



Processing, compatibilization and properties of ternary composites of Mater-Bi with polyolefins and hemp fibres

Md. Minhaz-Ul Haque^a, Vera Alvarez^b, Massimo Paci^a, Mariano Pracella^{c,*}

^a Department of Chemical Engineering and Materials Science, University of Pisa, Via Diotisalvi 2, Pisa 56122, Italy

^b Materials Science and Technology Research Institute, INTEMA-CONICET, University of Mar del Plata, B7608FDQ Mar del Plata, Argentina

^c Institute of Composite and Biomedical Materials, IMCB-CNR, Via Diotisalvi 2, Pisa 56122, Italy

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ABSTRACT

Ternary composites of a biodegradable thermoplastic matrix, Mater-Bi[®] (MB), with various polyolefins (PP, HDPE and PS) and hemp fibres (H) were obtained by melt mixing and characterized by SEM, OM, DSC, TGA and tensile tests. The properties of composites were compared with those of MB/polyolefin and MB/H blends. Maleic anhydride functionalized polyolefins were employed as compatibilizers. Crystallization behaviour and morphology of the composites were found to be affected by the composition, phase dispersion and compatibilizer. Thermogravimetric analysis indicated that the thermal stability of the polyolefin phase and fibres was influenced by the composition and phase structure. A significant improvement of tensile modulus and strength was recorded for composites of MB with PE and PS as compared to MB/H composites. The results indicate that incorporation of polyolefins in the biodegradable matrix, compared to binary matrix/fibre system, may have significant advantages in terms of properties, processability and cost.

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1. Introduction

Biodegradable polymers, which constitute a family of polymers designed to be degraded by living organisms, offer a possible alternative to traditional non-degradable polymers when recycling is impractical or not economical, and they can be composted together with food and yard waste [1,2]. However, due to the high cost, processing problems and specific performances of these materials, an advantageous opportunity is that to use biodegradable polymers in blends with other plastics and/or natural fillers to obtain materials with satisfactory cost/performance ratio [3]. Within this framework, a great attention from both academy and industry has been addressed to the development of novel eco-compatible composites with natural fibres [4,5]. Natural fibres exhibit several advantages as reinforcement of biodegradable polymer: biodegradability, low density, high specific properties, low cost, nonabrasive processing characteristics and extended availability from renewable resources. The disadvantages of natural fibres mainly concern the moisture absorption, low thermal resistance and fire resistance, local or seasonal variations in quality, lower mechanical properties (impact) than glass fibre composites and low fibre-matrix adhesion (especially with thermoplastic matrices). However, in the case of polymer composites the fibre-matrix interactions play a funda-

mental role. In order to improve the adhesion between cellulosic fibres and polymers, and to minimize the moisture absorption, chemical treatments – such as the alkalization, acetylation, silanization, etc. [6] – and functional modification of fibres and matrix have been used [7,8].

The properties of composites based on biodegradable thermoplastics, such as polyesters, polysaccharides, starch and their blends, containing vegetal fibres (i.e., hemp, sisal, flax, jute, cellulose derivative, etc.) have been analyzed in several papers. Improvements in the tensile behaviour have been reported for composites of various grades of Mater-Bi[®] – a biodegradable plastic with starch and other components – and cellulosic fibres [9–11]. For composites of polylactic acid (PLA) reinforced with hemp fibres [12,13] and other natural fillers derived from oat husks, cocoa shells and apple [14] the morphology, crystallization processes, thermal and mechanical properties have been examined by varying composition and thermal history. Further, improvements of mechanical and thermal properties have been observed for composites based on poly(hydroxycanoates) as compared to the virgin polymer [15,16].

The growing interest toward the development of novel eco-compatible composites has led to the formulation of systems that include, in addition to intrinsically degradable polymers, also non-biodegradable polymers with additives that can facilitate the processes of environmental degradation. Several polyolefins, such as polyethylene and polystyrene, have been used in mixtures with

* Corresponding author. Fax: +39 0502217866.

E-mail address: mariano.pracella@diccism.unipi.it (M. Pracella).

starch or starch based products (thermoplastic starch/ethylene-vinyl alcohol copolymers, starch + prooxidants) [17], as well as cellulose fibres [18,19]. It is expected that both the advantageous properties of commodity plastics and the presence of low cost natural fillers provide a good opportunity of reducing the total costs of material while improving the processing and mechanical properties [20].

The aim of the present work was the preparation and characterization of composite materials based on biodegradable polyester/polyolefin blends and natural fibres that can be used mainly in packaging applications with optimized costs and properties. The presence of the polyolefin component, due to its intrinsic characteristics, was expected to affect crystallization, thermal and mechanical behaviour as well as the processing of the composites. To improve the phase dispersion and the polymer–fibre compatibility, various polymers and copolymers modified with reactive groups – able to give rise to specific interactions at the interface between the components – were used.

2. Materials and methods

2.1. Materials

A biodegradable and compostable thermoplastic, MaterBi-Z[®] (MB), based on polycaprolactone (PCL), thermoplastic starch and additives (biodegradation time under controlled conditions: 20–45 days), was kindly supplied by Novamont (Novara, Italy). Iso-tactic polypropylene (PP), Moplen X30S (MFR = 8–10 g/10 min, Mw = 350,000 Da and Mn = 46,900 Da), and polypropylene-graft-maleic anhydride (PP-g-MA) (MA content 0.5–1 wt.%) were supplied by Himont and Montell, Italy, respectively. High density polyethylene (HDPE), Eltex B5920 (MFR = 0.39 g/10 min) was supplied by Solvay; Polystyrene (PS) powder (density = 1.05 g/cm³) was supplied by Goodfellow, England. HDPE-g-MA, Polybond 3009 (MFR = 3–6 g/10 min, density = 0.95 g/cm³, MA content 4 wt.%) was supplied by Uniroyal Chemical, Italy. SEBS-g-MA, Kraton FG-1901X (MFR = 22 g/10 min (200 °C, 5 kg), density = 0.91 g/cm³, MA content 2 wt.%) was supplied by Shell Chem, Italy.

Hemp (*Cannabis sativa*) fibres were kindly supplied by Sassetti Agricoltura S.r.l. (Bientina, Italy). In order to remove the non-cellulosic components, the fibres were first washed with liquid soap and immersed in 6% NaOH solution for 24 h at 40 °C. The alkali treatment increases the number of free hydroxyl groups on the fibre surface and produces changes in the chemical composition by extracting lignin and hemicellulose [4]. After NaOH treatment the fibres were repeatedly rinsed with distilled water, dried at 105 °C and finally stored for use.

2.2. Preparation of blends and composites

Blends of MB with PP, HDPE and PS (MB/PP, MB/PE, MB/PS) and their composites with hemp (MB/PP/H, MB/PE/H, MB/PS/H) were prepared in a Brabender Plasti-corder internal mixer at a temperature of 175 °C. The mixing was carried out under nitrogen flux for 7 min using a rotor speed of 60 rpm. To increase the compatibility of the components in the various systems PP-g-MA, HDPE-g-MA and SEBS-g-MA copolymers were added (2 wt.%) to the respective blends and composites.

