Morphology, rheology, and mechanical properties of a new nanobiocomposite

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ABSTRACT: Nanobiocomposites are a new class of biodegradable polymer materials with an ultrafine phase dispersion of the order of a few nanometers in a biodegradable polymer matrix that shows very interesting properties often very different from those of conventional filled polymers. In this work the morphology and the rheological and mechanical properties of a new nanobiocomposite made of a biodegradable copolyester based blend with an organomodified montmorillonite have been investigated to evaluate its possible use in several applications. SAXS diffractograms and TEM micrographs show that the in both the adopted processing conditions an hybrid intercalated/exfoliated morphology is observed. Rheological behavior is significantly influenced by the presence of the filler and more important, depends on the type of the applied type of flow. As for the mechanical properties, the elastic modulus strongly increases, while the elongation at break remarkably decreases. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42128.

INTRODUCTION

Nanobiocomposites are a new class of biodegradable polymer materials with an ultrafine phase dispersion of the order of a few nanometers in a biodegradable polymer matrix that shows very interesting properties often very different from those of conventional filled polymers.[1–18] The presence of these nanoparticles improves several properties, in particular mechanical and thermal properties, of the biodegradable polymer matrix without any significant worsening of the biodegradability of the polymer matrix.

Bioflex is a blend made by PLA and biodegradable copolyesters.[19] To our knowledge only a very few articles have published on this system[20–23] and no article on Nanobiocomposites based on this biodegradable blend.

Aim of this work is to investigate the properties of a Bioflex based nanocomposite with organomodified clay. In the adopted compounding conditions, an intercalated/exfoliated morphology is observed. This morphology gives rise to a significant increase of the rigidity of the material, with a consequent loss of ductility. Very interesting is the rheological response of this nanobiocomposite that depends on the applied type of flow.

EXPERIMENTAL

Materials

The polymer matrix used in this work was a sample of a biodegradable polymer blend (Bio-Flex® F2110 by FKUR) of proprietary composition made of PLA and other biodegradable copolyesters.[19] According to FKUR,[19] the melt flow index, MFI, is between 3 and 5 at 190°C and under a weight of 2.16 kg and the melt temperature is 145–160°C.

The nanofiller (DT) is a silicate sample (Dellite 72T from Laviosa Chimica Mineraria). DT is a montmorillonite modified with ditallow dimethylammonium with an average diameter of 7–9 μm.

Bioflex has been compounded with the silicate at a concentration of 5% (wt/wt) in a Brabender mixer at two temperatures, namely 170 and 200°C, for about 5 min, time enough to reach a constant value of the torque in both investigated processing conditions. Pure polymer blend was subjected to the same treatments. Before processing Bioflex and Dellite were dried under vacuum for two hours at a temperature of 90°C and overnight at 120°C, respectively. The compounding conditions have been chosen in order to avoid the degradation of the matrix and of the organomodifier.

Characterization

Transmission electron microscopy (TEM) observations and Small angle X-ray scattering (SAXS) measurements were performed at the Centro Grandi Apparecchiature–UninetLab, University of Palermo. Small angle X-ray scattering (SAXS) measurements and were taken by means of Bruker AXS Nanostar-U instrument using Cu Ka radiation emitted by a
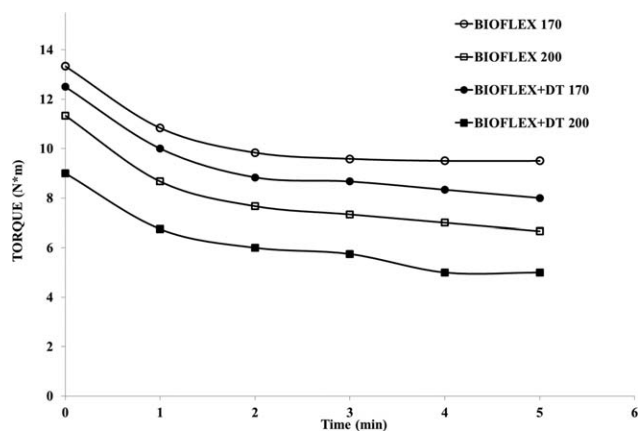
Figure 1. Torque curves of the pure Bioflex and of the nanobiocomposite sample.

rotating anode source set to 40 kV and 18 mA. X-rays were made parallel with a pair of Gobel mirrors and were collimated using a series of three pinholes with diameters of 500, 150, and 500 mm. Samples were directly mounted on the sample stage to avoid additional scattering of the holder. Data, collected at room temperature, were recorded using a two dimensional multiwire proportional counter detector placed at 26 cm from the sample, obtaining a Q range between 0.02 and 0.75 $A^{\circ -1}$. The momentum transfer, Q, is equal to

$$Q = 4\pi \sin\theta/\lambda$$

where 2θ is the scattering angle.

