How can Nanohybrids Enhance Polyester/Sepiolite Nanocomposite Properties?

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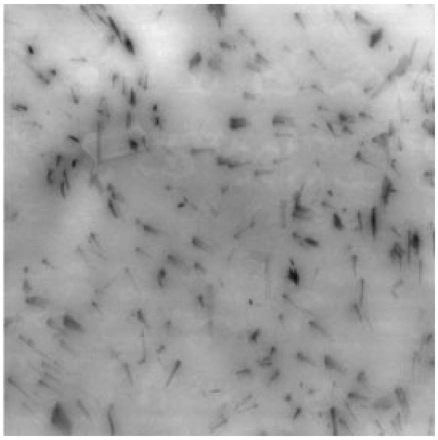
PCL/sepiolite (nano)composites are prepared by melt blending in a twin-screw mini-extruder, and PCL/sepiolite nanohybrids are synthesized by ROP of ε-CL. The nanohybrids have been used as masterbatches and dispersed in a commercial PCL matrix. Composites with 3 wt.-% nanofiller were prepared and characterized thermally, mechanically, and morphologically. Sepiolite addition has a profound effect on the mechanical properties of the PCL/sepiolite nanocomposites. Sepiolite disperses well in PCL, which leads to a significant increase in Young's modulus. The use of a PCL nanohybrid as masterbatch further improves the stiffness but also the toughness of the material in the elastic range.



Introduction

Polymers filled with inorganic nanoparticles have been widely studied during the last few years. The use of nanofillers in polymer matrices has opened the way to new properties and, therefore, nanocomposites have attracted considerable attention. Polymer nanocomposites are very attractive because a small amount of filler can lead to a large improvement in terms of thermal, mechanical, or barrier properties of the polymer matrix. The properties of these nanomaterials strongly depend on the intrinsic properties of the constituents, the amount of nanofiller, as well as the dispersion state. The effectiveness of a filler on material properties depends on the filler characteristics such as size and shape of the particles.[1] Indeed, the effect on the composite properties could be quite different for highly anisotropic particles such as needles or nanoplatelets than for spherical fillers. Amongst all the used nanofillers, layered silicates (such as montmorillonite are probably the most reported in the literature. The different techniques used to obtain polymer-layered silicate nanocomposites and the improved properties that the materials can display have been reported in several reviews.[2–7] Acicular (needle-like) type nanofillers such as sepiolite or palygorskite (attapulgite) have received much less attention than layered silicates for the preparation of nanocomposite materials.

Sepiolite is a magnesium silicate of fibrous morphology, with fine microporous channels of dimensions $0.37 \times 1.06\ \text{nm}^2$ running parallel to the length of the fibers. The

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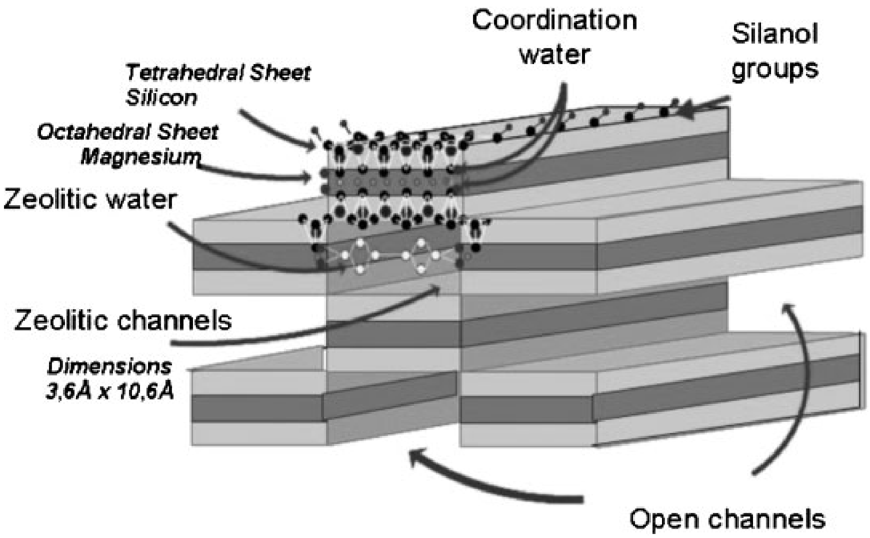

Figure 1. Structure of sepiolite.

size of the fibers varies widely, but in most cases they are 10–5 000 nm long, 10–30 nm wide, and 5–10 nm thick (Figure 1).