The composites were prepared by using a two-step mixing procedure: in the first step masterbatches of MB with NaOH treated hemp (60/40 w/w) were processed in Brabender, then in the second step, 80 wt.% of masterbatch was melt mixed with 20 wt.% of polyolefin under the same conditions. In order to analyze the effect of compatibilizer amount on the morphology and final properties of blend and composite, various amounts of PP-g-MA (2–10 wt.%)

were added to MB/PP matrices. All the examined systems are enlisted with their code in Table 1.

2.3. Scanning electron microscopy (SEM)

SEM analysis was carried out on the surfaces of samples cryogenically fractured in liquid nitrogen. The sample surfaces were sputter coated with a fine layer of gold in an Edward Sputter Coater and analyzed by a Jeol JSM-5600LV scanning electron microscope. The sizes of dispersed polyolefin phases in blends were measured with semi-automatic software (Scion Image 1.62) from SEM micrographs.

2.4. Differential scanning calorimetry (DSC)

DSC analyses were carried out in a Perkin Elmer Pyris-Diamond differential scanning calorimeter under nitrogen flow. Samples (about 10 mg) were heated from 0 to 180 °C at a rate of 10 °C/min and held at 180 °C for 1 min to eliminate the previous thermal history (1st heating run), then they were cooled to 0 °C at 10 °C/min and heated again to 180 °C under the same conditions (2nd heating run). Crystallization and melting data were recorded for each sample from the maxima and areas of the crystallization and second run melting peaks. The degree of crystallinity X_c of PP and HDPE in the composites was calculated from the ratio between the values of melting enthalpy (from the second heating run) and the heat of fusion of 100% crystalline polymer.

The crystallization behaviour of blends (MB/PE, MP/PP, MB/PP*2) was also examined with an optical polarized light microscope (Leitz Ortholux II POL-BK) equipped with a hot stage (Linkam, model THMSE 600). In this experiment, films were sandwiched between microscope glass slides, heated up at temperature of about 20° above the melting point at a controlled rate and kept at this temperature for 3 min to destroy any trace of crystallinity. Then the films were cooled down at a rate of 5 and 10 °C/min to room temperature, or isothermally crystallized at fixed temperatures. Micrographs of the growing crystal phases were taken at different times during the crystallization process.

2.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of blends and composites was carried out in a TGA Q500 TA Instruments analyzer. The

Table 1
Compositions and sample codes of examined materials.

Sample code	Components	Compositions (wt.%)
MB/PE	Mater-Bi/HDPE	70/30
MB/PE*2	Mater-Bi/HDPE/HDPE-g-MA	70/28/2
MB/PE/H	Mater-Bi/HDPE/Hemp	48/20/32
MB/PE*2/H	Mater-Bi/HDPE/HDPE-g-MA/Hemp	48/18/2/32
MB/PP	Mater-Bi/PP	70/30
MB/PP*2	Mater-Bi/PP/PP-g-MA	70/28/2
MB/PP*5	Mater-Bi/PP/PP-g-MA	70/25/5
MB/PP*10	Mater-Bi/PP/PP-g-MA	70/20/10
MB/PP/H	Mater-Bi/PP/Hemp	48/20/32
MB/PP*2/H	Mater-Bi/PP/PP-g-MA/Hemp	48/18/2/32
MB/PP*5/H	Mater-Bi/PP/PP-g-MA/Hemp	48/15/5/32
MB/PP*10/H	Mater-Bi/PP/PP-g-MA/Hemp	48/10/10/32
MB/PS	Mater-Bi/PS	70/30
MB/PS*2	Mater-Bi/PS/SEBS-g-MA	70/28/2
MB/PS/H	Mater-Bi/PS/Hemp	48/20/32
MB/PS*2/H	Mater-Bi/PP/SEBS-g-MA/Hemp	48/18/2/32
MB/H	Mater-Bi/Hemp	68/32
MB/H2	Mater-Bi/Hemp	60/40

Note: The codes with the asterisk indicate blends or composites containing compatibilizer.

samples (6–15 mg) were heated from 50 to 600 °C at 5 or 10 °C min⁻¹ under nitrogen flux, after equilibrating at 50 °C. The change of weight loss percent and its derivative (DTG) were recorded as a function of temperature. The temperature calibration was carried out with a Nickel standard sample. For MB, PP and MB/PP blend a high resolution TGA analysis (Hi-Res) was carried out in the same instrument.

2.6. Mechanical properties

Uniaxial tensile tests were carried out at room temperature (23 °C) on oar-shaped specimens using a Universal Testing Machine (Instron 4467) at a rate of 1 mm/min, according to ASTM D 638 M-93 standard recommendations. The specimens were prepared by a Proma WL-5 micro-injector setting the cylinder and mould temperature at 170 °C and 40 °C, respectively. Sample dimensions were measured to an accuracy of 0.01 mm. Three to six specimens were tested for each sample after conditioning at 50% relative humidity. Average values of Young's modulus, tensile strength and elongation at break were calculated from the stress-strain curves.

2.7. Rheological test

Measurements of rheological properties were performed by a MCR 301 Anton Paar rheometer with parallel-plate geometry. Tests were carried out in steady rate mode in the molten state at 180 °C. Tests were done in a frequency range from 0.1 to 500 s⁻¹. For all experiments, the strain amplitude was maintained constant at 2%. Before starting dynamic frequency sweep tests, the linear viscoelastic range was determined through a strain sweep test. G' (storage modulus) and G'' (loss modulus) were registered as function of deformation (γ). It was observed that G' and G'' remained constant until 3% of deformation, showing the linear viscoelastic range.

3. Results and discussion

3.1. Thermal behaviour

Fig. 1 shows the DSC cooling thermograms of MB, blends of MB with polyolefins and ternary composites of MB, polyolefins and hemp (without compatibilizer). The values of phase transition temperatures (T_c : crystallization peak temperature, T_m : melting peak temperature) and enthalpies (ΔH_c : crystallization peak area, ΔH_m : melting peak area) recorded by DSC on 2nd heating run

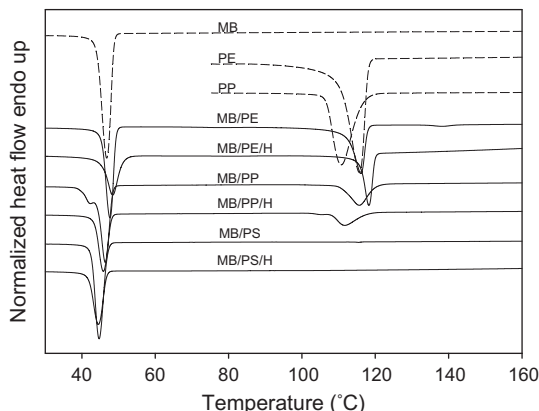


Fig. 1. DSC cooling thermograms of MB and its blends and composites with PP, PE, PS and hemp (cooling rate: 10 °C/min).

are summarized in Table 2. The degree of crystallinity of the crystallizable polymer components was calculated by the following equation:

$$X_c(\%) = (\Delta H_m / W \cdot \Delta H_m^0) \cdot 100 \quad (1)$$

where ΔH_m is the experimental heat of fusion, W is the matrix weight fraction and ΔH_m^0 is the heat of fusion of 100% crystalline polymer, with ΔH_m^0 (HDPE) = 293 J/g and ΔH_m^0 (PP) = 165 J/g [21].

As shown in Table 2, incorporation of a polyolefin into the biodegradable material produced only minor changes in the crystallization and melting behaviour of MB, as a consequence of phase separation phenomena due to the lack of miscibility between the polyolefin and other polar components (i.e., polyester and starch), even if the existence of crystalline interactions have been reported for blends of PCL with polyethylene and polypropylene [22]. The data in Table 2 indicate that, on cooling from the melt, the crystallization temperatures (and enthalpies) of MB/polyolefin blends did not display significant variations. According to the phase separation phenomena, the crystallinity degree of PE and PP in the blends remained almost unchanged with respect to plain polymers. Investigations by polarized optical microscopy on MB/PP films cooled from melt at 10 °C/min, showed that the growth of phase separated PP spherulites took place near to 120 °C, then the crystallization of MB matrix was initiated at about 50 °C at the boundary surface of PP spherulites and rapidly completed over all the mass of MB phase (Fig. 2). On subsequent heating (10 °C/min) the melting of the two polymer phases took place at the usual temperatures of pure polymers. Further, DSC data indicated that the presence of fibres in MB/H blends did not have nucleating effect on the crystallization behaviour of the MB matrix.

In the case of ternary systems a different thermal behaviour was recorded for MB/PE/H and MB/PP/H, that can be related to the differences observed in phase morphology. An increase of T_c of both polymer components was noticed for MB/PE/H sample, accompanied by a significant decrease of the heat of crystallization of MB phase as compared to plain MB. These changes could be accounted for by the effect of highly dispersed polyolefin phase and the presence of fibres on the crystallization of MB matrix. For MB/PP/H sample no nucleating effect of hemp on PP crystallization was evidenced, unlike that reported for the crystallization process of binary PP/hemp composites where the presence of fibres resulted in a neat increase of T_c and crystallinity of PP matrix [7]. However, it is expected that in ternary composites the interfacial interactions between polyolefin and fibres are limited owing to the dispersion of the polyolefin phase and fibres within the MB matrix (following the two-step mixing procedure). For MB/PS and MB/PS/H systems a little decrease of T_c of MB was found.

In the presence of compatibilizer a different crystallization behaviour was observed. Fig. 3 shows the effect of PP-g-MA content on the crystallization behaviour of MB/PP blends and MB/PP/H composites respectively, analyzed by DSC on cooling from melt at 10 °C/min. In all cases the crystallization peak temperature of PP increases with the compatibilizer content: for a PP-g-MA amount of 5 wt.%, T_c of PP increased from 110.8 °C (pure PP) to 125 °C in MB/PP*2 blends and to 120 °C in MB/PP*2/H samples respectively. The changes in the crystallization behaviour can be ascribed to nucleating effects induced by the presence of PP-g-MA copolymer. DSC analysis also indicated that for all examined composites both crystallization and melting temperatures of MB matrix were not influenced by the type and content of compatibilizer.

3.2. Morphology

SEM micrographs of fracture surfaces of the examined blends (with and without compatibilizer) are presented in Fig. 4. For all

Table 2

Thermal characteristics of components in blends and composites.

Sample code	MB				PE					PP				
	T_c (°C)	ΔH_c^a (J/g)	T_m (°C)	ΔH_m^a (J/g)	T_c (°C)	ΔH_c^a (J/g)	T_m (°C)	ΔH_m^a (J/g)	X_c (%)	T_c (°C)	ΔH_c^a (J/g)	T_m (°C)	ΔH_m^a (J/g)	X_c (%)
MB	46.8	81.4	63.5	81.3	–	–	–	–	–	–	–	–	–	–
PE	–	–	–	–	115.6	152.7	129.7	151.3	52	–	–	–	–	–
PP	–	–	–	–	–	–	–	–	–	110.8	94.6	162.8	94.1	57
MB/PE	47.6	74.4	63.9	73.6	116.3	161.7	129.2	163	52	–	–	–	–	–
MB/PP	46.4	80.6	63.0	79.9	–	–	–	–	–	115.6	89.5	160.2	88.0	53
MB/PS	44.7	81.4	62.8	81.6	–	–	–	–	–	–	–	–	–	–
MB/H2	46.4	76.2	63.8	75.7	–	–	–	–	–	–	–	–	–	–
MB/PE/H	48.5	66.7	62.9	69.0	118.0	154.5	131.0	156.2	53	–	–	–	–	–
MB/PP/H	45.8	77.7	63.0	80.8	–	–	–	–	–	111.7	87.5	159.7	85.6	52
MB/PS/H	44.5	75.1	63.0	77.7	–	–	–	–	–	–	–	–	–	–

^a The values of heat of crystallization and heat of fusion were calculated per gram of polymer component.

