



Macromolecular Nanotechnology

Probing the chain segment mobility at the interface of semi-crystalline polylactide/clay nanocomposites

A. Saiter^{a,*}, N. Delpouve^a, E. Dargent^a, W. Oberhauser^b, L. Conzatti^c, F. Cicogna^d, E. Passaglia^{d,*}^a AMME-LECAP EA 4528 International Lab., Av. de l'Université, BP12, Normandie Univ. France, Université de Rouen, 76801 St Etienne de Rouvray, France^b ICCOM-CNR Firenze, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Firenze, Italy^c ISMAC-CNR Genova, Via De Marini 6, 16149 Genova, Italy^d ICCOM-CNR UOS Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy

ARTICLE INFO

Article history:

Received 8 January 2016

Received in revised form 4 March 2016

Accepted 22 March 2016

Available online 24 March 2016

Keywords:

PLA
Nanocomposite
Exfoliated
Crystalline fractions
Chain mobility
Cooperativity

ABSTRACT

The concept of Cooperative Rearranging Region (CRR), an efficient probe of the interaction level in nanocomposites, has been used in Poly(lactic acid) (PLA)-based composites with phyllosilicates prepared in the melt with organomontmorillonite (O-MMT) and using poly(butylene adipate-co-terephthalate) (PBAT) as coupling agent. The samples were crystallized from various thermal treatments in order to obtain a wide range of morphologies and microstructures and accurately characterized by XRD, TEM, standard DSC and MT-DSC with the aim to highlight the effect of lamellae dispersion and distribution at nanoscale onto the thermal features of resulting nanocomposites. The presence of different interaction levels at the interface PLA/O-MMT, even tuned by the presence of PBAT, affects both the crystalline phase structure (by differently promoting crystallization of α and α' forms) and the distribution between the amorphous fractions (rigid and mobile). The variations of molecular dynamics are classified in two categories depending on the composite microstructure. Only in amorphous materials the cooperativity is driven by the filler/matrix interactions. In semi-crystalline materials, the morphological features linked to the presence of O-MMT and PBAT are overwhelmed by the confinement of the amorphous phase. Comparison between the two crystallization modes evidences a stronger change in the glass transition dynamics for systems exhibiting preponderant nucleation and high percentage of rigid amorphous fraction.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The key parameter in obtaining reinforced material by adding fillers is the interactions between the constituents. The interactions at interface between the materials forming the composite structure might involve multiple types of bonds depending upon the structure of the additive used with the matrix polymer. Usually these interactions are difficultly quantifiable as the structural description of the composite is restricted to its morphology obtained from X-ray diffraction and to the homogeneity of the filler dispersion obtained from electronic microscopy. However, during the last ten years many studies [1–8] have correlated the level of interactions at the interface between the filler and the matrix to the average size of one domain relaxing at the glass transition or Cooperative Rearranging Region (CRR) [9]. This idea of Cooperative Rearranging

* Corresponding authors.

E-mail addresses: allison.saiter@univ-rouen.fr (A. Saiter), passaglia@pi.iccom.cnr.it (E. Passaglia).

Region (CRR), which is defined as the amorphous domain where a conformational rearrangement may occur without causing rearrangements in the surrounding, has been introduced by Adam and Gibbs [9] and has given birth to many approaches aiming at calculating the characteristic length of the glass transition. Among them there is the thermodynamic approach proposed by Donth [10] which relates the CRR to the dynamic heterogeneity deduced from the temperature fluctuation associated with the glass transition. This approach provides a picture of the relaxation time at the glass transition which is directly observable through calorimetric measurements [11] and has been widely used to analyze the molecular mobility in amorphous domains of complex systems at the glass transition [12–17]. An increasing number of studies relate the degree of cooperativity to the number and ratio of weak physical inter-chain bonds [15,18–22]. Furthermore, it is speculated that, in nanoconfined environments, the exfoliated nanoclays can anchor polymer chains leading to a cooperativity increase [1,5], whereas in intercalated morphologies the macromolecules are confined in the galleries of clays [3,5,7], leading to a decrease of the cooperativity. However the number of studies considerably reduces when the systems contain other additives than the filler, with additional structural heterogeneities induced by microstructure changes, although these procedures are common in industry.