TEM analyses were carried out on ultrathin films with a thickness of about 100 nm for TEM observation were prepared via cutting from the epoxy block with a Leica (Solms, Germany) Ultramicrotome EM-UC6. Ultrathin slides of the samples were mounted on the lacey carbon films on 300-mesh copper grids and were then observed by a JEOL (Tokyo, Japan) JEM-2100 instrument under an accelerated voltage of 200 kV.

Rheological tests in shear flow were performed with a rotational rheometer Mars III (Thermofisher) in a plate-plate mode at a test temperature of 170°C, and with a capillary viscometer Rheologic 1000, (CEAST, Italy) at the same temperature. The tests in the rotational rheometer were carried out using a strain of 5% and a gap of 1.3 mm. The tests with the capillary viscometer were carried out with a capillary having $D = 1$ mm and length-to-diameter ratio of 40. Because of the high value of the length-to-diameter ratio Rabinowitsch correction was not applied.

Melt flow index (MFI) values have been measured at 190°C in a CEAST instrument under a weight of 2.16 kg.

Mechanical tests were carried out with an universal Instron machine mod 4443 according to ASTM D882. The elastic modulus (E) was measured at a speed of 1 mm/min. When the deformation was about 10%, the crosshead speed was increased to 100 mm/min until break. The values for E, tensile strength (TS), and elongation at break (EB) were calculated as the average of 10 tests.

The samples for all the tests were prepared by compression molding at 170°C. The thickness of the samples was about

600 μm for the tensile tests and about 1.4 mm for the rheological tests. Before testing all the samples were dried under vacuum for two hours at a temperature of 90°C.

RESULTS AND DISCUSSION

Compounding and Rheological Characterization

The torque recorded during the compounding in the mixer is a measure of the shear viscosity of the melt in those processing conditions and then of the processability of the polymer system. In Figure 1 the torque curves of the pure Bioflex and of the nanobiocomposite are shown. The data refer to tests carried out at 170 and 200°C and at a rotational speed of 60 rpm.

All the torque curves quickly decrease at the beginning of the process because the material melts quite quickly became almost flat after about 4–5 min of mixing in both processing conditions. This means that all the melts achieve a thermorheological equilibrium suggesting that the dispersion occurs in this mixing time and no significant degradation of the polymer matrix occurred. The two curves of the materials processed at the same temperature run very near but the presence of the filler slightly decrease the torque, then this dispersed nanofiller improve the processability of the biodegradable matrix.

The flow curves of all the systems prepared at $T = 170$ and at 200°C are reported in the Figures 2 and 3. In the figures, the data collected on both the rotational rheometer and on the capillary viscometer are reported. The flow curve of unfilled Bioflex sample has been measured on the processed material to take into account the effect of the thermomechanical treatment. The viscosity of the matrix decreases after processing and this decrease is more pronounced with increasing the mixing temperature. The nanobiocomposite shows a drastic rise of the flow curves, being this rise higher for the sample processed at lower temperature. The first behaviour is related to some thermomechanical degradation undergone by the matrix during the mixing that, of course, increases with increasing of the temperature. The second behaviour has been attributed to the presence of intercalated or exfoliated nanoparticles[24,25] that increase the resistance to the flow. Moreover, at low shear rate a very small upturn is shown by the pure matrix and this behavior is more pronounced—the
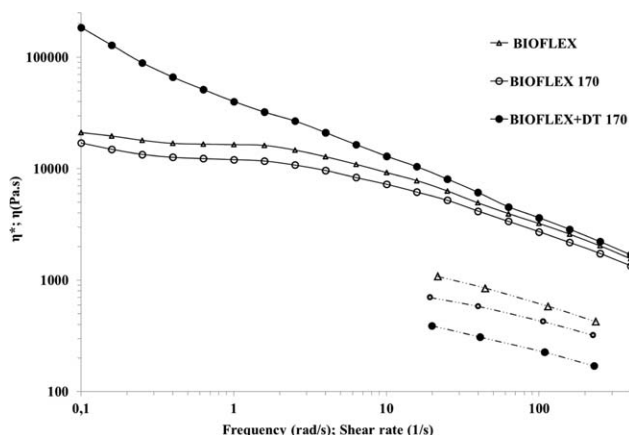

