



Macromolecular Nanotechnology

Superparamagnetic nanocomposites obtained by dispersion of ultrafine magnetic iron oxide nanoparticles in poly(3-hydroxybutyrate)



David D'Amico^a, Laura A. Fasce^a, Cristina E. Hoppe^{a,*}, M. Arturo López-Quintela^b, Viviana P. Cyras^{a,*}

^aInstituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA), Universidad Nacional de Mar del Plata, Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Juan B. Justo 4302, 7600 Mar del Plata, Argentina

^bDepartamento de Química Física, Facultad de Química, Universidad de Santiago de Compostela (USC), 15782 Santiago de Compostela, Spain

ARTICLE INFO

Article history:

Received 20 December 2013

Received in revised form 25 March 2014

Accepted 30 March 2014

Available online 4 April 2014

Keywords:

Biodegradable polymers

Poly(hydroxybutyrate)

Superparamagnetic materials

Nanocomposites

ABSTRACT

Superparamagnetic nanocomposites were obtained by dispersion of oleic acid-coated magnetic ultrafine iron oxide nanoparticles (NPs) in poly(hydroxybutyrate) (PHB), a semicrystalline, biodegradable and biocompatible polymer. Film nanocomposites displayed an optically homogeneous structure formed by sub-micrometric clusters created by a strong NPs segregation that occurred during solvent evaporation and polymer crystallization. Number and size of clusters increased with the concentration of NPs producing a controlled shift in the blocking temperature but hardly affecting PHB crystallinity and melting temperature. The presence of NPs decreased the elastic modulus of PHB and slightly reduced its hardness, leading to materials with improved resistance to permanent damage. This softening effect was attributed to the oleic acid shell covering the iron oxide core of the NPs. The present results shed some light on the mechanisms controlling morphology of semicrystalline-based nanocomposites modified with ultrafine NPs, opening interesting possibilities for the design of materials with controlled functional properties.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The design of polymer nanocomposites with predictable properties is a challenge that requires an efficient way to control the dispersion level of the nanoparticles (NPs) in the host matrix and a deep understanding concerning how these structures affect the final properties of the materials [1–5]. While it is well accepted that NPs dispersion strongly affects nanocomposites properties, it is not clear that a single state of dispersion or arrangement should optimize any given or all macroscale properties [5].

Sometimes, even the presence of NPs aggregates could be required in a solid material or colloidal dispersion for a specific function or property optimization [6]. The use of gold NPs aggregates as efficient photothermal heaters [7] and the application of stable colloidal aggregates formed by the assembly of individual magnetic NPs in MRI imaging [8] are some examples that prove the importance of the formation of aggregates in the design of new applications. In a similar way, both catalytic and optical properties [9] can be enhanced through the formation of controlled NPs aggregates. These effects are a consequence of the strong influence that magnetic and dipolar interactions between particles have on the properties of final assemblies and show that aggregates are not always a problem

* Corresponding authors. Tel.: +54 2234816600 (V.P. Cyras).

E-mail address: vpcyras@fi.mdp.edu.ar (V.P. Cyras).

but can be used as a design strategy for the synthesis of films with new and specific properties. Chemical affinity, polymer crystallinity, polymer crystallization kinetics, size and shape of NPs and relative sizes of these nanostructures respect to the polymer gyration radius, as well as processing conditions, can profoundly influence the level of dispersion attained [1–5]. Thus, relationship between all the variables of the fabrication processes and final states of NPs dispersion are important issues at the time of controlling reproducibility and material behavior for a specific function.

Compared with the preparation of materials based on amorphous polymers, dispersion of NPs in semicrystalline hosts is linked to the control of much more variables. Presence of a crystalline phase limit the location of modifiers (polymers, NPs, etc.) to the amorphous region (interspherulitic, intraspherulitic or interlamellar regions) [10,11] decreasing the available volume for NPs incorporation and making the morphology of these nanocomposites very dependent on the crystalline degree of the host, kinetic of crystallization and processing conditions (crystallization kinetics, annealing steps, presence of solvent, etc.) [12,13]. This idea was first reported by Kahn et al., which studied the effect of crystallization on the dispersion of small PMMA coated silica NPs (15 nm) in PEO and found a behavior that resembles that of molecular systems, in which the host “push” impurities out of the way of the crystal to maintain the crystallization process minimally perturbed [14]. They compared crystallization of nanocomposites formed by small NPs with crystallization behavior of polymer blends with a crystallizable and an amorphous component in which, for slow enough crystallization rates, the amorphous polymer can be completely expelled from the spherulites. This is not the common result found in the case of polymer nanocomposites synthesized with platelet fillers or large micrometer sized particles, too large to be easily maneuvered by the growing lamellae.

