.5 % and MFR=50 g/10 min was more efficient than the one with 1 % of maleic groups and MFR= 110 g/10 min.

Dennis *et al.* [12] have shown that the type of an extruder used for mixing of components is crucial; application of a co-rotating double screw extruder gave better results than a single screw extruder. Further improvement was achieved when a tangential extruder was used. In addition, the exfoliation improved with an increased residence time.

Pluta [13] demonstrated that increasing the time of mixing of polylactide (PLA) with 3 wt. % of o-MMT ["Cloisite 30B" modified with methyl-bis(2-hydroxyethyl) tallowalkyl ammonium cations, produced by Southern Clay Products, USA] enhanced the exfoliation of the clay. XRD studies proved that the peak originated from periodic structure of the clay was still visible after 6 min of mixing. However, it disappeared when the mixing time was increased to 30 min, as it is shown in Fig. 1, although no compatibilizer was applied. Transmission electron microscopy (TEM) confirmed the good exfoliation and dispersion of the clay.

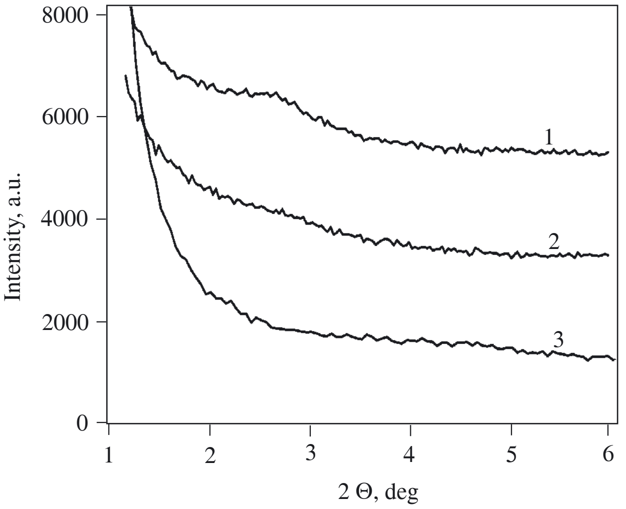

Fig. 1. XRD diffractograms of PLA (3) and PLA/o-MMT nanocomposites after 6 min (1), and 30 min. (2) of mixing, data from ref. [13]. The diffractograms shifted vertically for clarity

Golebiewski and Galeski [14] used a twin-screw corrotating extruder to obtain iPP/o-MMT nanocomposites compatibilized with PP-*g*-MA. The study utilized "Cloisite 15A", modified with dimethyl, dehydrogenated tallow quarternary ammonium chloride, Southern Clay Products, USA. The authors have found that intensity of mixing was a crucial factor. Increasing the mixing intensity by changing the screw configuration allowed to improve the exfoliation, as it was documented by XRD (Fig. 2) and TEM studies.

It is of importance to notice that the peak originating from a periodic structure of the clay was decreasing but not shifting to lower 2 theta angles. Clearly, in this case exfoliation was not achieved *via* intercalation and increase of interlayer distance but according to a mechanism proposed recently by Iwasa *et al.* [15]. According to ref. [15] the exfoliation proceeds by removal of MMT

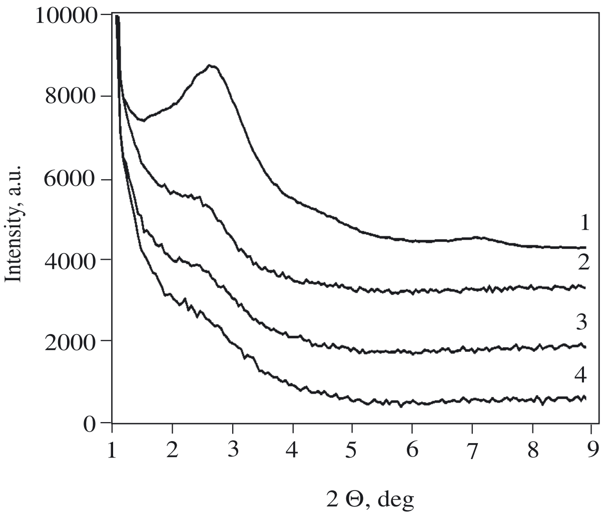

Fig. 2. XRD diffractograms of o-MMT "Closite 15A" (1) and compatibilized iPP nanocomposites with 5 wt. % of o-MMT mixed with different intensity: 2 — premixed components, rotational speed of the screws 250 l/min, temperature profile of a plasticizing system 185, 195, 195, 195 °C, head temperature 195 °C, 3 — the nanocomposite (2) was extruded again in the same conditions, 4 — two-step extrusion, i.e. extrusion of the compatibilizer with o-MMT and then extrusion of the concentrate prepared in this way with iPP; from ref. [14]. Diffractograms shifted verticaly for clarity

