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Characterization of clay platelet orientation in polylactide–montmorillonite nanocomposite films by X-ray pole figures

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The film samples of polylactide/montmorillonite (PLA/MMT) nanocomposite were formed by compression molding, film extrusion or melt blowing. The orientation of the single-layer platelets of fully exfoliated MMT was probed in these films with X-ray diffraction utilizing analysis of 2-D WAXS patterns and the pole figure technique. The reflections of the (020) and (210) crystallographic planes of MMT, both perpendicular to the plane of the platelet, were studied.

It was found that the texture of MMT created upon processing is the (100) planar texture, i.e. with MMT platelets oriented preferentially parallel to the film plane. That texture becomes significantly stronger and sharper with increasing shear deformation, according to the following order: compression molding → extrusion → blow molding. At the blow ratio of 7 the maximum of MMT orientation distribution reaches value of 8 m.r.d. and the estimated Hermans orientation factor of the platelet normal with respect to the film normal, is very high, $f_{001} = 0.96$.

The results obtained by X-ray pole figure technique were verified positively by direct TEM observations.

1. Introduction

The growing concern over the environmental issues and the decreasing reserve of fossil-based resources has led numerous research groups to focus on the development of new, environment–friendly materials, which can be obtained from renewable resources, and demonstrate a reduced negative impact on the environment [1]. Among these, poly(lactic acid) (PLA) appears a very promising polymer, especially for use in applications requiring short-life spans such as biomedical, packaging and agricultural [2,3]. PLA demonstrates many physical properties that renders it suitable as a replacement for conventional commodity polymers. Unfortunately, some of its properties, including the mechanical performance or barrier properties, are too poor for certain applications. To overcome these drawbacks and extend the application range, much work has been aimed on its modification. The success of nanocomposites, especially those with layered silicates (nanoclays), as e.g. montmorillonite (MMT) (for reference see the reviews and books, e.g. [4–12]) has fostered the search for systems with biopolymers matrix.

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The resulting 'nano-biocomposites' have been the subject of extensive research [1,5,13–17].

Layered silicates consist of stacked crystalline layers around 1 nm thick and of typical lateral dimensions 0.1–1.0 μm [12]. To benefit fully nanoclay as polymer reinforcement the grains of powder must be disrupted upon compounding into separate platelets, each consisting of a single basic silicate layer (exfoliated). When the nanoclay is exfoliated properly and individual platelets are dispersed evenly in the polymer matrix a significant improvement in mechanical properties can be achieved with already low level of the nanoclay filler, which is probably the most distinguishing characteristic of nanocomposites [4–12]. It can be attributed to extremely high specific surface area of nanoclay (of the order of 800 m^2/g), the rigidity and high aspect ratio of individual platelets together with the good affinity through interfacial interaction between polymer matrix and dispersed nanoclay platelets. The polymer–clay nanocomposites frequently have also excellent barrier properties against gases (e.g., O_2 and CO_2) and water vapor [4,5,18], which is explained by the concept of tortuous path: when impermeable nanoparticles are incorporated into a polymer, the permeating gas molecules are forced to wiggle around them in a random walk, and hence diffuse by a tortuous pathway through the matrix [5,18]. The best gas barrier properties are expected for nanocomposites with fully exfoliated clay platelets of large aspect ratio, oriented preferentially parallel to the film surface [17,18]. Such a sheet-like morphology is particularly efficient in maximizing the path length, as compared to other orientation modes or other filler shapes [4,5,18].

It is well known that the shear forces acting during melt processing and related flow can lead to significant orientation of highly anisometric clay particles in addition to polymer chain orientation. That platelet orientation can influence markedly mechanical as well as barrier properties of the nanocomposite product, as demonstrated e.g. for polyethylene blown films [19,20], syndiotactic polypropylene extruded tapes [21], uniaxially drawn isotactic polypropylene [22] or blown polylactide films [23,24].

The effect of shear on the orientation of the clay platelets in several nanocomposites was studied in detail by many authors [25–33]. Transmission electron microscopy (TEM) seems to be the most widely used method. It was frequently supported by X-ray techniques: 2-D SAXS [30,33], and 2-D WAXS [21,28,29,33,34]. In studies on preferential orientation of nanoclay platelets and polymer crystallites in nylon–clay nanocomposite extruded films, Kojima et al. [28] observed that both clay platelets and polymer crystallites align parallel to the surface of the film and along the machine direction (i.e. flow axis). In injection molded nylon–clay nanocomposite samples, they found that the clay platelets aligned either parallel to the sample surface (skin layer of high shear) or were oriented nearly randomly in the core region of very low shear [29]. Similar observations were reported by Varlot et al. [30]. In contrary, Fong et al. [25] observed that polymer crystallites aligned perpendicular to the clay platelets in nylon–clay electrospun fibers, where exceedingly high elongational strain rates were expected. Bafna et al. [33] studied 3-D orientation of silicate intercalated layers in extruded films of polyethylene–clay nanocomposites with 2-D WAXS. They found that the clay layers were oriented preferentially parallel to the film thickness, similarly to extruded nylon–nanoclay system.

The 'tilted film' transmission FTIR spectroscopy method was developed and then applied to PP/MMT nanocomposite blown films to quantify the clay platelet orientation [35]. This method was used also to determine platelet orientation in blown films of LDPE/MMT nanocomposite [20]. In both systems the preferred orientation of MMT platelets in plane of the blown film was observed.

Given the influence of orientation of nanoclay platelets, it is obviously important to characterize it well to facilitate correlation with other properties of a nanocomposite. The goal of this paper was to develop the method suitable for 3-D quantitative analysis of orientation of silicate single-layer platelets in nano-biocomposites, like PLA reinforced with exfoliated montmorillonite, and to apply it to analyze the MMT platelets orientation. Samples of the same PLA/MMT nanocomposite, yet of much different level of MMT orientation were selected for this study – the films produced by various processing routes, including compression molding, film extrusion and melt blowing. These samples were expected to show a relative low, moderate and high orientation of MMT, respectively). The commonly used microscopic techniques, although good in direct visualization of the nanofiller orientation, have a disadvantage that they illustrate orientation only locally, in the scale limited to the field of view of a microscope. Spectroscopic or scattering methods that probe much larger volume of the sample seem much better suited for quantitative characterization of MMT orientation in a global scale. Unfortunately, a relative simple and elegant method of 'tilted film' transmission FTIR spectroscopy [35], developed for polyolefin-based nanocomposites, is not suitable for the PLA/MMT system studied here since the Si–O vibration bands of MMT (1100–1000 cm^{-1}) used in this approach strongly overlap with C–O bands characteristic for PLA, thus cannot be analyzed precisely enough. Therefore, we decided to use X-ray scattering instead, including the pole figure technique [36] that allows to determine 3-D orientation distribution of crystallites, here the MMT platelets, on the basis of X-ray diffraction measurements. That technique has not been used for nanocomposites characterization before. It seemed very promising in the case of PLA/MMT system as the PLA matrix was amorphous and did not give any diffraction peak that could coincide with diffraction of MMT. It should be possible to use it also to study of orientation in other nanocomposites. The results obtained by X-ray were verified with TEM observations.

2. Experimental

2.1. Materials

The following materials were used in this study to prepare nanocomposites: