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Melt compounding of syndiotactic polypropylene nanocomposites containing organophilic layered silicates and in situ formed core/shell nanoparticles

Dirk Kaempfer, Ralf Thomann, Rolf Mülhaupt*

Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie der Albert-Ludwigs Universität, Stefan-Meier-Strasse 31, D-79104 Freiburg i.Br., Germany

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Abstract

Syndiotactic polypropylene (sPP) compounds containing organophilic layered silicates were prepared by means of melt extrusion at 220 °C using a corotating twin screw extruder in order to examine the influence of the silicate modification and the addition of maleic-anhydride-grafted isotactic polypropylene (iPP-*g*-MA) as compatibilizer on morphology development and mechanical properties. Synthetic sodium fluoromica was used as water-swellable layered silicate, which was rendered organophilic by means of cation exchange with protonated octadecylamine. Only compounding of the modified silicate in conjunction with iPP-*g*-MA afforded exfoliation and dispersion of individual silicate layers, encapsulated in an iPP-*g*-MA shell, within the polypropylene matrix. Interlayer distance increased with increasing content and increasing molecular weight of the compatibilizer. The Young's modulus of the nanocomposite increased fivefold from 490 to 2640 MPa. This was attributed to silicate nanoreinforcement and nucleation of sPP crystallization via the iPP-*g*-MA shell of the dispersed organophilic silicate nanoparticles. The yield stress was increased to 29 MPa with respect to 16 MPa for the bulk sPP. Morphology and mechanical properties were examined as a function of the silicate—and compatibilizer content. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Nanocomposite; Syndiotactic polypropylene; Core/shell

1. Introduction

Polypropylene exhibits an attractive combination of low cost, low weight and the extraordinary versatility in terms of properties, applications, and recycling [1]. In order to improve polypropylene's competitiveness in engineering resin applications, it is an important objective to simultaneously increase dimensional stability, stiffness, strength and the impact resistance. The production of polypropylene composites containing fiber reinforcement requires special processing technology involving fiber impregnation and prepreg formation [2]. Therefore, special emphasis is being placed upon the development of filled polypropylene, which is produced by means of conventional melt processing technology. Traditional fillers for polypropylene are calcium carbonate, talc, glass fibers, wollastonite, mica, glass beads and wood flour. It is well known that filler anisotropy, i.e. large length/diameter ratio 'aspect ratio'), is especially favorable in matrix reinforcement [3]. Although anisotropic nanofillers were found to afford attractive combinations of stiffness and toughness, limited commercial availability and dispersion problems due to strong interparticle interactions of nanofillers have limited their application [4]. Therefore, attempts have been made to generate anisotropic nanoparticles in situ during melt processing by means of in situ exfoliation of organophilic layered silicates during polymerization or processing, respectively.

Polymer/organoclay nanocomposite formation was reviewed by Dubois [5], Camino [6], Lagaly [7], Akelah [8], Giannelis [9], Pinnavaia [10] and Mülhaupt [11]. Such nanocomposites were found to exhibit unique property combinations, e.g. higher heat distortion temperature combined with higher stiffness, strength and improved barrier properties such as lower gas and liquid permeabilities. Recently, improved flame retardency was attributed to nanocomposite formation [12]. In contrast to talcum, which is a neutral layered magnesium silicate,

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* Corresponding author. Tel.: +49-761-203-6273; fax: +49-761-203-6317.

E-mail address: mulhaupt@uni-freiburg.de (R. Mülhaupt).

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anionic layered magnesium silicates, known as hectorites, are formed when part of magnesium is replaced by monovalent cations such as lithium. Since sodium cations are present in the interlayers, such layered silicates are water-swellable. Ion exchange of sodium cations for alkyl ammonium cations renders the layers hydrophobic. Polymer nanocomposites are formed in situ by exposing organophilic layered silicates to shear forces either during polymerization or during processing.

Progress in the development of isotactic polypropylene (iPP) nanocomposites was reviewed by Chung [13]. Reichert et al. [14] reported the influence of silicate modification and compatibilizer addition on morphology development and mechanical properties of melt extruded iPP nanocomposites. Synthetic sodium fluoromica was used as water-swellable layered silicate, which was rendered organophilic by means of cation exchange with various protonated *n*-alkyl amines. Exfoliation and self-assembly of individual silicate layers within the polypropylene matrix was obeyed by using C12, C16 and C18 amine modifiers in conjunction with maleic-anhydride-grafted polypropylene (PP-*g*-MA) as compatibilizer.

Until now, no reports on syndiotactic polypropylene (sPP) nanocomposites based upon organophilic layered silicates have appeared in the open literature. In comparison to iPP, sPP exhibits higher impact resistance and improved adhesion on organic surfaces or glass fillers [15]. sPP is known to nucleate crystallization of iPP. The objective of this research was to prepare and evaluate sPP nanocomposites based upon organophilic layered silicates and iPP-*g*-MA as compatibilizer. The in situ exfoliation of organophilic fluorohectorite layers encapsulated in an iPP shell was examined as a new route to sPP nanocomposites with in situ nanoreinforcement of the sPP matrix.

