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Influence of the modification, induced by zirconia nanoparticles, on the structure and properties of polycarbonate

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ABSTRACT

Melt compounding was used to prepare polycarbonate (PC)–zirconia nanocomposites with different amounts of zirconia. The effect of the zirconia loading, in the range of 1–5 wt.%, on the structure, mechanical properties and thermal degradation kinetics was investigated. The zirconia nanoparticle aggregates were well dispersed in the PC matrix and induced the appearance of a local lamellar order in the polycarbonate as inferred by SAXS findings. This order could be a consequence of the intermolecular interactions between zirconia and the polymer, in particular with the quaternary carbon bonded to the methyl groups and the methyl carbon as inferred from the NMR results. The presence of zirconia caused a decrease in the storage and loss moduli below the glass transition temperature. However, the highest amount of zirconia increased the modulus. The presence of zirconia in PC slightly increased the thermal stability, except for the highest zirconia content which showed a decrease. The activation energies of thermal degradation for the nanocomposites were significantly lower than that for pure PC at all degrees of conversion.

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1. Introduction

Polycarbonate (PC) is an amorphous and inexpensive polymer known for its excellent optical and mechanical properties. PC nanocomposites have shown potential applications in UV protecting sheets and films [1–4]. There are a number of recent papers reporting on the mechanical properties, thermal stability and flame retardancy of PC nanocomposites containing different metal oxide nanoparticles [5–10]. The results indicate that metal oxides have an effect on the morphology, as well as mechanical and thermal behavior of PC. Some authors found that the well dispersed metal oxide nanoparticles in PC improved its surface, viscoelastic, and mechanical properties, and increased its thermal stability. They related these observations to the strong interactions at the polymer–filler interface [8–11].

PC–zirconia nanocomposites are promising materials due to the interesting optical properties of the final product [12–14]. The nanocomposites prepared by *in situ* polymerization were found to be highly transparent with up to 50 wt.% ZrO_2 nanoparticles, and exhibited good thermal stability, hardness and elastic modulus. These results were attributed to the interfacial interaction between the polymer and the nanoparticles. However, the hardness and thermal stability of the nanocomposites considerably decreased at high filler contents [12,13]. The deterioration in hardness was related to the agglomeration of the ZrO_2 nanoparticles in the polymer matrix, and the decrease in thermal stability to the evaporation of the entrapped organic solvent in ZrO_2 agglomerates and/or the unreacted monomer because of the low final conversion. Imai et al. [12] also modified the polycarbonate with sulphonic acid,

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and this was found to further reduce the thermal stability of the matrix polymer.

The purpose of this study was to obtain a deeper understanding of the interfacial interaction between zirconia nanoparticles and PC in PC–ZrO_2 nanocomposites prepared through a melt compounding method. The effect of the presence and amount of zirconia nanoparticles, prepared using a sol–gel method, on the structure, thermal and mechanical properties, as well as the thermal degradation kinetics, of the PC was investigated. The composites were characterized using transmission electron microscopy (TEM), X-ray diffractometry (XRD), Small Angle X-ray Scattering (SAXS), dynamic mechanical analysis (DMA), thermogravimetric analyses (TGA), and ^{13}C cross-polarization magic-angle spinning nuclear magnetic resonance ($^{13}C\{^1H\}$ CP-MAS NMR).

2. Experimental

2.1. Materials

Tetra-*n*-propylzirconate (Aldrich), capronic acid (Aldrich), ethanol (Eurobase), ammonium hydroxide (Aldrich) were used as received without further purification. Commercial grade bisphenol-A polycarbonate (PC, Makrolon® 2407 produced by Bayer Material Science, Germany and having a melt flow rate at 300 °C/1.2 kg of 20 g/10 min) was used in pellet form. The resin was dried at 120 °C overnight under static vacuum before processing.

2.2. Zirconia preparation

The ZrO_2 nanoparticles were prepared according to the method reported by Bondioli et al. [15]. The zirconia nanoparticles were precipitated by slow addition of an alcoholic solution containing capronic acid and tetra-*n*-propylzirconate, previously reacted for 30 min at room temperature, to a mixture of ethanol and water.

