

## Polymer/layered silicate nanocomposites by combined intercalative polymerization and melt intercalation: a masterbatch process

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### Abstract

Poly( $\epsilon$ -caprolactone) (PCL) and poly(vinyl chloride) (PVC) layered silicate nanocomposites were prepared by combination of intercalative polymerization and melt intercalation. In a first step, high clay content PCL nanocomposites were prepared by in situ polymerization of  $\epsilon$ -caprolactone intercalated between selected organo-modified silicate layers. The polymerization was catalyzed with dibutyltin dimethoxide in the presence of montmorillonites, the surface of which were previously exchanged with (functionalized) long alkyl chains ammonium cations. Then, these highly filled PCL nanocomposites were added as masterbatches in commercial PCL and PVC by melt blending. The intercalation of PCL chains within the silicate layers by in situ polymerization proved to be very efficient, leading to the formation of intercalated and/or exfoliated structures depending on the organo-clay. These masterbatches were readily dispersed into the molten PCL and PVC matrices yielding intercalated/exfoliated layered silicate nanocomposites which could not be obtained by melt blending the matrix directly with the same organo-modified clays. The formation of nanocomposites was assessed both by X-ray diffraction and transmission electronic microscopy. Interestingly, this so-called ‘masterbatch’ two-step process allowed for preparing PCL nanocomposites even with non-modified natural clay, i.e. sodium montmorillonite, which showed a material stiffness much higher than the corresponding microcomposites recovered by direct melt intercalation. The thermal stability of PCL nanocomposites as a function of clay content was investigated by thermogravimetry (TGA).

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### 1. Introduction

Polymer/layered silicate nanocomposites are a new class of materials with enhanced properties compared to parent conventional (micro)composites and unfilled polymers [1, 2]. As a rule, the homogeneous dispersion of 3–5 wt% of thin clay layers (ca. 1 nm thick platelets) improves the mechanical and thermal properties of the polymer matrix to the same extent as 30–50 wt% of micron-sized fillers. Among other improvements, tensile properties are

increased, permeability to oxygen and other gases are decreased and thermal stability and flame retardancy are enhanced [3,4].

The most representative nanofiller is sodium montmorillonite, i.e. a natural smectite clay (2:1 phyllosilicate) which consists of regular stacks of aluminosilicate layers with a high aspect ratio and a high surface area. Because of the hydrated sodium cations in the clay galleries, natural montmorillonite is hydrophilic, which is a problem to have it homogeneously dispersed in organic polymers. Ion exchange of the interlayer inorganic cations by organic cations (i.e. alkylammonium ions) is an efficient method to provide the clay with organophilicity. In the last decade, a large variety of polymers, including thermoplastics (polyamides [5], polystyrene [6,7], polypropylene [8], etc.),

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thermosets (epoxy [9,10], etc.) and elastomers (polydimethylsiloxane [11], etc.), have been upgraded by tiny amounts of organo-modified layered silicates. Depending on the nano-scale dispersion of the layered silicate, the whole spectrum of structures ranging from intercalated to exfoliated nanocomposites can be observed. The intercalation of one monolayer of polymer chains between the silicate layers results in a well-ordered multilayer morphology. In contrast, exfoliated or delaminated structures result from the complete and uniform dispersion of the individual silicate layers in a continuous polymer matrix.

Melt intercalation of preformed polymers and in situ intercalative polymerization are the two techniques most commonly used to prepare polymer/clay nanocomposites. The first method is effective whenever the thermodynamics of the melted polymer/organo-clay pair allows the chains to crawl within the clay interlayer spaces, so pushing the individual sheets apart one from each other. The second method relies on the swelling of the organo-clay by the monomer, followed by the in situ polymerization initiated thermally or by addition of a suitable compound. The chain growth in the clay galleries triggers the clay exfoliation and the nanocomposite formation.

Nanocomposites based on poly( $\epsilon$ -caprolactone) (PCL) have already been prepared by in situ polymerization of  $\epsilon$ -caprolactone in the presence of montmorillonite modified by alkylammonium cations bearing a carboxylic acid [12], and a hydroxyl end-group [13,14], respectively. This type of nanocomposites has been used to prepare segmented PCL-based polyurethane/clay nanocomposites by step-growth polymerization of diphenylmethane diisocyanate, butanediol and preformed polycaprolactone diol [15]. Messersmith and Giannelis also reported on the direct preparation of PCL nanocomposites by heating  $\text{Cr}^{3+}$ -fluorohectorite in the presence of  $\epsilon$ -caprolactone [16]. Very recently, Jo et al. [17] reported on the preparation of poly(styrene-*co*-acrylonitrile) (SAN) layered silicate nanocomposites using PCL as compatibilizer. Indeed, the organo-clay was first melt blended with preformed PCL, and then compounded with SAN, which is known to be miscible with PCL. In addition to the in situ  $\epsilon$ -CL polymerization [13,14], some of us prepared PCL layered silicate nanocomposites by melt intercalation [18,19]. The key role of both the structure of the alkyl ammonium modifier and the dispersion technique, i.e. melt intercalation vs. in situ intercalative polymerization was accordingly highlighted.