2. Experimental part

2.1. Materials

The synthetic clay used for our studies was fluorohectorite produced by CO-OP CHEMICAL Co., Japan, by heating talcum and Na_2SiF_6 together. The trade name of this material is SOMASIF ME100 (ME). The cation exchange capacity (CEC) of ME is 0.7–0.8 mequiv./g. The interlayer spacing of the unmodified ME was 0.95 nm. The polypropylene (sPP) used for this studies was obtained from TOTALFINA, the trade name of the sPP is EOD 96-30, its melt flow index (MFI) is 4.4 g/10 min, its melting point 130 °C. The maleic anhydride-modified PP oligomer was Hostaprime HC5 (MA content ~4.2 wt%; $T_m \sim 150$ °C; $M_n \sim 7500$ g/mol; $M_w/M_n \sim 3.9$ from Clariant GmbH, abbreviated as compatibilizer HC) and Licomont AR 504 which is a subsequent product to the HC compatibilizer (MA content ~3.5 wt%; $T_m \sim 156$ °C; $M_n \sim 2900$ g/mol $M_w/M_n \sim 4.1$ from Clariant GmbH, abbreviated as compatibilizer AR).

2.2. Preparation of organophilic layered silicates

Typically 1.20 mol of the octadecylamine and 1.20 mol HCl were dispersed in 20 l of 80 °C hot water. Then 1 kg of the ME silicate was added to this mixture and stirred for 60 min. The precipitate was washed in a centrifuge with 150 l of deionised water. After the silicate had been dried at 80 °C for 48 h, it was ground in a mill (Retsch ZM100).

2.3. Compounding and preparation of polypropylene nanocomposites

sPP powder and the organoclay were premixed in a tumbling mixer together with 0.25 wt% of stabilizer (Irganox1010/Irgafos168 Ciba: 4/1). This mixture was melt-blended together with the PP-*g*-MA in a corotating twin screw extruder (Collin; ZK 25T) at 190–230 °C and at 120 rpm. The obtained strands were pelletized and dried at 80 °C. The dried pellets were injection-molded into test bars according to DIN 53455. The different test specimens for tensile strength and notched impact strength were injection-molded on a Ferromatic Milacron K40. The temperature of the cylinder was 200–235 °C and the mold was at 40 °C.

2.4. Polymer characterization

2.4.1. Mechanical characterization

The tensile modulus of the composites and nanocomposites was measured with a Zwick model Z005 (ISO/DP 527) and the notched impact strength was tested with an impact tester Zwick, model 5102 (ISO 180/1A). The data were taken at room temperature without preconditioning the samples.

2.4.2. Light microscopy

The samples were prepared by melting the composite between two cover glasses. The layer thickness between the glasses was about 40 μm. After 5 min at 180 °C, the samples were cooled to 135 °C and held for 85 min before the samples were slowly cooled down to room temperature. The light microscope investigations were carried out with an Olympus-Vanox AH2 microscope and a Linkam TMS90 hot stage that allowed the observation during the crystallization.

2.4.3. Differential scanning calorimetry

The thermal behavior was analyzed by differential scanning calorimetry (DSC) using a Netzsch DSC 200. The heating rate was 10 °C/min.

2.4.4. Wide angle X-ray scattering

The interlayer distance of the ME(C18) in the nanocomposites was studied by means of wide angle X-ray

Table 1
Mechanical properties of sPP-nanocomposites with standard deviation listed in parentheses

No.	Silicate (wt%)	Type of compatibilizer	Compatibilizer (wt%)	Young's modulus (MPa)	Yield stress (MPa)	IZOD impact strength (kJ/m^2)
1	–	–	–	490 (15)	16.1 (0.3)	3.0 (0.1)
2	5	–		580 (34)	16.1 (0.3)	3.9 (0.1)
3	10	–	–	660 (18)	15.1 (0.2)	3.8 (0.2)
4	20	–	–	910 (25)	15.1 (0.1)	4.6 (0.1)
5	–	HC	20	670 (33)	18.7 (0.3)	1.9 (0.1)
6	5	HC	5	910 (22)	18.7 (0.1)	3.6 (0.2)
7	5	HC	10	1180 (18)	21.1 (0.2)	2.1 (0.1)
8	5	HC	20	1530 (14)	26.1 (0.2)	1.3 (0.1)
9	10	HC	20	1950 (11)	28.0 (0.1)	1.0 (0.2)
10	20	HC	20	2640 (34)	28.7 (0.2)	1.0 (0.2)
11	–	AR	20	520 (20)	15.3 (0.2)	3.0 (0.1)
12	5	AR	5	690 (23)	16.9 (0.2)	3.3 (0.1)
13	5	AR	10	840 (17)	17.4 (0.1)	2.8 (0.2)
14	5	AR	20	1050 (21)	18.8 (0.1)	1.7 (0.1)
15	13	AR	20	1560 (24)	21.5 (0.1)	1.4 (0.1)

scattering (WAXS) using a Siemens D500 apparatus with the Cu $K\alpha$ radiation ($k = 1.5418$ nm) and a scanning rate of 0.3°/min.