The structural characteristics of sepiolite, its fibrous nature, and the presence of small channels are responsible for its absorption and adsorption properties and the derived applications. Indeed, sepiolite is widely used as a bleaching agent, filter aid, industrial absorbent, and catalyst carrier. Sepiolite has the structural formula $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4 \cdot 8H_2O$. The formula is written as such to indicate the two types of water present (Figure 1). Absorbed water is bonded by hydrogen bonds at the external surface or within the channels, called zeolitic water and crystal water, respectively. The hydrogen bonds complete the coordination of the octahedral cations at the edges of the ribbons. A third type of water can be identified in the sepiolite structure, which consists of 'constitution water' or hydroxy groups.

As far as sepiolite/polymer nanocomposites are concerned, only a few studies have been reported in the literature. For instance, Li et al. reported in 2001 on the preparation of palygorskite/polyethylene nanocomposites by in-situ polymerization.[8,9] Soon after, the same group dealt with the thermal, mechanical, and morphological properties of this family of palygorskite/polyethylene nanocomposites. These properties were compared to those of both nanocomposites prepared by conventional melt blending[10] and neat polyethylene matrix.[11] Quite simultaneously, Acosta et al. studied sepiolite as a reinforcement in hydrogenated poly(styrene butadiene) block copolymers for potential applications in polymer fuel cells.[12] More recently, sepiolite nanofibers have been considered for reinforcing elastomers,[13] natural rubber,[14] and silicone.[15] Finally, the beneficial effect of organo-modified attapulgite on the thermal and mechanical properties of poly(propylene) nanocomposites has also been investigated by Sheng and Wang.[16]

This contribution aims to report on the dispersion of sepiolite in a biodegradable aliphatic polyester matrix, i.e., a poly(ε-caprolactone) (PCL) matrix. PCL is well known for its high ductility but also for a rather low intrinsic rigidity. Therefore, it is expected that finely dispersing such a needle-like nanoclay as sepiolite within this polyester could allow a good stiffness/toughness performance to be attained. Accordingly the (nano)composites were prepared in a twin screw mini-extruder using three kinds of sepiolite samples : i) as received natural sepiolite, ii) the same sepiolite but previously organo-modified by γ-aminopropyltriethoxysilane (APTES), and iii) PCL-surface-grafted sepiolite nanohybrids as synthesized by ring-opening polymerization (ROP) of ε-caprolactone (CL) initiated from the aminopropyl-modified sepiolite and catalyzed by tin(II) bis(2-ethylhexanoate) ($Sn(Oct)_2$). These nanohybrids (highly filled with inorganics) were used as 'masterbatches' and dispersed in a neat commercial PCL matrix before studying their thermal, mechanical, and morphological properties.

Experimental Part

Materials

Commercial grade PCL ($\overline{M}_n = 50\,000\ g \cdot mol^{-1}$) was supplied by Solvay (Belgium) under the trade name CAPA6500. Sepiolite was supplied by TOLSA (Spain) and used as received. CL (99%, Acros) was dried for 48 h over calcium hydride and distilled under reduced pressure. Toluene (p.a., Labscan) was dried over calcium hydride and distilled. Tin(II) bis(2-ethylhexanoate) ($Sn(Oct)_2$, 95%, Aldrich) was used as received without any further purification. APTES from ABCR Gelest was used as received.

Surface Modification of Sepiolite

Natural sepiolite supplied by TOLSA was amino-functionalized following a reported procedure.[17] Sepiolite was dried under vacuum at 100 °C for 48 h before use. Typically, one gram of sepiolite and gradual amounts of APTES were dispersed into 50 mL of dried toluene under vigorous stirring and the mixture was refluxed overnight. After cooling to room temperature, the aminopropyl-modified sepiolite (sep-NH_2) was filtered off and thereafter thoroughly washed with toluene using a Soxhlet apparatus for at least 48 h. The aminopropyl-functionalized sepiolite was dried under vacuum to constant weight. The content of anchored amine groups was determined using a reported procedure.[18] Picric acid was reacted with the aminopropyl-functionalized sepiolite and then displaced by ethyldiisopropylamine, and the colored picrate formed was titrated by UV-vis spectrophotometry.

Nanohybrid Synthesis

In a typical experiment, dried and distilled CL was introduced into a previously flame-dried flask equipped with a three-way stopcock and that contained the amino-modified sepiolite previously dried overnight at 100 °C. The required amount of $Sn(Oct)_2$ in toluene solution was then added. The reaction was run at 100 °C for a desired polymerization time. The crude sepiolite/PCL nanohybrid (sep-PCL) was then recovered by dilution with toluene followed by precipitation from heptane to remove the unreacted CL monomer. The crude material was dried at 40 °C until constant weight and the monomer conversion was estimated by thermogravimetric analysis (TGA). Finally, the non-grafted PCL chains were removed from the nanohybrid by selective solubilization in toluene using a Soxhlet apparatus for at least 48 h. The grafting efficiency, i.e., the percentage of grafted PCL was calculated from the inorganic content in the nanohybrid as determined by TGA.