This paper aims at reporting on a new approach for the preparation of PCL and PVC layered silicate nanocomposites by combining the in situ intercalative polymerization and the melt intercalation process. A highly filled (organo)-clay/PCL masterbatch is first prepared by intercalative polymerization of  $\epsilon$ -caprolactone, followed by melt mixing with the polymer matrix (PCL or PVC). This method allows to prepare PVC-based nanocomposites with a high degree of exfoliation, which cannot be achieved by direct mixing of PVC and clay. This strategy that relies upon the unique

miscibility of PCL with PVC could be extended to all polymers known for miscibility with PCL, e.g. poly(styrene-*co*-acrylonitrile), poly(acrylonitrile-*co*-butadiene-*co*-styrene), bisphenol-A polycarbonate, nitrocellulose, cellulose butyrate, etc.

## 2. Experimental

### 2.1. Materials

Commercial grade poly( $\epsilon$ -caprolactone) (CAPA 650) was supplied by Solvay Chemicals sector-SBU. The number average molar mass was 49 000 with a polydispersity of 1.4, as determined by size exclusion chromatography. Stabilized and plasticized commercial grade poly(vinyl chloride) (PVC) was supplied by Solvay S.A. (Belgium). The clay minerals were supplied by Southern Clay Products (Texas, USA). The cation-exchange capacity of the non-modified sodium montmorillonite (Cloisite Na) (MMT-Na) was 90 mequiv./100 g. Two organophilic clays were used, i.e. Cloisite 25A (MMT-Alk) and Cloisite 30B (MMT-(OH)<sub>2</sub>) which are montmorillonite modified by 26 wt% dimethyl 2-ethylhexyl (hydrogenated tallowalkyl) ammonium cations and by 21 wt% methyl bis(2-hydroxyethyl) (hydrogenated tallowalkyl) ammonium cations, respectively.  $\epsilon$ -Caprolactone (purchased from Fluka) was dried over  $\text{CaH}_2$  and distilled under reduced pressure prior to use. Dibutyltin dimethoxide ( $\text{Bu}_2\text{Sn}(\text{MeO})_2$ ) was purchased from Aldrich and diluted with dry toluene.

### 2.2. Preparation of PCL/clay masterbatches

The native montmorillonite was dried under vacuum at 100 °C for one night and the organo-modified montmorillonites were dried at 70 °C in a ventilated oven for one night. They were further dried under vacuum at 70 °C for 3 h in a polymerization glass reactor equipped with a mechanical stirrer.  $\epsilon$ -Caprolactone was then added under nitrogen and the reaction medium was stirred at room temperature for 1 h. The reaction medium was then heated at 100 °C, and a known volume of  $\text{Bu}_2\text{Sn}(\text{MeO})_2$  solution in dry toluene was added to the reaction mixture such that the [monomer]/[Sn] molar ratio was 300. After a determined polymerization time, at 100 °C, the reaction was stopped by rapidly plunging the glass reactor in liquid nitrogen. Finally, the residual monomer was eliminated by evaporation under reduced pressure ( $10^{-2}$  mm Hg) at 80 °C for 2 days. The inorganic content of each PCL/clay masterbatch was measured by TGA.

### 2.3. Preparation of (nano)composites

PCL and PVC layered silicate composites were prepared by mechanical kneading with an Agila two-roll mill for 15 min, at 130 and 155 °C, respectively. The collected

material was compression-molded into 3 mm-thick plates by hot-pressing at 100 °C (PCL) or 130 °C (PVC) under atmospheric pressure for 10 min, under 150 bars for 10 s, followed by cold pressing at 15 °C under 150 bars for 5 min.

#### 2.4. Characterization

A reverse ion-exchange reaction was used to separate the PCL chains from the inorganic component of the nanocomposite masterbatches. The nanocomposite was dispersed under stirring in THF at room temperature for 2 h. This suspension was added to a 1 wt% solution of LiCl in THF, and the stirring was maintained at room temperature for 48 h. After centrifugation at 3000 rpm for 30 min, the supernatant was eliminated and the solid fraction was purified by dispersion in THF followed by centrifugation. The combined liquid phases were concentrated and precipitated from petroleum ether. The collected white powder was dried in vacuo at 50 °C. Absence of residual PCL in silicate was assessed by FT-IR (no carbonyl absorption at 1727 cm<sup>-1</sup>).

