Polymer 49 (2008) 3979–3986

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis of PCL/clay masterbatches in supercritical carbon dioxide

L. Urbanczyk[a], C. Calberg[b], F. Stassin[a], M. Alexandre[a], R. Jérôme[a], C. Jérôme[a], C. Detrembleur[a,*]

[a] Center for Education and Research on Macromolecules (CERM), University of Liege, Building B6, 4000 Liège, Belgium
[b] Department of Applied Chemistry, University of Liege, Building B6, 4000 Liège, Belgium

ARTICLE INFO

Article history:
Received 1 February 2008
Received in revised form 3 June 2008
Accepted 26 June 2008
Available online 5 July 2008

Keywords:
Supercritical CO_2
Masterbatch
Nanoclay

ABSTRACT

Pre-exfoliated nanoclays were prepared through a masterbatch process using supercritical carbon dioxide as solvent and poly(ε-caprolactone) as organic matrix. In situ polymerization of ε-caprolactone in the presence of large amount of clay was conducted to obtain these easily dispersible nanoclays, collected as a dry and fine powder after reaction. Dispersion of these pre-exfoliated nanoclays in chlorinated polyethylene was also investigated. All the results confirm the specific advantages of supercritical CO_2 towards conventional solvents for filler modification.

1. Introduction

In the last two decades, a great deal of attention has been focused on developing reinforced materials with incorporation of nanometric fillers [1,2]. Amongst the different types of nanofillers, those based on layered silicates or clays, especially natural montmorillonite (MMT), have been most widely investigated. Compared to more classical fillers, only a small quantity of nanofiller is indeed required to enhance various properties such as gas permeability, fire resistance and mechanical properties. This difference is due to the higher specific surface of the nanometric fillers and their rather large aspect ratio (sheet-like structure of the primary particles).

However, the nanocomposite performances are strongly dependent on the clay nanosheet dispersion. The challenge consists thus in achieving a good delamination of nanofillers in order to obtain sheets totally independent from each other. For this reason, the Na^+ cations lying in the interlayer galleries of the natural montmorillonite clay are usually exchanged with organic cations bearing one or several long hydrocarbon chains (C_{12}–C_{18}) in order to lower the hydrophilic character of the interlayer galleries, hence improving compatibility with hydrophobic polymers.

There are two common processes to prepare polymer/clay nanocomposites: melt intercalation and *in situ* intercalative polymerization. Melt intercalation, i.e. dispersion of the clay in the molten polymer matrix, is the preferred method in industry due to the flexibility of the process and cost reasons [3–5]. However, an extensive exfoliation is only achieved by this way in a few cases, such as in polyamide 6/clay systems [6]. *In situ* intercalative polymerization is another technique to prepare these nanocomposites where the monomer swells the clay, penetrates into the interlayer galleries and then polymerizes either upon addition of an initiator or a polymerization catalyst, leading to the formation of polymer chains intercalated in-between the clay nanosheets. The chain growth in the clay galleries triggers the clay delamination, leading to exfoliated nanocomposites [7,8]. However, this efficient technique is hardly transferable to industrial process for practical and cost reasons.

In order to improve the clay dispersion via melt blending techniques, several authors [9–13] report on the use of masterbatches (polymer/clay blends with a high weight content of clay, prepared by melt mixing), that are redispersed (diluted) into polymer matrices [9,12], but this technique generally leads to semi-intercalated/semi-exfoliated morphology.

An interesting process for masterbatch production has been previously described by Dubois et al. [14], which leads to a more efficient clay delamination after melt redispersion in a host matrix. First, a highly filled polymer/clay nanocomposite is synthesized by *in situ* intercalative polymerization of the monomer in the presence of a high amount of clay (>10 wt%). The polymer can even be anchored onto the clay nanosheet surface when initiating species are borne by the ammonium organomodifier fixed at the clay sheet surface. The final nanocomposite is obtained by melt blending a suitable amount of the resulting masterbatch into a polymer matrix in order to obtain a nanocomposite containing a few percent of well-dispersed clay. An exfoliated morphology is generally obtained in the final nanocomposite, as long as the matrix is compatible with the intercalated compatibilizer. Dubois et al. were the first to describe the synthesis of such masterbatches, and they

---

* Corresponding author. Tel.: +32 43663465; fax: +32 43663496.
E-mail address: christophe.detrembleur@ulg.ac.be (C. Detrembleur).

0032-3861/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.06.052

mainly focused their study on the poly(ε-caprolactone) (PCL)/clay system. They conducted their synthesis in bulk, with a tin(IV) initiator, and a low monomer conversion was used in order to reach a high inorganic content. An efficient dispersion of clay platelets was achieved after redispersion of such masterbatches into polymers miscible with PCL, such as in poly(vinyl chloride) (PVC) [14] or styrene/acrylonitrile copolymer (SAN) [10]. Despite of these encouraging results, this process is characterized by some drawbacks such as the complexity to recover the aggregated bulk masterbatch and the necessity to purify it before use.

In this paper, we propose an alternative way for masterbatch production by preparing PCL/clay masterbatches by *in situ* intercalative polymerization in supercritical carbon dioxide ($scCO_2$), a non-toxic, cheap and environmentally friendly solvent for which parameters for supercritical state can be easily reached ($T_c = 31.1$ °C, $P_c = 73.8$ bar). This unusual medium has been chosen because of some non-negligible advantages compared to more conventional media, like the possibility to produce a ready-to-use masterbatch powders in one step and the ease of product recovery. This solvent is also convenient as a polymerization medium [15–20] because of its unique transport properties in the supercritical state related to its high density (liquid-like property) and high diffusivity (gas-like property). This allows the synthesis of a polymer in the presence of high clay content without any viscosity problem. This is never the case for bulk polymerization processes, where the clay loading is limited to ~30 wt%.

In the literature, several papers can be found regarding the *in situ* synthesis of polymer/clay nanocomposites in $scCO_2$, but only two of them report about an increasing content of clay up to 20 wt% [21,22]. In these papers, the PS and PMMA/organoclays are obtained after *in situ* radical polymerization of the monomers in the presence of a clay content ranging from 4 to 20 wt% [21] and even 40 wt% [22]. These highly filled materials have been characterized but they have not been dispersed to our best knowledge in a host matrix yet.