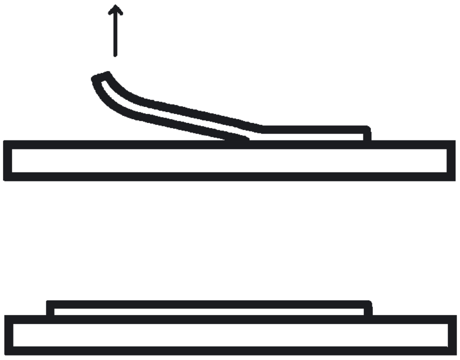

Fig. 3. Illustration of newly described [15] mechanism of the clay exfoliation

platelets sheet by sheet from the edges of platelets. The attachment of the functionalized compatibilizer to the edges of a platelet provides a good leverage for its detachment from the stack as it is shown schematically in Fig. 3.

Fig. 4 showing the structure of iPP/PP-*g*-MA/o-MMT composite can serve as an illustration of this mechanism; clay platelets curved and partially separated from clay stacks are clearly visible. It is worth to note that also in ref. [14] the peak resulting from tactoids of o-MMT was decreasing but not shifting to lower 2 theta angles with increasing mixing time which was suggestive that the Iwasa mechanism was responsible for exfoliation although no compatibilizer was used.

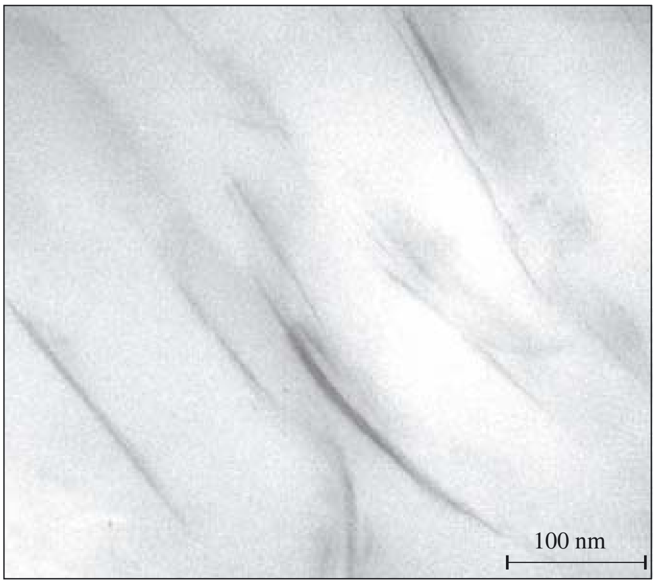

Fig. 4. TEM micrograph of compatibilized nanocomposite of iPP with 6 wt. % of o-MMT "Nanomer I30P"

Pluta [13] demonstrated also that o-MMT may contain a significant fraction of a micron and submicron size inclusions, most probably silica, which do not undergo exfoliation and have poor adhesion to PLA matrix. Undoubtedly, these impurities worsen the mechanical performance of nanocomposites.

NEW ROUTES OF EXFOLIATION OF THE CLAY DURING MELT PROCESSING

It is well established that MMT has to be organo-modified to be exfoliated within a hydrophobic polymeric matrix. A novel route, allowing to avoid organo-modification of the clay was elaborated in Toyota laboratories [16]. Water was injected into a molten iPP being mixed with a nanoclay in a twin-screw extruder. By controlling the pressure of the water vapor the exfoliation of the clay was achieved. It should be underlined that the method does not require the organo-modification of the clay. On the other hand, the authors found that the compatibilization was advantageous for a better dispersion of the clay within iPP matrix. This new type of polypropylene nanocomposite had almost the same properties as a conventionally prepared iPP based nanocomposite with o-MMT.

