



Macromolecular Nanotechnology

Structure–property relationships of nanocomposites based on polylactide and MgAl layered double hydroxides



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ABSTRACT

Nanocomposites based on poly(L-lactide) (PLA) and organically modified MgAl Layered Double Hydroxides (MgAl-LDH) were prepared by melt blending and investigated by a combination of Differential Scanning Calorimetry (DSC), Small- and Wide-Angle X-ray Scattering (SAXS, WAXS), and dielectric spectroscopy (BDS). Scanning microfocus SAXS investigations show that the MgAl-LDH is homogeneously distributed in the matrix as stacks of 6 layers and/or partly exfoliated layers. DSC and WAXS show that the degree of crystallinity decreases linearly with the content of LDH. The extrapolation of the dependencies (DSC and WAXS) to zero estimates a limiting concentration of LDH C_{crit} of ca. 21 wt% where the crystallization of PLA is completely suppressed by the nanofiller. The dielectric behavior of neat PLA show two relaxation regions, a β -relaxation at low temperatures related to localized fluctuations and the α -relaxation at higher temperatures due to the dynamic glass transition. The dielectric spectra of the nanocomposites show several additional relaxation processes compared to neat PLA which are discussed in detail. For the nanocomposites around 260 K ($f = 1$ kHz) an additional process is observed which intensity increases with increasing concentration of LDH. This process is mainly attributed to the exchanged dodecylbenzene sulfonate (SDBS) molecules which are adsorbed at the LDH layers and form a mixed phase with the polymer close to the layers and stacks. An analysis of this process provides information about the molecular dynamics in the interfacial region between the LDH layers and the PLA matrix which reveal glassy dynamics in this region. In the temperature range around 310 K ($f = 1$ kHz) a further process is observed. Its relaxation rate has an unusual saddle-like temperature dependence. It was assigned to rotational fluctuations of water molecules in a nanoporous environment provided by the LDH filler. Above the glass transition temperature a further process is observed at temperatures above. It is related to Maxwell/Wagner/Sillars polarization due to the blocking of charges at the nanofiller.

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Abbreviations: PLA, polylactide; LDH, layered double hydroxide; SEC, Size Exclusion Chromatography (SEC); DSC, Differential Scanning Calorimetry; SAXS, Small Angle X-ray Scattering; WAXS, Wide Angle X-ray Scattering.

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1. Introduction

Aliphatic polyesters especially polylactides (PLA) encounter nowadays various applications due to their biodegradable and/or biocompatible properties. Firstly, they are involved in the preparation of medical devices or therapies (bone surgery, suture, chemotherapy, etc.) [1,2]. Secondly, they are intensively studied as an alternative solution to partially reduce the plastic waste accumulation especially in packaging. Thirdly, there is also an increasing interest on PLAs as a promising replacement of petroleum-derived plastics, since they are extracted entirely from renewable agricultural products. Due to its biodegradation properties the polymer can enter in the natural cycle implying its return to the biomass [3–5].

However PLA, with a glass transition temperature around 329 K, is a relatively stiff and brittle polymer with a low deformation at break. One way to improve the properties of PLA is to incorporate nanoparticles to form polymer based nanocomposites. Among other nanoparticles like carbon nanotubes (see for instance Ref. [6]), layered aluminosilicates such as montmorillonite (clay), have been studied to some extent [7–15]. As a result it was found that a melt blending of the polyester with the clay leads to an intercalated or to a semi-intercalated/semi-exfoliated nanocomposite, relatively independent from the properties of the clay surface [16,17].

