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Nanocomposites with Biodegradable Polycaprolactone Matrix

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Summary: Biodegradable polymer/clay nanocomposites and/or composites based on poly(ε-polycaprolactone) (PCL) were prepared by conventional melt mixing. Three kinds of clays, organomodified Cloisite 15A and Cloisite 10A with different ammonium cations located in the silicate gallery and unmodified Cloisite with Na cations were used for composites preparation. The degree of dispersion of silicate layers in the matrix was determined by X-ray diffraction and transmission electron microscopy. Oscillatory rheological measurements were used for characterization of the physical network formed by the filler. The presence of intercalated and exfoliated structures were observed for the composites PCL/Cloisite 15A and PCL/Cloisite 10A, indicating that nanocomposite structure was formed. Changes of viscoelastic properties to more solid-like behavior, especially in the low frequency range were explained by formation of silicate network structure, which can be detected by modified Cole-Cole plots.

Keywords: melt mixing; nanocomposites; organoclay; polycaprolactone; silicate network structure

Introduction

Biodegradable plastics-based materials (BDPs) are considered to be a viable alternative for conventional commodity plastics because of both convenient dealing with plastics waste and in most cases production from renewable resources. However, to meet the target of partial substitution of commodity plastics by BDPs, mainly in packagings, more versatile properties of the materials must be reached to cover the full range of properties provided by commodity oil – based plastics. Additionally, a decrease in the price of basic materials must be dealt with as well.

Besides looking for new plastics, either from natural renewable resources or produced by synthesis, both goals can be addressed by appropriate physical and/or chemical modification of currently produced BDPs. From this point of view, application of various fillers is an obvious and straight forward approach. However, the selection of fillers is limited because of requirements of standards, e.g. ISO 14855, defining the maximal content of all non-biodegradable components to be below 5 wt % if the material should be declared as "biodegradable" (the abovementioned standard is even more specific regarding the additional requirements). Therefore, two ways seem to be acceptable, first, to use biodegradable cheap organic fillers, e.g. wood flour, or various organic fibers such as flax and cotton[1,2] or, alternatively, an application of nanofillers where even one percent of the additive can affect the properties of the composite significantly.[3] Number of papers has been focused on preparation and characterization of biodegradable composites and nanocomposites using inorganic particulate fillers, especially clays.[3–11]

From this point of view, layered silicates have been broadly investigated, mainly with polycaprolactone or polylactic acid as a polymeric matrices.[3] Polycaprolac-

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tone seems to be an important matrix for design of biodegradable nanocomposites because of its application in medicine and packagings. Nevertheless, to achieve broader applications, low melting temperature (around 60 °C only) and consequently low shape stability at temperature slightly above RT must be dealt with.

Various ways of nanocomposite's preparation were reported. Messersmith[6] and Kubies[7] investigated the preparation of PCL nanocomposites by solution polymerization in the presence of layered silicate. Although in-situ intercalative polymerization is a valuable procedure for preparation of rather homogeneous PCL - based nanocomposites,[7,9] a possibility of nanocomposite formation via melt mixing resulting in intercalation or partial exfoliation is the most important process for industrial application because of its simplicity and possibility of using conventional technologies for plastics processing.

The application of nanofillers in polycaprolactone was reported to improve mechanical as well as barrier properties,[6,8] and thermal stability.[8,11] An important increase of stiffness (Young's modulus growth from 216 up to 399 MPa) was reported by Lepoittevin et al[8] as a result of addition of 10 wt % of organomodified montmorillonite. At the same time, the material was found to be brittle (elongation at break decreased from 750% to 7% only) and a decrease of tensile strength was also observed as a result of substantial change of the stress–strain curve. Much lower changes, especially regarding toughness, were observed if lower amount of MMT was used, e.g. with 5 wt % of nanofiller elongation at break still reached values around 600%, with Young's modulus values well above 300 MPa. A detailed survey aimed to PCL –layered silicate- based nanocomposites is summarized in literature,[3] featuring also properties of the materials, concerning morphology, mechanical and barrier properties as well as thermal behavior. Important data on rheology and thermal stability of the PCL-based nanocomposites prepared by melt mixing were also reported.[4,11–14]