Average molar mass of PCL was determined by size exclusion chromatography in THF at 35 °C, with a Polymer Laboratory (PL) liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC1120 (flow rate: 1 ml/min), a Basic-Marathon Autosampler, a PL-RI refractive index detector and three columns: a PL-gel 10 µm guard column (50 × 7.5 mm<sup>2</sup>) and two PL-gel mixed-B 10 µm columns (300 × 7.5 mm<sup>2</sup>). Molar masses were calculated by reference to a PS standard calibration curve, using the Mark–Houwink relationship,  $[\eta] = K \times M^a$ , for PS ( $K_{PS} = 1.2510^{-4}$  dl/g,  $a_{PS} = 0.707$ ) and PCL ( $K_{PCL} = 1.0910^{-3}$  dl/g,  $a_{PCL} = 0.600$ ).

Morphology of composites were analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD patterns were recorded with a Siemens D5000 diffractometer with the Cu Kα radiation. Samples were prepared by hot-pressing at 100 °C (PCL) or 130 °C (PVC). XRD data were collected between 1.5 and 30° by step of 0.04° using an X-ray generator equipment with  $\lambda = 0.15406$  nm. TEM observations were performed with a Philips CM100 apparatus using an acceleration voltage of 100 kV. Ultrathin sections of composites (ca. 80 nm thick) were prepared at -130 °C with a Reichert-Jung Ultracut 3E, FC4E ultra-cryomicrotome equipped with a diamond knife. Because of the large difference in the electron density between silicate and polymer, no selective staining was required to observe the internal structure.

Thermogravimetric analysis (TGA) was performed under an air flow (75 cm<sup>3</sup>/min) at a heating rate of 20 K/min from room temperature to 600 °C with a Hi-Res TGA 2950 from TA Instruments. The clay content of each composite was assessed by TGA as the residue left at 600 °C. A previous comparative TGA study was carried out in triplicate on a separate sample attesting the excellent

reproducibility in terms of temperature ( $\pm 2$  °C) and weight loss ( $\pm 1$  wt%).

Tensile testing was performed at 20 °C at a constant deformation rate of 50 mm/min with a Lloyd LR 10 K tensile tester using dumbbell-shaped specimens prepared from compression molded samples according to the ASTM 638 type V norm. Tensile data were the average of five independent measurements. The ultimate tensile strength (in MPa), elongation at break (in %), and Young's modulus (in MPa) have been measured with relative errors of max. 9%.

### 3. Results and discussion

#### 3.1. Preparation of PCL/clay masterbatches

PCL/clay masterbatches were prepared by ring-opening polymerization of  $\epsilon$ -caprolactone using dibutyltin dimethoxide as catalyst. Three layered silicates were used, i.e. the native sodium montmorillonite (MMT-Na) and two organo-modified montmorillonites MMT-Alk and MMT-(OH)<sub>2</sub>, that result from the exchange of the Na<sup>+</sup> cations by dimethyl 2-ethylhexyl (hydrogenated tallow alkyl) ammonium and methyl (hydrogenated tallow alkyl) bis(2-hydroxyethyl) ammonium cations, respectively. Polymerization was conducted in bulk at 100 °C in the presence of 15–33 wt% of (organo)-clay depending on the filler and its dispersion in liquid  $\epsilon$ -caprolactone. In order to collect PCL composites with a high inorganic content, only low monomer conversion was envisioned and residual monomer was eliminated by vacuum distillation. The clay content of the final PCL/clay masterbatches was measured by thermogravimetry. Average molar mass of PCL extracted from the composite by a lithium chloride solution in THF was analyzed by size exclusion chromatography. Table 1 lists the number average molar mass, the polydispersity index and the clay content of the masterbatches prepared with MMT-Na, MMT-(OH)<sub>2</sub> and MMT-Alk, respectively.

The PCL molar mass lies in the range of 1000–10 000 g mol<sup>-1</sup> and the clay content ranges from 25 to 50 wt%. The polydispersity index is close to 2, except for the masterbatch M1 prepared from the native montmorillonite (MMT-Na). This very narrow molar mass

Table 1

Preparation of PCL/clay masterbatches by in situ intercalative polymerization of  $\epsilon$ -CL in presence of MMT-Na, MMT-Alk and MMT-(OH)<sub>2</sub> ([monomer]/[Bu<sub>2</sub>Sn(OMe)<sub>2</sub>] = 300; 100 °C)

Masterbatch	Clay	$M_n^a$	$M_w/M_n$	Filler content <sup>b</sup> (wt%)
M1	MMT-Na	1000	1.10	51
M2	MMT-Alk	9800	1.90	25
M3	MMT-(OH) <sub>2</sub>	2700	1.65	32

<sup>a</sup> Estimated by SEC, molar mass in PCL equivalent.