2.4.5. Transmission electron microscopy

The morphology of the samples was examined by transmission electron microscopy (TEM). For TEM measurements, ultra thin sections were prepared at -120 °C with an Ultracut E, Reichert & Jung, ultramicrotome using a diamond knife. The measurements were carried out on a LEO 912 Omega (120 kV).

3. Results and discussion

The synthetic fluorohectorite (Somasif ME100) was rendered organophilic by means of ion exchange of sodium cations, located in the interlayers, for protonated octadecylamine. In order to achieve exfoliation of the organophilic fluorohectorite combined with in situ encapsulation of the silicate layers, two different iPP compatibilizers grafted with maleic anhydride were employed. Melt compounding was preformed using a corotating twin screw extruder (Collin ZK 25T) at 200 °C, a screw speed of 120 rpm, and a throughput of 2 kg/h. Preferred feed stock was a powder blend of sPP, PP-*g*-MA, and organophilic fluorohectorite. The iPP-*g*-MA compatibilizer was required to improve the interfacial adhesion between the organophilic fluorohectorite and the polypropylene matrix. In order to examine the influence of the organophilic fluorohectorite on the morphology and the mechanical properties of the composite system, the content of the modified silicate was varied from 0 to 20 wt% at a constant iPP-*g*-MA compatibilizer content of 20 wt%. For comparison, compatibilizer-free systems were also investigated. The influence of the compatibilizer was studied by comparing PP-*g*-MA with a molecular weight of 7200 g/mol (compatibilizer HC) and 2900 g/mol (compatibilizer AR). In Table 1, the properties of the prepared compounds are listed.

All samples showed an increased modulus with

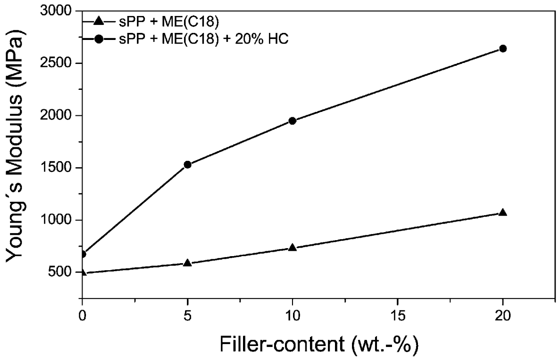

Fig. 1. Young's modulus of sPP/organohectorite compounds prepared in the presence (●) and absence (▲) of the iPP-*g*-MA compatibilizer with the higher molecular weight.

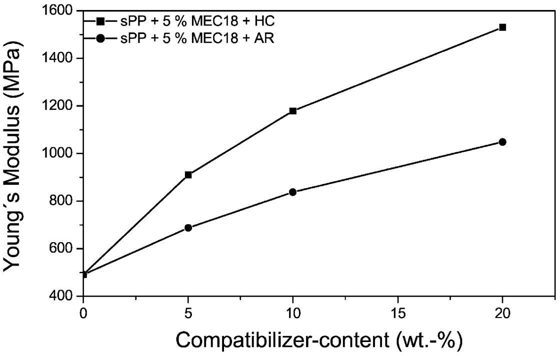

Fig. 2. Young's modulus of sPP/organohectorite composites prepared with the low (●) and the high molecular weight (■) iPP-*g*-MA compatibilizer.

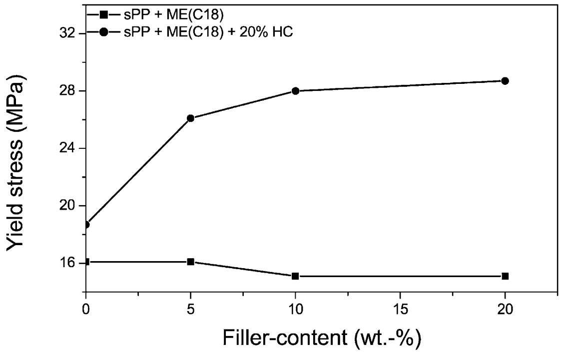

Fig. 3. Yield stress of sPP/organohectorite compounds prepared in the presence (●) and absence (■) of the high molecular weight iPP-*g*-MA compatibilizer.