Preparation of Nanocomposites

PCL/sepiolite nanocomposites were prepared by melt blending CAPA6500 with sepiolite (as received, amino-modified, or sep-PCL nanohybrid) by using a twin screw mini-extruder ThermoHaake MiniLab for 10 min at 80 °C. The collected material was compression-molded with an AGILA PE 20 hydraulic press by hot pressing at 80 °C under atmospheric pressure for about 10 min, under 50 bars for 2 min 30 s after three degassing steps, followed by cold pressing at 15 °C under 100 bars for 5 min.

Characterization

Transmission electron microscopy (TEM) images were obtained with a Philips CM200 apparatus using an accelerator voltage of 120 kV. Nanocomposite samples were 70 nm thick and prepared from 3 mm hot-pressed plates with a LEICA Ultracut UCT ultracryomicrotome cutting at −100 °C.

Morphology of the composites was analyzed by TEM using a Philips CM200 microscope. TGA analysis was performed under air or under He flow at 20 °C · min^{-1} from room temperature to 800 °C using a TA Instrument Q50 thermogravimetric analyzer. Tensile testing was performed at 20 °C at a constant deformation rate of 50 mm · min^{-1} on a Lloyd LR10K tester using dumbbell-shaped specimens prepared from compression molded samples according to the ASTM638 type V norm. Tensile data were the average of five independent measurements and the relative error was estimated to be equal to ±5%.

Results and Discussion

Morphology and Thermal Properties of Natural and Organo-Modified Sepiolite

The morphology of the as received natural sepiolite has been evidenced by TEM analysis. In Figure 2, one can observe a bundle-like aggregation of sepiolite needles of various sizes (Figure 2a) as well as some almost individualized needles (Figure 2b).

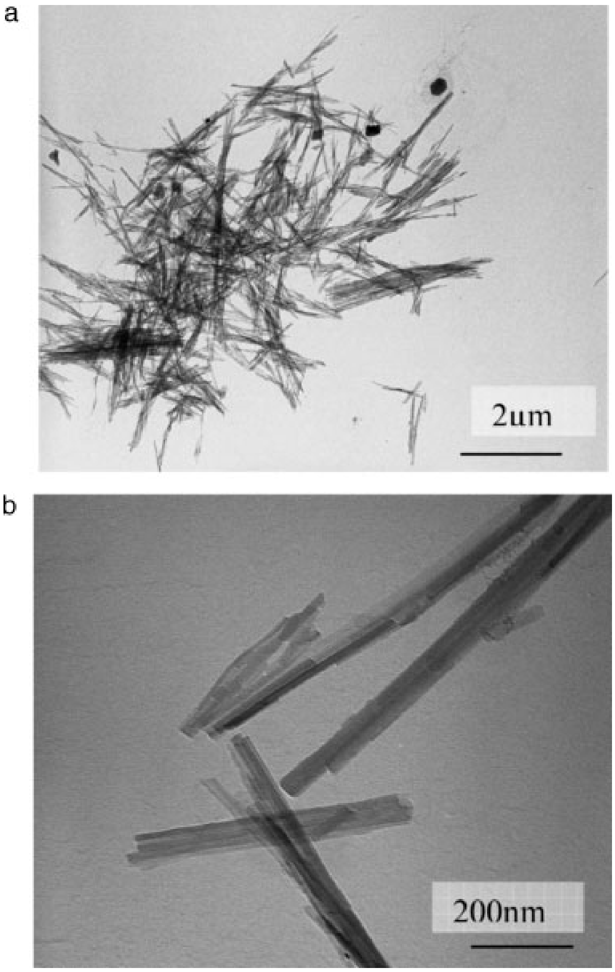

Figure 2. TEM pictures of a bundle (a) and almost individual needles (b) of natural sepiolite.

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The organo-modified sepiolite has been synthesized from natural sepiolite using gradual amounts of APTES in order to determine the optimal quantity of the silanization agent for sepiolite surface modification. The experiments were carried out using 1 g of natural sepiolite dispersed in 50 mL of dried toluene. The so-modified sepiolite was washed thoroughly with toluene in a Soxhlet apparatus and dried. The primary amine content was determined by UV-vis after back-titration of picric acid using a reported procedure.[18] The results are reported in Table 1.

Table 1. Amine derivatization of natural sepiolite using APTES as silanization agent.

Entry	**Vol. silane, mol silane**	**Amount of fixed NH_2**
	mL, mmol	**$mmol \cdot g^{-1}$**
1	0.1, 4	0.295
2	0.5, 21	0.566
3	1, 43	0.564
4	2, 86	0.610

Using gradual amounts of APTES leads to an increase in amine content fixed at the surface of sepiolite. However, it seems that the sepiolite surface is saturated when the amount of primary amine reaches $0.6\ mmol \cdot g^{-1}$. Consequently, for the synthesis of PCL-grafted sepiolite (sep-PCL) nanohybrids initiated from the primary amine groups present at the surface of sepiolite (sep-NH_2), a new batch of sep-NH_2 has been prepared using the conditions reported for the sample referenced as entry 2 in Table 1.