The ring-opening polymerization of ε-caprolactone in supercritical carbon dioxide has already been studied by Stassin and Jérôme [23–25]. This is a dispersion polymerization, since the monomer is soluble in this media but not the polymer, under classical supercritical conditions ($P < 500$ bar). ε-Caprolactone polymerization in $scCO_2$ using $Bu_2Sn(OMe)_2$, $Sn(oct)_2$ or $Al(OiPr)_3$, was controlled and good yields were obtained. However, the polymerization rate was decreased in the supercritical gas in comparison to polymerization in more classical solvents due to a carbonation reaction on the catalyst, resulting from an electrostatic interaction between a Lewis base (CO_2) and a Lewis acid (Sn or Al). In this study, $Sn(oct)_2$ has been chosen as the polymerization catalyst, since it has been shown to be less sensitive to such carbonation phenomenon, and because of its lower sensitivity to protic impurities.

In the second part of this paper, the obtained masterbatches have been dispersed in a commercial chlorinated polyethylene, known to be miscible with PCL [26], in order to compare the quality of clay delamination with the direct melt blending of classical organoclay.

2. Experimental part

2.1. Materials

ε-Caprolactone (ε-CL) and bis(2-ethylhexanoate)tin(II) ($Sn(oct)_2$), from Sigma–Aldrich (95%), were dried over molecular sieves for 48 h prior to use. CO_2 was supplied by Air Liquide Belgium (purity 99.95%) and used as-received. Three different clays were selected from Southern Clay Products (Texas, USA). These montmorillonite clays are either sodium-based (Cloisite® Na^+) or organo-modified either with dimethyl (dihydrogenated tallowalkyl) ammonium cation (Cloisite® 20A) or with bis-(2-(hydroxyethyl)methyl)(tallowalkyl)ammonium cation (Cloisite® 30B). The characteristics of these clays are described in Table 1. Commercial chlorinated polyethylene Tyrin® 3611P (CPE) was provided by Dupont-Dow Elastomers, and is characterized by a chlorine content of 36 wt%, a glass transition temperature of −20 °C and a crystallinity of about 4%.

2.2. Polymerization process

Polymerization was conducted in a 100 ml stainless steel high pressure reactor equipped with a helical stirring system. Pressure, temperature, and stirring speed were monitored on a digital display control rack. The clay (8 g) was dried in the reactor under vacuum at 85 °C for 1 night and then dry ε-CL (8 ml) was introduced under nitrogen flow, followed by $Sn(oct)_2$ (0.14 ml). The desired temperature was set (85 °C) and the desired pressure was attained (28 MPa) with a high-pressure pump. After 7 days of polymerization, the reactor was cooled down to room temperature and depressurized. The product was collected as a beige fine powder, in line with the intrinsic coloration of the selected clays. Nanocomposites containing 33–66 wt% of clay (inorganic part) were produced.

2.3. Redispersion process

Nanocomposites containing 5 wt% of clay were prepared by melt blending the masterbatches with the CPE matrix in a twin screw counter rotational mixer (Brabender®), at 165 °C for 5 min with a screw rotation speed of 75 rpm. The resulting material was then pressed into 3 mm sheets for 5 min at 165 °C.

2.4. Characterization

Thermogravimetric analysis (TGA) has been used on a TA Instrument TGA Q500 thermal analyser in the Hi-Res dynamic mode, under N_2 flow, in order to determine the clay content in the masterbatches. Measurements have been performed in triplicate and precision on clay content values lies around 2%.

Organic fractions (poly(ε-caprolactone) and ammonium salts) have been extracted from masterbatches by an ion-exchange reaction between the ammonium functions and lithium cations, by mixing a few grams of the nanocomposite in a THF solution saturated with LiCl. After 48 h, the clay was separated from the solution by filtration and the liquid fraction was concentrated and then precipitated in a 10-fold quantity of *n*-heptane. The polymer was recovered and the average molar mass of PCL was determined by size exclusion chromatography (SEC) in THF at 45 °C at a flow rate of 1 ml/min with a SFD S5200 autosampler liquid chromatograph equipped with a SFD refractometer index detector 2000. PL gel 5 μm (10^5 Å, 10^4 Å, 10^3 Å and 100 Å) columns were calibrated with polystyrene standards. The universal calibration curve was set up on the basis of the viscosimetric relationships for PS and PCL ($[\eta]_{PS} = 1.25 \times 10^{-4}\,M^{0.717}$, $[\eta]_{PCL} = 1.09 \times 10^{-3}\,M^{0.6}$). The extraction of organics (PCL + ammonium salts) from the masterbatch was quantitative within ~10% according to TGA analysis made on the clays recovered after ion exchange.

Table 1
Characteristics of the commercial clays used

Filler	Cation	Organic fraction (wt%)	Interlayer spacing (nm)
Cloisite® Na^+	Na^+	–	~1.1
Cloisite® 20A	$(CH_3)_2N^+(C_{18}H_{37})_2$	29	2.4
Cloisite® 30B	$(C_2H_4OH)_2N^+(C_{18}H_{35})CH_3$	20	1.8

XRD analysis was carried out with a powder diffractometer Siemens D5000 (Cu Kα radiation with $\lambda = 0.15406$ nm, 50 kV, 40 mA, Ni filter, $\theta/2\theta$ geometry) at room temperature for 2θ varying from 1.65° to 30° by 0.04 steps, in order to characterize the masterbatches and the final nanocomposite morphologies.

The powder recovered after masterbatch synthesis was observed by scanning electron microscopy (SEM; JEOL JSM 840-A) after metallization with Pt (30 nm) in order to estimate the particle size.

Nanocomposite morphology was directly observed by transmission electron microscopy (TECNAI G2 TWIN, LaB6, 200 kV). Ultrathin sections (50–80 nm) were prepared with an Ultramicrotome Ultracut FC4e, Reichert-Jung. No staining was used since the aluminosilicate sheets are contrasting enough in the polymer matrix.