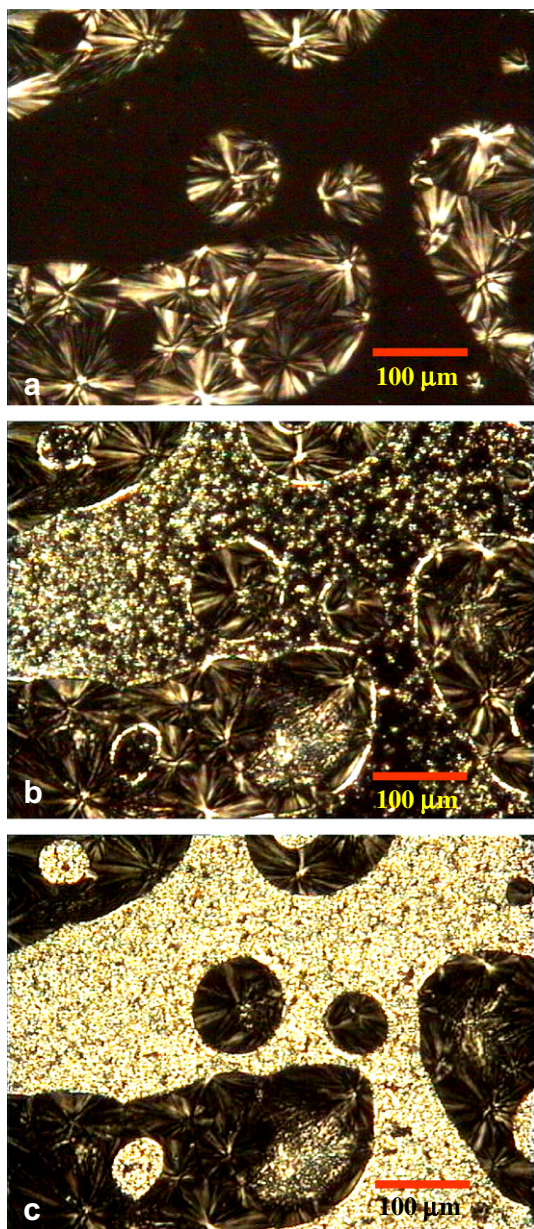


Fig. 2. Polarized optical micrographs of MB/PP 70/30 film during crystallization on cooling from the melt at 10 °C/min: (a) $T = 115$ °C (crystallized PP phase), (b) $T = 50$ °C (starting of MB crystallization) and (c) $T = 40$ °C (complete crystallization of PP and MB phases). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

samples, MB matrix and dispersed polyolefin phase appear as separated phases, due to the immiscibility of components. Blends MB/PP exhibited a characteristic droplet-like morphology with rather homogeneous size distribution (Fig. 4a), and a similar morphology was observed for MB/PE (Fig. 4e), whereas MB/PS blends displayed a large size distribution of the dispersed phase with irregular shape resembling a co-continuous morphology (Fig. 4g).

The micrographs of compatibilized systems indicated an improved phase dispersion and interfacial adhesion between polyolefins and MB. Generally, the number average size of PP dispersed

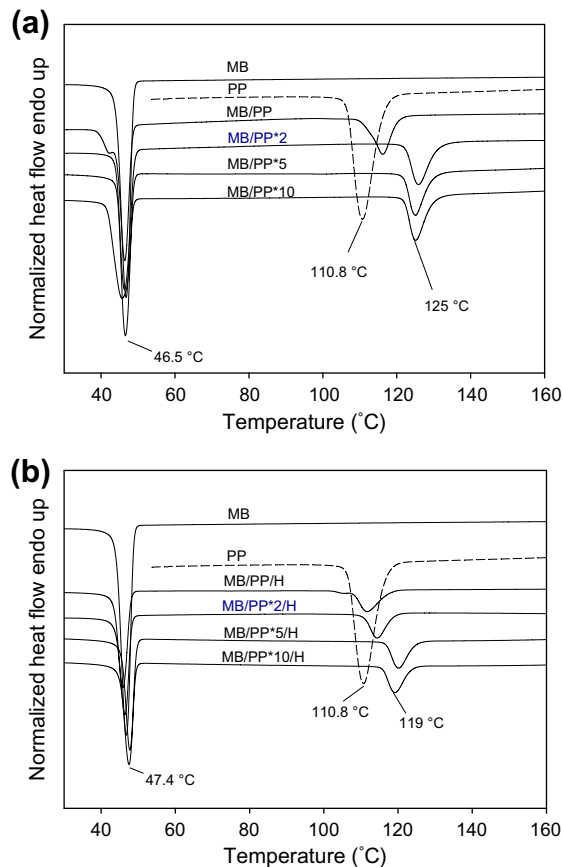


Fig. 3. DSC cooling thermograms of (a) MB, PP and MB/PP blends compatibilized with various PP-g-MA amounts, and (b) MB, PP and their composites compatibilized with various PP-g-MA amounts (cooling rate: 10 °C/min). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

particles is larger than that of PE particles, even if the two blends displayed a different size distribution. For MB/PP blends it was found a remarkable effect of PP-g-MA content on the average particle size which decreased from a value of about 28 μm for the uncompatibilized sample (Fig. 4a and b) to about 9 μm for the sample with 10 wt.% compatibilizer (Fig. 4d); however, it must be noticed that the addition of 2 wt.% compatibilizer caused a significant size reduction of PP particles to a value near 12 μm (Fig. 4c). For

MB/PE blends the average size of dispersed phase was around 5 μm , without any significant variation upon addition of 2 wt.% HDPE-g-MA (Fig. 4f).

Fig. 5 shows the SEM micrographs of fracture surfaces of composites with hemp. MB/H2 sample generally showed weak interactions between matrix and fibres and at higher fibre content (40 wt.%) the fibre dispersion became worse (Fig. 5a). On the other hand, for ternary composites the dispersion of fibres and polyolefin