Besides two basic methods for nanocomposite characterization, namely X-ray diffraction (XRD) and transmission electron microscopy (TEM), useful data have been published based on rheological measurements. Various aspects of rheological data related to the structure of layered silicate polymeric nanocomposites were described in detail by Krishnamoorti and Giannelis,[15] using end-tethered montmorillonite (MMT) nanocomposite with either PCL or polyamide–6 matrix. In this case solution polymerization in the presence of MMT was applied resulting in well dispersed nanofiller in the matrix with only marginally entangled chains due to controlled molecular weight. A broad variety of rheological properties were described and discussed, indicating a number of important conclusions, such as the primary importance of interactions between filler surface and polymeric matrix (the good dispersion of the filler is not sufficient) and features of saturation effect of the filler content (around 5 wt % in the reported case).

In the present paper, biodegradable PCL composites prepared by conventional mixing process have been investigated regarding morphology, rheological, and mechanical properties. Three types of MMT with different modification were applied with the aim to prepare nanocomposites by conventional melt mixing process. The prepared samples were characterized by X-ray diffraction, mechanical tests, as well as scanning and transmission electron microscopies (SEM, TEM) and oscillatory rheology for clarifying the composite nanostructure. Oscillatory rheology data can be also used to compare the materials prepared by melt mixing (this paper) and solution polymerization (published in [15]).

Experimental Part

Materials

Biodegradable PCL (CAPA 6800 from Solvay Interox Ltd., United Kingdom) was used as the polymeric matrix. Three kinds of montmorillonite commercially available from Southern Clay Products, Inc. (United States) were chosen for nanocomposite preparation. Two of them are organomodified materials containing different quarternary ammonium cations: dimethyl dehydrogenated-tallow ammonium for Cloisite 15A (C15A, $d_{001} = 31.5$ Å) and dimethyl benzyl hydrogenated-tallow ammonium for Cloisite 10A (C10A, $d_{001} = 19.2$ Å). Natrified clay Cloisite Na (CNa, $d_{001} = 11.7$ Å) was used for comparison as a filler without hydrophobic surface modification.

The composities were prepared by conventional melt mixing at 75 °C for 10 minutes at 30 rpm in a 50 ml mixing chamber of Plastograph Brabender PLE 330. The filler content in the samples varied between 1 to 10 wt %. After mixing, the samples were compression molded at 70 °C for 2 minutes to 1 mm thick slabs.

Methods

Morphology of the composites was studied by SEM and TEM methods. Fracture surfaces of the notched samples were prepared at a liquid nitrogen temperature and observed by JSM 6400 microscope (JEOL, Japan). The specimens were sputter-coated (SCD 050, BALTEC) with a thin layer of platinum (cca 4 nm). To be able to observe the filler in the samples, the fracture surfaces were treated by cold air-plasma for 5 minutes to remove the thin layer of the polymer matrix covering the filler particles near the surface. The cryo-ultramicrotomed sections of the samples were investigated using JEOL 200CX transmission electron microscope.

X-ray diffraction data were obtained by Philips PW1830/PW1050 using the CuKα radiation and operating at 40 kV and 35 mA.

The rheological measurements were carried out using a Rheometer AR2000 (TA Instruments) at 75 °C in oscillatory mode in the frequency range of 0,01–100 Hz with specimens of diameter 20 mm and thickness 1 mm. The amplitude of deformation was 1% being in the linear elastic region as revealed by an amplitude sweep. Strain sweeps were performed at a constant frequency of 1 Hz to investigate the strain-dependent behavior of the composites.

Measurements of mechanical properties were carried out at room temperature on an Instron 4301 tensile tester. The crosshead speed was 50 mm/min. The dog-bone specimens (working area 30 mm long and 3,5 mm wide) were cut from compression molded 1 mm thick slabs at room temperature using a specially shaped knife.