It is worth noting that all samples have been characterized by TGA. A 'high-resolution' method has been used in order to separate as finely as possible the different degradation steps that occur between 150 and 650 °C. In high-resolution TGA, the thermogravimetric analyzer modulates the temperature rate and applies quasi isothermal conditions as soon as a weight loss is measured. The resulting thermograms are reported in Figure 3.

As far as natural sepiolite is concerned (Figure 3a), four distinct weight losses are detected. Two are ascribed to dehydration and two to dehydroxylation. The first step occurs at 100 °C and is attributed to the loss of water physically bonded to sepiolite, i.e., adsorbed on the external surface and in the structural channels. Therefore, this first weight loss will depend on the atmospheric relative humidity. The second step is observed around 300 °C and can be attributed to the loss of two of the four crystallization water molecules that are more weakly bonded. The third step, observed around 525 °C, is a result of the elimination of the two

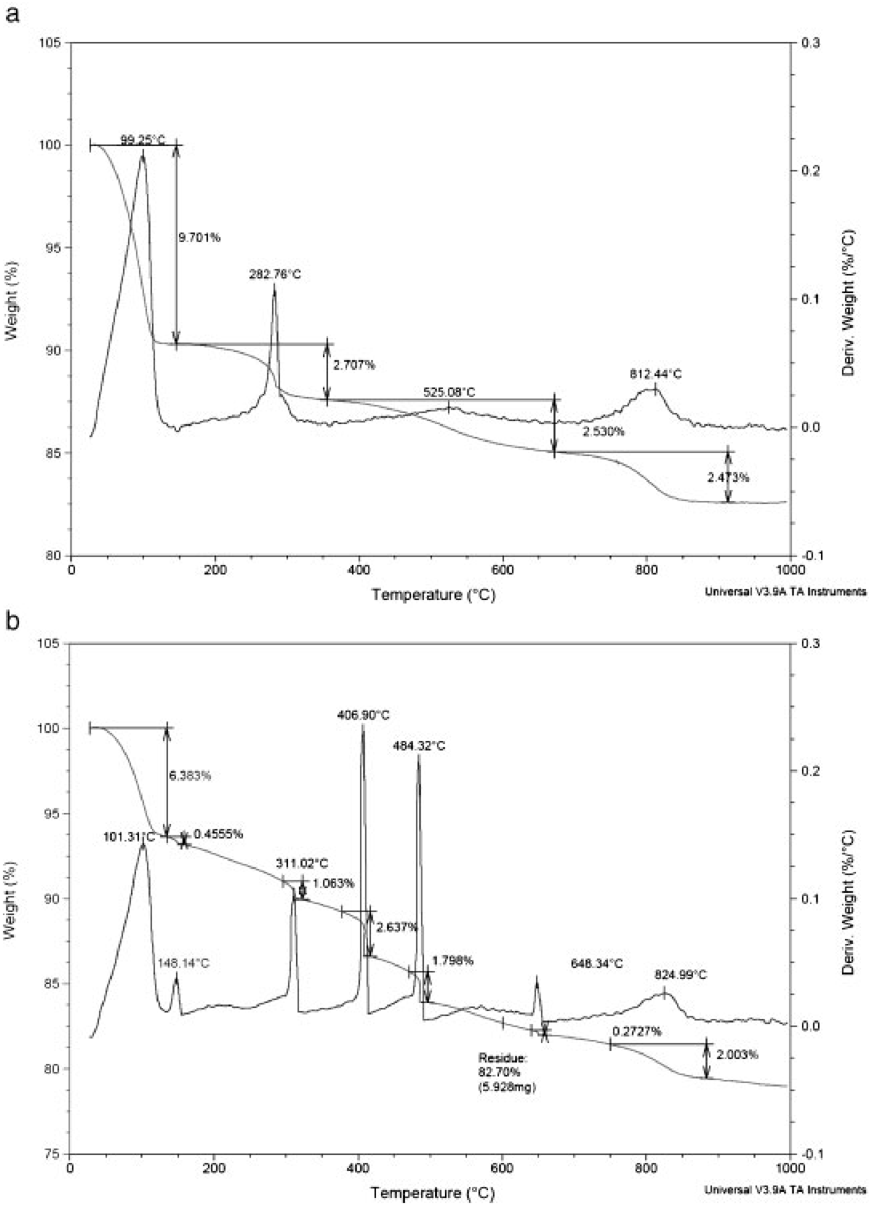

Figure 3. 'High-resolution' TGA thermograms of a) natural and b) amino-modified sepiolite.

other more strongly bonded crystallization water molecules. The final step is observed around 800 °C and corresponds to the loss of constitution water or hydroxy groups.[19] For the amino-modified sepiolite (Figure 3b), clearly, even if it is quite difficult to perform any precise quantification of the primary amine content, in addition to the loss of water, new weight losses appear at 406 and 464 °C, which more likely attest to the thermal degradation of the grafted aminopropyl groups. In addition, one can detect the presence of a low amount of non-grafted APTES simply adsorbed onto the filler even after Soxhlet treatment as attested by the degradation step around 150 °C. These observations qualitatively confirm the covalent grafting of APTES onto sepiolite, as quantitatively determined by the previously discussed UV-vis back-titration of primary amine functions by picric acid.

