Composites Part B 78 (2015) 1–7

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Processing and characterization of highly oriented fibres of biodegradable nanocomposites

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ARTICLE INFO

Article history:
Received 9 December 2014
Received in revised form
5 March 2015
Accepted 16 March 2015
Available online 21 March 2015

Keywords:
A. Polymer-matrix composites (PMCs)
B. Mechanical properties
B. Rheological properties
E. Melt-spinning

ABSTRACT

Biodegradable polymeric materials are becoming day by day ever more important in packaging, agriculture, single-use cutleries and other large consumer applications. The major part of those materials is used under the form of film, i.e. subjected to elongational flow, but the main problem is that they often offer poor mechanical properties. Adding nanofillers, like Multi Walled Carbon Nanotubes (MWCNTs) may solve this problem but only if there is a full control of their orientation inside the material. Aim of this work is to investigate the processing-properties-morphology relationships for a system prepared under elongation flow of MaterBi and commercial MWCNTs. The materials were characterized both in shear and non-isothermal elongational flow and mechanical tests have been done on hot and cold drawn fibres. The morphology has been investigated by TEM.

The shear viscosity increases dramatically in the presence of the MWCNTs, and the Cox–Merz relation does not hold.

The mechanical properties of the hot stretched fibres strongly increase with the draw ratio but the increase is larger for the filled fibres because of the orientation of the MWCNTs. This is not true for the cold drawing because the very low mobility of the MWCNTs hinders their further orientation and the final properties seem driven by the matrix.

1. Introduction

Nanobiocomposites are systems having a biodegradable polymer matrix filled with very small amounts of nanoparticles. Their interest from a scientific and industrial point of view is due to the possibility to conjugate the important characteristic of the biodegradability of the matrix with the reinforcing action of the nanoparticles. Although it is true that the nanoparticles remain in the environment after the complete biodegradation of the nanobiocomposites, given the very small amounts of inorganic nanoparticles used, the environmental sustainability and the features of the biodegradable matrix are not compromised.

Moreover, these last two considerations are very important due to the not satisfactory properties of the majority of the biodegradable polymers for many applications [1–3]. It is therefore necessary to improve their properties in order to make them competitive with conventional fossil fuel based polymers.

The scientific literature reports several papers about the preparation and the characterization of bio-polyesters based nanocomposites and in particular poly(lactic acid) (PLA) [4–18] and polycaprolactone [19–23] mixed with different types of lamellar silicates or carbon nanotubes.

Among the biodegradable nanocomposites based on starch containing polymers, systems mainly based on clays and silicates [24–31] or incorporating other organic fillers [32,33] have been studied and reported in scientific literature. However, only a few works report studies on starch-based systems with carbon nanotubes and, in all the cases, prepared by solvent casting [25].

To our best knowledge there is no systematic study regarding the preparation by melt compounding of nanocomposites based on commercial starch-derived polymers and carbon nanotubes and in particular on the effects of the spinning and of the cold drawing on the mechanical properties of these nanobiocomposites. In this work, therefore, we have prepared nanocomposites based on a starch-derived matrix (MaterBi®) and carbon nanotubes via melt mixing and cold stretching. In particular, the effects of the elongational flow on the dispersion and the possible aligning of the nanotubes along the flow direction were investigated. Rheological,

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http://dx.doi.org/10.1016/j.compositesb.2015.03.054
1359-8368/

morphological and tensile characterization showed also that the properties were found remarkably different upon varying processing and concentration of the nanotubes.

2. Experimental section

2.1. Materials and processing

The biodegradable polymer system used in this work (MB) belongs to MaterBi® family produced by Novamont (Italy). In particular, a CF04P grade was used (measured melt flow rate = 7 g/10 min at 160 °C and 5 kg load) which is a mixture of biodegradable thermoplastic polyesters of proprietary composition. Multi-walled carbon nanotubes, MWCNTs, supplied by Sigma–Aldrich (USA), were obtained through chemical vapour deposition. The main properties are: the average outside diameter (external diameter) about 120 nm and length 5–9 μm, carbon content >90%, density 2.1 g/ml at 25 °C. The MWCNTs were added at 1 and 2% wt/wt.

MWCNTs were also treated in a plasma reactor with radio-frequency polarized anode (Gambetti, Italy). The nanotubes were dried under vacuum at 120 °C overnight, fractionated in a mortar, put on a watch glass and then fed to the reactor, using oxygen as gas, a power of 120 W and a treatment time of 10 min, according to our previous studies [34–36]. The functionalized MWCNTs (fMWCNT) were added at 1% wt/wt.

The preparation of the MB/MWCNTs system was carried out using a corotating twin-screw extruder (OMC), having D = 19 mm and length to diameter ratio of 35 with the following temperature profile: 90–100–110–120–130–140–150 °C, screw rotation speed of 220 rpm and feed rate of 25 g/min. Under these conditions, the residence time measured by feeding a colour tracer to the extruder was about 80 s. The molten material coming out the die of the extruder was cooled on line in a water bath, pelletized and then used for further processing and characterization.