Differential scanning calorimetry (DSC) has been used to study the crystallization kinetics of the PCL intercalated chains in masterbatches. The measurements have been done on a TA 2010 DSC thermal analyzer calibrated with indium. Samples were encapsulated in aluminum pans and the following cycle has been used: heated at 10 °C/min from room temperature to 100 °C, held at 100 °C for 5 min and then cooled at 10 °C/min to -50 °C and finally heated to 100 °C at 10 °C/min. Measurements have been performed twice and enthalpy values were reproducible within 5%.

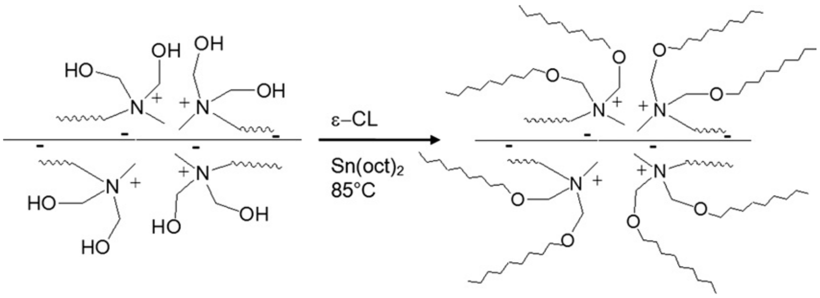
3. Results and discussion

3.1. Masterbatch synthesis and morphology

Three different types of clays were selected in order to prepare PCL/clay masterbatches: Cloisite® Na$^+$ (MMT–Na$^+$), Cloisite® 20A (MMT–Alk) and Cloisite® 30B (MMT–(OH)$_2$). The first one is a highly purified natural clay whereas the two others were organomodified with a non-functional (Cloisite® 20A) or a functional (Cloisite® 30B) quaternary ammonium salt. This organic treatment induces an increase of the interlayer spacing (see Table 1) and enhances the monomer/clay affinity. Both effects should have a beneficial impact on the clay impregnation by ε-caprolactone. In the case of Cloisite® 30B, the hydroxyl groups borne by the quaternary ammonium cations are also expected to initiate the polymerization of ε-caprolactone according to Scheme 1. This should allow a direct grafting of the polymer onto the clay surface and thus favour the delamination of the clay sheets.

Polymerization of ε-CL was carried out in scCO$_2$ (85 °C, 28 MPa) in the presence of clay by using Sn(oct)$_2$ as a catalyst, in a 100 ml high pressure reactor. After 7 days, the reactor is depressurized and the product is obtained as a dry fine powder. In clear contrast with the other methods for masterbatch preparation by *in situ* intercalative polymerization (bulk or classical organic solvents), the preparation of the masterbatch in scCO$_2$ allows to obtain the material as a dry fine powder instead of solidified blocks or soft pastes (bulk synthesis) or wet aggregated powders (organic solvents). The use of scCO$_2$, which is a gas at ambient pressure and temperature, explains this fine morphology of the final product, and the extraction of the residual monomer during depressurization also helps to get a dry powder. The monomer extraction has been confirmed by TGA analysis of the recovered masterbatches (data not shown) which does not show any mass loss between 80 and 200 °C, typical for ε-caprolactone vaporization.

As observed in Table 2, results are clearly dependent on the clay used. The best monomer conversion is obtained with Cloisite® 20A as polymerization may be considered to be complete within 7 days. The molar masses of the extracted polymer chains lie in the 1500–4000 g/mol range, according to measurements carried out on three different polymerization tests. The predicted molar mass is fixed by the initiator content, that are in this case protic impurities (residual water). This explains the variation in the molar masses obtained for the three polymerizations. Cloisite® 30B possesses hydroxyl functions that can act as initiator together with protic impurities, thus the molar mass of the *in situ* synthesized polyester obtained in MB30B is lower than MB20A and MBNa. This means that hydroxyl functions contained in the organoclay take part in the polymerization initiation, leading to some polyester chains grafted onto the clay surface. This behavior has also been observed in bulk or in organic solvent [27], where most of the hydroxyl groups grafted into the clay act as initiator. In order to prove polymer grafting, the masterbatches have been treated with pure THF for 2 days followed by filtration and drying of the recovered clay. In opposition to classical extraction with a THF solution saturated with LiCl where ion exchange occurred to extract the whole organic



Scheme 1.

Table 2
Characteristics of the PCL/clay masterbatches synthesized in supercritical carbon dioxide

Code	Type of clay	Clay (wt%)	PCL (wt%)	N$^+$ (wt%)	Conv.[a] (%)	Molecular weight (g/mol)[b]	PDI[b]	Interlayer spacing[c] (nm)
MBNa	Na$^+$	66	34	–	68	2400	1.7	1.9 and 3.3
MB20A-1	20A	32.5	50	17.5	100	3900	1.8	3.5
MB20A-2	20A	35	46	19	91	2400	1.8	3.4
MB20A-3	20A	35	46	19	91	4000	1.6	3.6
MB30B	30B	53	34	13	68	1500	1.8	3.2

[a] Determined by thermogravimetric analysis.
[b] Determined by size exclusion chromatography using polystyrene standards.
[c] Determined by X-ray diffraction.

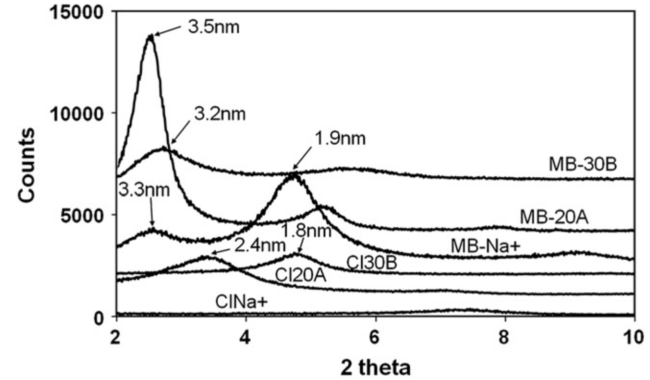


Fig. 1. XRD patterns of the commercial clays and the corresponding PCL/clay masterbatches synthesized in $scCO_2$.

content from the clay, here, only the non-grafted organic content is expected to be extracted. Final organic content in the filtrated and washed insoluble fraction was determined by TGA. We observed that ~60–70% of PCL was extracted by this way from MBNa and MB20A (100% non-grafted polymer). This means that polymer extraction is not quantitative, showing the difficulty for the intercalated PCL to leave the interlayer gallery. Anyway, the same experiment realized on MB30B (partially grafted polymer) leads to extraction of only ~20% of PCL initially present in this masterbatch. This tends to prove the partial grafting of PCL onto the clay surface via the organomodifier but the technique is not accurate enough to quantify the degree of polymer grafting.

