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Effect of biaxial stretching on thermomechanical properties of polylactide based nanocomposites

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ABSTRACT

This work focuses, for the first time, on the structural evolution of Polylactide (PLA) and PLA-Talc nanocomposites upon biaxial stretching. Biaxial stretching is a widely used technique to improve the end-use properties of polymer films. Encountered in a large number of elaboration processes it involves important structural changes into the material which directly govern the properties gain. In this work the influence of both stretching conditions and clay content were addressed. Besides it is observed that while relatively low clay content, i.e. below 10 wt%, has a limited impact on the mechanical behavior, higher contents dramatically modify the latter and particularly decreases the stretchability of the material. It was also evidenced that both the stretching conditions and clay content influence the strain-induced structure. Particularly the presence of talc favors the formation of a crystalline structure upon stretching due to its nucleating ability.

The mechanical behavior of the biaxially stretched samples has also been investigated. As a key point it was observed that while the as elaborated materials are brittle when uniaxially stretched at room temperature, the biaxially stretched ones exhibit a ductile behavior with achieved strains at break up to 100%. The origin of this brittle to ductile transition, assessed by means of *in situ* SAXS experiments, was found in the inhibition of the crazing mechanism for samples biaxially oriented under appropriate conditions.

1. Introduction

Polylactide (PLA) is currently one of the most promising polymer issued from renewable resources and it is actually produced at a large scale. Even if this polymer exhibits properties similar to the ones of polystyrene [1] allowing its use in a wide range of applications, PLA mainly suffers from its brittleness and from its relatively low barrier properties. In this way, in order to improve its physico-chemical properties, the elaboration of PLA based nanocomposites has given rise to a large number of studies. Besides it was shown that this route allows some properties improvement such as an increase of fire resistance [2] or barrier properties [3], allowing thus to consider new applications fields for PLA. However consideration to use PLA in a wider application range such as bottles or films involves to know the behavior of PLA upon biaxial stretching which is the commonly deformation route applied to the material during these processes.

A review of the literature reveals that this topic remains scarcely addressed in the case of PLA. Ou et al. have studied the structural evolution induced upon biaxial stretching of PLA in the rubbery state [4]. They found that simultaneous biaxial stretching leads to the formation of an in-plane isotropic structure with poorly ordered crystalline regions. They have also showed that sequential biaxial stretching induces a less organized structure as compared to the simultaneous mode due to the fact that the crystals formed along the stretching direction during the first stretching step are destroyed or damaged during the second stretching step. In a subsequent study these authors highlight the fact that a constrained annealing of biaxially oriented (BO) films leads to the enhancement of the structural order by increasing crystal size and perfection [5]. Regarding the effects of biaxial stretching on PLA properties, Delpouve et al. have showed that biaxial stretching is an efficient route to improve water barrier properties of PLA [6]. Besides while crystallinity has only very limited effect on the

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permeability of PLA, a significant improvement was observed in the case of BO-PLA. Tsai et al. also report a significant improvement of PLA crystallization kinetics induced by biaxial stretching [7]. Finally, a positive effect regarding mechanical behavior of PLA has been also reported [8]. This point was recently in-depth studied by Jariyasakoolroj and coworkers who have evidenced that biaxial stretching may involve a brittle to ductile transition. Indeed while PLA is known to be intrinsically brittle when stretched at room temperature, these authors report in their study strains at break as high as 100% in the case of BO-PLA [9]. They assumed that the crystalline structure induced upon biaxial stretching, which consists in isotropically small crystalline lamellae, is the key parameter to obtain super-tough PLA.

The mechanical behavior upon biaxial stretching of PLA based nanocomposites is meanwhile a poorly addressed topic. Only a study of Tabatabaei et al. addresses this topic in the case of PLA/Cloisite nanocomposites [10]. In this work authors show that even if mechanical treatments and particularly biaxial stretching did not modify the dispersion degree of the clay, it strongly infers on the crystal unit cell alignment. They also report that the presence of the filler also increases the orientation degree of the crystal unit cell. However the impact of BO on the end-use properties of the material was not addressed. Moreover this study does not provide information about the influence of the filler on the mechanical behavior of PLA upon biaxial stretching in spite of the fact that this is of prime interest as it determines the processing capacities of the material. Indeed, in most of applications such as bottles or films, a biaxial mechanical treatment is applied to PLA. However there are no data available in the literature regarding how the presence of the filler influences the mechanical behavior.