The materials were prepared by premixing them in the solid state and then feeding them into the extruder. Virgin MB was subjected to the same processing for comparison.

The fibres were spun using a capillary viscometer (Rheologic 1000, CEAST, Italy) operating under a constant extrusion speed (5 mm/min), with a die of 1 mm diameter (D_0) at 145 °C and 150 °C. At the exit of the capillary, the filaments were drawn at constant speed and free cooling at room temperature using a collecting pulley. The take-up velocity was varied in order to obtain fibres with different hot draw ratio (DR_H). The hot draw ratio, DR_H, has been evaluated by dividing the square diameter of the die by that of the fibre. The fibre diameter varies between 250 and 80 μm.

The spun fibres were drawn with the aid of an Instron machine at room temperature and at a crosshead speed of 10 mm/min. The initial length was in all the cases 30 mm. Fibres with a DR_H of about 15 were used for the cold drawing The amount of drawing is characterized by the draw ratio: $DR_C = L_f/L_0$, were L_f is the final length and L_0 the initial length of the fibre. L_f was measured after the recovery of the fibre.

2.2. Characterization

The rheological characterization was performed using a plate–plate rotational rheometer Mars (Thermofisher), operating at two temperatures, namely, 145 °C and 150 °C. The instrument has been set to operate in the frequency sweep mode in the range 0.1–500 rad/sec with a strain of 5%.

The rheological behaviour in shear flow and non-isothermal elongational flow was tested using the same capillary viscometer (Rheologic 1000, CEAST, Italy) above described, equipped with the same drawing system. The capillary diameter was 1 mm, the length-to-diameter ratio was 40 and the testing temperatures 145 °C and 150 °C. Due to the high value of the length-to-diameter ratio, Bagley correction was not applied, while Rabinowitsch correction was applied throughout. As for the measurement of the non-isothermal elongational flow, the extruded filament coming out from the capillary viscometer was driven through a pulley system and is then drawn by using two counter-rotating rolls. The run was carried out by pulling the filament, extruded at a given flow rate, at a rotational speed which increases with a linear acceleration of 100 rpm s^{-1}, i.e. the rotational velocity increases of 100 rpm in 1 s. The test ends when the filament breaks. The force at break of the molten filament was read directly and is known as melt strength (MS). The breaking stretching ratio (BSR) was calculated as the ratio between the drawing speed at break and the extrusion speed at the die.

All rheological test were performed in triplicate and the maximum deviations have been in the range ±5%.

Mechanical tests of the fibres were carried out using an universal Instron machine, according to ASTM D882 (crosshead speed of 100 mm/min). The average values for elastic modulus, E, tensile strength, TS, and elongation at break, EB, were calculated.

Transmission Electron Microscopy, TEM, observations were performed at Centro Grandi Apparecchiature – UninetLab, University of Palermo. The analyses were carried out on the radial surface of the fibres. The ultrathin slides of the fibres at different DR were mounted on a lacey carbon films on 300 mesh copper grids and then observed by JEOL JEM-2100 under the accelerated voltage of 200 kV.

3. Results and discussion

Fig. 1 reports the rheological curves of the neat polymer and of the nanocomposites, measured by using both the rotational and the capillary rheometer at 145 °C and at 150 °C.

It can be observed that the rheological curves obtained at the capillary rheometer do not fit the corresponding ones obtained at the plate–plate rheometer. This implies that the Cox–Merz rule does not apply to both the matrix and the nanocomposite systems here investigated, in agreement with the results already found in other studies on heterogeneous, multiphase systems [37–40]. The effect of temperature is very important and the increase of viscosity is very relevant as the viscosity increases of about three times with a decrease of temperature of only 5 °C. This remarkable effect can be interpreted considering that the matrix is a mixture of

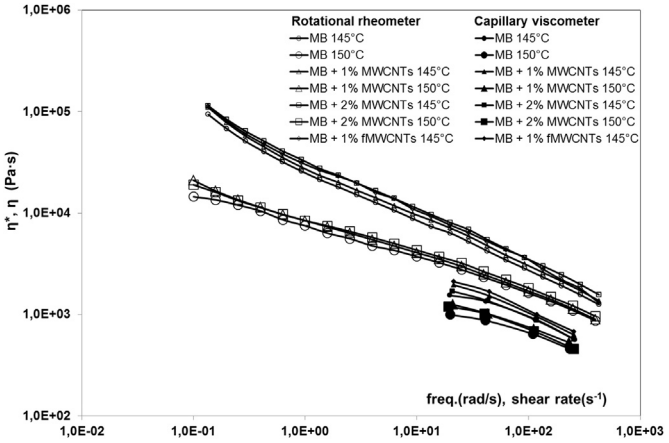

Fig. 1. Flow curves of all the investigated polymer systems at two different temperatures in the rotational rheometer and in the capillary viscometer.