The polydispersity indices determined for MB20A and MB30B, about 1.6–1.8, are in accordance with the values usually found with this kind of catalyst when polymerization is carried out in a heterogeneous medium.

MB30B is characterized by a higher clay content compared to MB20A, as the monomer conversion reaches only about 70% after 7 polymerization days. This difference in kinetics can be explained by a variation in protic impurities' content that is difficult to control, despite of the careful cleaning. A similar monomer conversion has been reached in MBNa (68%).

Fig. 1 compares the XRD analysis of the initial clays and the synthesized masterbatches. The signal in the low 2θ region for all masterbatches corresponds to an interlayer distance of about 3.2–3.6 nm, according to Bragg's law. As the interlayer distance in the initial clays lay around 1.1–2.4 nm (Fig. 1), we can conclude to an increase of distance in-between nanosheets during masterbatch formation, which proves the polymer formation between the clay sheets, typical for an intercalated system. These nanocomposites can then be qualified as "pre-exfoliated" masterbatches, since true exfoliation cannot be reached at such high clay contents. As far as

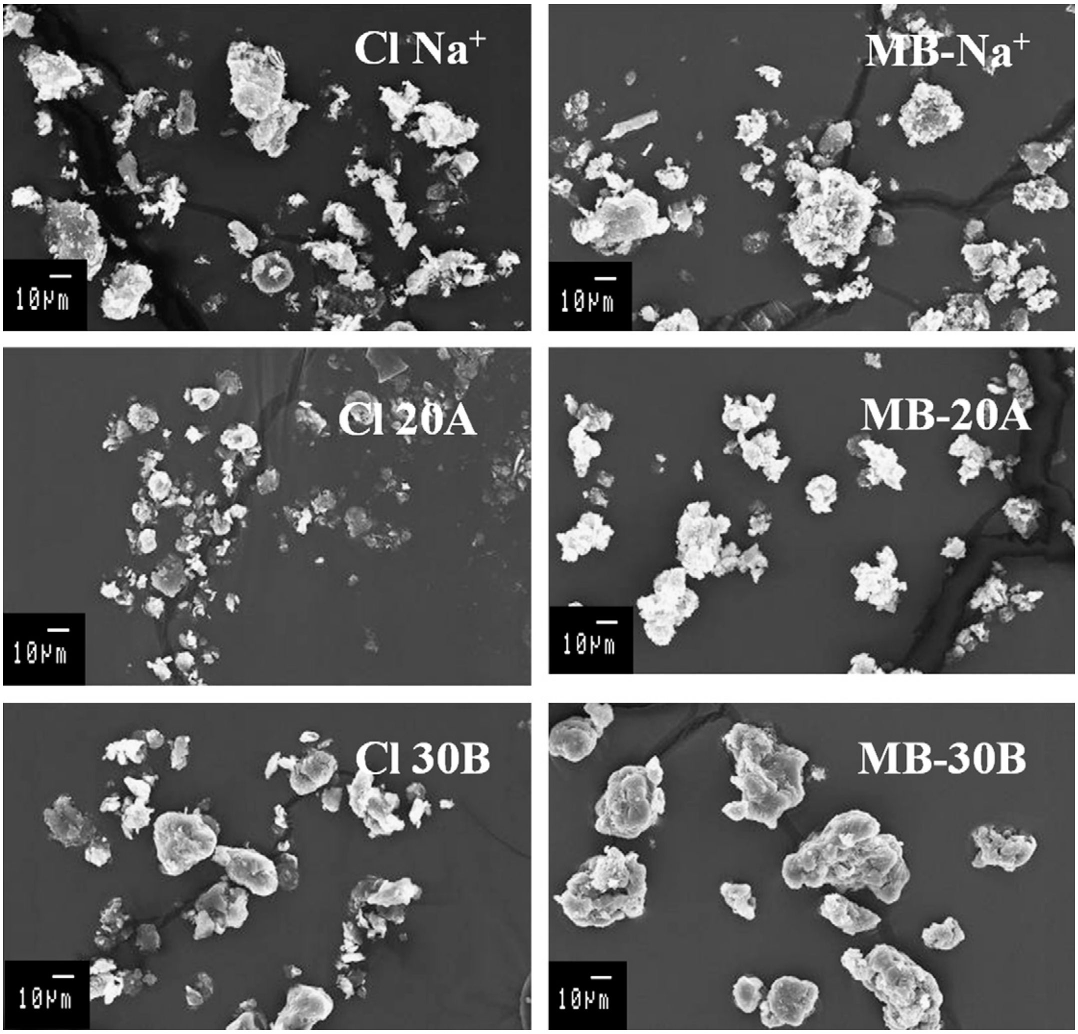


Fig. 2. SEM analysis of the original clays and the corresponding PCL/clay masterbatches.