Results and Discussion

The virgin powdered fillers form aggregates as shown in Fig 1. Larger aggregates have been observed in natural unmodified Cloisite CNa (Fig 1c) than in organomodified C15A and C10A (Fig 1a, 1b). SEM observations allow indicating the filler dispersion in the polymer matrix. In Fig 2

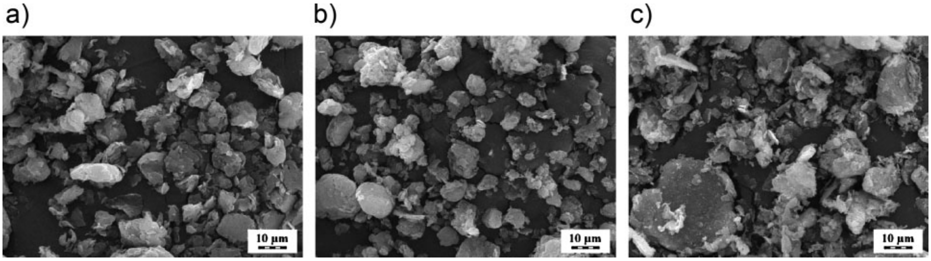

Figure 1.
SEM micrographs of the MMT fillers C15A (a), C10A (b) and CNa (c).

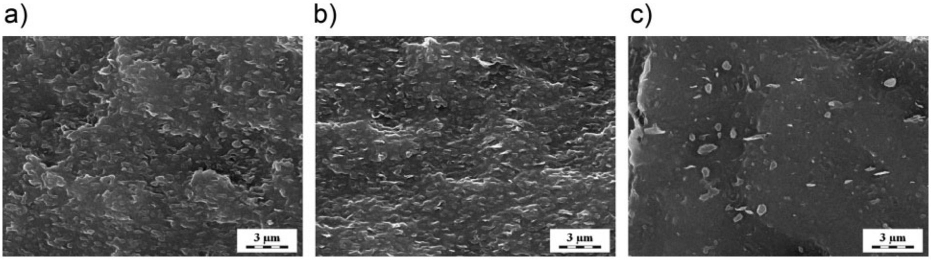

Figure 2.
SEM micrographs of PCL filled with 3 wt.% of C15A (a), C10A (b) and CNa. c).

SEM micrographs are shown for PCL composites with 3 wt % of the fillers. The samples filled with organomodified clays (C15A and C10A) exhibit good filler dispersion in the matrix (Fig 2a, 2b). On the contrary, for the composite filled with unmodified filler (CNa), dispersion of the filler consists of rather large clay clusters present in the polymer matrix (Fig 2c).

TEM micrographs of the composites provide direct observation of intercalated and/or exfoliated clay in the matrix. The samples filled with organomodified clays C15A and 10A C10A show good dispersion of the filler in PCL matrix without the presence of the original organoclay clusters (Fig 3a, 3b). The existence of the hybrid structures with intercalated tactoids but also exfoliated platelets is evident in the micrographs (Fig 3a, 3b). More extended intercalation and higher degree of exfoliated layers have been observed in the sample PCL/C15A with larger interlayer distance in C15A (Fig 3a). These observations indicate clearly that the nanocomposites are formed during conventional melt mixing when the organomodified clays are used. When unmodified CNa clay is applied, in fact no signs of exfoliation were found although some changes are indicated in Fig 3c. where small stacks are seen. Certain increase of the interlayer space occurs as determined from XRD analysis discussed below (Fig 6).

XRD is a suitable method to confirm the polymer/clay nanocomposites formation by intercalation of polymer chains between the clay layers. As the polymer penetrates, the intergallery space increases leading to better interactions between filler and polymeric matrix and easier exfoliation of the clay layers.[4] XRD patterns of PCL/C15A samples are shown in the Fig 4. The shift of the main diffraction peak to lower 2θ° indicates that interlayer spacing has increased. In comparison with C15A powder, apparently the position of the diffraction peak shifts to lower 2θ° values, moreover the peak splits to two parts. This may indicate a presence of the filler with