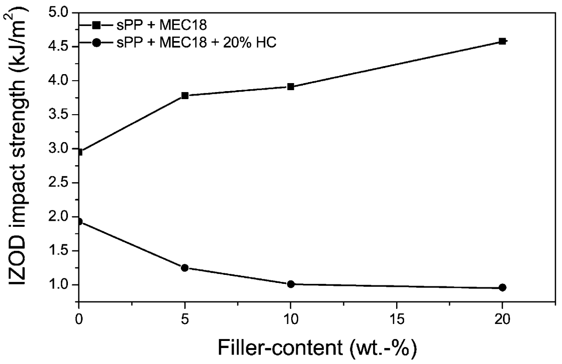

Fig. 5. Notched IZOD impact strength of sPP/organohectorite compounds prepared in the presence (●) and absence (■) of the high molecular weight iPP-*g*-MA compatibilizer.

increasing organophilic fluorohectorite content. It is apparent from Fig. 1 that the utilization of a compatibilizer is essential to achieve higher stiffness. The compound containing 20 wt% of the organophilic fluorohectorite and 20 wt% of the compatibilizer with the higher molecular weight showed a 2.9 times higher stiffness with respect to that in the absence of a compatibilizer and a 5.4 times higher stiffness with respect to that of the bulk sPP. Compounds containing 5 and 10 wt% of the organophilic fluorohectorite and 20 wt% of the compatibilizer gave a Young's modulus that was 2.2 and 2.9 times higher than that of bulk sPP, respectively.

As shown in Fig. 2, the stiffness of the polymer was influenced by both the organophilic fluorohectorite content and the presence of the iPP-*g*-MA compatibilizer. In the presence of the lower molar mass iPP-*g*-MA (AR type), the resulting sPP/organohectorite compound exhibited only 66% of the stiffness of the corresponding compound prepared with the HC-type iPP-*g*-MA. By varying the compatibilizer content, the Young's modulus increased from 580 MPa for a system containing 5 wt% of the organohectorite and without a compatibilizer to 1530 MPa for the compound containing the same amount of the organohectorite but 20 wt% of compatibilizer with the higher molecular weight.

The yield stress (Fig. 3) of the compounds prepared in the absence of iPP-*g*-MA decreased with increasing silicate content. In the presence of iPP-*g*-MA compatibilizers, yield stress increased with the organohectorite content. Fig. 4 shows that the HC-type compatibilizer with the higher molecular weight gives up to 1.3 times higher yield stress than the AR-type iPP-*g*-MA. The best results were achieved with the system containing 20 wt% of the organohectorite and 20 wt% of the HC-type compatibilizer.

The notched IZOD impact strength was affected by the organohectorite and the iPP-*g*-MA compatibilizer content. As shown in Figs. 5 and 6, the toughness decreased with increasing organohectorite and compatibilizer content. By adding 20 wt% of the organohectorite and 20 wt% of HC-type compatibilizer, the impact strength was reduced to 1/3rd of the impact strength of the bulk sPP. In the absence of a compatibilizer, the toughness was up to 1.5 times higher than that of the bulk polymer. At elevated compatibilizer

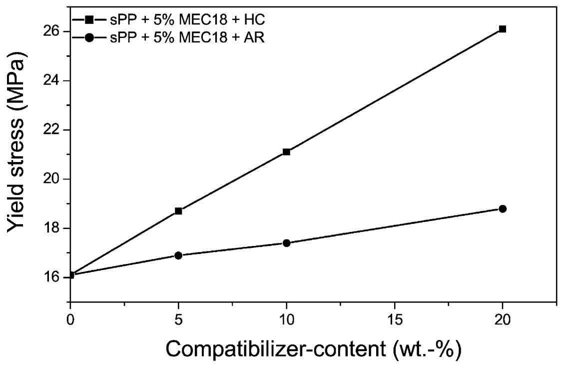

Fig. 4. Yield stress of sPP/organohectorite compounds prepared in the presence of the high (■) and low (●) molecular weight iPP-*g*-MA compatibilizer.

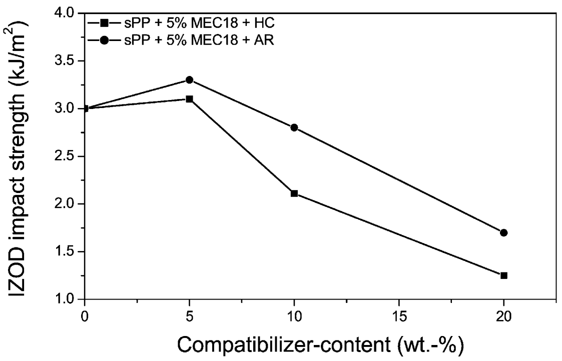

Fig. 6. Notched IZOD impact strength of sPP/organohectorite compounds prepared in the presence of the high (■) and the low (●) molecular weight iPP-*g*-MA compatibilizer.

