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Poly(ϵ-caprolactone)/Clay Nanocomposites by in-Situ Intercalative Polymerization Catalyzed by Dibutyltin Dimethoxide

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ABSTRACT: Poly(ϵ-caprolactone)/clay nanocomposites were prepared by in-situ ring-opening polymerization of ϵ-caprolactone by using dibutyltin dimethoxide as an initiator/catalyst. A nonmodified Na^+−montmorillonite and two montmorillonites surface-modified by dimethyl 2-ethylhexyl (hydrogenated tallow alkyl) and methyl bis(2-hydroxyethyl) (hydrogenated tallow alkyl) ammonium cations, respectively, were used. The evolution of molecular weights was followed in relation to silicate surface modification and clay concentration. The alcohol-bearing organo-modified clay was a co-initiator for the polymerization reaction and thus controlled the molecular weight of the PCL chains. Furthermore, the number-average molecular weight of the growing PCL chains linearly increased with the monomer conversion. Nanocomposites were analyzed by small-angle X-ray diffraction, transmission electron microscopy, and thermogravimetry. The clay dispersion depended on the structure of the alkylammonium used to make the clay more hydrophobic. Exfoliated nanocomposites were formed when hydroxyl-containing alkylammonium was used; otherwise, intercalated structures were reported. Thermogravimetric analyses showed a higher degradation temperature for the exfoliated structures than for the intercalated ones, both of them exceeding the degradation temperature of unfilled poly(ϵ-caprolactone).

Introduction

During the past decade, polymer nanocomposites based upon organophilic layered silicates have rapidly grown.[1,2] Because of the nanometric dispersion of the silicate layers, this new family of materials exhibits properties that are completely different from those of composites in which the inorganic component is dispersed at micrometric level. Unexpected properties, such as a large increase in thermal stability, mechanical strength, and permeability to gases such as oxygen and moisture, have been observed.[1] Smectite clays, e.g. montmorillonite, are of particular interest because of the high aspect ratio of silicate nanolayers and the high surface area, making them suitable for reinforcement purposes. Na^+−montmorillonite is a crystalline 2:1 layered clay mineral in which a central alumina octahedral sheet is sandwiched between two silica tetrahedral sheets. The lamellae thickness is ca. 1 nm, and the space between the nearest-neighbor lamellae is a van der Waals gap known as a gallery or an interlayer. Although dispersion of the hydrophilic monolayers in a hydrophobic polymer is usually a problem, the ion exchange of the interlayer sodium cations by alkylammonium surfactants is an efficient way to improve the polymer/clay compatibility. In some examples, the alkylammonium cations can bear a functional group able either to react with the polymer or to initiate in-situ polymerization.

The characteristic properties of nanocomposites are usually observed at clay contents as low as 1−5 wt % compared to more than 20 wt % whenever properties of conventional microcomposites have to be optimized. The reinforcing action of organoclays has been studied in a series of polymers including polypropylene,[3] nylon-6,[4] poly(ethylene terephthalate),[5] polystyrene,[6] unsaturated polyesters,[7] polyimide,[8] polyolefins,[9] poly(methyl methacrylate),[10] ethylene−vinyl acetate copolymers,[11,12] and poly(ethylene oxide).[13]

Depending on the polymer, different methods have been reported for nanocomposite preparation, the most important ones being melt intercalation and in-situ intercalative polymerization. In the first method, clay is mixed within the melted preformed polymer, whereas the polymer is formed within the clay galleries in the second method. Two extreme structures have been reported for nanocomposites, i.e., *intercalated nanocomposites* in which polymer chains are intercalated between the silicate layers with formation of well-ordered multilayers with a repetitive thickness of a few nanometers and *delaminated or exfoliated nanocomposites* in which the individual silicate sheets are dispersed in the polymer matrix. Moreover, intermediate structures in which silicates are partially delaminated/partially exfoliated can also be obtained.[1]

Poly(ϵ-caprolactone)/clay nanocomposites are of a special interest because of the biocompatibility and biodegradability of the aliphatic polyester and the expected enhancement of the mechanical and thermal properties of this matrix. Giannelis et al. reported the intercalative polymerization of ϵ-caprolactone at 170 °C in protonated 12-aminododecanoic acid exchanged montmorillonite.[14] X-ray diffraction analysis showed that the silicate layers were delaminated in the poly(ϵ-caprolactone) (PCL) matrix. The same authors[15] also conducted the intercalative polymerization of ϵ-caprolactone in

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Cr^{3+}-exchanged fluorohectorite, a synthetic mica-type silicate. Recently, we reported[16] on the preparation of PCL nanocomposites by melt intercalation in montmorillonite modified by a variety of quaternary ammonium cations. The thermal stability of PCL was improved, together with a remarkable flame resistance.