Synthesis and Characterization of Sepiolite/PCL Nanohybrids

Sepiolite/PCL (sep-PCL) nanohybrids have been synthesized in order to further modify the sepiolite surface and to prepare PCL-grafted sepiolite to be used as 'masterbatches'. In order to graft PCL chains at the surface of sepiolite through an amide bond, the primary amines of sep-NH_2 have been used as initiating species for the ring-opening polymerization of CL catalyzed by $Sn(Oct)_2$. The polymerization of CL was conducted at 100 °C either in bulk (in absence of solvent) or in toluene solution (see Experimental Part). Experimental conditions such as the polymerization time, the catalyst-to-initiator and monomer-to-initiator molar ratios, as well as the monomer concentration have been varied and their influence on the polymerization rate (in terms of monomer conversion) as well as the grafting efficiency (percentage of grafted PCL after tentative Soxhlet extraction) has been investigated. The results are reported in Table 2.

Influence of Polymerization Time

From entries 1 to 3 (Table 2), it is revealed that the monomer conversion increases as a function of time, which attests to an efficient polymerization process. Indeed, in bulk and using equimolar amounts of initiator and catalyst, a high monomer conversion is reached after 5 h. However, after Soxhlet extraction of the non-grafted PCL chains, whatever the monomer conversion, only a limited percentage of the in-situ synthesized polyester chains (ca. 12 wt.-%) remains anchored onto the nanofiller, which is quite acceptable with regards to the used conditions. Indeed, even if the sepiolite nanofiller is systematically dried before the ROP of CL, one cannot exclude the presence of protic impurities (water for instance) able to initiate the polymerization in solution.

Influence of $[Sn]_0/[NH_2]_0$

As expected, decreasing the amount of catalyst with regards to the initiator (entries 4 and 5, Table 2) leads unavoidably to a marked slowing of the polymerization rate. Indeed, only 18% of the monomer is converted into polymer chains after 24 h of reaction time. Nevertheless, it seems that even if the kinetics is slowed down, almost all the polymer chains remain grafted onto the nanofiller since the amount of grafted PCL as measured by TGA remains around 12 wt.-%.

Influence of the Monomer Concentration

There is no significant influence of the monomer concentration on the polymerization kinetics. Indeed, the monomer conversion reached after 24 h remains around 85%.

Table 2. Sepiolite-PCL nanohybrids as synthesized by in situ ROP of CL initiated from the amine functions of the amino-modified sepiolite and using $Sn(Oct)_2$ as the catalyst ($T = 100$ °C).

Entry	$[CL]_0$	t	$[CL]_0/[NH_2]_0$	$[Sn]_0/[NH_2]_0$	Monomer conversion	Grafted PCL
		h			%	wt.-%
1	Bulk	1	128	1	20	12
2	Bulk	3	128	1	59	13
3	Bulk	5	128	1	78	12
4	Bulk	5	128	0.1	4	12
5	Bulk	24	128	0.1	18	11
6	6.0 M	24	128	1	85	30
7	3.0 M	24	128	1	84	34
8	Bulk	5	159	1	67	57
9	Bulk	5	191	1	58	40
10	Bulk	5	223	1	56	43

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However, simply by adding a small quantity of toluene, one can increase the grafting efficiency as attested by the quite high grafted PCL content in the nanohybrids (30 to 34 wt.-%) even after Soxhlet extraction (entries 6 and 7, Table 2).

Influence of the Monomer-to-Initiator Ratio (Theoretical Degree of Polymerization)

As expected, increasing the targeted polymer chain length leads to a decrease of the monomer conversion. Indeed after 5 h polymerization time (in bulk), the monomer conversion decreases from 67 to 56% when the initial monomer-to-initiator molar ratio is increased from 159 to 223 (entries 8–10, Table 2). Interestingly, the percentage of grafted PCL chains remains high as attested by the PCL content in the nanohybrid after Soxhlet extraction (40 to 57 wt.-% grafted PCL).