Figure 2. Flow curves of the Bioflex/Dellite system compounded at 170°C. Full lines refer to rheometer and dashed lines to capillary viscometer.
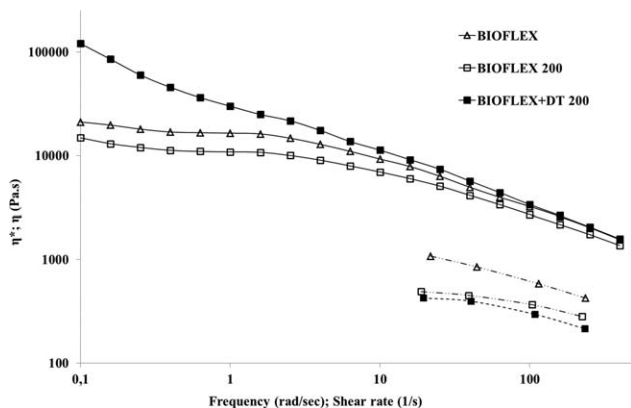
Figure 3. Flow curves of the Bioflex/Dellite system compounded at 200°C. Full lines refer to rheometer and dashed lines to capillary viscometer.

Figure 4. G' and G'' curves of the Bioflex/dellite system compounded at 170°C.

Newtonian plateau is almost disappeared—in presence of the nanofiller at both the processing temperatures. This behavior is typical of some heterogeneous systems and in particular of the nanocomposites and attributed to the formation of a some structured morphology in the melt.[24,25] The presence of this small amount of organo-modified clay dramatically increases the value of the viscosity in the low shear rate range. With increasing the shear rate all the flow curves approach one another and that of the pure polymer, but the curves of the nanobiocomposite remain higher than that of the matrix, Also for the nanobiocomposite, the viscosity is lower for the sample compounded at 200°C not only for the degradation of the matrix, as already observed, but also for some possible small degradation of the organomodified filler that can occur at this temperature.[26]

These data do not confirm the results and the comments previously done on the torque measurements. The flow curves, indeed, clearly show that the viscosity in shear flow at high shear rates—the shear rates involved in the compounding operation—is higher in the presence of the nanoparticles and this is the contrary of that observed for the torque curves. To explain this contradictory result, the flow curves measured at high shear rates in the capillary viscometer are also reported. These curves do not superimpose to that in the rotational rheometer for the same material. This implies that the Cox-Merz rule does not apply to the nanocomposite systems here investigated, in agreement with the results already found in other studies on heterogeneous, multiphase systems[27–30] and attributed to both the multiphase nature of the systems and some orientation phenomena of the nanofiller particles during the flow in the capillary. Moreover, the curves of the nanobiocomposite are lower than that of the matrix. This behaviour fits that observed for

Table I. MFI Values for All the Materials

Sample code	MFI, g/10 min
Bioflex 170	3.8
Bioflex 200	4.5
Bioflex + DT 170	4.4
Bioflex + DT 200	5.3
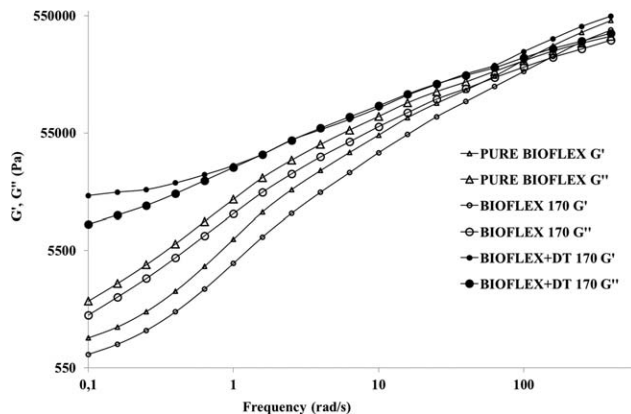
the torque curves and also the melt flow index values reported in Table I. The values of the MFI are higher for the nanocomposites prepared in both compounding processes indicating a lower viscosity of these materials with respect those of the pure matrix.