As an example, poly(lactic acid) (PLA) is a biodegradable, linear, aliphatic poly-ester, produced from renewable resources and thus its use is appealing for different industrial applications. In the last decade, the growing interest for poly(lactic acid) (PLA) as a promising substitute to petroleum issued polymers has led researchers to investigate how its macroscopic properties could be tailored by controlling its microstructure. Similar to the conventional plastics, PLA-based composites made by employing inorganic or natural fillers are the potential methods to improve its mechanical properties and even its functional features. Reinforcement of biodegradable polymers through the addition of macro or nano-scale reinforcements can be a useful method in production of eco-friendly nanocomposites for various applications [23,24]. With reference to layered inorganic systems both montmorillonite (MMT) and layered double hydroxides as hydrotalcite (LDH) have been used to provide PLA based nanocomposites. In both cases the use of suitable surfactants (ionic salts used as organomodifiers) is necessary to promote interactions, to enlarge the intergalleries spacing and to provide morphologies suitable to reach the target features (mechanical improvements and/or barrier properties) [25–28]. In addition, in some cases, a reactive coupling agent or polymer compatibilizer were employed [29,30].

In order to better characterize the structure of PLA-based nanocomposites, the thermal analysis is a very useful tool [31]. While their thermal stability is well characterized by means of thermogravimetric analysis (TGA), the Differential Scanning Calorimetry (DSC) investigations have been used in order to determine not only the characteristic temperatures as the glass transition temperature, the cold crystallization temperature and the melt temperature, but also the enthalpies of melting and crystallization, and then the crystallinity degree. As an example, in Ref. [32], W.S. Chow et al. examined the effects of the organo-montmorillonite (O-MMT 1% w/w) and the maleic anhydride-grafted ethylene propylene rubber (EPMgMA) as compatibilizer, on the thermal properties of PLA by using TGA and DSC. They showed that the thermal stability of PLA_O-MMT was greatly enhanced by the addition of EPMgMA. Furthermore, the crystallinity degree of the PLA was increased by the O-MMT incorporation, and conversely reduced by EPMgMA addition. They showed that even the crystallization temperature of PLA was decreased by adding both O-MMT and EPMgMA. Recently, Mohapatra et al. [29] studied the thermal behavior of nanocomposites based on PLA/poly(butylene adipate-co-terephthalate) (PBAT) blends with cloisite 30B as nanofiller provided by a reactive blending procedure employing maleic anhydride and peroxide to promote efficient PLA/PBAT interfacial interactions. Very similar approach was used by Kumar et al. [31] by using glycidyl methacrylate (GMA) as reactive compatibilizer. Thermo-mechanical and morphological investigations showed the improvement of the final properties of nanocomposites as compared with virgin PLA, even if the role of PBAT and reagents onto the confinement effects were not fully investigated.

The goal of this work is also to investigate by DSC the influence of the crystalline phase on the chain segment mobility in PLA_O-MMT nanocomposites, obtained by dispersing O-MMT even in the presence of PBAT, used here as surfactant/compatibilizer in a very low amount. The materials have been analyzed as formulated, then annealed with different procedures generating the α and/or α' crystalline forms [33]. The results obtained in terms of chain segment mobility were compared to the experimental results obtained by XRD and TEM, all aimed at investigating the starting morphology of PLA nanocomposites. In addition, to understand how the PBAT interferes with the morphology of PLA_O-MMT nanocomposites, we carried out modulated temperature DSC (MT-DSC) experiments in order to estimate the degree of cooperativity at the glass transition as a probe of the chain segment mobility. Indeed, recent works have validated this approach to obtain a structural representation of the physical interaction landscape in a material which undergoes structural hindrances [34], including the addition of nanofillers [35].

2. Materials and methods

2.1. Materials

Poly(lactic acid) PLA 2002D, 96% L-lactic acid (PLA) supplied by NatureWorks[®], (Minnetonka, MN, USA) [melt flow index (MFI) (2.16 kg, 190 °C) 4–8 g (10 min)⁻¹], was used as the polymer matrix. Before processing, PLA was dried in a vacuum oven at 110 °C for 18 h.

Download English Version:

<https://daneshyari.com/en/article/1394645>

Download Persian Version:

<https://daneshyari.com/article/1394645>

[Daneshyari.com](https://daneshyari.com)