Morawiec *et al.* [17] employed the two step procedure, in a way similar to that described in [10], to obtain nanocomposites of low density polyethylene (LDPE) with o-MMT ("Nanomer I30P"). Maleic anhydride grafted LDPE (PE-*g*-MA) was utilized in order to compatibilize the components. The XRD studies proved the exfoliation of the clay. TEM micrographs have also shown the exfoliated clay platelets. It is important to note that the exfoliated platelets remained clustered resembling "frog eggs" and were not dispersed uniformly within

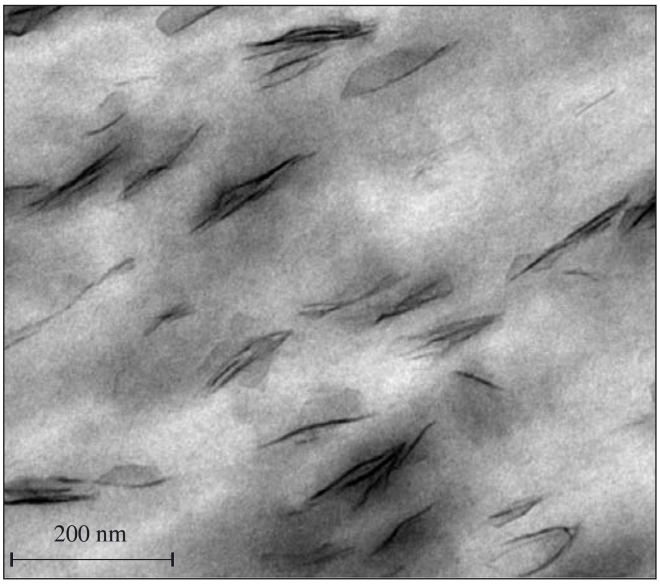

Fig. 5. TEM micrograph of LDPE/o-MMT nanocomposite compatibilized with PE-g-MA

LDPE matrix, as it is illustrated in Fig. 5. Further research [18] led us to the conclusion that in LDPE/o-MMT compositions, compatibilized with PE-*g*-MA, the clay platelets were surrounded most probably by PE-*g*-MA and not in contact with LDPE matrix.

A new way to produce polymer/o-MMT nanocomposites was proposed by Galeski *et al.* [19, 20]. According to the invention o-MMT is mixed with an exfoliation promoter and then added to a polymer. In the case of LDPE and iPP an efficient exfoliation promoter appears to be glicydyl methacrylate (GMA), a liquid with a boiling point at 189 °C. During melt processing GMA evaporates from the compositions leaving the clay platelets exfoliated and dispersed within a polymeric matrix GMA is added in the proportion much lower than that in which usually a compatibilizer is added for the same purpose. The proper weight ratio of exfoliation promoter to clay could be as low as 1:4 or less. An example of the XRD diffractogram of compositions of LDPE with o-MMT ("Nanofil 8", modified with distearyldimethyl ammonium chloride, produced by Süd-Chemie) obtained with the help of GMA is shown in Fig. 6. Comparison with a diffractogram of LDPE mixed with "Nanofil 8" at the same conditions, but without GMA, leads to the conclusions that the (100) peak o-MMT decreases and shifts to lower 2 theta angles when the clay was mixed with GMA. That evidenced the intercalation and exfoliation of the clay.

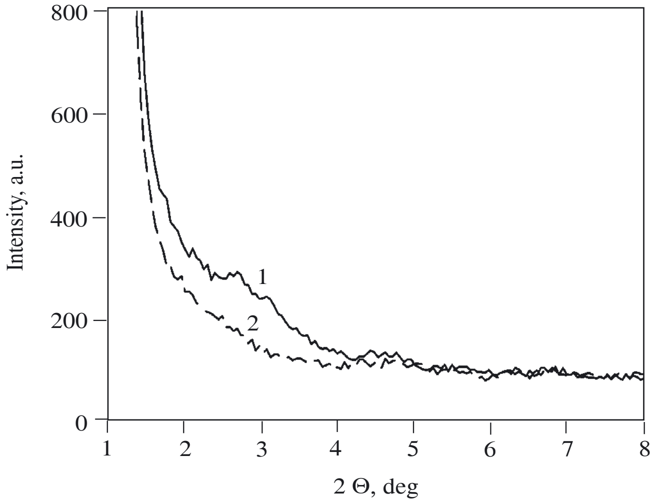

Fig. 6. Comparison of XRD difractograms of LDPE based nanocomposites with 6 wt. % of o-MMT obtained with (2) and without (1) application of GMA from ref. [19]

It is of importance that while a compatibilizer remains within a nanocomposite affecting its crystallization, crystallinity level and mechanical properties [8, 17], an exfoliation promoter mostly evaporates and does not influence the properties of a nanocomposite allowing the clay to come in contact with a polymer. Thus, the new route leading to exfoliation and dispersion of the clay within a polymer matrix will allow for more precise control of the properties of nanocomposites.