In this paper, we report on a convenient route to poly(ϵ-caprolactone)/clay nanocomposites by in situ intercalative polymerization catalyzed by dibutyltin dimethoxide. Nonmodified Na^+−montmorillonite and the same clay modified by nonfunctional alkyl chains and by alkyl chains bearing two hydroxyl groups have been studied. The effect of the surface modification, surface reactivity, and concentration of the clay on the molecular weight of the in situ formed PCL has been investigated. The grafting of the polyester chains from the surface of the clay layers is expected to occur when hydroxyl groups are part of the modification agent. Moreover, the PCL molecular weight should be controlled by the hydroxyl content, i.e., by the clay content. The morphology of the three series of nanocomposites has been characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Resistance against thermal degradation has been also compared by thermogravimetric analysis (TGA).

Experimental Part

Materials. ϵ-Caprolactone (Fluka) was dried over CaH_2 and distilled under reduced pressure prior to use. Dibutyltin dimethoxide ($Bu_2Sn(MeO)_2$) was purchased from Aldrich and diluted with dry toluene. Three types of clay were kindly supplied by Southern Clay Products (Gonzales, TX). Cloisite Na^+ (MMT-Na) is a purified montmorillonite with a cation exchange capacity (CEC) of 92 mequiv/100 g. Cloisite 25A (MMT-C_8H_{17}) and Cloisite 30B (MMT-$(CH_2CH_2OH)_2$) are montmorillonites modified by dimethyl 2-ethylhexyl (hydrogenated tallow alkyl) ammoniums and by methyl bis(2-hydroxyethyl) (hydrogenated tallow alkyl) ammoniums, respectively. The organic content of the organo-modified montmorillonites was determined by TGA, i.e., 26 wt % for MMT-C_8H_{17} and 21 wt % for MMT-$(CH_2CH_2OH)_2$. Before polymerization, the nonmodified montmorillonite was dried under vacuum at 100 °C for one night and the organo-modified montmorillonites were dried in a ventilated oven at 70 °C for one night.

Preparation of Polymer/Clay Nanocomposites. The desired amount of clay was added into a polymerization tube and dried under vacuum at 70 °C for 3 h. A known amount of ϵ-caprolactone was then added under nitrogen, and the reaction medium was stirred at room temperature for 1 h. A solution of $Bu_2Sn(MeO)_2$ in dry toluene was finally added, such that the $[monomer]_0/[Sn]$ molar ratio was 300. The polymerization was allowed to proceed at room temperature for 24 h.

Recovery of PCL by Clay Extraction. PCL chains were separated from the clay by a reverse ion-exchange reaction. In a representative experiment, 2 g of the nanocomposite was suspended under stirring in 30 mL of THF for 2 h at room temperature. This suspension was then poured into 50 mL of 1 wt % solution of LiCl in THF and maintained stirred at room temperature for 48 h. After centrifugation at 3000 rpm for 30 min, the PCL containing supernatant was collected and the solid phase was washed by redispersion in 30 mL of THF followed by centrifugation. The supernatants were combined, concentrated, and precipitated into petroleum ether. The white powder was dried in vacuo at 50 °C. FT-IR analysis of the recovered silicate confirmed the complete extraction of PCL (no carbonyl absorption at 1727 cm^{-1}).

Characterization. Size exclusion chromatography was carried out in THF (sample concentration: 1 mg/mL) at 35 °C with a Polymer Laboratory (PL) liquid chromatograph equipped with a PL-DG802 degazer, an isocratic HPLC pump LC1120 (flow rate: 1 mL/min), a Basic-Marathon autosampler, a PL-RI refractive index detector, and three columns: a guard column PLgel 10 μm (50 × 7.5 mm) and two columns PLgel mixed-B 10 μm (300 × 7.5 mm). Molecular weights were calculated by reference to a PS standard calibration curve, using the Mark−Houwink relationship $[\eta] = KM^a$ for PS and PCL ($K_{PS} = 1.25 \times 10^{-4}$ dL/g, $a_{PS} = 0.707$, $K_{PCL} = 1.09 \times 10^{-3}$ dL/g, $a_{PCL} = 0.600$).

