Macromol. Symp. ***183,*** *95–102 (2002)*

Layered Silicate/Polyester Nanohybrids by Controlled Ring-Opening Polymerization

Bénédicte Lepoittevin[1,3], *Nadège Pantoustier*[1,3], *Michael Alexandre*[1,3], *Cédric Calberg*[2,3], *Robert Jérôme*[2,3], *and Philippe Dubois*[1,3]*

[1]Laboratory of Polymeric and Composite Materials (LPMC), University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium
[2]Center for Education and Research on Macromolecules (CERM), B6, Sart-Tilman, 4000 Liège, Belgium
[3]Inter-university Research Center in Polymeric Materials Science (CRESMAP), Belgium

Summary: In this study, layered silicate/aliphatic polyester nanohybrids were synthesized by ring-opening polymerization of ε-caprolactone as promoted by the so-called coordination-insertion mechanism. These nanocomposites were formed in presence of montmorillonite surface-modified by ammonium cations bearing hydroxyl group(s), such as bis(2-hydroxyethyl)methyl (hydrogenated tallow alkyl) ammonium. The lactone polymerization could be initiated by all the hydroxyl functions available at the clay surface, after activation into either tin(II) or Al(III) alkoxide active species. Hybrid nanocomposites were accordingly generated through the covalent grafting of every polyester chain onto the filler surface. Surface-grafted polycaprolactone (PCL) chains were untied and isolated by ionic exchange reaction with LiCl in THF solution and molar masses were measured by size exclusion chromatography. The PCL molar masses could be controlled and readily tuned by the content of hydroxyl groups available at the clay surface. Interestingly, initiation reaction by aluminum trialkoxide active species yielded grafted PCL chains characterized by very narrow molecular weight distribution (M_w/M_n~1.2). These polyester-grafted layered silicate nanohybrids displayed complete exfoliation of silicate sheets as shown by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

Introduction

Polymer/clay nanocomposites represent a new class of materials that display improved mechanical, thermal and chemical properties, even at very low clay content (≈ 3 wt%), by comparison to more conventional polymer microcomposites filled with more than 20 wt% particles.[1] Poly(ε-caprolactone) layered silicate nanocomposites present a particular interest because of the biocompatibility and biodegradability of the aliphatic polyester matrix and the

CCC 1022-1360/00/$ 17.50+.50/0

high property enhancements that could result from the silicate dispersion. Interestingly, biodegradable poly(ε-caprolactone) nanocomposite can be obtained by *in-situ* ring-opening polymerization of ε–caprolactone in the presence of organophilic clay such as organo-modified montmorillonite.[2,3] By dispersing these layered nanoparticles within the aliphatic polyester matrix, two types of nanocomposite structures can be obtained. Intercalated structures are formed when a single polymer monolayer is sandwiched between the clay layers with a corresponding small increase in the interlayer spacing of a few nanometers.[4] In the exfoliated structure, the silicate sheets are individually delaminated and fully dispersed in the continuous polymer matrix.[5] The alkaline cations located in the gallery between two successive layers are usually exchanged by substitution reaction with onium ions, e.g. alkylammonium cations. Such a cation exchange reaction is required in order to render the platelets surface more organophilic and to favor the insertion of the polyester chains within the galleries.[1]

This contribution aims at reporting on the synthesis of poly(ε-caprolactone)-grafted clay nanohybrids by *in situ* intercalative polymerization directly initiated by hydroxyl functions available at the surface of the organo-modified montmorillonite. For so doing, the surface-anchored alcohols have been adequately activated in tin(II) or Al(III) alkoxide active species. The PCL molar mass can be readily tailored by the hydroxyl concentration. The nanocomposites have been further characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM).