SHEAR INDUCED CRYSTALLIZATION OF NANOCOMPOSITES

Nowacki *et al.* [8] and Somwangthanaroy [21] have shown that even a weak shear enhances strongly the overall crystallization kinetics of iPP/o-MMT nanocomposites compatibilized with PP-*g*-MA. In ref. [8] it was clearly demonstrated that the shear enhanced greatly the nucleation. In the nanocomposite containing 3 wt. % of the clay, crystallized at 132 °C under shear at the rate of 0.68 s^{-1} the nucleation density increased roughly 10^3—10^4 times. In the neat iPP and in the blends of iPP with PP-*g*-MA the effect of such a weak shear was negligible.

Further efforts were focused on the effect of shear on the structure of nanocomposites [22]. Shear induced crystallization was carried out in an apparatus described in details in ref. [23], consisting of a polarizing light microscope and a cell containing two heated glass-rails positioned on microscope stage. Sample in the form of film was placed between the glass-rails and the entire sandwich was heated up to 220 °C. The melt annealing at 220 °C for 5 min allowed to relax some possible orientation and the entire sandwich was cooled down to the crystallization temperature of 136 °C. When the isothermal condition was reached a simple shear was applied by a displacement of the lower rail during 10 s at a speed which fixed the shear-rate at either 1 s^{-1} or at 2 s^{-1}. Crystallization occurred after shearing.

Fig. 7 shows light micrographs of nanocomposite containing 3 wt. % of the clay, crystallized isothermally at 136 °C a in static conditions and after shearing at the