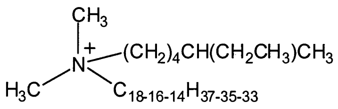
X-ray diffraction (XRD) patterns were recorded between 1.5° and 30° (by steps of 0.04°) with a Siemens D5000 diffractometer and Cu Kα radiation. TEM micrographs were observed with a Philips CM100 apparatus using an acceleration voltage of 100 kV. Ultrathin sections (ca. 80 nm thick) were cut at −130 °C from 3 mm thick hot-pressed plates by using a Reichert-Jung Ultracut 3E, FC4E ultra-cryomicrotome equipped with a diamond knife. Because of a large difference in electron density between silicate and PCL, no selective staining was required.

Thermogravimetric analysis (TGA) was performed under an air flow (74 cm^3/min) at a heating rate of 20 °C/min from room temperature to 600 °C by using a Hi-Res TGA 2950 from TA Instruments. The clay content of each composite was assessed by TGA.

Results and Discussion

Preparation of PCL/Clay Nanocomposites. ϵ-Caprolactone was polymerized in bulk with various amounts of layered silicates. The polymerization was activated at room temperature by dibutyltin dimethoxide. Metal alkoxides[17] are indeed known to be effective initiators of the ring-opening polymerization of lactones and lactides according to a "coordination−insertion" mechanism.[18,19] Polymerization proceeds through the insertion of the monomer into the "metal−O" bond of the initiator via the selective acyl-oxygen cleavage of the lactone ring. Three layered silicates were used: natural nonmodified montmorillonite (MMT-Na) and two organo-modified montmorillonites (MMT-C_8H_{17} and MMT-$(CH_2CH_2OH)_2$) prepared by Na^+ exchange with dimethyl 2-ethylhexyl (hydrogenated tallow alkyl) ammonium (**1**) and methyl (hydrogenated tallow alkyl) bis(2-hydroxyethyl)ammonium (**2**), respectively. Prior to polymerization, the clay is dried in order to eliminate water molecules that solvate the gallery cations. It is then swollen by the monomer. In the case of the organo-modified clays, the reaction medium turns into a gel.

1



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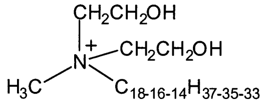


C_{18} : 65 %, C_{16} : 30 %, C_{14} : 14 %

The targeted content of filler was 1, 3, 5, and 10 wt %. Whenever the ϵ-caprolactone polymerization was conducted in the presence of the nonmodified silicate MMT-Na and the organo-modified clay MMT-C_8H_{17}, Tables 1 and 2 show that the clay content has no effect on the polymer molecular weight and the polydispersity index. For all these samples, M_n lies in the 14 000−24 000 range with an average polydispersity index of 2.

Table 1. Polymerization of ε-Caprolactone in the Presence of MMT-Na ($[\mathrm{Monomer}]_0/[\mathrm{Bu_2Sn(OMe)_2}] = 300$; 24 h at Room Temperature)

samples	filler content (wt %)	conv (%)	M_n[a] (g mol^{-1})	M_w/M_n
NC1−1	1	90	23 500	2.35
NC1−3	3	98	17 500	1.90
NC1−5	5	74	20 000	1.85

[a] Molecular weight in PCL equivalent.

Table 2. Polymerization of ε-Caprolactone in the Presence of MMT-C_8H_{17} ($[\mathrm{Monomer}]_0/[\mathrm{Bu_2Sn(OMe)_2}] = 300$; 24 h at Room Temperature)

samples	filler content (wt %)	conv (%)	M_n[a] (g mol^{-1})	M_w/M_n
NC2−1	1	94	14 500	2.05
NC2−3	3	93	16 000	2.05
NC2−5	5	88	17 500	2.05

[a] Molecular weight in PCL equivalent.