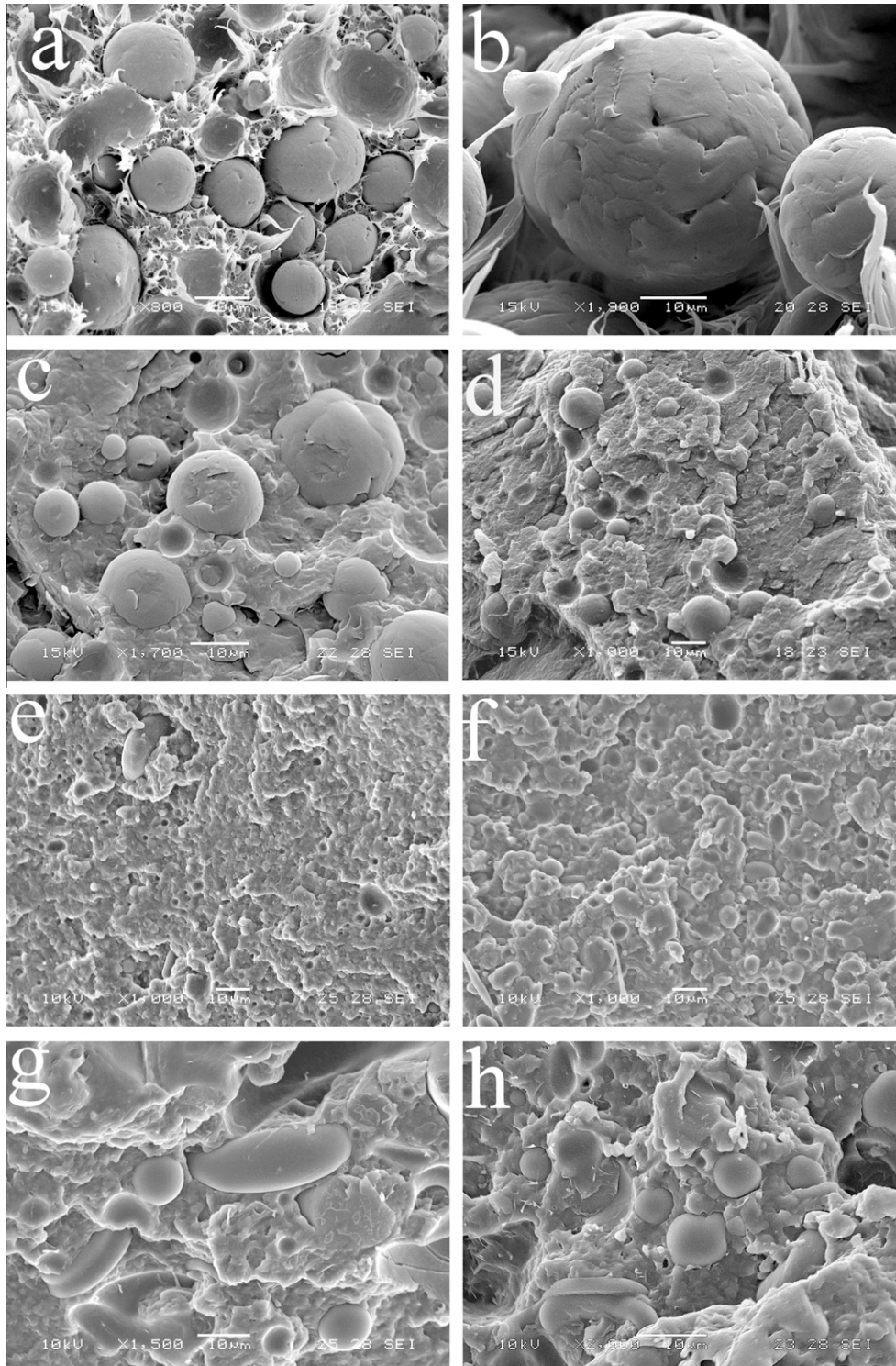


Fig. 4. SEM micrographs of (a) MB/PP, (b) PP particle (showing the growth of spherulites) in MB/PP blend, (c) MB/PP*2 (2 wt.% PP-g-MA), (d) MB/PP*10 (10 wt.% PP-g-MA), (e) MB/PE, (f) MB/PE*2 (2 wt.% HDPE-g-MA), (g) MB/PS, (h) MB/PS*2 (2 wt.% SEBS-g-MA) blends.

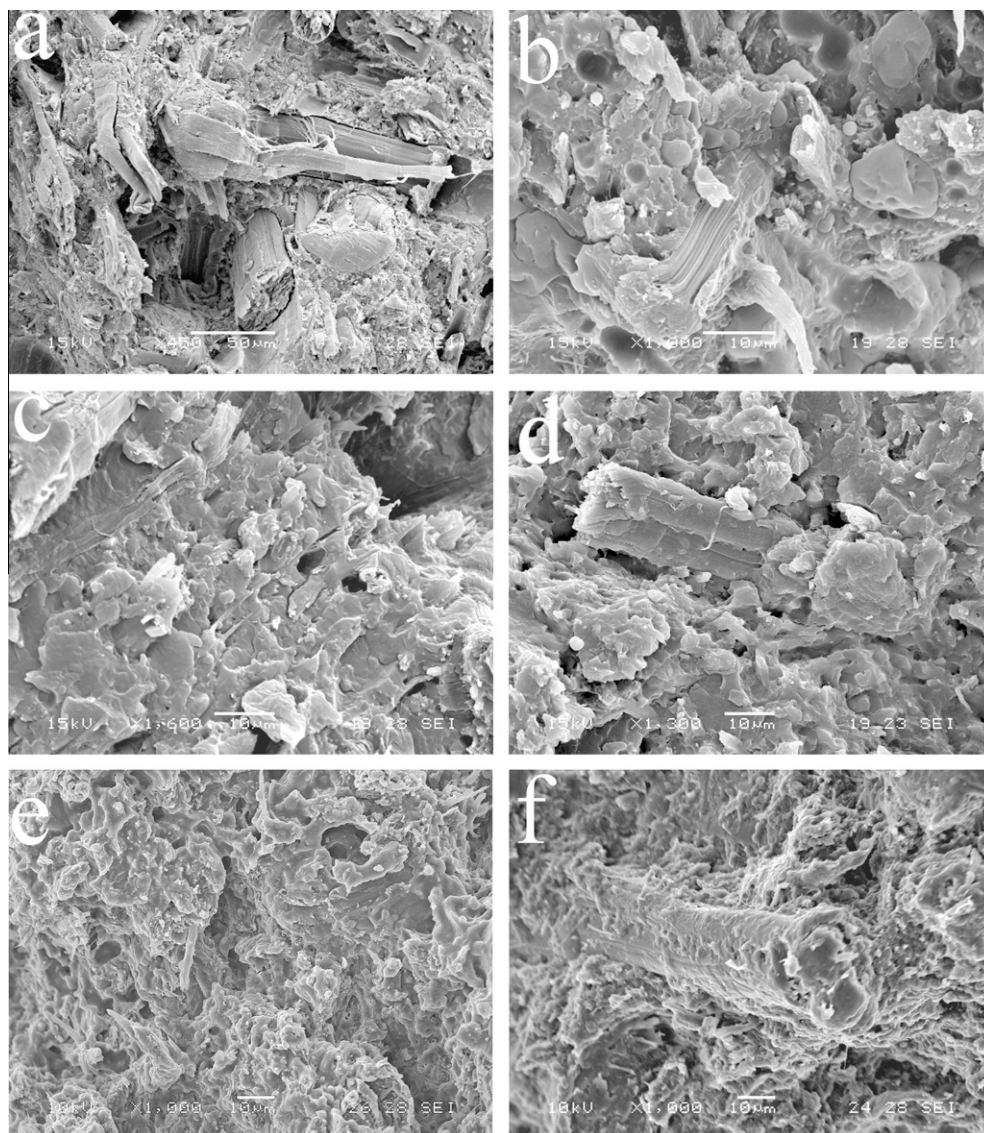


Fig. 5. SEM micrographs of (a) MB/H2, (b) MB/PP/H, (c) MB/PP+2/H (2 wt.% PP-g-MA), (d) MB/PP+10/H (10 wt.% PP-g-MA), (e) MB/PE+2/H (2 wt.% HDPE-g-MA), (f) MB/PS+2/H (2 wt.% SEBS-g-MA) composites.

in the matrix appeared almost uniform. The addition of compatibilizer contributed to reduce the particle size of dispersed polyolefin and improve the adhesion between fibre and matrix (Figs. 5c–f), as a consequence of interactions between the anhydride groups and hydroxyl groups of polysaccharide chains (i.e., starch and cellulose). The occurrence of such interactions has been reported for several polyolefin composites compatibilized with maleated PP [23–25].

3.3. Thermogravimetry

Exemplary TG and DTG thermograms of MB, blends and composites with hemp, at a heating rate of 10 °C/min, are shown in Fig. 6.