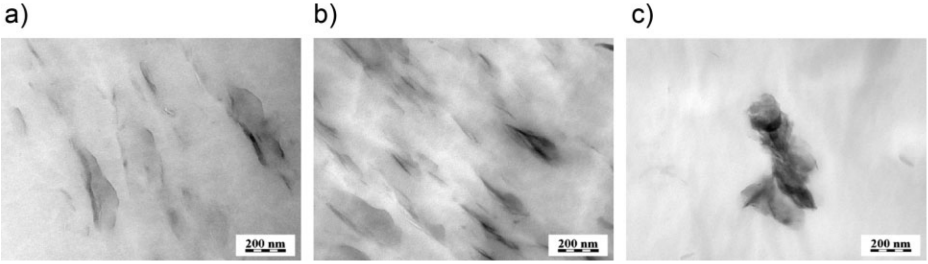

Figure 3.
TEM micrographs of PCL filled with 3 wt.% of C15A (a), C10A (b) and CNa (c).

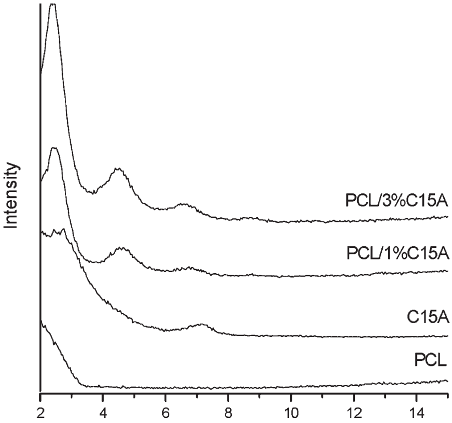

Figure 4.
XRD patterns of neat PCL, C15A powder and PCL/C15A nanocomposites with different wt.% of C15A.

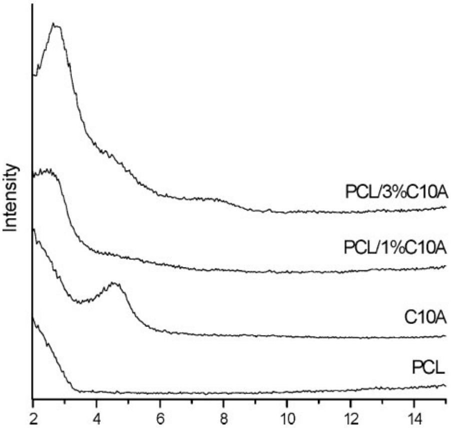

Figure 5.
XRD patterns of PCL/C10A nanocomposites with different wt.% of C10A.

different interlayer distances in PCL/C15A corresponding with uneven intercalation of the sample, although the reason and mechanism of the process is not quite clear. The formation of second order peak might be considered indicating a high level of ordering remaining in the filler tactoids in spite of the increase of the gallery spacing. More pronounced shift of the diffraction peak to lower values of diffraction angles was observed for the composite with C10A (Fig 5). For the sample containing 3 wt.% of C10A the peak corresponding to basal spacing of C10A is also seen, while this peak is absent in composite containing only 1 wt.% of the clay.

The XRD patterns for the composites with unmodified filler CNa show a slight shift to lower values of 2θ° (certain increase of gallery spacing) but the values indicate that relatively large stacks of platelets persist (Fig 6), as already been mentioned when discussing the TEM (Fig 3c).

The lowest values of 2θ° were obtained when 1 wt.% of the filler was applied in all prepared samples which is in agreement with literature.[4] The XRD results are in accordance with TEM observation and it can be suggested that with organomodified clays, nanocomposites with the hybrid nanostructure of intercalated and exfoliated layers are formed during conventional melt mixing process.

More detailed information on the structure and interactions in the composites was obtained from rheological measurements. The viscoelastic properties of particulate suspensions depend on particle structure, size and shape, therefore rheology can be used to examine the structural evolution and the quality of dispersion of polymer/MMT in the melt. Nanocomposites PCL/C15A and PCL/C10A exhibited a much higher complex viscosity than the neat PCL; if 5 and more wt. % of filler was present, significant shear-thinning behavior in the low frequency range was observed.