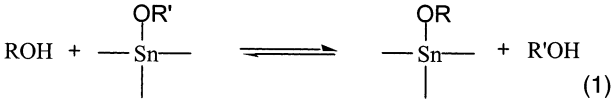
Table 3. Polymerization of ε-Caprolactone in the Presence of MMT-$(CH_2CH_2OH)_2$ ($[\mathrm{Monomer}]_0/[\mathrm{Bu_2Sn(OMe)_2}] = 300$; 24 h at Room Temperature)

samples	filler content (wt %)	conv (%)	$M_{n,th}$[a] (g mol^{-1})	M_n[b] (g mol^{-1})	M_w/M_n
PCL	0	96	17 100	21 000	2.05
NC3−1	1	91	13 700	16 000	1.95
NC3−3	3	95	11 200	13 500	1.80
NC3−5	5	87	8 800	9 000	1.65
NC3−10	10	82	5 600	4 500	1.55

[a] $M_{n,th} = [M]_0/[I] \times M_{CL} \times$ conversion, assuming that all the alkoxide groups of $Bu_2Sn(MeO)_2$ and the hydroxyl groups of MMT-$(CH_2CH_2OH)_2$ are active. [b] Molecular weight in PCL equivalent.

In contrast, Table 3 shows that when the modified silicate is MMT-$(CH_2CH_2OH)_2$, the number-average molecular weight M_n decreases with increasing clay content. This observation indicates that the hydroxyl functions act as co-initiator/chain transfer agents.

Indeed, the addition of an alcohol to tin alkoxide results in a rapid alkoxide−alcohol exchange as schematized by eq 1:[20]



$$\mathrm{ROH} + -\overset{\mathrm{OR'}}{\underset{|}{\overset{|}{\mathrm{Sn}}}}- \rightleftharpoons -\overset{\mathrm{OR}}{\underset{|}{\overset{|}{\mathrm{Sn}}}}- + \mathrm{R'OH} \qquad (1)$$

Therefore, the propagating species (metal alkoxide) are temporarily converted into dormant hydroxyls and vice versa. This equilibrium between active and dormant species (reversible chain transfer) contributes to the polymerization control. The final degree of polymerization (DP_n) is given by $DP_n = [M]_0/([I]_0 + [\text{transfer agent}]_0)$. Figure 1 illustrates how the experimental degree of polymerization changes with the $([CL]_0 - [CL])/(2[Sn] + [OH])$ molar ratio, i.e., with the total concentration of initiating groups. A linear relationship is observed with a slope of 1, which indicates that all the hydroxyl groups associated with the ammonium ions are active. Two types of polymer chains thus coexist, i.e., chains initiated by the methoxy groups of $Bu_2Sn(MeO)_2$ and chains initiated by the hydroxyl groups at the clay surface which participate in the reversible exchange with tin methoxides.

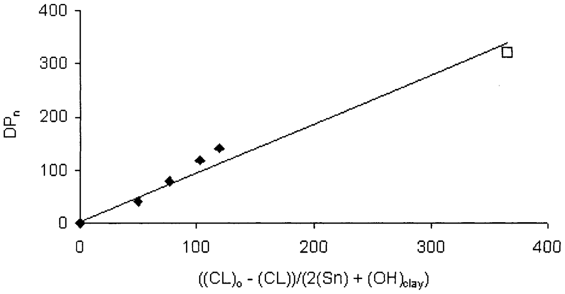


Figure 1. Dependence of the PCL polymerization degree (DP_n) on the $([CL]_0 - [CL])/(2[Sn] + [OH])$ ratio for nanocomposites prepared in the presence of various amounts of MMT-$(CH_2CH_2OH)_2$ (conditions: see Table 3). □ refers to an experiment in which the hydroxyl groups of the clay have been converted into alkoxides before polymerization.

Table 4. Polymerization of ε-Caprolactone in the Presence 3 wt % of MMT-$(CH_2CH_2OH)_2$ at Room Temperature

samples	polymerization time (h)	conv (%)	$M_{n,th}$[a] (g mol^{-1})	M_n[b] (g mol^{-1})	M_w/M_n
NC4−0.5h	0.5	<5			
NC4−1h	1	16	1900	2500	1.02
NC4−2h	2	72	8800	11000	1.50
NC4−24h	24	95	11200	13500	1.80

[a] $M_{n,th} = [M]_0/[I] \times M_{CL} \times$ conversion, assuming that all the alkoxide groups of $Bu_2Sn(MeO)_2$ and the hydroxyl groups of MMT-$(CH_2CH_2OH)_2$) are active. [b] Molecular weight in PCL equivalent.