The DTG curve (i.e., the temperature dependence of the degradation rate) of plain MB in nitrogen displayed a large peak in the region 300–450 °C with maximum at 410 °C – which is to be ascribed to degradation of PCL (the major component of MB) while the starch degradation is at about 320 °C – followed by a minor peak near to 460 °C, which can be ascribed to the presence of additives (Fig. 6a); for plain polyolefins the maximum degradation rate

was recorded at about 411 °C for PS [26], 458 °C for PP [27] and 477 °C for HDPE [17] respectively (Fig. 6a). DTG curves of blends generally show a main peak above 400 °C characteristic of the MB matrix (PCL component) accompanied by peaks at higher temperature (Fig. 6a): for MB/PS the peak of PS coincides with that of PCL at 410 °C (the lower peak at about 460 °C is due to MB), while for MB/PE the peak at 472 °C corresponds to the degradation of the polyolefin. For MB/PP the peak at about 450 °C is due to the overlap of the peak of PP with the high temperature peak of MB. DTG thermograms carried out at 5 °C/min display very similar degradation behaviour but with maxima shifted to lower temperature.

As shown in Fig. 6b the degradation peak of hemp fibres was centered at 363 °C. The thermal degradation of hemp is mostly a two-stage process, the first at temperatures in the range 220–315 °C is generally associated with degradation of hemicellulose (270 °C) and the second at higher temperatures, in the range 315–400 °C, is ascribed to degradation of cellulose (360 °C) [28]. The DTG curves of ternary composites containing hemp fibres generally display three main peaks corresponding to the degradation of hemp (350–363 °C), PCL (408–415 °C) and polyolefin (415–475 °C) respectively (Fig. 6b). The composite containing PS

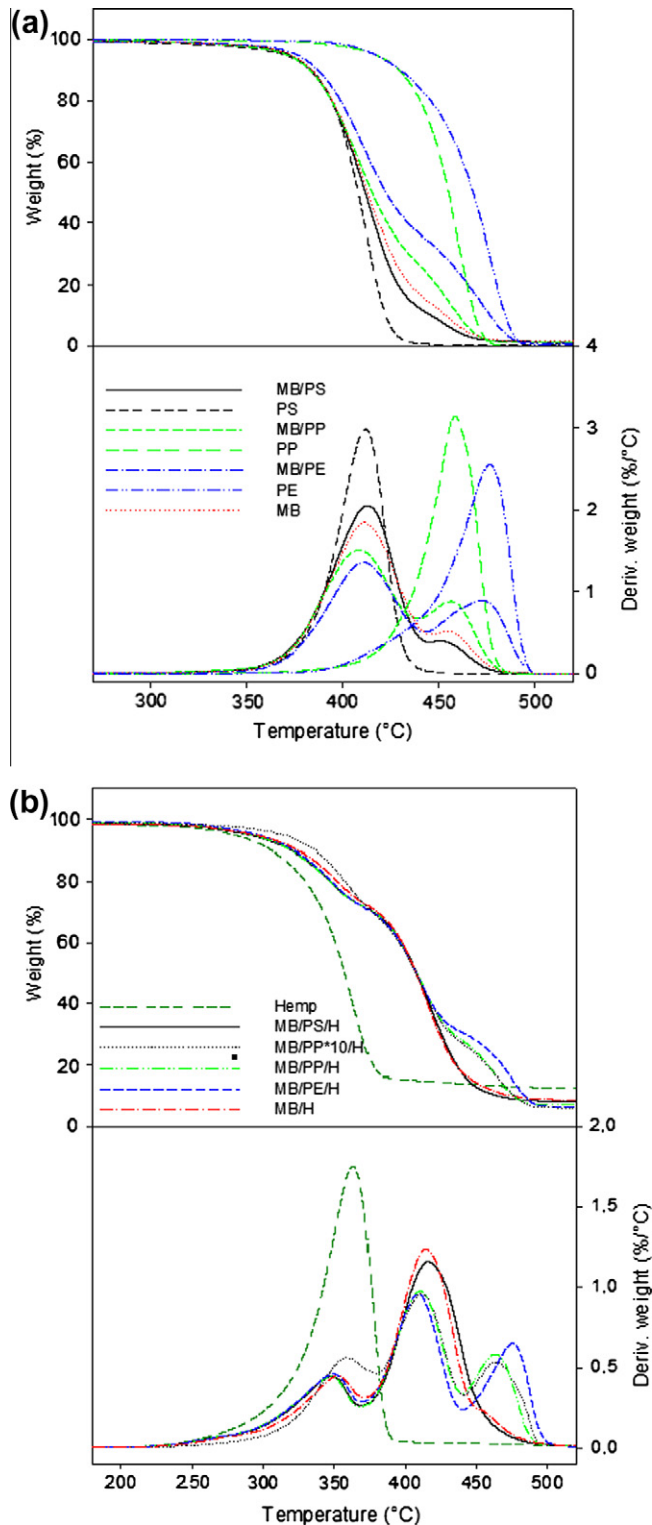


Fig. 6. TGA and DTG curves of (a) MB, PP and their blends, and (b) ternary composites as a function of temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

displayed a double peak with a pronounced maximum at 415 °C as a result of overlap of polyester and polyolefin peaks (with maximum at higher temperature respect to MB/PS blend). The degradation behaviour of the fibres in the composites appears to be influenced by the polyolefin type, likely owing to differences in the morphological features and crystallinity of these systems; in

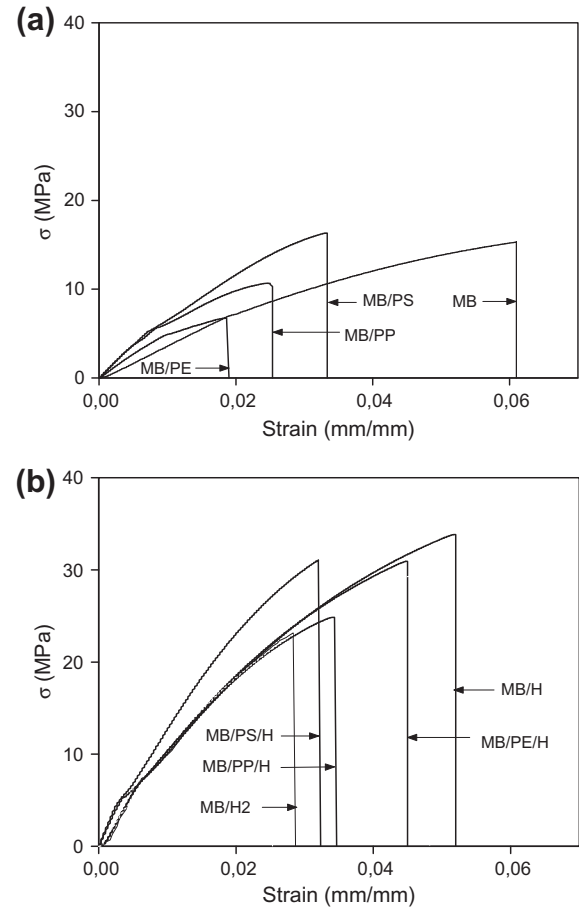


Fig. 7. Stress–strain curves of tensile tests for (a) blends of MB with polyolefins, and (b) MB/H and ternary composites.

ternary composites temperature corresponding to the maximum weight loss rate of the fibres was decreased (348 °C) as compared to the compatibilized systems (360 °C). In particular, for the compatibilized MB/PP*10/H sample a decrease of the degradation rate was observed in the range 230–350 °C, that can be accounted for by a higher polymer/fibre interfacial adhesion due to the interactions between the functional groups of PP-g-MA and hemp [7,29]. In the DTG curves of composites and blends the peaks of PP and PE are shifted to lower temperature with respect to plain polyolefins, suggesting a lower thermal stability of the polyolefins when they are dispersed within the biodegradable matrix. Similar effects, which can be associated with lower values of the activation energies for the degradation of polyolefin (and starch) have been reported for composites of HDPE and LDPE with MB [17].