Experimental

Materials : ε-Caprolactone (Fluka) was dried over CaH_2 and distilled under reduced pressure prior to use. Triethylaluminum ($AlEt_3$) and bis(2-ethylhexanoic acid) tin(II) salt (tin(octoate); $Sn(Oct)_2$) were purchased from Fluka and Goldschmidt, respectively, and diluted with dry toluene. $AlEt_3$ and $Sn(Oct)_2$ solutions were stored in glass ampoules under nitrogen atmosphere. Cloisite® 30B ($MMT\text{-}(CH_2CH_2OH)_2$), provided by Southern Clay Products (Texas, USA), is a montmorillonite organically-modified with bis(2-hydroxyethyl) methyl (hydrogenated tallow alkyl) ammonium cations. Montmorillonites organo-modified with various contents in monohydroxy-functionalized ammonium cations were also synthesized. Actually a purified natural sodium montmorillonite with a cation exchange capacity (CEC) of 92 meq/100 g (Cloisite® Na^+ from Southern Clay Products) was intercalated by given mixtures of monohydroxy-functionalized ammonium cation, $(CH_3)_2(C_{16}H_{33})N^+(CH_2CH_2OH)$, together with non-functionalized ammonium cation, $(CH_3)_3N^+(C_{16}H_{33})$. This co-intercalation with various monohydroxy-functionalized ammonium relative contents equal to 0, 25, 50, 75 and 100% (leading to organo-clays coined MMT-$(CH_2CH_2OH)_x$ with x = 0, 25, 50, 75 and 100), was performed in water at 85°C by ionic exchange reaction of the interlayer sodium cations with the corresponding ammonium iodide salts. The modified clays were extensively washed with hot water and isolated by freeze-drying. The intercalated ammonium composition strictly corresponds to the initial ammonium composition as attested by NMR analysis of the remaining aqueous solutions after clay intercalation. Intercalation was evidenced by XRD analysis with a basal spacing increasing from 1.21 nm for Cloisite® Na^+ to ca. 1.90 nm for the different organo-clays. The organic content of all these organo-modified montmorillonites was close to 21 wt% as determined by TGA.

Polymerization procedure : Before polymerization, the organo-modified montmorillonites were dried in a ventilated oven at 70°C for one night. Then, in a polymerization tube, the desired amount of layered silicate was further dried under vacuum at 70°C during 3h. A given amount of ε-caprolactone was then added under nitrogen and the reaction medium was stirred at room temperature for 1h. A predetermined volume of $AlEt_3$ (or $Sn(Oct)_2$) solution was added to the suspension and the polymerization was allowed to proceed for 24h at room temperature (for Al alkoxides active species) or at 100°C (for catalysis by $Sn(Oct)_2$). The inorganic content of each composite was checked by TGA. A reverse ion-exchange reaction was used to isolate the PCL chains from the inorganic fraction of the nanocomposite. A colloidal suspension was obtained by stirring the nanocomposite in THF at room temperature for 2h. The nanocomposite suspension was reacted with a solution of 1 wt% of LiCl in THF and left to stir at room temperature for 48h. The resulting solution was centrifuged. The supernatant was decanted and the solid phase was washed with THF before precipitation of PCL chains from petroleum ether. The white powder was dried in vacuum at 50°C. The absence of residual PCL in the silicate was checked by FT-IR (absence of PCL carbonyl absorption band at 1727 cm^{-1}).

Characterization : Size exclusion chromatography measurements were carried out in THF at 35°C using a Polymer Laboratory (PL) liquid chromatograph with a refractive index detector and a set of three columns: a guard column PLgel 10 μm (50*7.5 mm) and two columns PLgel mixed-B 10 μm (300*7.5 mm). Molar masses were calculated by reference to a PS standard calibration curve, using the Mark-Houwink relationship $[\eta] = K.M^a$ (K_{PS} = 1.25 10^{-4} dl/g, a_{PS} = 0.707, K_{PCL} = 1.09 10^{-3} dl/g, a_{PCL} = 0.600). X-ray diffraction (XRD) patterns were obtained from a Siemens D5000 diffractometer with Cu-K_α radiation. Measurements were carried out on sheets obtained by hot-pressing the samples at 100°C. XRD data were collected by an X-ray generator equipment (λ = 0.15406 nm) between 1.5 and 30° by step of 0.04°. TEM observations were performed with a Philips CM100 apparatus using an acceleration voltage of 100 kV. Ultrathin sections of the composites with a thickness of approximately 80 nm 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.

Results and Discussion

The nanocomposites were first produced by ε-caprolactone (CL) polymerization in bulk and in the presence of an organo-modified silicate exchanged by a functional ammonium bearing two hydroxyl groups (MMT-$(CH_2CH_2OH)_2$). Different nanocomposites were prepared in order to reach 1, 3, 5 and 10 wt% of inorganic fraction (Table 1). The polymerization was initiated by the surface hydroxyl groups previously activated in diethylaluminum monoalkoxides by reaction with an equivalent amount of triethylaluminum. Such aluminum alkoxides are known for their high efficiency in promoting controlled ring-opening polymerization of lactones according to a "coordination-insertion" mechanism.[6] Aluminum alkoxide initiated polymerizations proceed through the insertion of the monomer into the "Al-O" bond of the initiator via a selective acyl-oxygen cleavage of the lactone ring. Therefore every growing polyester is end-capped by the alkoxide residue of the initiator attached through an ester linkage. As expected and confirming selective initiation by the hydroxyl functions spread all over the organo-clay surface, the PCL chains proved to be quantitatively anchored at the silicate surface leading to very rapid gelation of the reaction medium. Surface-grafted PCL chains could only be untied and isolated by ionic exchange reaction with lithium chloride in THF solution (see experimental).