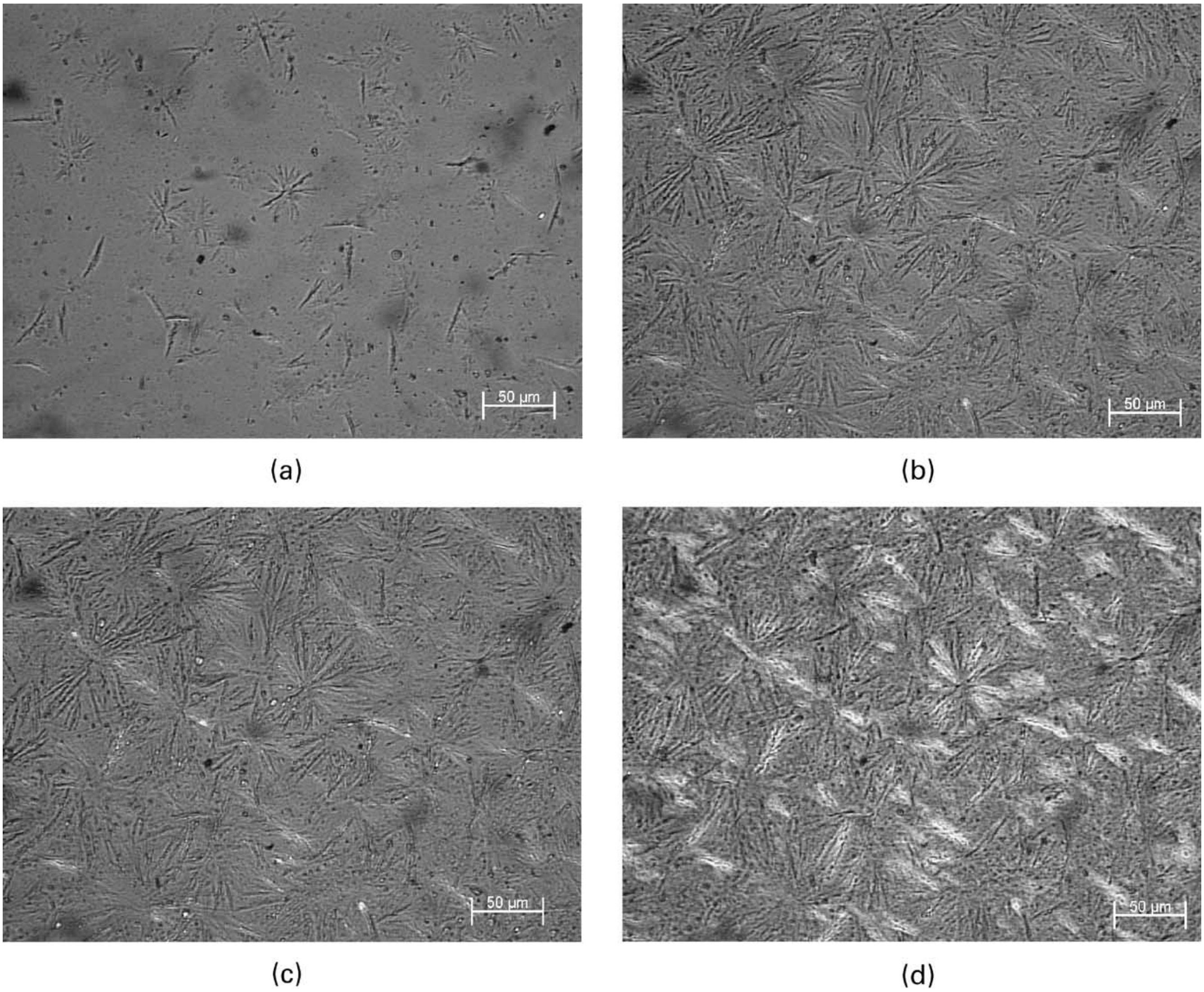

Fig. 7. (a)–(d) Light microscopy images of sPP containing 20 wt% of the high molecular weight iPP-*g*-MA compatibilizer. (a) SPP 20% HC; 135 °C; 20 min. (b) sPP 20% HC; 135 °C; 80 min. (c) sPP 20% HC; 100 °C; 85 min. (d) sPP 20% HC; 25 °C; 100 min.

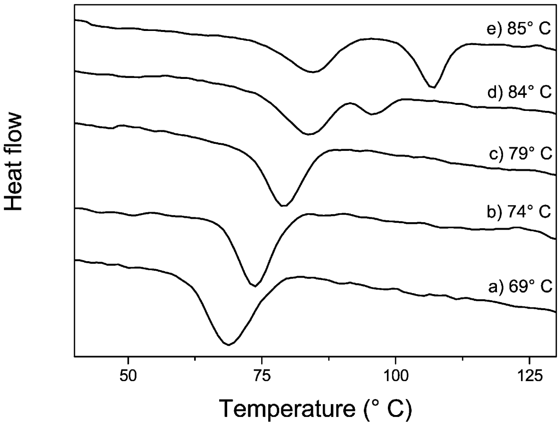

Fig. 8. DSC thermograms of sPP compounds containing 5 wt% of the organohectorite and up to 20 wt% of the high molecular weight iPP-*g*-MA compatibilizer. (a) sPP; (b) sPP 5ME(C18); (c) sPP 5ME(C18) 5 HC; (d) sPP 5ME(C18) 10 HC; (e) sPP 5ME(C18) 20 HC.

contents, the lower molecular weight iPP-*g*-MA compatibilizer gave better impact resistance with respect to that with the higher molecular weight.