The increase in complex viscosity with the rising amount of organoclay indicates strong interaction between organoclay (C15A or C10A) particle surface and PCL macromolecules.[8] The strong interaction also leads to an increase in both the dynamic storage modulus (G′) and loss modulus (G″). Fig 7 shows the frequency-dependent dynamic moduli for PCL/C15A composites. The shapes of the curves are similar to those published in,[15] the differences in absolute values may result from different grade of MMTs and partially also because of differences in molecular weight of the polymers used. An increase in both G′ and G″ of the composites (Fig 7) was observed with rising amount of C15A and for composites containing 5 and more wt.% C15A both moduli were also found to be

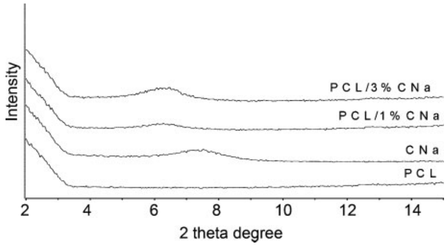

Figure 6.
XRD patterns of and PCL/CNa composites with different wt.% of CNa.

less frequency dependent in the low frequency range compared to the virgin PCL. Viscoelastic behavior of nanocomposites above this filler concentration appeared to be more solid-like especially in the low frequency region. This behavior can be explained by an existence of a kind of a rheological percolation threshold at which a remarkable increase in the modulus is achieved indicating the onset of network formation. This formation of silicate network structure was analyzed in detail via a Cole-Cole plot evaluating the structural changes in dependence on filler concentration[16] as well as the frequency dependence of dynamic viscosity and complex viscosity (Fig 8a). The formation of a network structure leads to the increase of the elastic component of viscosity, therefore relaxation parameters of the network during dynamic deformation differ from those for the homogeneous melt of unfilled polymer; deviation from a semicircle shape is observed and an upward turn in the low frequency part of the circles (at the right hand side of the semicircle). On the other hand, in the case of composites PCL/CNa, both the G′ and G″ grow and no deviation in low frequency region is observed. At the same time, the Cole-Cole plot (Fig 8b) did not show any changes concerning structural changes due to network formation. These results, together with TEM micrographs of composites PCL/CNa confirmed that only exfoliated stacks or individual layers may form the network.

While the rheological data correspond to those of TEM and XRD, mechanical tensile properties only partially confirmed the expected tendency as seen in Fig 9. The Young's modulus increase with rising filler content is obvious and expected. Higher values of E for composites with organo-modified clays is worth to mention although the difference compared to CNa-filled materials is not big, but significant enough to demonstrate intercalation and exfoliation effect leading to higher surface area of the filler. Rather small decrease in elongation at break due to filler addition, even after addition of 10 wt % of the fillers is certainly of interest, especially when considering the data of Lepoittevin et al,[8] who reported a decrease of elongation below 10 wt %, while in our case more than 900%

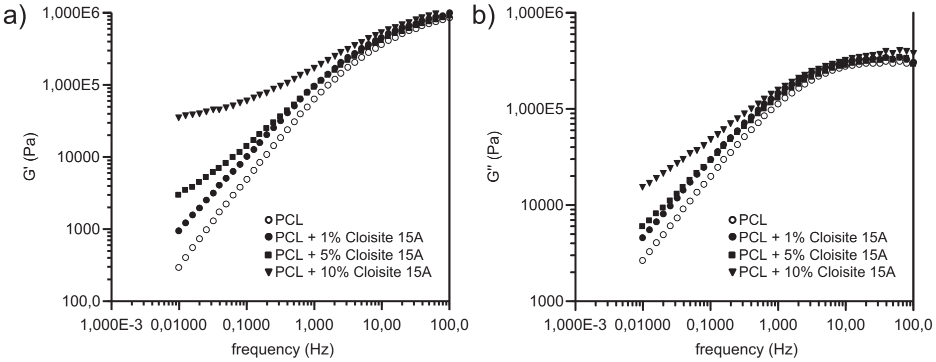

Figure 7.
Storage modulus (a) and loss modulus (b) for PCL/C15A nanocomposites as a function of frequency at various filler loading.