It is also possible to convert quantitatively the hydroxyl groups at the clay surface into tin alkoxides by reaction with $Bu_2Sn(OMe)_2$ in toluene at room temperature. The alcohol/alkoxide equilibrium is totally shifted toward alkoxide by distilling off the azeotropic mixture formed by toluene with the released methanol. The surface-treated clay was dispersed in ε-caprolactone at room temperature. Polymerization is very fast as shown by the reaction medium which turns rapidly into a gel and ultimately into a solid as result of crystallization of the PCL chains. After 24 h at room temperature, the polyester was recovered by extraction of polymer from clay with a yield of 96%. The number-average molecular weight of the PCL chains is in good agreement with the expected value on the assumption of a quantitative initiation by the surface-hydroxyl groups ($M_{n,exp}$ = 37 000 g mol^{-1} compared to $M_{n,theor}$ = 41 500 g mol^{-1}).

A decrease in the polydispersity index is observed when the content of the MMT-$(CH_2CH_2OH)_2$ modified clay is increased. The confinement of the propagating chains within the clay interlayers is thought to impose limitations on the mobility of the tethered PCL chains, which are less prone to participate to transesterification reactions. This protective effect is lost when the chains are long enough to come out of the galleries.

During the CL polymerization in the presence of 3 wt % of MMT-$(CH_2CH_2{-}OH)_2$, PCL molecular weight is followed as a function of polymerization time (Table 4). Figure 2 shows a linear increase of M_n with monomer conversion in agreement with the control of the CL polymerization promoted by tin(IV) alkoxides. The molecular weight distribution is very narrow at the first stage of polymerization (1.02 for 16% monomer conversion) and gradually broadens with increasing monomer conversion. This is likely due to the increasing extent of intermolecular transesterification reactions.

Because the hydroxyl groups attached to the alkylammonium cations in the clay galleries are potential binding sites for the initiators, the average length of the PCL chains tethered onto the organo-modified layered silicates can be predicted from the clay content with respect to the monomer. Another way to control the

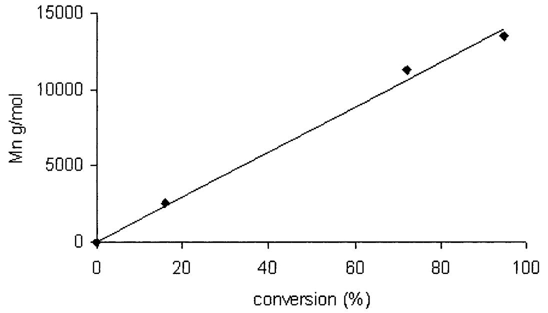


Figure 2. Dependence of the PCL molecular weight on monomer conversion for nanocomposites containing 3 wt % of MMT-$(CH_2CH_2OH)_2$ (conditions: see Table 4).

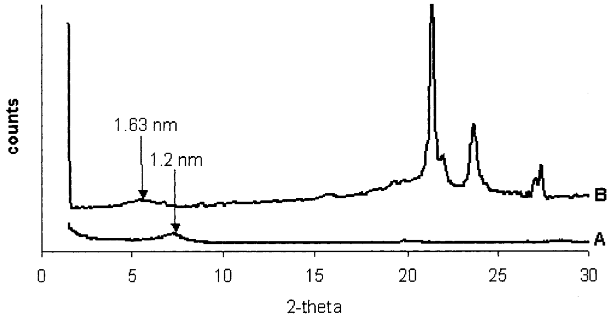


Figure 3. XRD profiles for (A) native montmorillonite (MMT-Na) and for (B) a PCL nanocomposite containing 3 wt % of this clay (sample NC1−3, see Table 1).

molecular weight of PCL while keeping the clay content constant would be to use the montmorillonite modified by a mixture of nonfunctional alkylammonium and hydroxyl-bearing ammonium cations. At constant monomer/clay ratio, the molecular weight of PCL is expected to decrease whenever the relative content of hydroxyl groups in the clay is increased. This strategy will be the topic of a forthcoming paper.[21]

Morphological Characterization. The montmorillonite dispersion within the aliphatic polyester matrix has been analyzed by both X-ray diffraction (XRD) and transmission electronic microscopy (TEM). Figure 3 shows the XRD pattern for the composite that contains 3 wt % of nonmodified montmorillonite (MMT-Na) (sample NC1−3). The XRD pattern for the pristine MMT-Na filler, i.e., Cloisite-Na^+, is also shown for comparison. In addition to the diffraction peaks characteristic of the semicrystalline PCL matrix ($20° < 2\theta < 30°$), the interlayer spacing is increased from 1.2 nm for the original clay to 1.63 nm for the 3 wt % PCL−clay nanocomposite, which attests to the formation of an intercalated structure. Only a few examples are known for nanocomposites directly prepared from nonmodified silicates.[22,23] Giannelis et al.[24] prepared poly(ethylene oxide) nanocomposites by solution and melt intercalation and explained that polymer chains were able to replace weakly adsorbed water molecules in the space between hydrated exchangeable cations. PCL chains thus appear to behave similarly when intercalated ϵ-caprolactone is polymerized in situ. Modeling of the lactone (polyester)/sodium cations interactions within the silicate galleries is under current investigation.