4. Morphology

As previously reported by Thomann and coworkers [16], blends of iPP and sPP are immiscible. Since sPP crystallizes at lower temperature, iPP can be applied as the nucleating agent for sPP. The nucleation of sPP nanocomposites was monitored by means of light microscopy during the controlled crystallization of a compound containing 20 wt% iPP-*g*-MA compatibilizer. At a temperature of 135 °C, the iPP slowly started to crystallize (Fig. 7a). After 80 min at 135 °C, the crystalliation of most of the

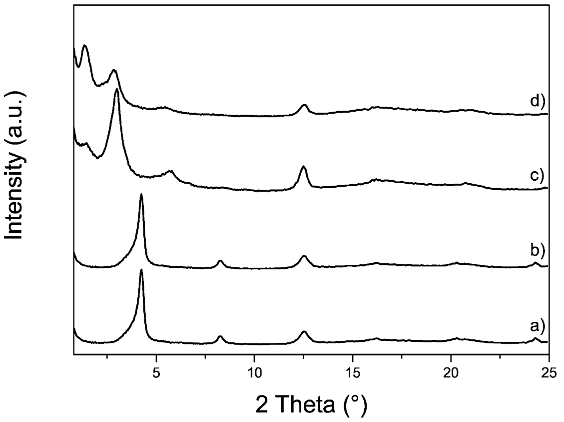

Fig. 9. WAXS traces of sPP/organohectorite compounds with varying compatibilizer content. (a) sPP 5ME(C18); (b) sPP 5ME(C18) 5 AR; (c) sPP 5ME(C18) 10 AR; (d) sPP 5ME(C18) 20 AR.

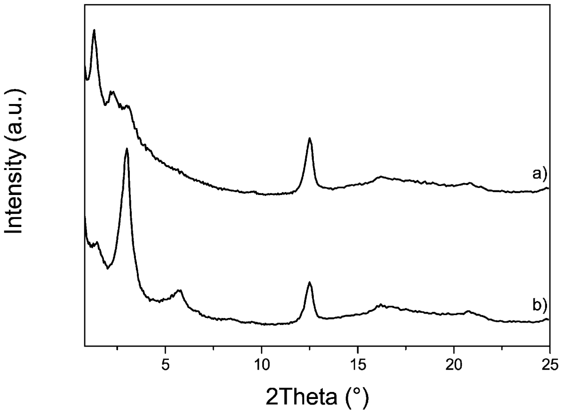

Fig. 10. WAXS traces of sPP/organohectorite compounds prepared with the two different compatibilizers. (a) sPP 5ME(C18) 10 HC; (b) sPP 5ME(C18) 10 AR.

compatibilizer had completed (Fig. 7b). At a temperature of 100 °C, the sPP started to crystallize (Fig. 7c). At room temperature, iPP was embedded in the sPP matrix (Fig. 7d).

The nucleation process can also be observed by means of DSC. It is apparent from Fig. 8 that the exothermic peaks of the cooling curves were shifted to higher temperatures with increasing compatibilizer content. The unmodified polypropylene showed a crystallization temperature of 69 °C. By adding 5 wt% of the compatibilizer with the higher molecular weight, the crystallization temperature was raised to 79 °C. For higher compatibilizer amounts, a much smaller temperature shift was observed. From 10 to 20 wt% the temperature difference was only 1 °C.

When iPP-*g*-MA compatibilizers were added together with organohectorite, exfoliation occurred, thus producing organohectorite layers encapsulated in a thin shell of iPP-*g*-MA. The resulting micro- and nanometer-scaled morphologies were monitored by means of WAXS and TEM. Fig. 9 shows the WAXS traces of sPP compounds containing 5 wt% of the modified silicate and up to 20 wt% of the AR-type compatibilizer. Clearly, the interlayer distance increased only marginally from 2.0 to 2.1 nm when 5 wt% of the compatibilizer was added. In contrast, an interlayer distance of 2.9 nm can be achieved by adding 10 wt% of the iPP-*g*-MA compatibilizer. By doubling the amount of compatibilizer a slightly higher interlayer distance of 3.1 nm can be obtained.

In addition to the amount of compatibilizer, the molecular weight plays an important role concerning the mechanical properties of the compounds. The comparison of samples containing the two iPP-*g*-MA compatibilizers with different molecular weights (Fig. 10) clearly indicates that the compatibilizer with the higher molecular weight afforded enhanced intercalation. The interlayer distance was increased from 2.9 nm for the compound containing 5 wt% of the organohectorite and 10 wt% of the compatibilizer with the lower molecular weight to 6.8 nm for the compound containing the compatibilizer with the higher molecular weight. In fact, higher toughness appeared to be associated with increased interlayer distance. According to TEM measurements, the length of the silicate particles is greater than 200 nm with an average thickness of a few nanometers, as expected for intercalated silicate stacks. This high aspect ratio accounts for the sPP matrix reinforcement.

