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Poly(ε-caprolactone)-based nanocomposites: Influence of compatibilization on properties of poly(ε-caprolactone)–silica nanocomposites

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Abstract

In the present paper, results about preparation and characterization of poly(ε-caprolactone) (PCL) based nanocomposites filled with silica nanoparticles are reported. In order to promote polymer/inorganic nanofiller compatibility and to increase the interfacial adhesion between the two components, silica nanoparticles surface has been functionalised by grafting a $M_w = 10{,}000$ Da PCL onto it. Successively, PCL based nanocomposites have been prepared by extrusion process. The relationships among size, amount of the nanofiller, organic coating and the final properties have been investigated. The morphological analysis has revealed that the silica functionalization can provide a useful method of preparation of the nanocomposites with the achievement of a fine, a good dispersion and a strong adhesion level. Thermal characterization has shown an improved thermal stability due to the presence of the silica nanoparticles, especially in the case of modified nanofillers. Finally mechanical tests revealed an increase of the Young's modulus in the PCL based nanocomposites.

Keywords: Polymers; Hybrid compounds; Coupling agent; Interface; Mechanical properties

1. Introduction

The recent developments of new materials based on nanometer sized filler particles in polymeric matrices represent a radical alternative to conventional-filled polymers or polymer blends resulting thus in a disruptive change in composite technology.

Polymeric nanocomposites combine the excellent flexibility, low density and easy processability of polymers with high strength, rigidity, heat resistance of inorganic materials, and may become the most important and practical materials [1–8].

Uniform dispersion of these nanoscopically sized filler particles produces ultra-large interfacial region per volume between the nanoelement and host polymer due to their high specific surface area. This enormous interfacial region represents the peculiar characteristic of the polymer based nanostructured materials and differentiates them from traditional composites and filled plastics containing micrometric reinforcements and fillers in the forms of fibres or powders (whiskers, talc, mica, calcium carbonate, etc.) [9,10].

In particular an interphase layer forms at the interface between organic and inorganic phases. The interphase

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polymer layer near the inorganic surface dramatically differs from the bulk polymer [11]. Because of this interphase layer, nanocomposites show enhanced properties with respect to constituents bulk properties.

As a result of the large surface area of nanoscopic fillers, significantly smaller amounts of the particles (1–6% by weight) compared to conventional composites (up to 60% by volume) can induce dramatic changes in host matrix properties [12,13]. In this way, it is possible to prepare materials characterized by a lower density and a better processability with respect to the use of conventional microfiller.

The different nature of the nanofiller (inorganic) with respect to that of the polymeric matrix (organic), and their high adsorption surface energies are responsible for a strong nanofillers tendency to form aggregates. At the same time, enhanced performances nanomaterials are correlated to an homogeneous nanoparticles dispersion and to a strong interfacial adhesion between filler/polymer. Hence, more versatile synthetic and/or preparative approaches are needed to obtain polymer based nanocomposites with controlled composition and microstructures. The key to any of these fabrication processes is the engineering of the polymer–nanoparticle interface.

Developing an understanding of the characteristics of this interphase region, its dependence on nanoelement surface chemistry, the relative arrangement of constituents and, ultimately, its relationship to the nanomaterials properties, is a current research frontier in nanocomposites. Equally important is the development of a general understanding of the morphology-property relationships for mechanical, barrier, and thermal response of these systems. As matter of fact, researchers currently focus most efforts on developing interfacial tailoring and on compatibilization promotion [14–19].

In the present research, results about PCL based nanocomposites filled with silica nanoparticles are reported. PCL is a synthetic semicrystalline polymer, which is characterized by low glass transition temperature (T_g), low modulus, high elongation at break and, overall, it is biodegradable. PCL is frequently found as a component in starch based formulations of biodegradable commodity films for packaging, but it is also proposed for nursery pots and transplantation bags [20]. In the area of biomedical devices, it is studied for suture filaments and as a component in polylactide based blends, where its resistance to hydrolysis, compared to Poly(lactic acid) (PLA), allows a longer permanence of the article within the body [21,22]. The main disadvantages of PCL reside in its low melting temperature ($T_m \sim 60$ °C) and, mainly, in its low modulus and abrasion resistance. The addition of silica nanoparticles should, in principle, be beneficial for all the above aspects, provided that an efficient control of the interfacial tensions in the composite formation is achieved [23]. In the present paper, a preliminary investigation on the chemistry of PCL grafting onto silica nanoparticles and on the influence of addition of modified nanoparticles in high molecular weight PCL matrix ($M_w = 60{,}000$ Da) on thermal, mechanical and morphological behaviour of nanocomposites is reported.

2. Experimental

2.1. Materials

Poly(ε-caprolactone) [molecular weight $M_w = 60{,}000$ Da] has been supplied by Solvay. Poly(ε-caprolactone) [molecular weight $M_w = 10{,}000$ Da] has been supplied by Poly-Sciences, Inc. γ-aminopropyltriethoxysilane (APTEOS), tetraethoxysilane (TEOS), Aldrich reagent-grade product, and hexamethylendiisocyanate (HMDI), Fluka reagent grade product, have been used without further purification.

2.2. Preparation of SiO_2 nanoparticles

Monodispersed silica particles have been prepared by the hydrolysis and polycondensation reaction of tetraethoxysilane (TEOS). The reaction has been carried out in a tightly screw-capped container by adding TEOS solution 0.025 M to a EtOH solution containing NH_4OH 0.5M and H_2O 8 M at 40 °C. After an equilibration time of 10 min, the suspension has been cooled, filtered, washed and dried in a vacuum oven at 100 °C for 24 h.

2.3. Modification of SiO_2 nanoparticles surface

Four hundred mg of γ-aminopropyltriethoxysilane (20% by weight of silica) have been dissolved in 40 ml of water and the aqueous solution (1% wt/wt) has been kept at room temperature for 2 h under mechanical mixing to hydrolysis reaction. A fine dispersion of 2 g of silica nanoparticles into 50 ml of ethanol has been added to this solution and kept at 70 °C for 24 h under stirring. After the reaction, the treated silica nanoparticles have been dried at 80 °C.

2.4. Preparation of coupling agent (SiO_2 CA)

Two g of silica nanoparticles modified with aminosilane have been dispersed into 40 ml of chloroform. To this dispersion, 1% by weight solution of HMDI in chloroform has been added with a separator funnel and kept for 24 h at room temperature under mixing. The amount of HMDI in mol is the same of γ-aminopropyltriethoxysilane, (2.23×10^{-3} mol).

This dispersion has been added dropwise to a solution containing 22 g of hydroxyl terminated PCL ($M_w = 10{,}000$ Da) dissolved in chloroform (HMDI/PCL molar ratio 1:1); the mixture was kept for 24 h at reflux under mixing.

2.5. Preparation of PCL/SiO_2 nanocomposites

PCL based nanocomposites have been prepared by mixing PCL ($M_w = 60{,}000$ Da) and SiO_2-CA into a