Therefore, a batch of sep-PCL nanohybrids has been synthesized in a larger amount (20 g) and used as a masterbatch for the preparation of PCL-sepiolite nanocomposites. This batch was prepared following the experimental conditions of the sample reported in entry 10 (Table 2). TGA characterization evidenced a monomer conversion of 67% and a content of grafted PCL chains around 58% (as determined after Soxhlet extraction), which is in perfect agreement with the previous experiment conducted on a smaller scale and, therefore, fully attests to a fair reproducibility. This sep-PCL nanohybrid has been considered a masterbatch for the preparation of PCL-sepiolite nanocomposites and thus dispersed with CAPA6500 by extrusion (see experimental) in order to reach 3 wt.-% of inorganic filler. The so-produced nanocomposites have been compared to the other blends (prepared with either native or amino-modified sepiolite) in terms of mechanical, thermal, and morphological properties (by tensile testing, TGA, DSC, and TEM, respectively). It is worth noting that the sep-PCL nanohybrid has been dispersed within commercial PCL either crude, i.e., as recovered from the in-situ polymerization/grafting (thus in the presence of residual non-grafted polyester chains) or purified, that is to say after elimination of the non-grafted PCL chains by Soxhlet extraction. In the following section, these two sep-PCL nanohybrids will be coined as 'crude sep-PCL' and 'purified sep-PCL' nanohybrids, respectively.

Preparation and Characterization of PCL/Sepiolite Nanocomposites

PCL/sepiolite nanocomposites have been prepared by extrusion using a 7 mL twin-screw micro-compounder. The blends were formed at 80 °C under relatively high shear (75 rpm) for 10 min. The thermal, mechanical, and morphological properties of the materials prepared from the nanohybrids were investigated and compared to the neat polymer matrix (CAPA6500) on the one hand and to the PCL/sepiolite simple blends as prepared from natural and amino-modified sepiolite (sep-NH_2) samples.

Thermal Properties

In order to check the influence of the sepiolite nanofiller on the melting temperature as well as the degree of crystallinity of the PCL matrix, DSC measurements have been carried out. The samples have been analyzed under nitrogen with a heating ramp of 10 °C · min^{-1} and the data collected after the second heating scan (Table 3).

From Table 3, it is revealed that the presence of sepiolite, either natural, primary amine derivatized, or the nanohybrid form, has no significant influence on the melting temperature of the PCL. Moreover, even if the crystallinity is slightly enhanced in some cases, it does not vary to a large extent.

In addition, the degradation temperatures of the nanocomposites have been measured by TGA under helium with a heating ramp of 20 °C · min^{-1} and the results reported in Table 4 and Figure 4.

At this stage, surprisingly, it seems that with an inorganics content of 3 wt.-% the sepiolite has no significant effect on the thermal degradation of the PCL matrix (entries 2 and 3 in Table 4). Such a lack of influence of nanofiller on the thermal stability of PCL under an inert atmosphere has also been very recently observed by Bikiaris et al.[20]for sodium montmorillonite (a layered clay) and multiwalled carbon nanotubes. A large decrease in thermal stability is observed for the sample containing the crude sep-PCL nanohybrid (entry 4 in Table 4). For the Soxhlet-purified nanohybrid (purified sep-PCL), a two-step degradation is observed with a first small step in the temperature area of the nanocomposite based on the crude nanohybrid followed by a main step in the temperature range of neat commercial PCL (entry 5 in Table 4). This is clearly evidenced in Figure 3, which shows the

Table 3. Melting temperature (T_m) and degree of crystallinity (χ_c) for PCL and PCL/sepiolite nanocomposites (3 wt.-% inorganics) prepared by twin-screw mini-extrusion.

Entry	Sample	T_m	$\chi_c$$^{a)}$
		°C	%
1	CAPA6500	59	41
2	CAPA6500 + natural sepiolite	59	41
3	CAPA6500 + sep-NH_2	60	45
4	CAPA6500 + crude sep-PCL	58	47
5	CAPA6500 + purified sep-PCL	59	40

$^{a)}$$\Delta H_m^0 = 136\ J \cdot g^{-1}$.

Table 4. Temperature of maximum thermal degradation rate as measured by TGA (20 °C · min^{-1} under helium) of PCL and PCL-sepiolite nanocomposites (3 wt.-% inorganics) prepared by twin-screw mini-extrusion.

Entry	**Sample**	$T_{d,max}$ °C
1	CAPA6500	435
2	CAPA6500 + natural sepiolite	431
3	CAPA6500 + sep-NH_2	434
4	CAPA6500 + crude sep-PCL	406
5	CAPA6500 + purified sep-PCL	354, 435

thermograms of the nanohybrid-containing samples. This observation could be explained by the presence of residual tin octoate able to catalyze the degradation of the polyester chains.[21] A relatively large amount of this residue remains in the crude nanohybrid, which triggers thermal degradation of the resulting nanocomposite at a lower temperature while a significant amount of the catalyst residue seems to be eliminated or inactivated after Soxhlet extraction, which therefore limits at least partially its effect on the PCL thermal degradation.