Both dispersion and encapsulation of the silicate particles were imaged by means of TEM. Fig. 11a shows the compound containing 5 wt% organohectorite in the absence of a compatibilizer. Fairly large silicate particles are visible. From Fig. 11b, it is obvious that composites containing the iPP-*g*-MA compatibilizers exhibit different architectures. The silicate particles are much better dispersed within the sPP matrix. A comparison of Fig. 11c and d clearly indicated that higher molecular weight (HC-type) iPP-*g*-MA affords better exfoliation. As mentioned earlier, iPP and sPP are immiscible. This can also be confirmed because the RuO_4-stained TEM micrograph (Fig. 12a) shows the embedded iPP-*g*-MA compatibilizer as darker parts in the sPP matrix. From Fig. 12b, showing a sample consisting of 5 wt% of the organohectorite and 5 wt% of the lower molecular weight iPP-*g*-MA compatibilizer, it is apparent that the organophilic silicate is encapsulated in a thin iPP-*g*-MA shell. The compounding of sPP in the presence of immiscible iPP-*g*-MA represents an example of phase-selective filling with in situ prepared nanofillers.

5. Conclusions

Melt compounding of sPP with organohectorite, obtained via cation exchange of fluorohectorite with octadecylammonium cations, in a corotating twin screw extruder represents

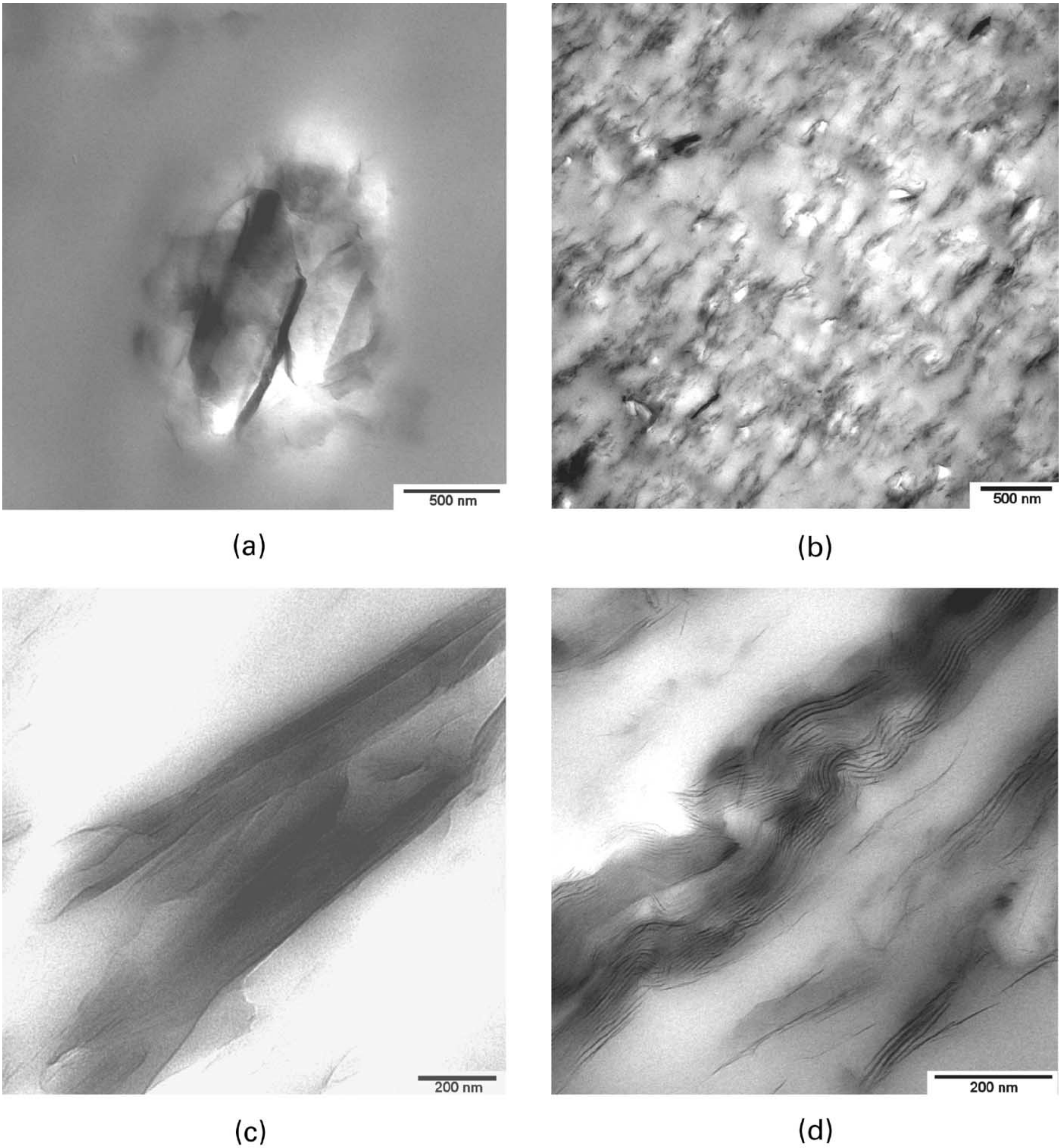

Fig. 11. (a)–(d) TEM micrographs of sPP compounds containing 5 wt% of the organohectorite and different amounts of the high molecular weight iPP-*g*-MA compatibilizer. (a) sPP 5% MEC18. (b) sPP 5% MEC18 20% HC. (c) sPP 5% MEC18 20% AR. (d) sPP 5% MEC18 20% HC.