The unexpected lower values of the viscosity of the nanocomposite measured in the capillary can be attributed to the convergent flow at the inlet of the capillary that orient the inert particles along the flow direction and reduces the resistance to the flow. With respect to other nanocomposite materials, in a polymer blend like the Bioflex investigated in this work, this phenomenon is magnified, as the particles of the minor phase can also be oriented enhancing the reduction of the viscosity. The convergent flow is present at the inlet of the capillary of the viscometer and of the melt indexer, but also is present, although in small amount, in the mixing chamber.[31] In all these conditions, then, the viscosity of the nanobiocomposite is lower that that of the matrix.

In the Figures 4 and 5 the values of the in-phase and out-of-phase moduli are reported for the same samples. The complex moduli curves of the samples compounded at both processing temperatures reflect, of course, the same behavior observed in the flow curves. In particular, the G' curves of the
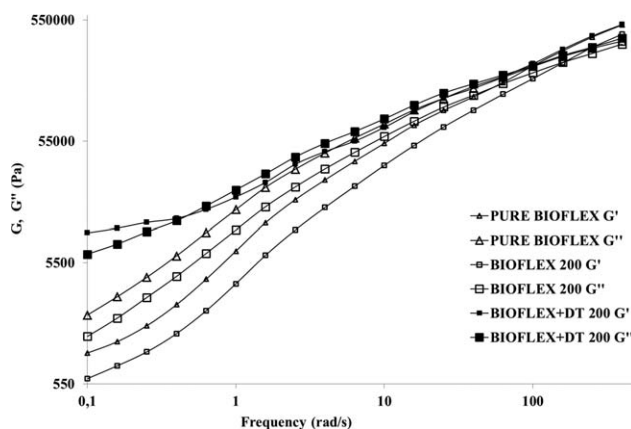

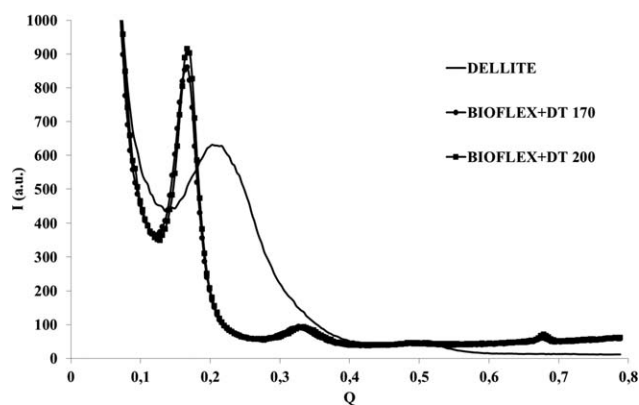**Figure 5.** G' and G'' curves of the Bioflex/dellite system compounded at 200°C.

Figure 6. SAXS diffractograms of the dellite sample and of the nanobiocomposite samples.

Table II. Mechanical Properties of All the Samples

Sample	E (MPa)	TS (MPa)	EB (%)
Bioflex 170	145 ± 8	11.4 ± 0.5	120 ± 9
Bioflex 200	140 ± 9	11.2 ± 0.5	125 ± 10
Bioflex + DT 170	210 ± 12	9.8 ± 0.8	29 ± 3.5
Bioflex + DT 200	192 ± 13	9.7 ± 0.9	27 ± 3.9

$$d = n\lambda/2\sin\theta$$

The interlayer distance of the pure organomodified montmorillonite is about 3.1 nm, while the interlayer distance of the filler nanoparticles in the nanobiocomposite is about 3.80 nm for the sample compounded at 170°C and about 3.85 nm for the sample compounded at 200°C. In both cases a significant increase of the interlayer distance is observed.

In order to better put in evidence the morphology of these samples, the TEM micrographs have been reported in Figure 7. In both samples both tactoids of about 25 nm and exfoliated lamellae are observed. This picture confirms the presence of intercalated nanoparticles but clearly indicates the presence of an exfoliated morphology. An intercalated/exfoliated hybrid morphology is then observed, being very small the influence of the compounding temperature.

In Table II the mechanical properties, elastic modulus, E, tensile strength, TS, and elongation at break, EB, are reported for the pure Bioflex and for the nanobiocomposites compounded in the two processing conditions.