<sup>b</sup> Determined by TGA as the residue left at 600 °C, after drying at 80 °C in vacuo for 2 days.

distribution ( $M_w/M_n = 1.1$ ) might be related to the high clay content (51 wt%) and the restricted mobility of the growing chains confined in between the silicate layers that could prevent transesterification side reactions from occurring at least at this stage of the polymerization reaction. Indeed, the PCL polydispersity is observed to increase with the reaction time (and thus the monomer conversion) until ca. 2. In agreement with previous observations for PCL layered silicate nanocomposites prepared by the same technique and containing a low amount of clay (1–10 wt%) [13,14], intercalated nanocomposites are collected when the nanofiller is sodium montmorillonite (MMT-Na) and montmorillonite modified by alkylammonium cations deprived of any functional group (MMT-Alk). In contrast, partially exfoliated/partially intercalated structures are formed in the presence of montmorillonite modified by alkylammonium cations bearing two hydroxyl groups MMT-(OH)<sub>2</sub>, the exfoliation extent of which is reduced at higher clay content due to limited room remaining available for delaminating every silicate layer [13]. Exfoliation actually results from the grafting of PCL chains all along the clay surface. Indeed, the hydroxyl groups immobilized in the clay galleries are co-initiators of the  $\epsilon$ -CL polymerization because of a fast exchange with the initiating and propagating tin alkoxides [13,14]. At low MMT-(OH)<sub>2</sub> content (<5 wt%) quantitative exfoliation has been observed by TEM and XRD. This complete delamination of the silicate layers could be explained by the grafting of the PCL chains via the hydroxyl groups attached to the alkylammonium cations. By direct melt blending of preformed PCL chains with the same MMT-(OH)<sub>2</sub> organo-clay, intercalated nanocomposites have been exclusively recovered [13]. In other words, delamination of the clay platelets is triggered by the grafting reaction occurring at the initiation step rather than by an improved compatibility between the PCL matrix and the MMT-(OH)<sub>2</sub> surface. Although the clay content of the masterbatches prepared in this study is much higher than previously (>25 wt%), their XRD patterns remain similar to the previously published ones [13], however and as expected, with a less exfoliated morphology in case of masterbatch M3. The interlayer distance is observed at ca. 1.7, 2.8 and 3.3 nm, respectively, for the masterbatches prepared with MMT-Na, MMT-Alk and MMT-(OH)<sub>2</sub>.

### 3.2. PCL/(organo)-clay nanocomposites

PCL-based nanocomposites containing decreasing amounts of inorganics were prepared by melt blending the PCL/clay masterbatches with a commercially available PCL (molar mass of 49 000 g mol<sup>-1</sup>) at 130 °C for 15 min. The blend composition was such that the final clay content was 1, 3, 5 and 10 wt%.

Composites were analyzed by XRD and TEM in order to estimate the extent of the filler dispersion in the PCL matrix. Fig. 1 shows the XRD patterns for neat (organo-)clays and