2.3. Composites preparation

The PC pellets were thoroughly mixed with 1, 2 and 5 wt.% zirconia for 10 min at 240 °C and 30 rpm in a 50 mL internal mixer of a Brabender Plastograph (Duisburg, Germany). The total batch size was approximately 40 g. The mixed samples were melt-pressed into 150×150 mm^2, 1 mm thick sheets at 240 °C for 5 min.

2.4. Analysis methods

TEM micrographs were acquired using a JEM-2100 (JEOL, Japan) electron microscope operating at 200 kV accelerating voltage. The obtained nanocomposites were cut into 100 nm thick slices using a Leica EM UC6 ultramicrotome. Slices were put onto a 3 mm Cu grid "lacey carbon" for analysis.

XRD patterns were recorded in the 2–70° 2θ range at steps of 0.05° and a counting time of 5 s/step in a Philips PW 1050 diffractometer, equipped with a Cu tube and a scintillation detector beam. The X-ray generator worked at 40 kV and 30 mA. The instrument resolution (divergent and antiscatter slits of 0.5°) was determined using standards free from the effect of reduced crystallite size and lattice defects.

SAXS measurements were taken using a Bruker AXS Nanostar-U instrument whose source was a Cu rotating anode working at 40 kV and 18 mA. The X-ray beam was monochromatized at a wavelength λ of 1.54 Å (Cu Kα) using a couple of Göbel mirrors and was collimated using a series of three pinholes with diameters of 500, 150 and 500 μm. Samples were directly mounted on the sample stage to avoid additional scattering of the holder. Data were collected at room temperature for 1000 s by using a two-dimensional multiwire proportional counter detector placed at 24 cm from the sample allowing the collection of data in the Q range 0.02–0.78 Å. The measurements were repeated in two different portions of each sample to check its homogeneity.

^{13}C cross polarization – magic angle spinning nuclear magnetic resonance ($^{13}C\ \{^1H\}$ CP-MAS NMR) spectra were obtained at room temperature with a Bruker Avance II 400 MHz (9.4 T) spectrometer operating at 100.63 MHz for the ^{13}C nucleus with a MAS rate of 8 kHz, 500 scans, a contact time of 1.5 ms and a repetition delay of 2 s. The optimization of the Hartmann–Hahn condition [16] was obtained using an adamantine sample. Each sample was placed in a 4 mm zirconia rotor with KEL-F caps using silica as filler to avoid inhomogeneities inside the rotor. The proton spin-lattice relaxation time in the rotating frame $T_{1\rho}(H)$ was indirectly determined, with the variable spin lock (VSL) pulse sequence, by the carbon nucleus observation using a 90°-τ-spin-lock pulse sequence prior to cross-polarization [17]. The data acquisition was performed by ^1H decoupling with a delay time, τ, ranging from 0.1 to 7.5 ms and a contact time of 1.5 ms. The proton spin-lattice relaxation time in the laboratory frame $T_1(H)$ was determined, using the saturation recovery pulse sequence [18], by the carbon nucleus observation using a 90°–τ–90° pulse sequence prior to cross polarization with a delay time τ ranging from 0.01 to 3 s. The ^{13}C spin-lattice relaxation time in the rotating frame $T_{1\rho}(C)$ was determined, with the variable spin lock (VSL) pulse sequence, applying the spin-lock pulse after the cross-polarization on the carbon channel [17]. The data acquisition was performed by ^1H decoupling with a spin lock pulse length, τ, ranging from 0.4 to 30 ms and a contact time of 1.5 ms. The cross polarization time T_{CH} values for all the carbon signals of PC were obtained through variable contact time (VCT) experiments [19]. The contact times used in the VCT experiments were 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0, 1.2, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0 and 7.0 ms.

The dynamic mechanical analysis of the blends and composites were performed between 40 and 180 °C in the bending mode at a heating rate of 5 °C min^{-1} and a frequency of 1 Hz using a Perkin Elmer Diamond DMA (Waltham, Massachusetts, USA).

Thermogravimetric analysis (TGA) was done in a Perkin Elmer TGA7 (Waltham, Massachusetts, USA) under flowing nitrogen at a constant flow rate of 20 mL min^{-1}. Samples (5–10 mg) were heated from 25 to 600 °C at different heating rates. The degradation kinetic analysis was performed

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