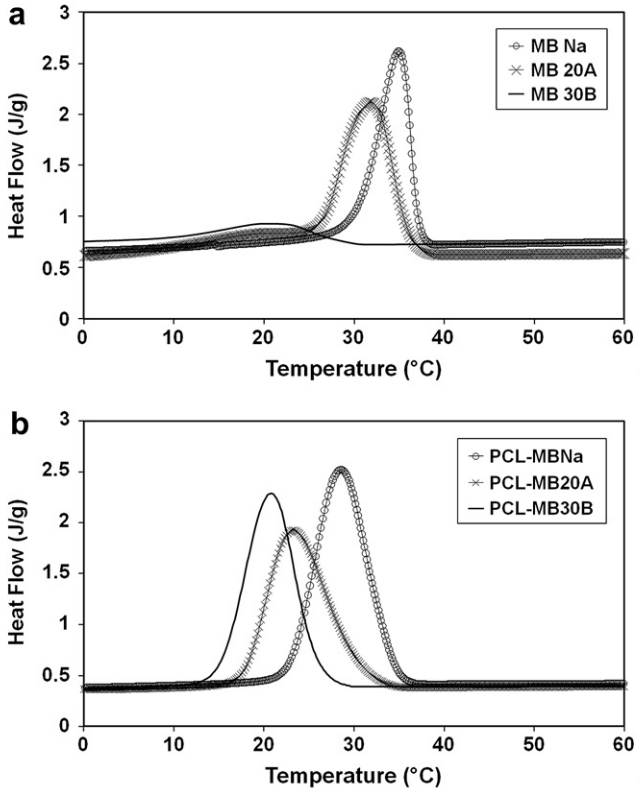


Fig. 3. Differential scanning calorimetry analysis on (a) the masterbatches and (b) the extracted PCL, cooling step.

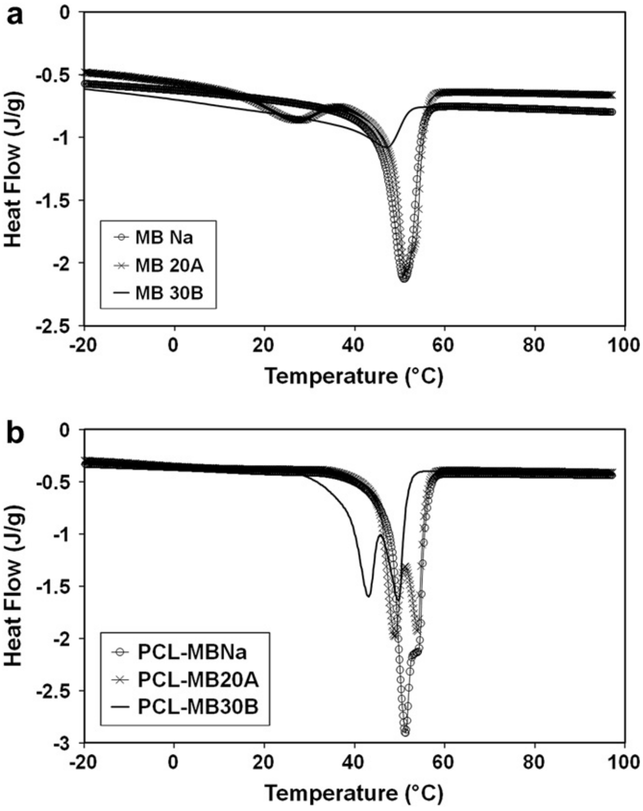


Fig. 4. Differential scanning calorimetry analysis on (a) the masterbatches and (b) the extracted PCL, second heating step.

MBNa is concerned, one can observe a second relatively intense diffraction peak at around 4.8° corresponding to an interlayer distance of 1.9 nm. Such bi-populated (3.3 and 1.9 nm) intercalated species may be interpreted as bi- and monolayers of PCL chains intercalated within the interlayer galleries as already demonstrated for PEO in hectorite [28].

The masterbatches have been studied by scanning electron microscopy in order to estimate the particle size before and after polymerization (Fig. 2). The original Cloisites show a broad particle size with an estimated diameter ranging from 5 to 20 μm. The powders recovered after ε-caprolactone *in situ* intercalative polymerization show only a small increase of particle size, which remains below 50 μm. This fine powder aspect is highly desirable to recover easily the sample and to facilitate its homogeneous dispersion into the molten polymer during the masterbatch dilution step. In fact, the masterbatches synthesized in bulk are usually agglomerated and can only be recovered after tedious treatments (agglomerates grinding or solubilisation/precipitation processes), which limits the practical use of this method in industrial development. When using supercritical CO_2 as a polymerization medium, we have developed a simple process, easy to scale up and which does not necessitate any purification step, as the remaining monomer is automatically extracted during gas venting. Considering these advantages, this process has been patented [29]. We should mention, however, that the catalyst is not fully extracted from the product during the depressurization step, as its solubility in the supercritical fluid is limited. Anyway, if its presence is really not desirable, further extraction step(s) with the supercritical fluid can be envisaged [23].

3.2. Masterbatch thermal characterization

Kiersnowski and Piglowski [10] have synthesized PCL/organoclay nanocomposites at 170 °C in bulk, using only water traces as initiator (activated monomer polymerization) with a final clay loading up to 50 wt%, and they have observed by DSC the influence of the clay content on the kinetics of PCL crystallization. They have found that a high clay loading slowed down the crystallization rate of the polymer. This was explained by a restriction in the mobility of

Table 3
Enthalpy and corresponding crystallinity values obtained from DSC analysis

Sample	PCL molecular weight[a] (g/mol)	ΔH_c[b] (J/g)	Crystallinity[c] (%)	ΔH_m[b] (J/g)	Crystallinity[d] (%)	$\Delta H_c - \Delta H_m$ (J/g)
MBNa	2400	62.6	46.0	57.5	42.3	5.1
MB20A-1	3900	90.1	66.2	82.2	60.4	7.9
MB30B	**1500**	**41.2**	**30.3**	**21.3**	**15.7**	**19.8**
PCL-MBNa	2400	88.9	65.3	92.2	67.7	−3.3
PCL-MB20A-1	3900	74.9	55.0	76.7	56.4	−1.8
PCL-MB30B	1500	79.3	58.3	81.3	59.7	−2.0

[a] Determined by size exclusion chromatography using polystyrene standards.
[b] Determined by differential scanning calorimetry measurements.
[c] Calculated with the formula $X_{PCL} = \Delta H_c \times w_{PCL}/\Delta H_0$, w_{PCL} being the weight fraction of the polyester and ΔH_0 value for a 100% crystalline PCL = 136.1 J/g.
[d] Calculated with the formula $X_{PCL} = \Delta H_m \times w_{PCL}/\Delta H_0$, w_{PCL} being the weight fraction of the polyester and ΔH_0 value for a 100% crystalline PCL = 136.1 J/g.

