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Mechanical characterisation of virgin and recovered polycarbonate based nanocomposites by means of Depth Sensing Indentation measurements

V. Lorenzo [a,*], M.U. de la Orden [a,b], C. Muñoz [c], C. Serrano [c], J. Martínez Urreaga [a,c]

[a] Polymers, Characterization and Applications Research Group, Universidad Politécnica de Madrid, José Gutiérrez Abascal 2, E-28006 Madrid, Spain
[b] Departamento de Química Orgánica I, E.U. Óptica, Universidad Complutense de Madrid, Arcos de Jalón s/n, E-28037 Madrid, Spain
[c] Departamento de Ingeniería Química Industrial y del Medio Ambiente, E.T.S.I. Industriales, Universidad Politécnica de Madrid, José Gutiérrez Abascal 2, E-28006 Madrid, Spain

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ABSTRACT

The preparation of recovered polycarbonate matrix nanocomposites filled with organic modified montmorillonites has been considered as a method for the secondary or mechanical recycling of these polymeric wastes. The mechanical properties of these nanocomposites have been evaluated by means of Depth Sensing Indentation measurements. The selection of the measurement conditions has been discussed and a method to evaluate the heterogeneity of these materials has been presented. It has been found that greater nanoclay contents do not always lead to increase in mechanical properties. This fact has been explained in terms of the competition between the reinforcement effect of the nanofiller and the thermal and mechanical degradation that experiments the matrix during the melt processing. This result provide a limit for the clay addition in the mechanical recovery of polycarbonate wastes.

1. Introduction

Bisphenol A polycarbonate, PC, is the second largest volume engineering thermoplastics after polyamides due to its outstanding combination of mechanical, optical and thermal properties and its relatively moderate price. As a consequence of its high consumption, the generation of waste PC increases every year. Hence, different strategies for the valorization of the waste PC have been proposed including the mechanical and the chemical recycling and the energy recovery [1]. Mechanical recycling is an interesting method for recovering waste polymers but its application to waste PC is not easy because PC undergoes an important degradation during its reprocessing [2–6] and a consequent worsening of the mechanical properties. One method that has been considered for mechanical recycling of waste PC is the blending with other polymeric materials [7,8]. An alternative procedure for improving the properties of the mechanically recycled PC can be the preparation of nanocomposites with layered clays by melt processing [9,10].

Polymer–layered clay nanocomposites have received considerable interest in the last years and, consequently, have been thoroughly reviewed [11–13]. The careful addition of small quantities of nanoclays can lead to a significant improvement of the mechanical, barrier and flame retardancy properties of the matrix. Organically modified montmorillonite, OMMT, fillers are relatively cheap, their shape factor is high and their incorporation to polymer matrices can be achieved easily by using the conventional melt processing techniques. Consequently, it is expected

* Corresponding author. Tel.: +34 913363167.
E-mail address: vicente.lorenzo@upm.es (V. Lorenzo).

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that the melt compounding with nano-OMMT can be used as a method for enhancing the properties of PC wastes.

It has been proved that hardness indentation is an adequate tool to evaluate the mechanical properties of polymers and polymer based systems [14]. But in this kind of experiments, hardness is evaluated after releasing the indentor and, consequently, most of the information about the loading and the unloading periods is lost. Depth Sensing Indentation, DSI, is an experimental technique that provides information on mechanical properties of materials by considering the whole load–penetration depth, *F*–*h*, curve. DSI experiments allow one to obtain information about different types of hardness, elastic modulus and recoverable energetic contributions to the indentation of elasto-plastic materials [15,16]. Even more, the analysis of the *F*–*h* DSI curve also enables the determination of parameters related to the time-dependent mechanical response that can be exhibited by some materials. Although DSI measurements on polymers are not as straightforward as DSI measurements on metallic or ceramic materials, the DSI characterisation of polymers and polymer based materials is an area of increasing interest. This is a consequence of the fact that a single DSI experiment allows one to obtain very precise information about the elastic, the plastic and the viscoelastic behaviours of these materials simultaneously [17–23].