In nanocomposites prepared from the MMT-C_8H_{17} modified clay (samples NC2−3), the interlayer distance of the silicate is shifted from 1.86 nm for the organo-modified clay to 2.68 nm (Figure 4). This significant increase of the interlayer distance is indicative of formation of an intercalated structure.

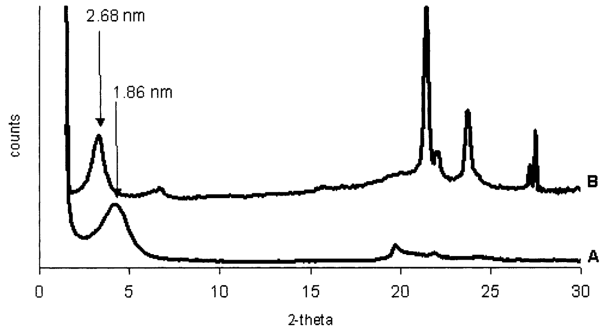


Figure 4. XRD profiles for (A) the montmorillonite modified by dimethyl 2-ethylhexyl (hydrogenated tallow alkyl) ammonium (MMT-C_8H_{17}) and for (B) a PCL nanocomposite containing 3 wt % of this modified clay (sample NC2−3; see Table 2).

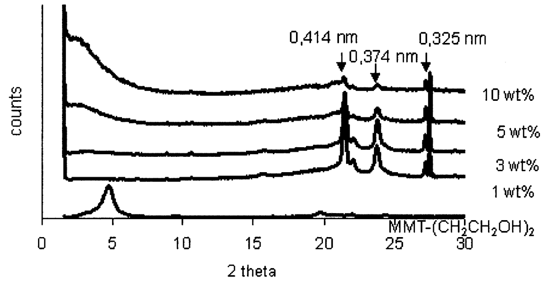


Figure 5. XRD profiles for the montmorillonite modified by methyl bis(2-hydroxyethyl) (hydrogenated tallow alkyl) ammonium (MMT-$(CH_2CH_2OH)_2$) and for PCL nanocomposites containing 1, 3, 5, and 10 wt % of this modified montmorillonite (see Table 3).

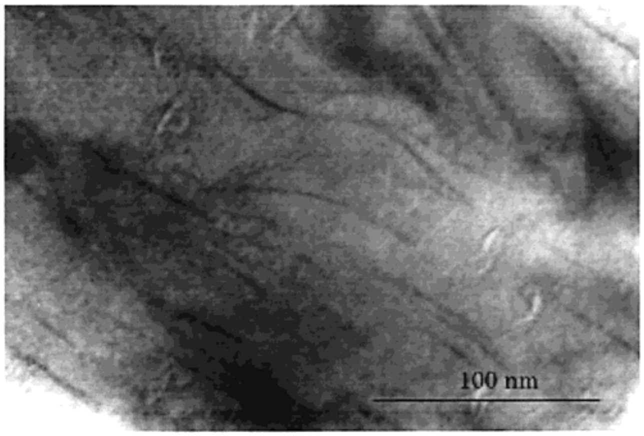


Figure 6. TEM image for a PCL nanocomposite containing 3 wt % of organo-modified montmorillonite MMT-$(CH_2CH_2OH)_2$ (sample NC3−3 in Table 3).

XRD analysis of nanocomposites that contain 3 wt % of the MMT-$(CH_2CH_2OH)_2$ hydroxyl-functionalized clay is consistent with an exfoliated structure. Indeed, no diffraction peak is observed as illustrated by Figure 5 for the NC3−3 sample. XRD patterns for different clay contents are also shown in Figure 5. For high clay content (10 wt %), a broad peak in the small-angle region might indicate the formation of partially exfoliated/partially intercalated structures. A decrease in the PCL crystallinity with increasing silicate content is assessed by the much lower intensity of the PCL characteristic diffraction peaks at 0.414, 0.374, and 0.325 nm. These observations are in agreement with data previously published by Giannelis et al.[14]

The exfoliated structure has been confirmed by TEM, as illustrated by Figure 6 that shows a typical TEM