Table 4
Composition of the nanocomposites obtained via direct mixing (DM) of the organoclay or via the masterbatch route (MB)

Code[a]	Type of clay	Clay (wt%)	Interlayer spacing[b] (nm)
NC-DM30B	30B	5	3.70
NC-MB30B	30B	5	No XRD signal
NC-DM20A	20A	5	3.60
NC-MB20A	20A	5	3.60
NC-DMNa	Na^+	5	No XRD signal
NC-MBNa	Na^+	5	No XRD signal

[a] NC stands for nanocomposite.

[b] The interlayer spacing between two clay sheets has been measured with XRD.

polymer chains caused by dispersed silicate nanolayers. However, they also showed that a small clay content (<10%) increased the PCL crystallization kinetics. Thus in this case, the clay acts as a nucleating agent. We have made some DSC analysis on our masterbatches too, to see the influence of the clay on the PCL crystallization behaviour. In Figs. 3 and 4, we compare the crystallization and melting peaks during, respectively, the cooling and last heating cycles in non-isothermal conditions (see Section 2) of the three masterbatches and the organic fraction extracted from these masterbatches. The melting and crystallizing enthalpies (ΔH_m and ΔH_c, respectively) have been measured for each curve and the PCL crystallinity degree has been deduced from these values, by using

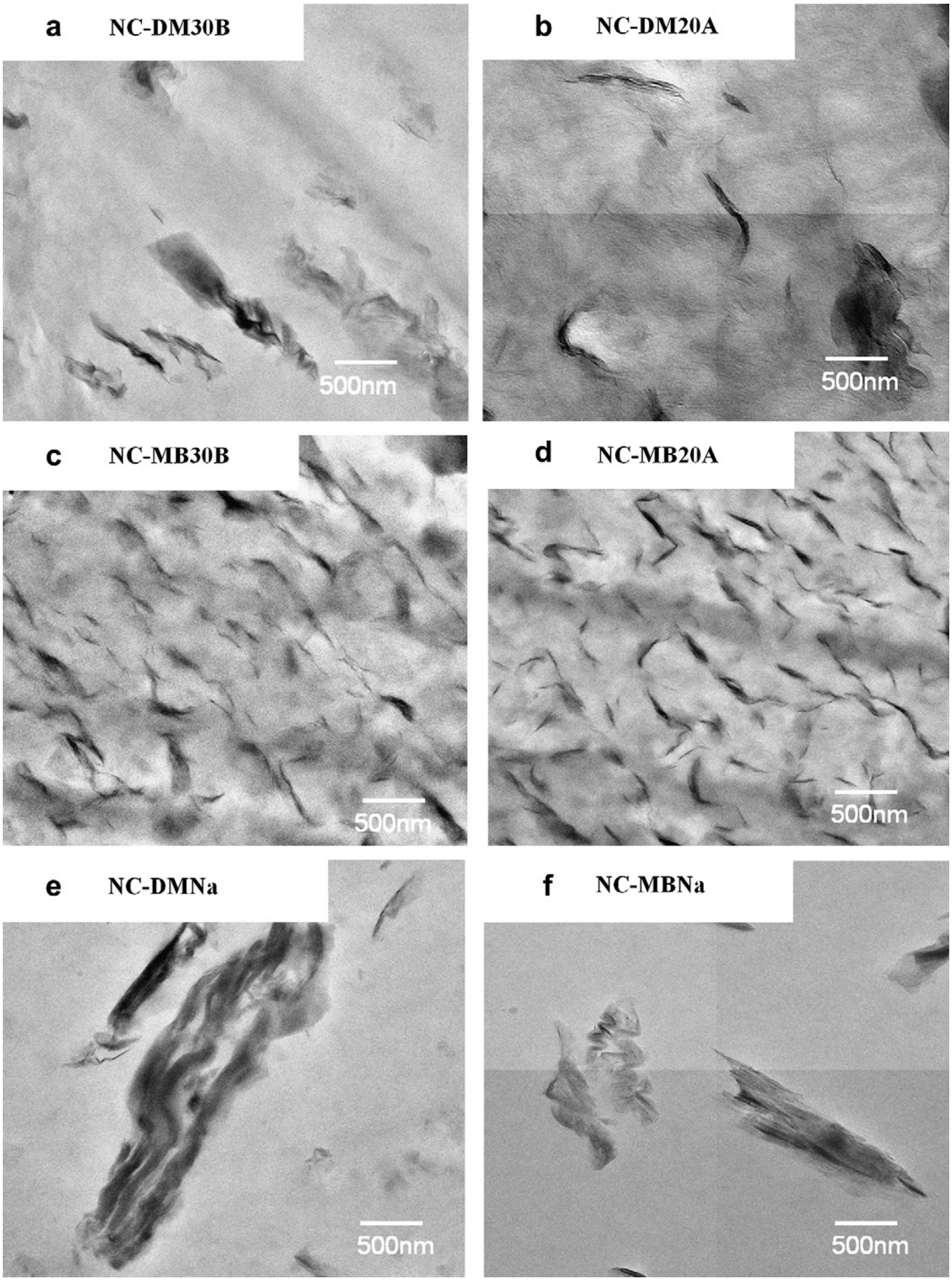


Fig. 5. TEM microscopy of CPE/clay nanocomposites, zoom 10 500×.

the formula $X_{PCL} = \Delta H \times w_{PCL}/\Delta H_0$, with X_{PCL} being the polycaprolactone crystallinity degree, w_{PCL} the weight fraction of the polyester and ΔH_0 the value for a 100% crystalline PCL, which is 136.1 J/g [13]. These results are summarized in Table 3. When comparing masterbatches' ΔH_m with ΔH_c values, ΔH_c values are always a little higher. This may be due to a melt–recrystallization–melt cycle during sample heating that reduces the real values for the melting enthalpy. This phenomenon had already been described by several authors when PCL was blended with amorphous polymers, such as SAN [30], chlorinated polyethylene [26], poly(hydroxy ether of bisphenol A) [31] or poly(styrene-*co*-maleic anhydride) [32]. They observed a PCL double melting peak during DSC analysis of the different polymer blends whereas the pure PCL had a single melting peak. The $\Delta H_c - \Delta H_m$ discrepancy is more pronounced for PCL in MB30B, where ΔH_c is doubled compared to ΔH_m. This reflects the strong effect of partial PCL grafting on its crystalline behavior, which favors the melt–recrystallization–melt cycle. In the literature, they explain this phenomenon by an imperfect crystallization of PCL. In our case, grafted chains are less mobile and thus may lead to the formation of less perfect crystals, supporting this explanation too.