Table 1 : Polymerization of ε-caprolactone in presence of MMT-$(CH_2CH_2OH)_2$ and promoted by *in situ* formed aluminum alkoxides ($[AlEt_3]=[OH]$; room temperature; 24 h). Effect of the clay content.

Clay (wt-%)	Conv. (%)	M_n	M_w/M_n	$M_{n,theor}$ [a)]
1	92	85,300	2.0	116,000
3	91	41,700	1.8	39,500
5	91	27,400	1.9	22,700
10	72	6,000	- [b)]	8,200

a) [CL]/[OH] x 114,14; b) bimodal molecular weight distribution

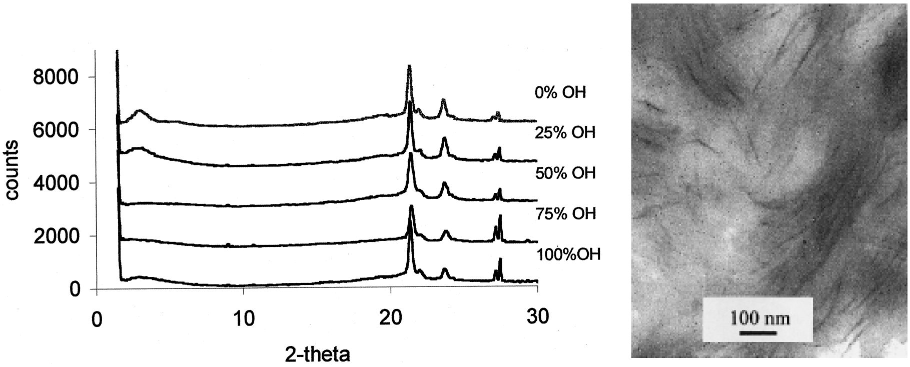
A continuous decrease of molar masses with clay content is measured by size exclusion chromatography (Table 1). Furthermore, the PCL molecular weights are in good agreement with the theoretical values expected from the initial monomer-to-alkoxide molar ratio. Such a behavior confirms that all polyesters chains are initiated by the hydroxyl functions available at the clay surface and grow away from every silicate layer. Thus the average length of the PCL chains therefore grafted onto the organo-modified layered silicates can be predetermined by taking into account the amount of the surface hydroxyl functions, that is to say the relative content in clay particles. The question that may be addressed at this stage is to know whether the molecular weight of the grafted polyester chains can be also predetermined and adjusted in the presence of a constant silicate content. For that purpose, montmorillonite has been co-intercalated by different mixtures of non-functionalized alkyl ammonium, $(CH_3)_3N^+(C_{16}H_{33})$, and monohydroxyl-functionalized ammonium cations, $(CH_3)_2(C_{16}H_{33})N^+(CH_2CH_2OH)$ (see experimental). Layered silicates surface-modified with relative molar contents in monohydroxy-functionalized ammonium equal to 0, 25, 50, 75 and 100% (MMT-$(CH_2CH_2OH)_x$) have been prepared and dispersed in liquid ε-caprolactone. The "coordination-insertion" polymerization has been catalyzed by $Sn(Oct)_2$ at 100°C for 24 h (Table 2). At a constant filling content (3 wt% inorganics), the molar mass of PCL chains decreases with the relative content of hydroxyl groups available on the clay surface, confirming the initiation of the polymerization by the surface hydroxyl groups, that time activated into Sn(II) alkoxides by reaction with $Sn(Oct)_2$.[7]

Table 2 : Polymerization of ε-caprolactone in presence of $MMT\text{-}(CH_2CH_2OH)_x$ (3 wt% inorganics) and catalyzed by $Sn(Oct)_2$ at 100°C for 24 h ([OH]/[Sn]=300). Effect of the relative content in surface hydroxyl functions.

$MMT\text{-}(CH_2CH_2OH)_x$ (OH content, x %)	Conv. %	M_n	M_w/M_n
100	93	28,200	1.8
75	96	36,300	1.8
50	97	47,100	1.9
25	98	53,700	1.9
0	98	56,200	2.0

The initiation reaction promoted by the surface hydroxyl groups and the concomitant grafting of polyester chains onto the organo-clay have a strong effect on the morphological structure of the PCL layered silicate nanocomposites. Indeed the extent of silicate exfoliation depends on their surface OH content as evidenced by both XRD and TEM. For instance, XRD patterns of PCL filled with $MMT\text{-}(CH_2CH_2OH)_x$ (3 wt% inorganics) show the disappearance of the diffraction peak at very low 2-theta angle (that is the characteristic feature of the intercalated structure) by increasing the hydroxyl content spread onto the layered silicates (Figure 1).