From the opposite point of view, the presence of NPs can affect crystallinity, lamellar thickness, spherulitic size and even crystalline structure of polymers, which are expected to have an important impact on mechanical and barrier properties and on chemical resistance of final materials [15,16]. In this regard, different and controversial effects have been reported. Larger crystallinity degrees have been produced thanks to an enhanced crystallization ability of the matrix in the presence of nanofillers, which behave as nucleating agents. Mitchell and Krishnamoorti [17] reported that for the carbon nanotubes/poly(ϵ -caprolactone) composite systems the nucleation activity was approximately 0.56, thus it can deduced that the nanotubes incorporation acts as a source of heterogeneous nucleation sites. On the other hand, a decrease of the percentage of crystallinity with the increase in NPs content has been produced as a consequence of partial inhibition on polymer crystal formations [14,18–21]. To further complicate this picture, recent reports have shown that moderate loadings of small NPs could have a negligible effect on crystallinity and melting temperature of highly crystalline polymers [22,23]. Therefore, under this complex scenario, the analysis of the inter-relationship between processing, morphology and properties of nanocomposites based on

semicrystalline polymers is of fundamental interest for scientists and technologists and it requires a deep research.

Modification of biocompatible polymers with inorganic nanostructures opens interesting possibilities for the development of new materials [24–26]. For example, the modification of highly semicrystalline biodegradable polymers, like poly(3-hydroxybutyrate) (PHB), poly(L-lactic acid) (PLLA) and poly(ethylene oxide) (PEO) with functional nanostructures, opens a broad range of potential applications in the biomedical field [24].

In particular, PHB is a biodegradable polyester, synthesized and intracellularly stored by several microorganisms in the form of granules, with properties that make it suitable for many applications in which petroleum-based synthetic polymers are currently used [27]. PHB can be produced from renewable sources through fermentation processes under restricted growth conditions [28]. It is a thermoplastic polymer with a high degree of crystallinity and with physical and mechanical properties close to those of isotactic polypropylene [28].

In this work, we evaluate the possibility of obtaining magnetic nanocomposites with reproducible and predictable properties, starting from PHB and ultrafine iron oxide NPs coated with oleic acid, one of the most common organic coatings used in the synthesis of iron oxide NPs [29]. We focus the investigation on the mechanisms that control dispersion of ultrafine NPs in highly crystalline nanocomposites as well as on the influence that their arrangement has on magnetic, thermal and mechanical properties. To this aim some of the results of PHB/iron oxide NPs are compared with those of a similar system (PEO/iron oxide NPs).

2. Experimental

2.1. Materials

Poly(3-hydroxybutyrate) (PHB) (kindly supplied by PHB Industrial S.A., Brazil, $M_v \approx 250,000$) and Poly (ethylene oxide) (PEO), with a molecular weight, $M_w \approx 300,000$ (Aldrich) were used as polymeric hosts. PEO was used for comparative purposes in magnetic measurements. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), cyclohexane, dichlorometane, chloroform, poly-oxyethylene-10-oleyl ether (Brij-97), oleic acid and oleylamine were purchased from Aldrich and used to prepare NPs and films. All the reagents of analytical grade were used as received. Deionized water was used in NPs preparations.

2.2. NPs synthesis

Ultrafine magnetite NPs with two different sizes were synthesized in order to study the effect of the size for certain selected formulations. NPs with an average size of 3.5 nm coated with oleic acid ($\gamma\text{-Fe}_2\text{O}_3\text{@OA-3.5}$) were obtained by a microemulsion method [30]. In brief, a (cyclohexane/Brij 97/aqueous phase) system was used with an aqueous phase formed by a 2:1 ferric-ferrous solution. Oleylamine was added to the microemulsion with magnetic stirring to form NPs. Final stabilization was

Download English Version:

<https://daneshyari.com/en/article/1399520>

Download Persian Version:

<https://daneshyari.com/article/1399520>

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