3.4. Mechanical tests

Typical curves of mechanical tests for MB/polyolefin blends and their composites with hemp are summarized in Fig. 7. The tensile parameters recorded for blends and composites, without and with addition of compatibilizer, are reported in the bar diagrams of Fig. 8. The tensile properties of MB are essentially unaffected by changes of the temperature used in the melt processing of the material (100 or 175 °C). The blends show higher values of modulus and lower strength with respect to plain MB (Fig. 8a). In particular, the strength of MB/PS results to be higher than that of MB/PP and MB/PE.

The incorporation of 32 wt.% fibres into MB (MB/H) caused a marked rise of the modulus from 440 to about 1300 MPa – with

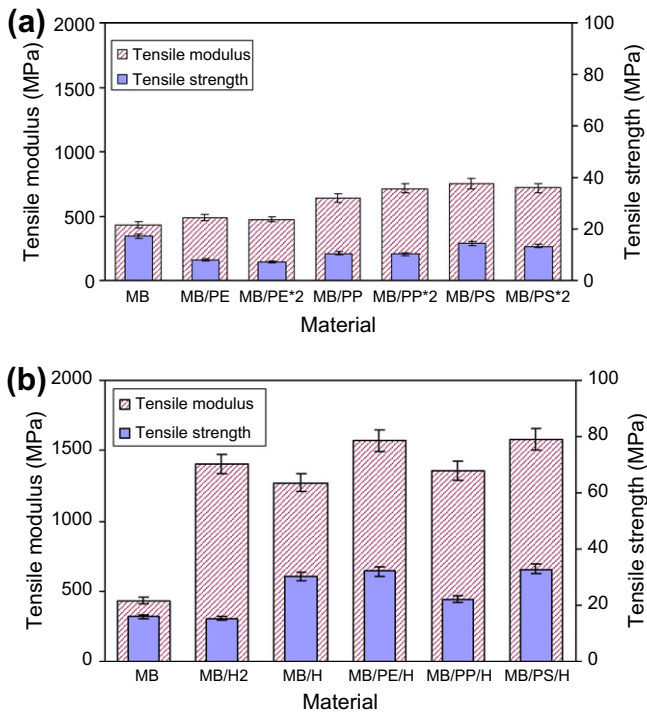


Fig. 8. Bar diagram of tensile modulus and strength for (a) MB and blends, and (b) MB/H and composites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

an increase higher than 200% – and of tensile strength from about 16 to 30 MPa. Increasing the fibre content to 40 wt.% (MB/H2), the modulus was further increased while the strength was reduced (Fig. 8b), likely due to the effect of dispersion of the fibres inside the matrix. A similar improvement of tensile properties has been described for composites of Mater-Bi Z[®] with flax cellulose pulp in the composition range 0–40 wt.% fibres [10].

In blends, the tensile modulus increased when MB was mixed with PP and PS, whereas no significant improvements were observed on mixing with HDPE; on the opposite, the values of strength were reduced for all blends as compared to MB alone (Fig. 8a). The addition of compatibilizers (2 wt.%) did not induce significant changes on the tensile properties; however, for MB/PP samples with increasing the compatibilizer content

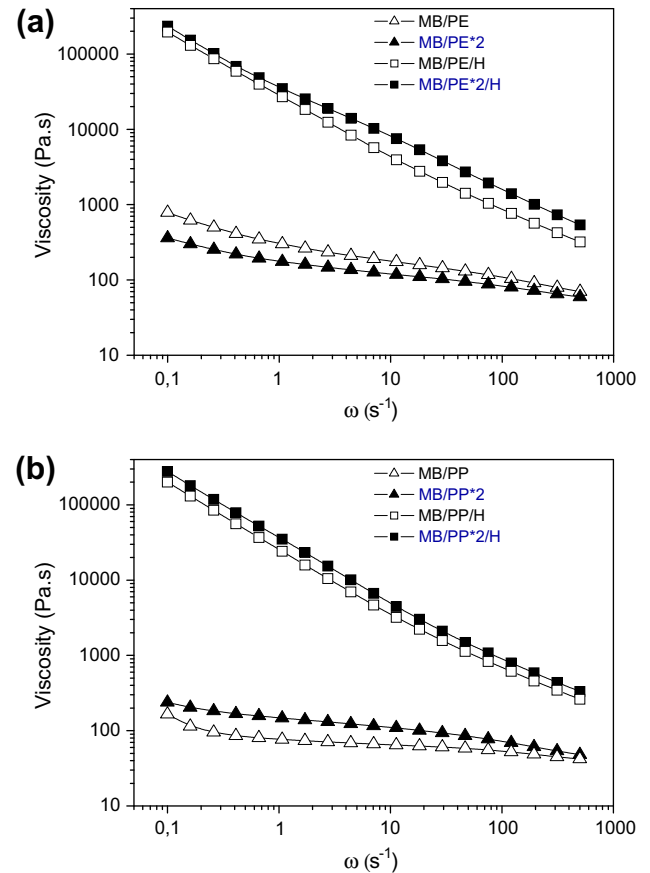


Fig. 9. Melt viscosity of (a) MB/PE and MB/PE/H, and (b) MB/PP and MB/PP/H as a function of shear rate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(5–10 wt.%) – as shown in Table 3 – an improvement of strength was observed suggesting the occurrence of effective interactions between the components, in accordance with the results of DSC and SEM analyses.

The ternary composites generally display higher properties than those of MB and blends (Fig. 8b). Tensile modulus was also improved with respect to MB/H and the strength, for systems with PE and PS, increased above 32 MPa. The addition of compatibilizer

Table 3
Mechanical properties of MB/PP blends and MB/PP/H composites.