Extracted PCL samples are characterized by a double melting peak (Fig. 4b). One hypothesis to explain this behavior is that PCL of very low molecular weight (oligomers, $M_n < 1000$ g/mol) crystallizes differently than higher PCL molecular weight ($M_n > 1000$ g/mol). This assumption has been verified with the following test: a 50:50 mixture of oligomeric PCL ($M_n = 530$ g/mol) and PCL of a higher molecular weight ($M_n = 3000$ g/mol) has been prepared by dissolution of the two polymers followed by solvent evaporation. This sample has been characterized by DSC and a double peak appears during melting, whereas the two pure PCLs exhibit a single peak (data not shown). Furthermore, we have extracted the PCL from our masterbatches with LiCl saturated THF solution, followed by precipitation in methanol instead of heptane, in order to eliminate short oligomers and/or alkylammonium salts. The recovered polyester chains exhibit a slightly higher average molecular weight due to the disappearance of a shoulder at long elution time (low molecular weight species) observed in the samples precipitated in *n*-heptane and they are characterized by a single melting peak in DSC. The melting temperatures measured on these curves lie in the same range than the second peak of the previous bimodal curves. We can thus conclude that the double melting peaks observed for the extracted PCL are due to different crystallization behaviors of oligomeric and longer polymer chains. The crystallinity degree of these extracted polymers is in the 55–65% range, which is rather common for this polymer. This value is nearly unchanged for PCL contained in MB20A and MBNa but is dramatically decreased in MB30B sample. This decrease is attributed to the high clay content in this masterbatch, combined with the partial polymer grafting onto the clay surface, which prevent the polymer from crystallizing efficiently.

These measurements have allowed us to highlight the striking difference between the non-grafted and grafted polymer crystallization behaviour in the PCL/clay masterbatches. We have also shown the differences in the crystallization behavior of PCL intercalated/grafted in the masterbatch and of the same polymer after extraction from the masterbatch.

3.3. Masterbatch dispersion in chlorinated polyethylene: morphological study

In order to evaluate the efficiency of the as prepared masterbatches to promote clay exfoliation, they have been dispersed by melt blending into a commercial chlorinated polyethylene (Table 4), which is known for its miscibility with PCL. Kim and White [33] already reported about commercial organoclay dispersion into chlorinated polymers with different degrees of chlorination. When using the melt blending method, it appears that the best organoclay dispersion occurs in PVC, whereas an intercalated morphology was observed in chlorinated polyethylene (36 wt% chlorine). This difference has been attributed to the higher polarity of PVC, thus increasing the affinity with the clay.

The various CPE-based nanocomposites have been prepared using the same mixing procedure in order to compare the direct melt blending of CPE with commercial organoclays and with the prepared masterbatches. The clay content has been kept constant at 5 wt% (inorganics part) in the resulting nanocomposites.

The clay dispersion has been observed directly by transmission electron microscopy (TEM). It is clear from Fig. 5 that the blend of CPE with the natural clay Cloisite Na^+ gives a microcomposite, even with the masterbatch route (Fig. 5e–f). This means that the high interlayer distance of MBNa was not sufficient to induce the delamination. This reflects the system instability at high temperature, where the intercalated polymer in MBNa leaves the clay interlayer gallery during melt mixing, leading to clay aggregates in the final composite, as observed in other systems such as some HDPE/clay nanocomposites prepared by *in situ* intercalative polymerization in non-organomodified clays [34]. This demonstrates the importance of the affinity between the clay surface and the polymer for the masterbatch to stay stable during the melt blending process.

In Fig. 5a–d, we can see that organomodified clays lead to at least partially exfoliated clays. The degree of exfoliation is clearly better in masterbatch-redispersed nanocomposites (NC-MB20A and 30B) than in nanocomposites prepared by direct dispersion of the organoclay (NC-DM20A and 30B). XRD analysis confirms this observation (Fig. 6), with a smaller peak intensity in the low 2θ angle region for NC-MB20A compared to NC-DM20A and even a broad shoulder for the NC-MB30B sample, typical of a disordered system. No XRD signal appears in the low angle region for NC-DMNa and NC-MBNa. This signal disappearance is typical of two extreme and opposite systems: either the clay is fully exfoliated or it is completely aggregated, giving rise to a microcomposite. Looking at the TEM analysis of these samples, we can affirm that the second assumption is the right one. This shows the complementarity of the two methods used to characterize nanocomposite morphology.

In conclusion, we have shown here the clear advantage to use a masterbatch to achieve efficient clay dispersion into a polymer miscible with PCL such as chlorinated polyethylene. Upon dispersion of the masterbatches based on organoclay in CPE, the clay is largely delaminated, whereas some very large clay stacks remain with the direct blending of the commercial clay. The investigation of the mechanical, thermal and flame retardant properties of the resulting nanocomposites are currently undertaken and will be reported in a forthcoming publication.

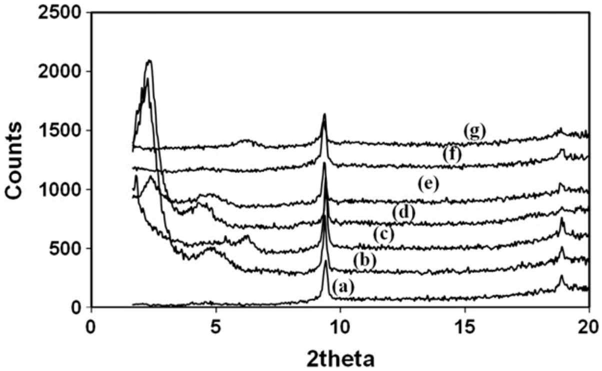


Fig. 6. XRD patterns of (a) CPE, and the nanocomposites: (b) NC-DM30B (c) NC-MB30B (d) NC-DM20A (e) NC-MB20A (f) NC-DMNa (g) NC-MBNa containing 5 wt% clay (inorganic part). Peak at 9.5° is typical for talc used as CPE additive.