The main objective of this work is to characterise the mechanical properties of recovered PC matrix nanocomposites filled with OMMT by means of DSI techniques. These properties will provide information about the interest of the addition of nanoclays in the mechanical recycling of PC wastes.

2. Experimental section

2.1. Materials

Two different PC were used to prepare the nanocomposites that have been studied. The former was a virgin PC without any additive and with a melt flow index of 6.5 g/10 min (1.2 kg at 300 °C) that was kindly supplied by SABIC Innovative Plastics (Cartagena, Spain). The latter was PC powder obtained during the mechanical recycling of polycarbonate bottles used in water dispensers that was gently provided by Montsia plastic (Tarragona, Spain). The starting waste polycarbonate is composed of neat polycarbonate and of impurities as adhesive, paper, ink and other unidentified substances. These impurities were removed by sieving and washing with water and 2-propanol successively. The virgin and recovered PC's have been labelled PCV and PCR, respectively.

In this study, we have used two OMMT, Cloisite® 15A, C15, and Cloisite® 30B, C30, which were kindly supplied by Southern Clay Products.

2.2. Nanocomposite preparation

Powdered PCV and PCR were dried at 120 °C in a vacuum oven during 24 h. This drying process removes most of the water, as it leads to a constant weight with a variation of less than 0.01%. C15 and C30 nanoclays were vacuum dried during 24 h at only 70 °C, in order to avoid the degradation of the organic modification. PC-OMMT mechanical mixtures were compounded in a Rondol 10 mm Twin Screw Extruder with a 20/1 *L*/*D* ratio. A barrel temperature profile of 150, 220, 250, 250 and 225 °C and a screw speed of 40 rpm were selected for obtaining the PC-clay nanocomposites. The estimated residence time was 3 min, approximately. Extruded materials were then cut to granules. To check the homogeneity of nanocomposites, some randomly selected granules were melted in a Differential Scanning Calorimeter, DSC, and no significant differences were observed. The nanocomposites were dried at 150 °C and then compression moulded at 250 °C in a press with hot plates. The four nanocomposites were labelled by the matrix identifier (PCR or PCV) followed by the numerical reference of the clay (15 or 30) and by the mass percent of the filler (2 or 4). For example, PCR302 reads for the PCR based nanocomposite that was reinforced with 2% of C30 clay.

The PCR and PCV samples were processed in the same way to equal the effect of the preparing conditions on the microstructure of the studied materials.

2.3. Structural characterisation

Fourier Transform Infrared, FTIR, spectra were recorded in a Nicolet iS10 spectrometer in transmission mode. Each spectrum was recorded at a resolution of 4 cm^{-1}, with a total of 25 scans.

The viscometric average molar masses, M_v, of neat PCR and PCV and those of the matrices of the nanocomposites were determined by dilute solution viscosimetry. The values of the intrinsic viscosities, $[\eta]$, of the samples in chloroform at 25 ± 0.5 °C were measured using an Ubbelohde viscometer by extrapolation to infinite dilution. The values of M_v were calculated by using the Mark–Houwink–Sakurada equation,

$$[\eta] = KM_v^{\alpha} \quad (1)$$

with the parameters $K = 0.0301$ ml/g and $\alpha = 0.74$ according to [24].

Microtomed sections of the different materials were examined by Transmission Electron Microscopy, TEM, at room temperature. A JEOL JEM-2100 transmission electron microscope, operated at 200 kV, was used to obtain images of the nanocomposite specimens.

2.4. Depth Sensing Indentation (DSI) measurements

DSI measurements were carried out by using a Shimadzu DUH211S Ultra-Microhardness Tester equipped with a Berkovich type diamond indenter at room temperature (20 ± 0.5 °C). The tester was calibrated with a fused silica and a steel certified standard specimens in order to evaluate the correction due to the compliance of the equipment and the contact area function of the indenter.

Each test was performed after a waiting period of at least half an hour for reaching thermal equilibrium before starting. A maximum load, P_0, of 12.5 mN and a loading