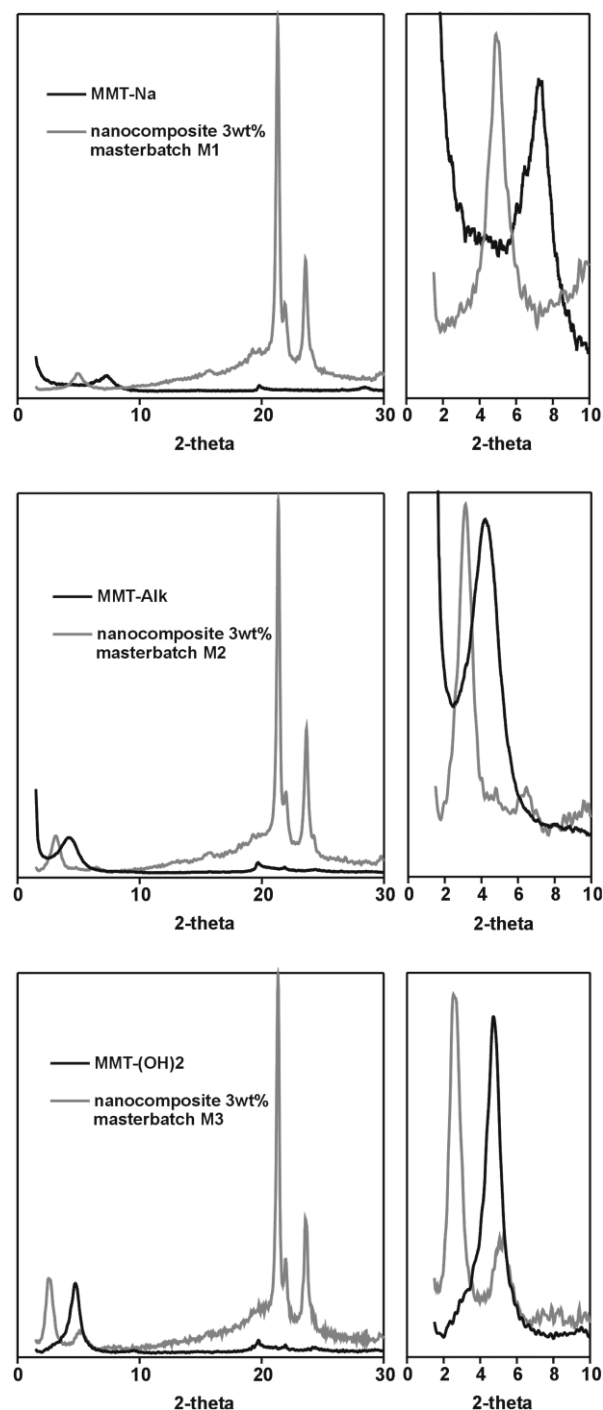


Fig. 1. XRD patterns for layered silicates and the corresponding PCL-based nanocomposites prepared from the masterbatches M1–M3 (Table 1). For every pattern, zoom view over the 0–10° 2-theta region is also presented.

for nanocomposites containing 3 wt% of them and prepared by melt blending a masterbatch with PCL.

Intercalated nanocomposites were collected as supported by the significant increase in the interlayer distance (diffraction observed at lower angles). In all the cases, the intercalated structure has been confirmed by TEM (not shown here). For instance, melt blending of PCL with the non-modified montmorillonite (MMT-Na)-filled PCL



masterbatch M1 has resulted in an increase of the interlayer distance from 1.17 to 1.79 nm consistent with an intercalated nanocomposite (Fig. 1). This situation is a remarkable progress compared to the microcomposite structure which is formed when PCL is directly melt blended with the native sodium montmorillonite (MMT-Na) [18]. It thus appears that the intercalated structure found in the PCL/MMT-Na masterbatch is preserved upon melt blending with high molar mass PCL chains. In case of the organo-modified clays, the interlayer distance has increased from 1.86 to 2.87 nm and from 1.85 to 3.33 nm for MMT-Alk and MMT-(OH)<sub>2</sub>, respectively.

Table 2 reports the mechanical properties for PCL/MMT-Na masterbatch (M1) nanocomposites, with different clay contents. For the sake of comparison, Young's modulus, ultimate tensile strength and elongation at break have been measured for the microcomposites prepared by direct melt blending of the non-modified montmorillonite (MMT-Na) with PCL under the same conditions.

The difference in properties observed for the two sets of composites is the expression of the difference in their morphology. PCL is quite a ductile polymer able to sustain large deformations consistent with a rather low elastic modulus. This characteristic feature is improved from 217 MPa for the unfilled PCL to 365 MPa for the PCL nanocomposite that contains 10 wt% of clay and has been prepared by melt blending with the masterbatch (M1). In contrast, microcomposites prepared from the native montmorillonite show only a small increase in stiffness (Fig. 2). PCL nanocomposites remain rather ductile, with an elongation at break higher than 300%. The stress at break decreases when the clay content is increased but remains at an acceptable level. Similar observations have been reported for the two organo-modified clays: increased stiffness and preserved ultimate tensile properties.

The thermal stability of the PCL-based nanocomposites prepared by the masterbatch process has also been studied by TGA with a heating rate of 20 K/min under an air flow. Fig. 3 shows the thermograms for the nanocomposites that contain 3 wt% of inorganic material and that originate from the masterbatches, M1 (MMT-Na), M2 (MMT-Alk) and M3

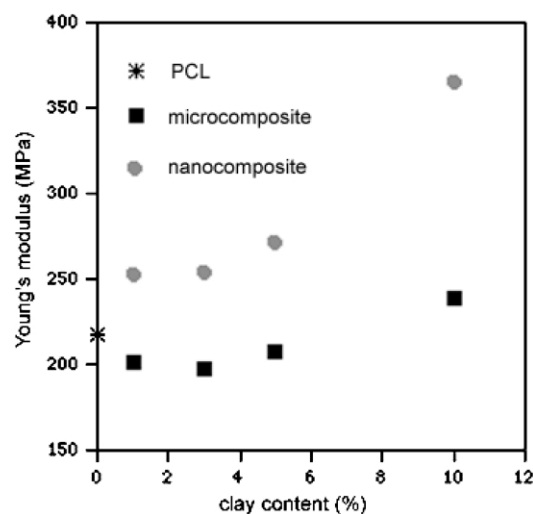


Fig. 2. Dependence of the Young's modulus on the clay content for composites containing MMT-Na. Comparison of microcomposites (direct melt blending of PCL with MMT-Na) and nanocomposites (melt blending of PCL with the masterbatch M1, Table 1).