Morphological Properties

The dispersion of sepiolite into PCL has been evidenced by TEM applied to thin (ca. 50 nm thick) slides as cut by ultra-cryomicrotomy. Two samples have been investigated: on the one hand, a natural sepiolite/PCL simple blend (entry 2 in Table 4) and on the other hand, a (purified) sep-PCL nanohybrid/PCL nanocomposite (entry 5 in Table 4). TEM pictures are shown in Figure 5.

As observed in Figure 5, whatever the nature of the sepiolite (natural or nanohybrid) the dispersion appears of high quality. Indeed, one can see only the presence of almost individualized needles without any remaining bundle-like aggregates. This observation, even if it was expected for the use of the nanohybrid, is quite surprising in the case of a sepiolite/PCL simple blend. Despite the presence of hydrophobic-hydrophilic interactions, simply by applying a relatively high shear (75 rpm) at relatively low temperature (80 °C), one can disaggregate the sepiolite bundle in a PCL matrix.

Mechanical Properties

Tensile tests have been performed at 20 °C at a constant deformation rate of 50 mm · min^{-1} using dumbbell-shaped specimens prepared from compression-molded samples according to the ASTM638 type V norm.

As expected, the dispersion of such a limited amount of a rigid filler into a polymer matrix slightly increases the Young's modulus. Unexpectedly, while the addition of natural sepiolite (entry 2 in Table 5) slightly increases the elastic properties of PCL, the use of sep-NH_2 (entry 3 in Table 5), which is more organophilic, does not reinforce the composite in terms of tensile properties at yield or Young's modulus when compared to the pure matrix (entry 1 in Table 5). In contrast, upon introduction of the PCL-grafted sepiolite nanohybrid (crude or purified sep-PCL) in the PCL matrix, the stiffness of the resulting composition proved to be significantly enhanced (entry 4 and 5 in Table 5). Indeed, the Young's modulus increases from 383 MPa for an unfilled PCL matrix up to ca. 510 MPa. This increase in stiffness cannot be explained by a finer dispersion of the coated nanofillers since both natural and polyester surface-treated sepiolite displayed a very similar quality of dispersion (as previously observed in Figure 4). Such a mechanical behavior might be attributed to some stronger nanoparticle/polyester interfacial interactions that would strengthen the nanohybrid materials. Indeed, besides the expected increase of interfacial adhesion because of the matrix and the grafted polymer chains being of the same chemical nature, other strong interactions such as chain entanglements and/ or co-crystallization of grafted-PCL

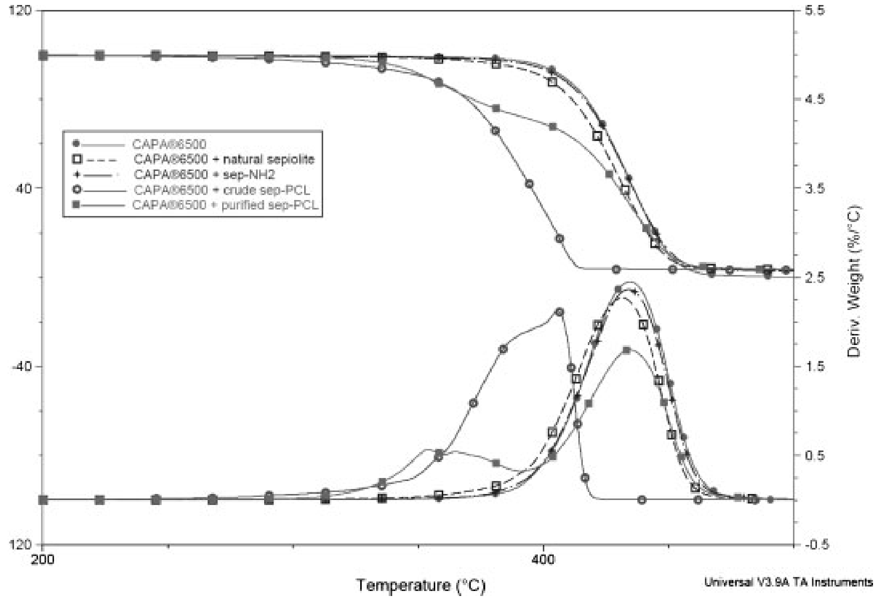

Figure 4. TGA curves of PCL-sepiolite nanocomposite samples that contain 3 wt.-% sepiolite. Effect of the sepiolite surface treatment.