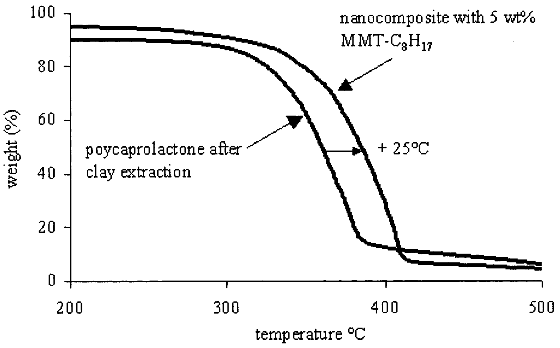


Figure 7. Temperature dependence of weight loss for a PCL nanocomposite containing 5 wt % (relative to inorganics) of MMT-C_8H_{17} (NC2−3 in Table 2) and for the poly(ϵ-caprolactone) matrix (heating rate: 20 °C/min, under an air flow).

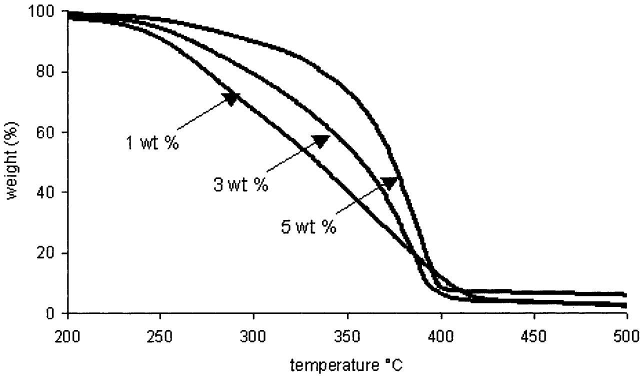


Figure 8. Temperature dependence of weight loss for nanocomposites containing 1, 3, and 5 wt % (relative to inorganics) of MMT-C_8H_{17} (heating rate: 20 °C/min, under an air flow).

micrograph for the nanocomposite containing 3 wt % of the MMT-$(CH_2CH_2OH)_2$ organo-modified clay (sample NC3−3; Table 3).

Individual clay platelets are randomly distributed in the poly(ϵ-caprolactone) matrix. Absence of aggregates confirms the high exfoliation of the layered silicate. Initiation of the ϵ-caprolactone polymerization from the clay surface accounts for the tethering of the chains onto the clay surface and for the clay delamination. As also reported elsewhere,[10,25−27] grafted and/or tethered polymer chains have a key role in preventing the exfoliated silicate layers from reaggregating during postthermal and processing treatments of the composites.

Thermogravimetric Analysis. Thermal degradation behavior of nanocomposites was studied by thermogravimetric analysis (TGA) under an air flow at a heating rate of 20 °C/min. Both intercalated and exfoliated nanocomposites are degraded at higher temperatures compared to PCL and PCL/clay microcomposites. Thermograms for nanocomposites containing 5 wt % MMT-C_8H_{17} (sample NC2−5 in Table 2) and for the PCL chains (M_n = 17 500 g mol^{-1}) recovered after clay extraction are compared in Figure 7. The temperature at which 50 wt % loss is noted is higher by 25 °C for the nanocomposite compared to PCL. This shift to higher temperature might be explained by a lower permeability/diffusivity of oxygen and volatile degradation products through the sample as result of barrier properties imparted by highly anisotropic nanoparticles and to char formation.[1]

Resistance to thermal degradation is improved when the clay content is increased up to 5 wt %. Beyond that content, the effect levels off independently of the clay.