First of all, the properties of the samples processed at the lowest temperature are better than those of the samples compounded at 200°C. This confirms the comments drawn from the viscosity data, i.e. that some thermomechanical degradation occurs during the compounding at higher temperature. As for the effect of the presence of the inert nanoparticles, in both processing conditions the elastic modulus significantly increases, while tensile strength and elongation at break decrease in the presence of the
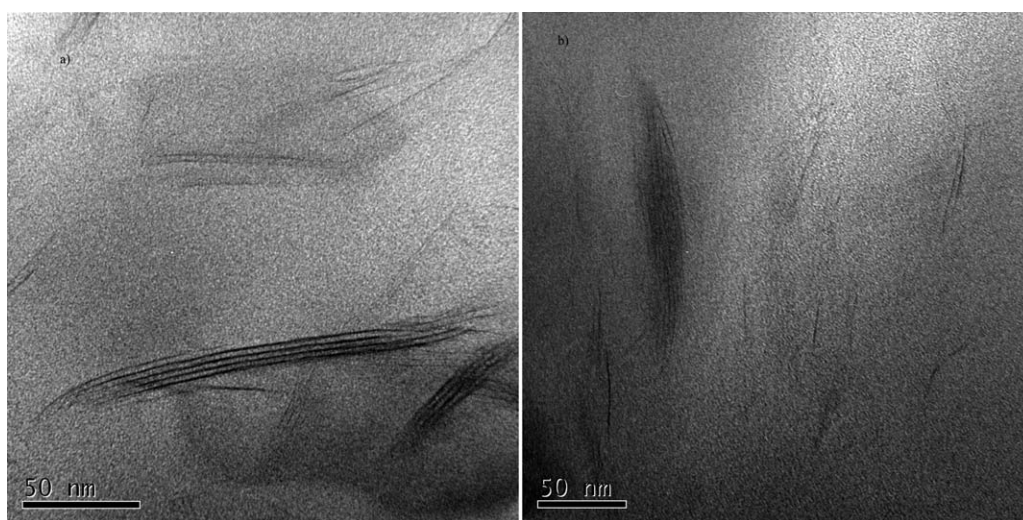
nanocomposites are significantly higher than that of the polymer matrix processed in the same conditions and tends to became flat at low frequency. This behavior indicates a transition toward a solid-like behaviour typical of more structured melt.

As for the loss modulus curves an increase similar to that shown by the storage modulus is observed for the nanocomposite with respect to the curve relative to the matrix.

Morphology

The SAXS diffractograms of the silicate and of the nanobiocomposite samples are reported in Figure 6. The characteristic peak of the nanofiller in the nanobiocomposites is shifted towards lower values of Q for both samples and no appreciable difference is observed as a consequence of the different processing temperature. The presence and the shift of this characteristic peak suggest the formation of an intercalated morphology. The macromolecules of the matrix penetrate the galleries of the tactoids increasing the interlayer distance between the layers. In particular the interlayer distance, d, can be calculated through the Bragg's formula:

Figure 7. TEM micrographs of the two nanobiocomposite samples, (a) sample processed at 170°C and, (b) sample processed at 200°C.

nanoparticles. The elongation at break, in particular is dramatically reduced by the presence of the organomodified clay particles. The presence of the intercalated/exfoliated nanoparticles are responsible for the increased rigidity of the biodegradable matrix. The small decrease of the tensile strength is a consequence of the reduction of the elongation at break. Indeed, the nanocomposite specimens show lower tensile strength because of the premature breaking.

CONCLUSIONS

Bioflex based nanobiocomposites with an organomodified montmorillonite present an intercalated/exfoliated morphology without any adding of compatibilizers. The nanobiocomposites show a very interesting rheological behavior. First, the flow curves obtained in the rotational rheometer present an increased viscosity in presence of the nanoparticles and an upturn of the flow curves at very low frequency. This behavior, together with the decrease of the slope of the G' curves at low frequencies suggest the presence of nanostructured, solid-like morphology. A completely different situation is shown by the flow curves of the nanobiocomposite in the high shear rates, indeed, they show viscosity lower than those of the matrix. This unusual behavior, confirmed by the MFI values, has been correlated with the convergent flow experienced by macromolecules and nanoparticles at the inlet of the capillary. This flow is able to orient the nanoparticles and the minor components of the blend, giving rise to melt with a lower resistance to the flow. The processability of the film grade Bioflex sample is then slightly improved because of the presence of the nanoparticles. The elastic modulus of the nanobiocomposite increases in presence of the organomodified montmorillonite, while the ductility id strongly reduced.

ACKNOWLEDGMENTS

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