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chains with the PCL matrix could strengthen the nanoparticle/matrix interphase and hence the stiffness of the materials through a better stress transfer from the matrix to the filler. Such an effect has already been observed in other studies that deal with the dispersion of polymer-grafted particles in a miscible polymer matrix.[22,23] On another side, the ultimate properties are unavoidably decreased upon filler addition. However, and interestingly enough, addition of the sep-PCL nanohybrids allows for an increase in the stress measured at the yield point to about 22–23 MPa (to be compared to 18.4 MPa for neat PCL). This observation again attests to a rather strong anchoring of the polyester chains onto the polymer-surface-treated sepiolite. The use of the sep-PCL nanohybrid can thus lead to an improvement of the mechanical properties of PCL in terms of rigidity as well as in terms of elastic deformation.

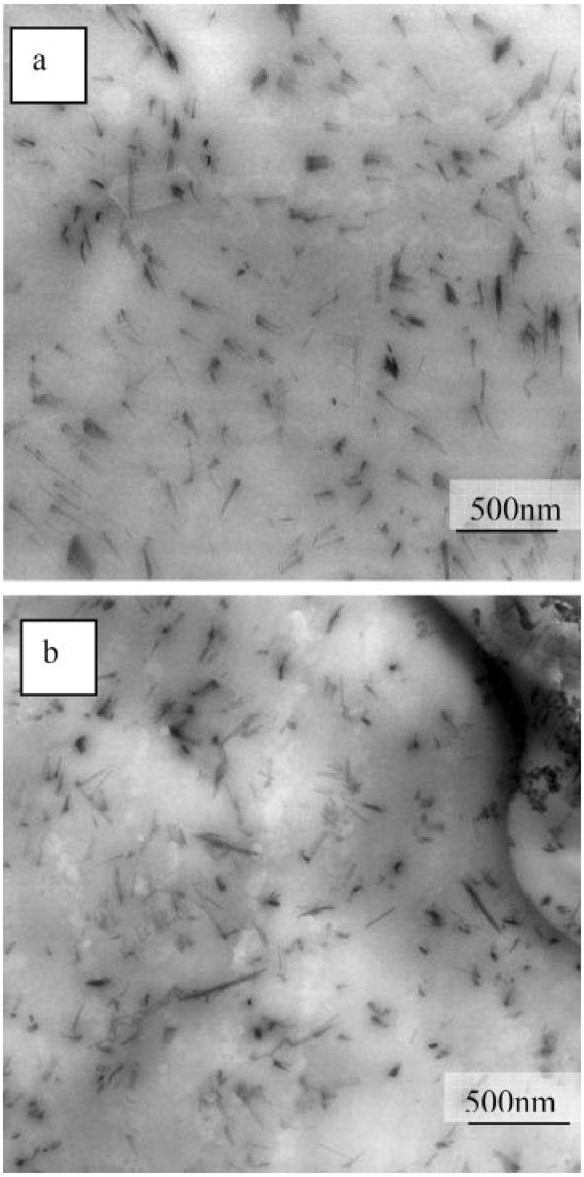

Figure 5. TEM pictures of a) natural sepiolite/PCL nanocomposite (entry 2 in Table 4) and b) sep-PCL nanohybrid/sepiolite nanocomposite (entry 5 in Table 4).

Conclusion

The preparation and characterization of PCL-sepiolite nanocomposites have been investigated. These nanocomposites have been prepared by extrusion under rather mild conditions. Natural sepiolite has been used either as received, after organo-modification using γ-aminopropyltriethoxysilane, or after PCL-surface grafting, i.e., to generate so-called sepiolite-PCL nanohybrids. These nanohybrids have thus been synthesized from the aminopropyl-functionalized sepiolite by the ring-opening polymerization of ε-caprolactone catalyzed by tin(II) octoate. Experimental conditions in terms of catalyst or monomer concentration have been optimized in order to ensure a high grafting efficiency. The as-prepared nanocomposite materials have been characterized in terms of thermal, morphological, and mechanical properties and compared to the pristine PCL matrix. A significant improvement of the mechanical properties occurs if sepiolite-PCL nanohybrids are used without affecting morphological properties. Indeed, the presence of covalent bonds between the polyester chains and the well-dispersed nanofiller allows for a strong enhancement of the interfacial adhesion as well as the

Table 5. Mechanical properties of PCL and PCL/sepiolite nanocomposites (3 wt.-% inorganics) prepared by twin-screw mini-extrusion.

Entry	Sample	Stress at yield	Strain at yield	Stress at break	Strain at break	Young's modulus
		MPa	%	MPa	%	MPa
1	CAPA6500	18.2	2.3	36.1	668	383
2	CAPA6500 + natural sepiolite	20.6	2.5	30.5	542	456
3	CAPA6500 + sep-NH_2	18.4	2.8	35.3	640	392
4	CAPA6500 + crude sep-PCL	22.7	2.1	17.0	284	510
5	CAPA6500 + purified sep-PCL	22.4	2.6	27.2	471	508

overall stiffness of the nanocomposites materials. Further studies dealing with the gas barrier and flame retardant performances are under current investigation and will be the object of a forthcoming paper.

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