(MMT-(OH)<sub>2</sub>). All the nanocomposites have a degradation temperature higher than neat PCL. It has been recently reported that the thermal degradation of PCL fits a two-step mechanism [21]. There is first a statistical rupture of the polyester chains by pyrolysis of ester groups with release of CO<sub>2</sub>, H<sub>2</sub>O and hexenoic acid. In the second step,  $\epsilon$ -caprolactone is formed as result of an unzipping depolymerization process. Whereas the temperature dependent weight loss curve recorded for neat PCL displays two consecutive steps, the PCL nanocomposites are characterized by a single weight loss with the beginning of the degradation shifted to much higher temperature. The temperature at which 50 wt% is lost is shifted by ca. 50 °C towards higher temperature when 3 wt% of inorganic material is added. This effect is explained by the fine dispersion of the clay layers, which decreases the polymer permeability to both oxygen and the volatile decomposition products. A similar thermal stabilization has been recently reported by Camino et al. for nanocomposition based on

Table 2

Tensile properties of neat PCL and PCL-based (nano)composites containing native montmorillonite (MMT-Na) and prepared by direct melt blending and by the masterbatch (M1) process

Preparation	Clay content <sup>a</sup> (wt%)	Ultimate tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
Neat PCL	0	37	746	217
Melt blending	1	35	715	201
	3	35	714	197
	5	32.5	666	207
	10	28	569	238
Masterbatch process	1	27	454	252
	3	26	448	253
	5	22	363	270
	10	22	397	365

<sup>a</sup> In inorganics.

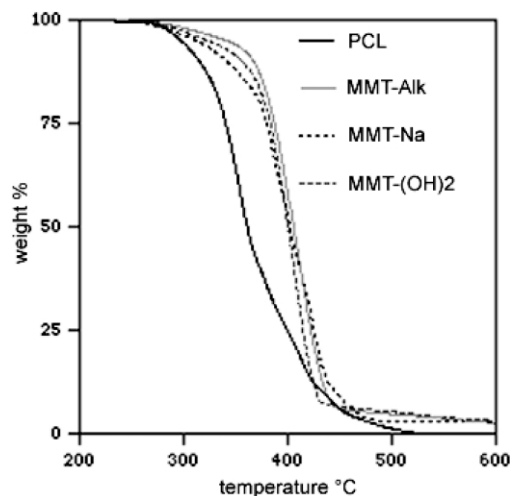


Fig. 3. Temperature dependence of weight loss under an air flow, for unfilled PCL and PCL-based nanocomposites prepared from the masterbatches M1–M3, and containing 3 wt% of inorganics (heating rate: 20 K/min).

ethylene-*co*-vinyl acetate copolymers (EVA) filled with organo-modified MMT [22,23].

The thermal degradation has also been studied as a function of the clay content in case of nanocomposites prepared with the masterbatch M3 (MMT-(OH)<sub>2</sub>). The temperature at which 50 wt% is lost is shifted by ca. 60 °C towards higher temperature at a clay content as low as 1 wt%. However, this beneficial effect is decreased when the clay content is increased (Fig. 4), as recently observed for PCL-based nanocomposites prepared by direct melt intercalation within (MMT-(OH)<sub>2</sub>) [18,19]. Such a continuous decrease of the improved thermal stability at higher clay content has been explained by a lower extent of clay delamination as a result of reduced free room within the thermoplastic matrix (as attested by XRD).

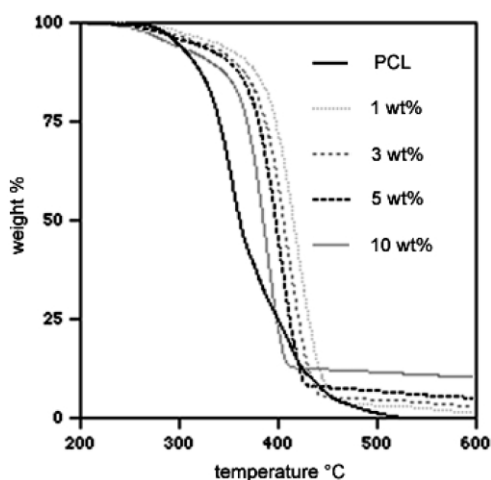


Fig. 4. Temperature dependence of weight loss under an air flow, for unfilled PCL and PCL-based nanocomposites prepared from the masterbatch (M1) and filled with 1, 3, 5 and 10 wt% of inorganics (heating rate: 20 K/min).

### 3.3. PVC/(organo)-clay nanocomposites

Although PVC is one of the most largely used thermoplastics, only little attention has been paid to PVC layered silicate nanocomposites. Very recently, Wang et al. [20] reported on the preparation of PVC/clay nanocomposites with organo-modified montmorillonites. Intercalated and partially exfoliated structures were formed by melt blending. Dioctyl phthalate, which is a common plasticizer for PVC, is favorable to the intercalation process, consistent with the swelling of the clay by this plasticizer (increased interlayer distance).