an attractive new route to reinforced sPP with considerably higher stiffness. The matrix reinforcement is achieved by in situ formation of silicate nanoparticles via exfoliation combined with simultaneous in situ encapsulation of the resulting nanosilicates in a thin shell of iPP-*g*-MA. The resulting anisotropic core/shell type nanoparticles, containing stacks of organohectorite layer as core and iPP-*g*-MA as shell, represent very effective new classes of nucleating agents for sPP crystallization. Adding 20 wt% of the organohectorite together with 20 wt% of the HC-type

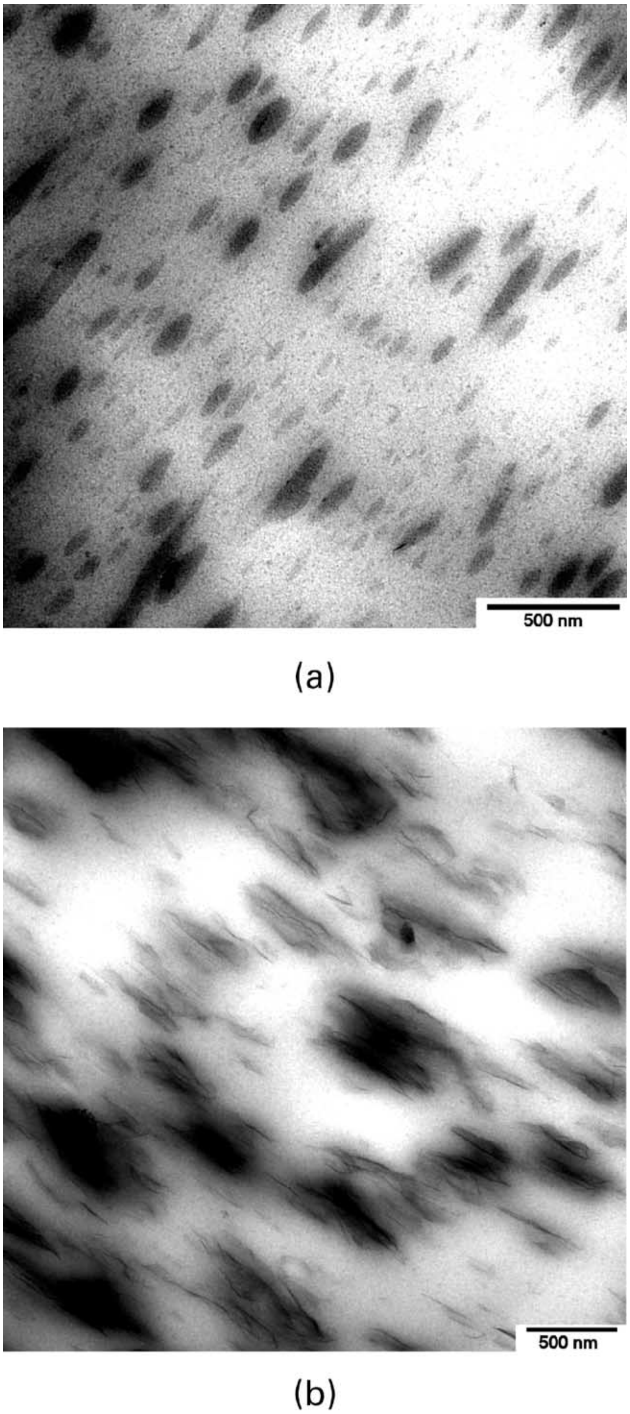

Fig. 12. (a)–(b) TEM micrographs of sPP compounds with and without 5 wt% of the organohectorite and the compatibilizer with the lower molecular weight. The samples were stained with ruthenium tetroxide. (a) sPP 20% HC. (b) sPP 5ME(C18) 5% AR.

compatibilizer and 60 wt% sPP afforded sPP nanocomposites exhibiting five times higher Young's modulus and a tensile-strength increase of 90%. Without a compatibilizer, the notched IZOD impact strength is increased by 50% whereas the addition of an isotactic compatibilizer reduces the impact strength by a factor of three. The formation of hybrid nanocomposites containing simultaneously dispersed rubber and anisotropic core/shell type nanosilicates is required to enhance the toughness/stiffness balance. The in situ formation of anisotropic core/shell nanosilicates encapsulated in a polymer shell represents an interesting new approach towards the design of novel nucleating agents, which can be tailored to match the compatibility requirements of other semicrystalline polymers. The phase-selective filling of immiscible polymers using in situ nanoparticles formation represents an attractive route to multiphase polymers with novel property profiles.

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