Starting from these findings, one of the aims of this study is to address this point. Besides this study will focus, for the first time, on the strain-induced structure upon biaxial stretching of moderately but also highly filled PLA-clay materials. For this purpose, PLA-Talc nanocomposites films with clay contents varying from 5 wt% to 30 wt% were elaborated and their mechanical behavior upon biaxial stretching was studied. Particularly the influence of the stretching parameters, i.e. drawing temperature and stretching speed, on both mechanical behavior and strain-induced structure were analyzed. The second goal of this work is to characterize the thermomechanical properties of the biaxially stretched samples so as to highlight the potential beneficial effect of this mechanical treatment.

2. Experimental

2.1. Materials

The Polylactide (PLA) grade PLE003 used in this study was purchased from NaturePlast (France). The number-average and weight-average molar weights are $M_n = 92$ kDa and $M_w = 164$ kDa as measured by means of GPC. The Melt Flow Index (MFI) and density of the pristine material are equal to 2–10 g/10 min and 1.24 g/cm^3 respectively. Talc (grade Luzenac 00, Imerys, France) was used as filler. Talc is a magnesium silicate of formula $Mg_3Si_4O_{10}(OH)_2$; which is composed of an octahedral layer of magnesium being sandwiched between two tetrahedral silica layers.

2.2. Elaboration

It is well known that PLA is a hydrophilic polymer that may undergo hydrolysis at elevated temperatures. Pellets were dried under vacuum at 40 °C for 12 h before extrusion in order to avoid hydrolysis of PLA which may occurs at elevated temperatures [11]. The elaboration of the nanocomposites was carried out in two steps. The compounding of PLA with talc, at contents varying from 5 wt% to 30 wt%, was carried out on a Coperion CS Separate twin screw extruder. In the process used, PLA is first melted and sheared at 180 °C in a first region of the extruder. Then clay is added into molten PLA in a second part of the extruder heated at 190 °C. In a second step, 200 μm thick films were elaborated by extrusion casting using a Collin extruder. Heating temperatures as well as rolls speed were adjusted in order to prevent or at least minimize any orientation into the sample.

For sake of clarity, samples will be denoted as PLA-T-*X* with *X* being the clay content (wt%). Finally a specimen of neat PLA (denoted as PLA-0) was extruded in the same conditions for the sake of comparison.

2.3. Structural characterization

On the one hand the structure of the samples, biaxially oriented or not, was determined by means of *ex situ* WAXS measurements using the synchrotron radiation on the BM02 beamline at European Synchrotron Radiation Facility (Grenoble, France). WAXS experiments were carried out using an energy of 22 keV (i.e. $\lambda = 0.5635$ Å) and a sample to detector distance of 20 cm.

On the other hand the plastic deformation mechanisms involved during the uniaxial stretching at room temperature of the materials were assessed by means of *in situ* SAXS experiments carried out at an energy of 8 keV (i.e. $\lambda = 1.54$ Å) using a sample to detector distance of 1.2 m. For this purpose mechanical tests have been performed on a portable homemade stretching device designed so as to adapt on the beamline and allowing symmetrical stretching. Tensile tests were performed at an initial stretching speed of 10^{-3} s^{-1} at a drawing temperature (T_d) of 20 °C.

Through-view 2D-patterns were recorded using a CCD camera from Princeton Instruments. Standard corrections were applied to the patterns before their treatment. The intensity profiles were obtained by 360° azimuthal integration of the 2D patterns using the fit2D software®.

2.4. Morphology

The composites' morphologies were assessed by means of both Scanning Electronic Microscopy (SEM) and Transmission Electronic Microscopy (TEM). SEM analyses were carried out using a HITACHI S4700 scanning electron microscope operating at an accelerating voltage of 5 kV. The analyzed samples were prepared using a Leica UM EC7 microtome in order to reduce topological contrast as much as possible. Samples were cut perpendicularly to the film's thickness in order to observe the bulk morphology. Finally samples were also coated with chromium prior to the observation.

TEM observations were carried out on a Tecnai G2 20 (FEI) transmission electron microscope operating at 200 kV. Analyzed samples, having a thickness of approximately 70 nm, were microtomed from bulk samples at room temperature using a Leica Reichert FCS microtome and collected on a 300 mesh copper grid.

In order to describe the orientation of the clay platelets in the films, the extrusion direction of the film will be labelled as MD (Machine Direction) while the perpendicular direction to MD in the film plane will be denoted as TD (Transverse Direction). Finally, the Normal Direction (ND) is defined as the direction perpendicular to the film plane, i.e. perpendicular to MD and TD.

2.5. Biaxial stretching

A KaroIV biaxial stretcher (Brückner) was used for the biaxial drawing of the specimens. Experiments were carried out on