Figure 1 a) XRD patterns of the PCL grafted $MMT\text{-}(CH_2CH_2OH)_x$ samples prepared in Table 2. Effect of the relative content in surface hydroxyl functions on the extent of exfoliation, b) TEM of fully exfoliated PCL-grafted $MMT\text{-}(CH_2CH_2OH)_{100\%}$



It comes out that intensive exfoliation occurs only if the silicate sheets are surface-modified by a OH content higher than 25 %, i.e. for MMT-$(CH_2CH_2OH)_x$ with x > 25%. Below this threshold, partially intercalated/partially exfoliated nanocomposites are recovered.[1] This observation is of key importance since the properties improvement usually reported for polymer layered silicate nanocomposites, such as material stiffness, thermal stability or flame retardant behavior, strictly depends on the extent of exfoliation. Such an effect in case of PCL-based nanocomposites has been discussed elsewhere.[4,5]

The coordination-insertion polymerization of ε-caprolactone thus allows to control both the polyester grafting reaction and the molecular weight of the surface grafted PCL chains. However the so far obtained polyesters are characterized by a broad molecular weight distribution (MWD) as a result of the occurrence of transesterification reactions. Interestingly enough, an additional control over the MWD have been achieved by activating the surface hydroxyl groups into aluminum trialkoxide active species. For instance, the hydroxyl groups of MMT-$(CH_2CH_2OH)_x$ (with x = 100%) have been transformed in aluminum trialkoxides by reaction with $AlEt_3$ ([OH]/[Al]=3). The surface activated organo-clay has been dispersed in ε-caprolactone (3 wt% inorganics) and the polymerization has been carried out in bulk at room temperature for 24 h. Again the grafted PCL chains could only be isolated by ionic exchange reaction with lithium chloride in THF solution. Confirming the previously discussed control, there is again an excellent agreement between the theoretical molecular weight (M_n = 19,800) and the M_n value determined by SEC, i.e. 21,000. It is worth pointing out the symmetrical and narrow molecular weight distribution of the PCL chains with a polydispersity index as low as 1.2. It does mean that all molecular parameters of these polyester/silicate nanohybrids are under control : inorganic content, extent of dispersion/exfoliation, quantitative surface grafting, number of polyester chains per clay surface as well as the polymer chain length and molecular weight distribution.

Conclusions

This study has emphasized that polyester-grafted layered silicate nanohybrids can be synthesized by intercalative *in situ* ring-opening polymerization of ε-caprolactone via a coordination-insertion mechanism. The lactone polymerization is initiated selectively and quantitatively by all the hydroxyl functions fixed on ammonium cations organo-modifying the nanoclay surface. The hydroxyl groups are accordingly activated in metal alkoxides active species and more particularly, initiation by aluminum trialkoxides allows to perfectly well control the polymerization reaction. The silicate sheets can be surface-grafted by predetermined number of PCL chains of predictable molecular weight and narrow molecular weight distribution. These layered silicate/aliphatic polyester nanohybrids display complete exfoliation of silicate sheets as shown by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Consequently these materials exhibit much higher thermal stability than unfilled PCL or the corresponding simply intercalated nanocomposites (without polyester chain grafting) as will be reported in a forthcoming paper.

Acknowledgements

LPCM is much indebted to the *Région Wallonne* and the *Fonds Social Européen* for support in the frame of *Objectif 1-Hainaut : Materia Nova*. XRD analyses have been performed in the General Chemistry and Physics Chemistry Department at University of Liège. LPCM and CERM are grateful to the *Région Wallonne* for support in the frame of the W.D.U. program : *TECMAVER*, including a grant to N.P. CERM thanks the "*Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles*" for support (PAI 4/11).

References

(1) Alexandre M., Dubois Ph., Mater. Sci. Eng., **R28**, 1 (2000)
(2) Messersmith P.B., Giannelis E.P., Chem. Mater., **5**, 1064 (1993); J. Polym. Sci., Part A : Polym. Chem., **33**, 1047 (1995)
(3) Lepoittevin B., Devalckenaere M., Alexandre M., Pantoustier N., Calberg C., Jérôme R., Dubois Ph., Macromolecules, Submitted for publication
(4) Pantoustier N., Alexandre M., Degée Ph., Calberg C., Jérôme R., Henrist C., Cloots R., Rulmont A., Dubois Ph., e-Polymer, **9**, 1 (2001)
(5) Pantoustier N., Lepoittevin B., Alexandre M., Kubies D., Calberg C., Jérôme R., Dubois Ph., Polym. Eng. Sci., accepted for publication (2001)
(6) Mecerreyes D., Jérôme R., Dubois Ph., Adv. Polym. Sci., Springer Ed., **147**, 1 (1999)
(7) Kowalski A., Duda A., Penczek St., Macromolecules, **33**, 689 and 7359 (2000)