From a general point of view, compared with micro or macro scaled composites, polymer-based nanocomposites attract an increasing interest because of the substantial improvements in material properties such as gas and solvent barrier, toughness, mechanical strength and flame retardancy [18–25]. The properties improvements can be attributed to the small size of the filler particles, its homogeneous dispersion on the nanoscale in the polymeric matrix, and thus the length scale of interaction with the polymer segments [26]. Moreover, due to the small size of the particles the surface to volume ratio is high, which results in a high volume fraction of an interfacial area between the polymer matrix and the nanoparticle [27]. The behavior of the polymer chains/segments in these interfacial regions like the packing density, the segmental molecular mobility or even the crystallinity can be different from those in the matrix polymer (see for instance Refs. [28–31]). Because of its high volume fraction, the interfacial area between the matrix polymer and the nanofiller is crucial for the properties of the whole composite. A basic understanding of the interplay of the properties of the matrix and that of the interfacial area is still lacking.

Recently, Layered Double Hydroxides (LDH) has attracted considerable interest as nanofiller for polymer based nanocomposites (see for instance Refs. [29,32–38]). From the mineral point of view LDHs belong to the general class of anionic clay minerals and well known for their catalytic activity [39]. Due to the large amount of tightly bound water [40] and other synergistic effects they are able to enhance the flame retardancy of polymeric materials [41,42]. The most common naturally occurring LDH is hydrotalcite. Besides that, a broad range of chemical composition can be obtained due to the fact that layered double hydroxides can be synthesized.

Here the structure/property relationships of nanocomposites based on poly(L-lactide) and synthetic organically modified MgAl LDH is investigated. In detail a combination of complementary methods like Differential Scanning Calorimetry (DSC), Small- and Wide-Angle X-ray Scattering (SAXS, WAXS), Size Exclusion Chromatography (SEC) and Broadband Dielectric Spectroscopy (BDS) are employed. Recently a similar combination of methods was employed to investigate nanocomposites based on polyolefins and LDH [36,37,43]. Some work on LDH filled poly(L-lactide) has been published recently [44,45].

2. Experimental section

2.1. Materials

Layered Double Hydroxides (LDH) are a special class of anionic clay minerals. Like layered silicates LDH materials have a crystalline constitution. Its structure is based on brucite-like layers ($\text{Mg}(\text{OH})_2$) where each magnesium cation is octahedrally surrounded by hydroxyl groups. An isomorphous substitution of Mg^{2+} by a trivalent cation (or by a combination of other divalent or trivalent cations) occurs in the LDHs. The layers become charged and therefore anions between the layers are necessary to balance the charge. LDH can be represented by the general formula $[\text{M}_{1-x}^{\text{II}}\text{M}_x^{\text{III}}(\text{OH})_2]^{x+} \cdot [(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}]^{x-}$ where M^{II} and M^{III} are the divalent and trivalent metal cations respectively, and A is the interlayer anion. A detailed discussion can be found in recent reviews [32,38]. The interlayer anions can be exchanged by bulky organic anionic species. This makes LDH especially suitable to prepare polymer nanocomposites because macromolecules can intercalate into the gallery of organically modified LDH and may result in the exfoliation of LDH layers.

Examples of divalent cations are Mg^{2+} , Ni^{2+} , and Zn^{2+} where for the trivalent ions are commonly found Al^{3+} , Cr^{3+} , Fe^{3+} , and Co^{3+} . Here Mg^{2+} and Al^{3+} are employed as di- and trivalent cations where the LDH is fully synthetically. Sodium dodecyl benzene sulfonate (SDBS) is used as organic anion in the layer galleries of the LDH.

The synthesis of organomodified MgAl-LDH (O-MgAl-LDH; O-LDH) was carried out by a one-step procedure [46]. A mixed magnesium and aluminum metal salt solution (with $\text{Mg}^{2+}:\text{Al}^{3+}$ ratio equal to 2:1 and a total metal ion concentration of 0.3 M) to a SDBS solution under continuous stirring at 50 °C. During the synthesis the pH value was kept constant at 10 ± 0.2 by adding a 1 M NaOH solution in the required amounts. After the addition of the mixed metal salt solution, the resulting slurry was further continuously stirred at the same temperature for 0.5 h. Finally a thermal treatment was applied at 75 °C for 18 h. The final products were filtered and washed several times with distilled water to remove non-reacted surfactant molecules until the pH of the supernatant solution was about 7. The organomodified MgAl-LDH was then dried at

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