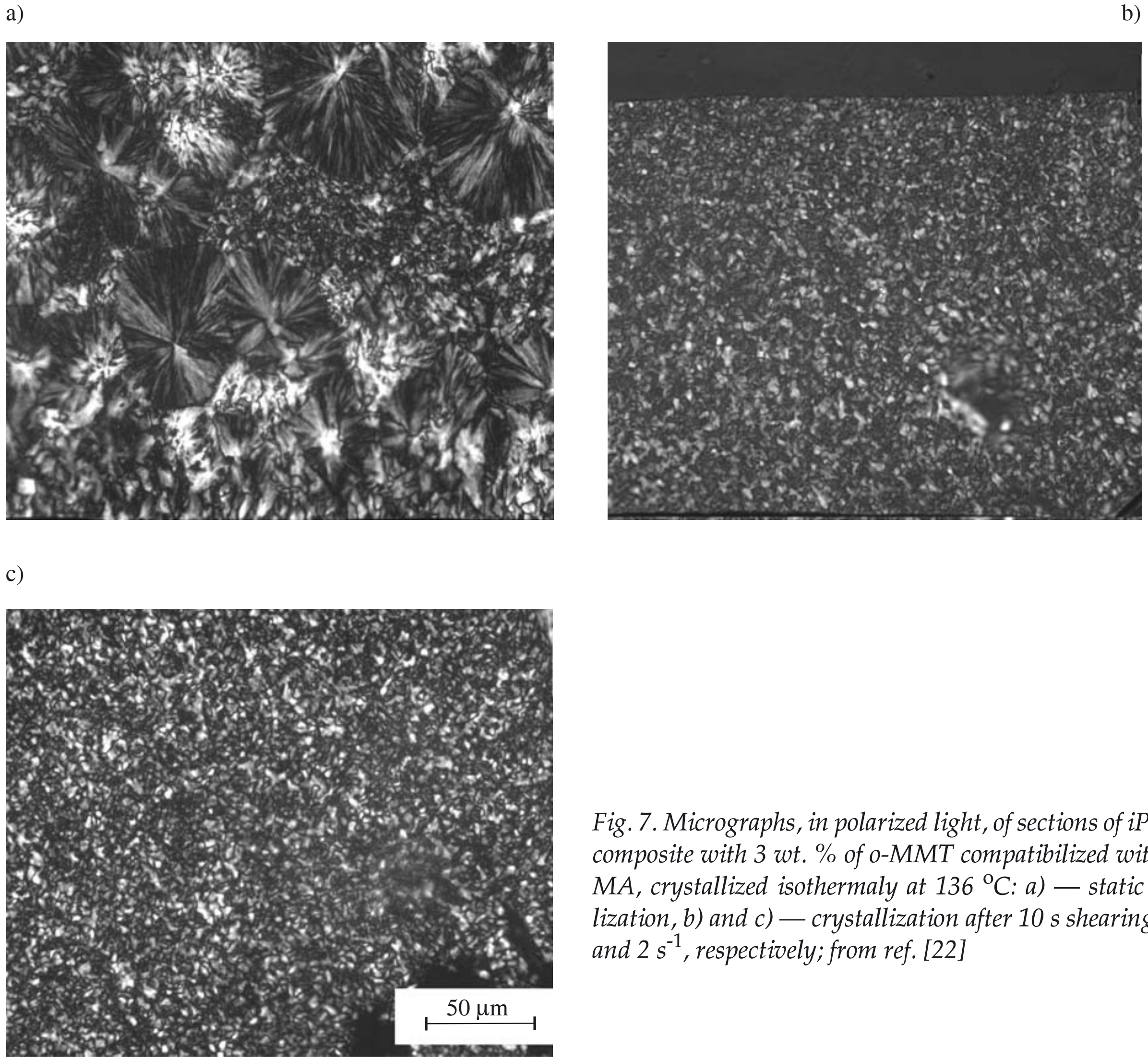

Fig. 7. Micrographs, in polarized light, of sections of iPP nanocomposite with 3 wt. % of o-MMT compatibilized with PP-g-MA, crystallized isothermaly at 136 °C: a) — static crystallization, b) and c) — crystallization after 10 s shearing at 1 s^{-1} *and 2 s*$^{-1}$*, respectively; from ref. [22]*

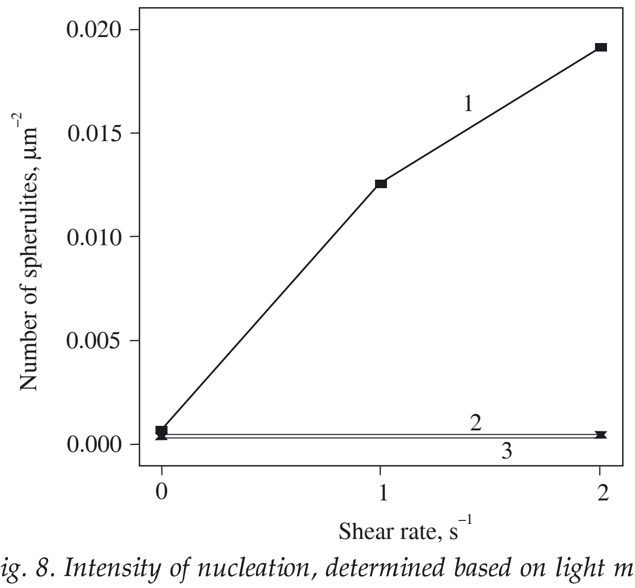

Fig. 8. Intensity of nucleation, determined based on light microscopy of thin sections, in PP-g-MA compatibilized iPP nanocomposite with 3 wt. % of o-MMT (1), composite of iPP with 3 wt. % o-MMT (3) and blend of iPP with 11 wt. % of PP-g-MA (2) vs. shear rate [22].

rate of 1 s^{-1} and 2 s^{-1}. The number of spherulites per unit area of sample cross-section is plotted in Fig. 8. It is clear that also the shear applied prior to crystallization enhanced the nucleation in a nanocomposite with exfoliated clay. The enhancement of nucleation is accompanied by orientation of crystals. X-ray diffraction with pole figures analysis allowed to establish that (040) are parallel to shear direction while (110) planes are normal to the shear direction. These findings indicate that the iPP chains are aligned in the plane normal to the shear direction. Usually, during shear induced crystallization of neat iPP, chains tend to assume the direction parallel to shearing [24], although much higher shear rates are required. However, Li and de Jeu [24] observed also that shear induced smectic layers in iPP can rotate and align in the velocity gradient direction. In our system the unusual direction of chain orientation has to be also related to the orientation of the exfoliated clay and correlated with enhanced nucleation of crystallization, especially that evolution of a texture component, in which the chains are aligned within a plane normal to shear direction was also found by us in LDPE based nanocomposites [25].

CONCLUSIONS

In spite of intense efforts undertaken by numerous research groups worldwide during past years, nanocomposites of polymers with layered silicates are still challenging materials. Their production involves most often melt-processing. The clay exfoliation in a polymer matrix is therefore influenced by a number of factors including a type of machine used, mixing conditions, molecular weight of polymers, including that of a compatibilizer.

In addition, new methods to achieve exfoliation of the clay were recently developed that permit to avoid either organo-modification of the clay or application of a compatibilizer.

While the clay may affect the static crystallization of a polymer matrix in a limited way, the situation changes when the nanocomposite is processed, *i.e.* it is subjected to a shear. Even a weak shear, which hardly affects a neat polymer, induces orientation of clay platelets and also orientation of polymer chains and accelerates the crystallization in nanocomposites. Thus, the solidification of nanocomposites during injection moulding or film blowing might differ substantially from that of neat polymers, even if quiescent crystallization in either isothermal or nonisothermal conditions is similar.

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