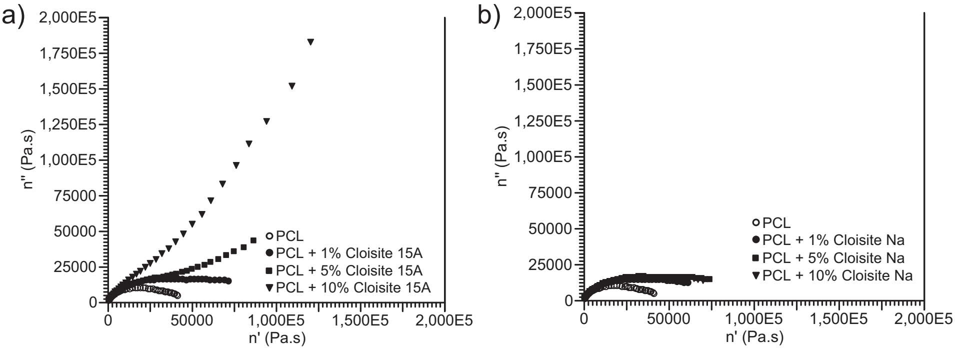

Figure 8.
Cole-Cole plots of PCL and PCL/C15A (a) and PCL/CNa (b) for nanocomposites with different filler content.

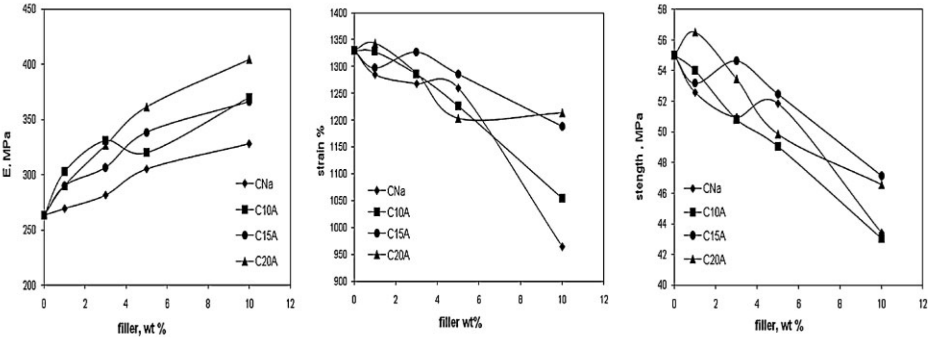

Figure 9.
Mechanical properties (Young's modulus, elongation at break, tensile strength) of the composites in dependence on the clay content for PCL/C15A, PCL/C10A and PCL/CNa nanocomposites.

was measured even for addition of 10 wt % of unmodified filler while for the composites with C15A and C20A only marginal decrease of the elongation was observed. On the other hand, the data for tensile strength do correspond neither to above-mentioned mechanical properties nor to characteristics obtained from TEM, XRD and rheological measurements, moreover, the data for all composites are similar including the one containing unmodified CNa. This tendency is difficult to explain; perhaps it may be caused by a presence of small amount of aggregates in spite of generally good exfoliation of the organo-modified fillers. In that case the modulus would depend on the total summation of filler particle surface, elongation at break on good particle surface – polymeric matrix interaction keeping the material together while tensile strength, being more complex parameter may be influenced by several factors, a presence of a small amount of aggregates, acting as stress concentrator and decreasing the effective crossection of the testing specimen, being one of them. In this case, the aggregates presence itself is of primary importance, while the increase in their concentration has additional but low effect.

Conclusion

Three kinds of commercial montmorillonites Cloisites were used to prepare nanocomposites based on biodegradable PCL by conventional melt mixing. XRD diffractograms of the composites with organomodified clays C15A and C10A showed the intercalation of clay layers by polymer matrix. The morphological study by TEM confirmed a formation of nanostructure and also the existence of the exfoliated layers of clay. If unmodified clay CNa was used as the filler, the stacks of platelets persist. SEM observations confirmed a good dispersion of organomodified filler in the composites prepared by the conventional melt mixing.

With the increase of clay loading, the composites exhibited more solid like behavior consisting in a decrease of the slope in the low frequency region while low values of frequency-dependent modulus originate from the filler network structure, which can be detected very sensitively with Cole-Cole plots of the complex viscoelastic characteristics of composites melt.

The results obtained contribute to the view that biodegradable matrix - based nanocomposites can be prepared with substantially modified properties, still fulfilling the status of biodegradability according to the current standards.

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