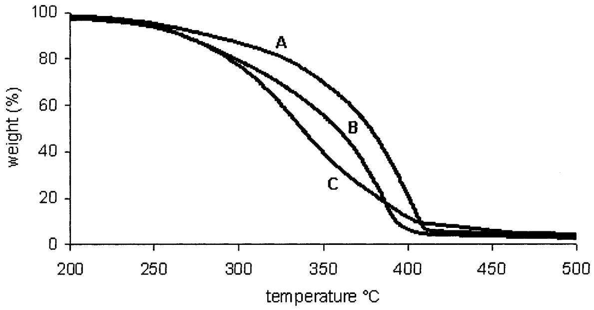
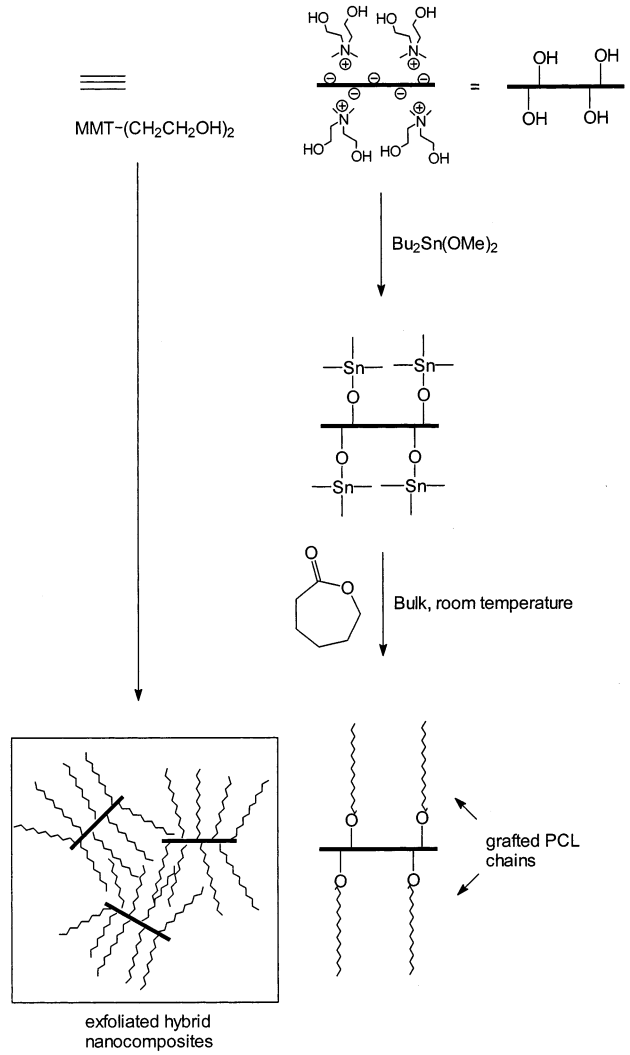


Figure 9. Temperature dependence of weight loss for nanocomposites containing 3 wt % (relative to inorganics) of (A) MMT-$(CH_2CH_2OH)_2$, (B) MMT-C_8H_{17}, and (C) MMT-Na (heating rate: 20 °C/min, under air flow).

Scheme 1



As an example, Figure 8 shows the thermograms for nanocomposites that contain 1, 3, and 5 wt % of MMT-C_8H_{17}.

Finally, Figure 9 compares the degradation profile for PCL nanocomposites that contain 3 wt % of MMT-Na, MMT-C_8H_{17}, and MMT-$(CH_2CH_2OH)_2$. The lower thermal stability is noted for the natural sodium montmorillonite. When nanocomposites containing the organo-modified clays are compared, the exfoliated nanocomposites prepared in the presence of MMT-$(CH_2CH_2OH)_2$ are degraded at much higher temperatures.

This difference in thermal stability cannot be attributed to the PCL molecular weight which is comparable for the three samples (M_n of ca. 15 000 g mol^{-1}). Difference in morphology as previously observed by X-ray diffraction and by TEM would be a reasonable explanation. The complete delamination of the clay platelets whose the surface is grafted by PCL chains is at least partly responsible for degradation of MMT-($CH_2CH_2OH)_2$ containing nanocomposites at higher temperature.

Conclusion

PCL nanocomposites have been prepared by polymerization of ϵ-caprolactone initiated by dibutyltin dimethoxide in the presence of either sodium montmorillonite or two montmorillonites surface-modified by dimethyl 2-ethylhexyl (hydrogenated tallow alkyl) and methyl bis(2-hydroxyethyl) (hydrogenated tallow alkyl) ammonium cations, respectively. Intercalated structures are formed in the presence of natural sodium montmorillonite as assessed by XRD analysis. In contrast, montmorillonite surface-modified by ammonium cations bearing hydroxyl groups is exfoliated by the in-situ formed PCL chains (see Scheme 1). The lactone polymerization is initiated by the hydroxyl groups available at the clay surface which are activated by tin(IV) dialkoxide. Size exclusion chromatography of PCL shows that the chain length is controlled by the amount of this reactive clay with respect to the monomer. PCL/clay nanocomposites are degraded at higher temperature than the unfilled polymer. The grafting of the polyester chains from the filler surface improves further the thermal stability compared to montmorillonite modified by nonfunctional ammonium cations.

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