In this study, plasticized and stabilized commercial grade PVC has been melt blended with the PCL masterbatches M1 (native montmorillonite (MMT-Na)) and M3 (montmorillonite modified by methyl (hydrogenated tallow alkyl) bis(2-hydroxyethyl) ammonium cations (MMT-(OH)<sub>2</sub>)). Melt blending was carried out at 155 °C for 15 min, and the final inorganic content was 3 wt%. PVC has also been mixed directly with MMT-Na and MMT-(OH)<sub>2</sub> (3 wt% of inorganics) under the same conditions.

Fig. 5 shows the XRD patterns for neat MMT-(OH)<sub>2</sub>, and for the PVC/MMT-(OH)<sub>2</sub> composite prepared by direct melt intercalation and by the masterbatch (M3) process. The *d*-spacing of MMT-(OH)<sub>2</sub> is increased from 1.85 to 3.88 Å as result of blending with PVC, which agrees with formation of an intercalated nanocomposite. In contrast, when the masterbatch M3 is melt blended with PVC, no diffraction peak at low 2θ angle is observed anymore, consistent with the formation of an exfoliated PVC nanocomposite. The exfoliation of the organo-modified layered silicate by PVC has been confirmed by TEM analysis, as well as the clay dispersion within the PVC matrix as observed at low magnification (not shown here). Fig. 6 shows indeed that an intercalated structure results from the direct mixing of PVC

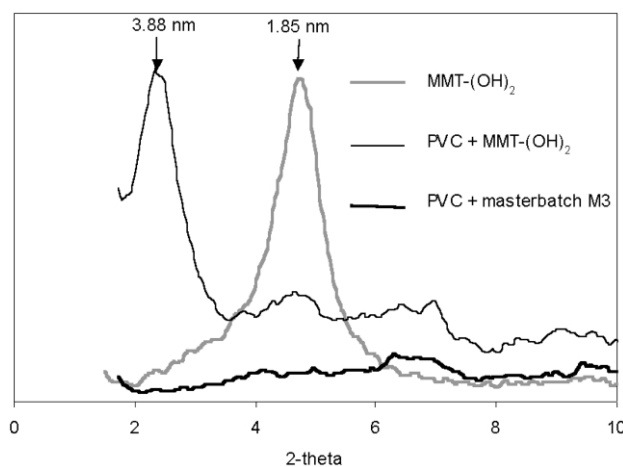
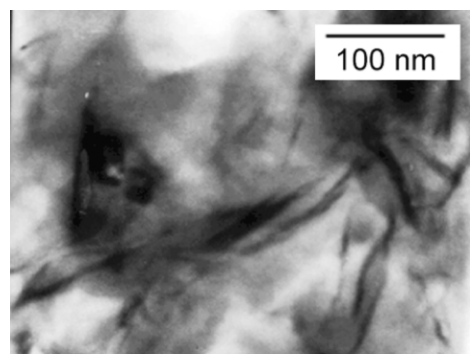
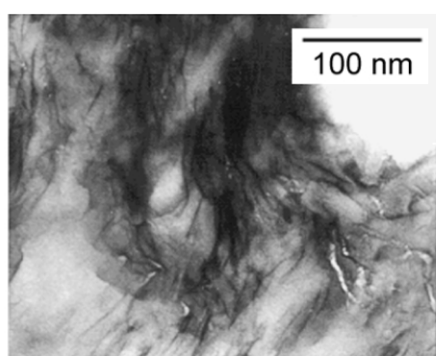


Fig. 5. XRD patterns for montmorillonite modified by methyl bis(2-hydroxyethyl) (hydrogenated tallow alkyl) ammonium (MMT-(OH)<sub>2</sub>), for PVC composites filled with 3 wt% of MMT-(OH)<sub>2</sub> and prepared either by direct PVC and MMT-(OH)<sub>2</sub> melt blending or by the masterbatch (M3) process.

PVC + MMT(OH)<sub>2</sub> (3 wt%)

PVC + masterbatch M3 (3 wt%)

Fig. 6. TEM images of the PVC-based nanocomposites filled with 3 wt% of MMT-(OH)<sub>2</sub>. (a) Direct melt blending, (b) masterbatch (M3) process.

with MMT-(OH)<sub>2</sub> (Fig. 6(a)), whereas the clay is exfoliated when the masterbatch (M3) is used instead of MMT-(OH)<sub>2</sub> (Fig. 6(b)).

It thus appears that the known miscibility of PVC with PCL is a driving force strong enough to exfoliate the silicate layers, to which PCL chains are grafted.

Mechanical properties for some PVC nanocomposites are reported in Table 3 for the PVC/MMT-Na composites prepared either from the masterbatch M1 or by direct blending with MMT-Na (3 wt% of inorganics). The masterbatch M1 has been used rather than M3, because it contains less PCL (49 wt% as determined by TGA, Table 1), which is known to plasticize PVC. Mechanical properties of the PVC matrix will thus be less modified by M1 than by

M3, so making comparison with the PCL-free PVC/clay nanocomposite more reliable.