4. Conclusions

The masterbatch technique is known to be an efficient way to enhance the clay delamination into organophilic polymers where the direct melt blending of the clay fails. In this study, we have successfully *in situ* synthesized PCL/clay masterbatches in supercritical carbon dioxide. This unique medium allows to reach a very high clay loading in the masterbatch. Also, the product obtained after depressurization is an easily recoverable fine powder. Another advantage of using supercritical CO_2 is its capacity to extract the residual monomer during depressurization, leading directly to a ready-to-use dry powder. These clear advantages show the superiority of this process compared to the classical synthesis in bulk and have pleaded to patent the process. In fact, all of these advantages allow this process to be upgraded to an industrial scale, which was not feasible with the classical process. However, it should be mentioned that the process time has not been yet optimized and could certainly be reduced with varying different parameters such as T°, P, catalyst content, ….

Three types of clays have been tested. They all lead to intercalated masterbatches with a clay loading ranging from 32.5 wt% to 66 wt% and an upper interlayer distance of around 3.2–3.6 nm. The PCL crystallinity has been studied by DSC and it appears that the crystallization behavior is different when the polymer is free or intercalated/partially grafted between a high amount of clay sheets. This phenomenon has been explained by the polymer confinement due to the high clay content, as well as the partial polymer grafting onto the clay surface, which prevent the polymer from efficiently crystallizing.

The redispersion of organomodified clay/polymer masterbatches into CPE has proven to be of a higher efficiency in terms of quality of clay delamination than direct blending of commercial clay.

The properties of the final nanocomposites and the redispersion of these masterbatches into poly(styrene-*co*-acrylonitrile) will be detailed in forthcoming papers.

Acknowledgements

CERM thanks the Region Wallonne in the frame of the WIN-NOMAT program PROCOMO. The authors are grateful to Interuniversity Attraction Poles Programme PAI P6/27, Belgian State, Belgian Science Policy for financial support. C.D. is “Chercheur Qualifié” by F.N.R.S., Belgium.

References

[1] Pinnavaia TJ, Beal GW. Polymer–clay nanocomposites. New York: John Wiley & Sons; 2001.
[2] Vaia RA, Krishnamoorti R. Polymer nanocomposites. Washington DC: American Chemical Society; 2001.
[3] Ray SS, Pralay M, Masami O. Macromolecules 2002;35:3104–31.
[4] Giannelis EP. Appl Organomet Chem 1998;12(10):675–82.
[5] Lepoittevin B, Devalckenaere M, Panoustier N, Alexandre M, Kubies D, Calberg C, et al. Polymer 2002;43:4017–23.
[6] Fornes TD, Hunter DL, Paul DR. Macromolecules 2004;37:1793–8.
[7] Kubies D, Panoustier N, Dubois P, Rulmont A, Jérôme R. Macromolecules 2002; 35:3318–20.
[8] Lepoittevin B, Panoustier N, Devalckenaere M, Alexandre M, Kubies D, Calberg C, et al. Macromolecules 2002;35:8385–90.
[9] Ren J, Huang Y, Liu Y, Tang X. Polym Test 2005;24:316–23.
[10] Kiersnowski A, Piglowski J. Eur Polym J 2004;40:1199–207.
[11] Kiersnowski A, Dabrowski P, Budde H, Kressler J, Piglowski J. Eur Polym J 2004; 40:2591–8.
[12] Kim SW, Jo WH, Lee MS, Ko MB, Jho JY. Polymer 2001;42:9837–42.
[13] Pucciariello R, Villani V, Gorrasi G, Vittoria V. J Macromol Sci Phys 2005;44: 79–92.
[14] Lepoittevin B, Panoustier N, Devalckenaere M, Alexandre M, Calberg C, Jérôme R, et al. Polymer 2003;44:2033–40.
[15] Mingotaud AF, Cansell F, Gilbert N, Soum A. Polym J 1999;31:406–10.
[16] Clark MR, DeSimone JM. Macromolecules 1995;28:3002–4.
[17] Kendall JL, Canelas DA, Young JL, DeSimone JM. Chem Rev 1999;99:543–63.
[18] Canelas DA, DeSimone JM. Macromolecules 1997;30:5673–82.
[19] Cooper AI. J Mater Chem 2000;10:207–34.
[20] Woods HM, Silva MMCG, Nouvel C, Shakesheff KM, Howdle SM. J Mater Chem 2004;14:1663–78.
[21] Zhao Q, Samulski ET. Polymer 2006;47:663–71.
[22] Zerda AS, Caskey TC, Lesser AJ. Macromolecules 2003;36:1603–8.
[23] Stassin F. Utilization of Supercritical carbon dioxide for the preparation and the processing of aliphatic polyesters. Ph.D. Thesis, Belgium: University of Liège; 2005.
[24] Stassin F, Jérôme R. Macromolecules 2001;34:775–81.
[25] Stassin F, Jérôme R. Chem Commun 2003:232–3.
[26] Defieuw G, Groeninckx G, Reynaers H. Polymer 1989;30:595–603.
[27] Lepoittevin B, Panoustier N, Alexandre M, Calberg C, Jérôme R, Dubois P. J Mater Chem 2002;12:3528–32.
[28] Harris DJ, Bonagamba TJ, Schmidt-Rohr K. Macromolecules 1999;32:6718–24.
[29] Calberg C, Stassin F, Halleux O, Dubois P, Panoustier N, Alexandre M, et al. Patent WO/2002/081541.
[30] Rim PB, Runt JP. Macromolecules 1983;16:762–8.
[31] Defieuw G, Groeninckx G, Reynaers H. Polymer 1989;30:2164–9.
[32] Defieuw G, Groeninckx G, Reynaers H. Polymer 1989;30:2158–63.
[33] Kim Y, White JL. J Appl Polym Sci 2003;90:1581–8.
[34] Alexandre M, Dubois P, Sun T, Garces JM, Jérôme R. Polymer 2002;43:2123–32.