The Young's modulus measured for the PVC/MMT-Na nanocomposite prepared by the masterbatch process (entry 2) is substantially higher than the modulus of counterpart prepared by direct melt blending of PVC with MMT-Na (Table 3; entry 3). No significant change in elongation at break and ultimate tensile strength is however observed. Direct melt blending of PVC with MMT-Na triggers a substantial decrease of the Young's modulus (38 MPa compared to 133 MPa for the unfilled PVC). Such a behavior could be explained by some molecular degradation of the PVC backbone such as a deprotonation reaction of the PVC backbone catalyzed by the alkaline surface of MMT-Na at processing temperature. This degradation being out of the scope of the present study, no further investigation has been carried out. For sake of comparison, the tensile properties for unfilled PVC and PVC melt blended with 3 wt% of a low molar mass PCL ( $M_n = 1000$ ) have been measured, as well (entries 1 and 4, Table 3). Indeed, the PVC/MMT-Na nanocomposite prepared by melt blending with the masterbatch M1 (entry 2) contains ca. 3 wt% of PCL chains of 1000  $M_n$ . Expectedly, addition of PCL (plasticizer) to the unfilled PVC results in an important decrease of the Young's modulus (28 compared to 133 MPa) and the elongation at break (67 compared to 141%) (entries 1 and 4). Interestingly enough, addition of 3 wt% of sodium montmorillonite to PVC by the masterbatch process triggers a fivefold increase in the Young's modulus compared to the PCL-plasticized PVC (140 compared to 28 MPa), whereas the ultimate tensile properties are also increased. Clearly, PVC layered silicate nanocomposites prepared by the masterbatch technique display superior mechanical properties (material stiffness) compared to composites formed by direct melt intercalation of PVC in the clay galleries.

#### 4. Conclusions

PCL and PVC layered silicate nanocomposites have been prepared in two steps, the first one being an intercalative polymerization and the second one a melt blending process.

Table 3

Tensile properties of neat PVC, PVC filled with 3 wt% of MMT-(OH)<sub>2</sub> (prepared by direct melt intercalation and by the masterbatch process), and PVC added with PCL

Entry	Composition	Clay content <sup>a</sup> (wt%)	PCL content (wt%)	Ultimate tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
1	Commercial PVC	0	0	12	141	133
2	PVC + masterbatch M1	3	3	12	151	140
3	PVC + MMT-Na	3	0	11	179	38
4	PVC + PCL <sup>b</sup>	0	3	8.5	67	28

<sup>a</sup> Content in inorganics.

<sup>b</sup>  $M_n = 1000 \text{ g mol}^{-1}$ .

Indeed, highly filled PCL masterbatches (typical content of (organo)clay in the range of 25–50 wt%) were first prepared by the in situ  $\epsilon$ -caprolactone polymerization catalyzed by dibutyltin dimethoxide at 100 °C. The masterbatches were then melt blended with either PCL or PVC such that the final clay content was lower than 10 wt%. PCL-based nanocomposites were collected, even with native sodium montmorillonite. Stiffness of the PCL nanocomposites was significantly improved compared to microcomposites directly prepared by melt intercalation. Thermal stability of these nanocomposites is also enhanced as result of restricted permeation of oxygen and combustion gas by the silicate sheets. For instance, the 50% weight loss temperature is shifted towards higher temperature by ca. 50 °C.

Depending on the (functionalized) alkylammonium cation used to modify the montmorillonite surface, intercalated or exfoliated PVC/clay nanocomposites can be prepared by the masterbatch technique, as assessed by both XRD and TEM analyses. Again, the PVC/layered silicate nanocomposites display a significantly higher stiffness compared to composites prepared by direct melt intercalation. In addition to improved mechanical and thermal properties, other key properties, e.g. flame retardancy, transparency, gas barrier properties are expected to be enhanced. For instance, the gas barrier properties of PCL-based nanocomposites have been recently studied and proved to be largely enhanced by the dispersion of a tiny amount of adequately modified layered silicate [24].

Because of the unique miscibility of PCL with a variety of polymers, PCL-based nanocomposite masterbatches are ideal starting materials to prepare a range of new nanocomposites, e.g. based on poly(styrene-*co*-acrylonitrile), poly(acrylonitrile-*co*-butadiene-*co*-styrene), bisphenol-A polycarbonate, nitrocellulose and cellulose butyrate. Moreover, PCL is mechanically compatible with polypropylene, polyethylene, natural rubber, poly(vinyl acetate), ethylene/propylene rubber, etc. Whether the compatibility of PCL with these polymers is enough to prepare valuable nanocomposites from the masterbatches will be tested in the near future.

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