Samples	Tensile modulus, <i>E</i> (MPa)	Tensile strength, σ (MPa)	Elongation at break (%)
MB	433 ± 38	17.2 ± 0.8	7.8 ± 2.0
MB/PE	484 ± 24	7.8 ± 0.2	2.7 ± 0.2
MB/PE*2	475 ± 23	7.3 ± 0.3	2.5 ± 0.2
MB/PP	641 ± 70	10.5 ± 1.2	3.2 ± 0.6
MB/PP*2	713 ± 34	10.3 ± 1.1	2.2 ± 0.3
MB/PP*5	643 ± 47	11.2 ± 1.8	2.1 ± 0.2
MB/PP*10	670 ± 41	15.5 ± 0.5	3.2 ± 0.3
MB/PS	751 ± 26	14.5 ± 1.4	3.1 ± 0.3
MB/PS*2	717 ± 41	13.3 ± 2.0	3.0 ± 0.5
MB/H	1273 ± 71	30.4 ± 1.7	5.2 ± 0.7
MB/H2	1406 ± 71	15.2 ± 0.8	2.3 ± 0.3
MB/PE/H	1568 ± 74	32.0 ± 2.0	4.9 ± 0.5
MB/PE*2/H	1389 ± 368	29.6 ± 7.3	5.2 ± 1.1
MB/PP/H	1360 ± 45	22.1 ± 3.2	2.9 ± 0.7
MB/PP*2/H	1150 ± 70	20.2 ± 2.5	2.7 ± 0.2
MB/PP*5/H	1600 ± 30	22.3 ± 1.0	2.5 ± 0.3
MB/PP*10/H	1380 ± 40	20.2 ± 3.0	2.4 ± 0.2
MB/PS/H	1582 ± 72	32.8 ± 1.5	4.0 ± 0.6
MB/PS*2/H	1474 ± 81	26.5 ± 3.1	2.9 ± 0.2

Table 4
Rheological parameters of blends and composites at frequency $\omega = 1 \text{ s}^{-1}$.

Samples	G' (Pa)	G'' (Pa)	η (Pa s)
MB/PE/H	20,900	28,700	27,000
MB/PE*2/H	15,900	37,200	34,900
MB/PP/H	23,300	25,700	24,200
MB/PP*2/H	30,600	37,300	35,000
MB/PS/H	57,900	103,000	96,700
MB/PS*2/H	37,100	80,300	75,400

did not show significant effects on the tensile behaviour of the composites; for MB/PP/H the values of modulus and tensile strength underwent little changes with increasing the PP-g-MA amount.

3.5. Rheological behaviour

The melt viscosity behaviour of MB/polyolefin blends and their composites with hemp is shown in Fig. 9. The melt rheology curves were fitted to the power law expression [30]:

$$\eta = A_{RH} \omega^{(n_{RH})} \quad (2)$$

where η is the apparent viscosity, A_{RH} a preexponential factor, ω the oscillation frequency of the rheometer equivalent to shear rate and n_{RH} the shear thinning exponent. The values of rheological parameters – such as G' , G'' and η – of blends and composites, recorded at a frequency of 1 Hz, are listed in Table 4.

It is possible to notice that the melt viscosity and moduli (G' , G'') of HDPE based blend was generally higher than that of PP and PS based ones. On addition of compatibilizer (2 wt.%) an opposite behaviour was found: melt viscosity decreased in the presence of HDPE-g-MA for MB/PE (Fig. 9a), but increased with addition of PP-g-MA for MB/PP blends (Fig. 9b). This effect could be associated with the viscosity range of each polyolefin component, as well as with changes of the morphology (and size) of dispersed phases due to the interchain interactions promoted by the functional groups.

For the composites, the viscosity values were markedly higher than that of blends, which is an expected behaviour to be related with the incorporation of fibres [31]. This trend was affected by the type of polyolefin, the highest values being observed for composites with PS (Table 4). Similar tendencies were observed for the other rheological parameters, i.e. storage and loss shear modulus (G' and G''), as reported in Table 4. In general, it appears that the addition of compatibilizer does not affect the viscosity of the composites in the low shear range, whereas significant differences are observed at high shear rates (especially for composites with PE), most likely as a consequence of lower viscosity values.

4. Conclusions

Binary and ternary systems based on a biodegradable polyester matrix (MB) with polyolefins (PP, PE and PS) and hemp fibres as dispersed components were characterized by microscopic, thermal, mechanical and rheological analyses. Reactive compatibilizers (PP-g-MA; HDPE-g-MA and SEBS-g-MA, respectively) were added in order to improve the interfacial interactions between the polymers and fibres. It was found that the incorporation of a polyolefin in the biodegradable matrix influenced the crystallization behaviour of the components. Nucleating effects on MB crystallization were observed at the interface of polyolefin particles in MB/PP blends. SEM and DSC analyses revealed changes of morphology and phase transition temperatures both for blends and composites in the presence of compatibilizers. The addition of PP-g-MA (2–10 wt.%) in MB/PP and MB/PP/H systems resulted in an improved

phase dispersion with reduced particle size and better interfacial adhesion.

The thermogravimetric analysis showed that the maximum weight loss rate of PP and PE in the composites is shifted to lower temperature with respect to plain polyolefins, suggesting a lower thermal stability of the polyolefins dispersed within the biodegradable matrix. On the other hand, the degradation rate of the fibres in the composites appeared to be reduced by the presence of compatibilizer, likely due to the effect of chemical interactions between the functional groups at the interface.

Regarding the mechanical properties, tensile modulus increased when MB was mixed with polyolefins, while the strength was reduced; the addition of compatibilizers (2 wt.%) resulted in no significant changes of tensile parameters. An increase of strength was observed for MB/PP blends at higher PP-g-MA content. In the case of composites, modulus and tensile strength generally increased with polyolefin and fibres incorporation, the largest values being reached for composites with PE and PS.

It can be concluded that the results reported here for the ternary systems support the expectations expressed in the introduction: namely the introduction of the polyolefin component in the biodegradable (polyester) matrix, as compared to the binary matrix/fibre system, may have some significant advantages in terms of properties and processability, as well as cost. Indeed, morphological analysis showed that it is possible to obtain a sufficiently homogeneous dispersion of the polyolefin phase – especially in the case of PE and PP composites – along with the fibres (30 wt.%) by controlling the particle size (and interfacial adhesion) through the introduction of a compatibilizer (modified polyolefin). Moreover, the addition of polyolefin may have a positive effect on the processability (higher thermal stability of the ternary composites compared to MB/H). From the mechanical point of view, for ternary composites the tensile tests showed values of modulus and stress better than those observed for the MB/H batch product. An increase of the fraction of fibres in the composite (>30 wt.%) generally leads to a worsening of the processability in the melt (mixing, extrusion, etc.) and especially of the mechanical properties (low ductility and impact resistance, low stability, etc.); otherwise, the addition of the polyolefin component in low concentration (10–20 wt.%) – compared with an equivalent amount of fibre (as for the batch product MB/H2) – seems to lead to a positive balance of properties, and also of cost considering the overall reduction that can be obtained in the amount of matrix employed ($\leq 50\%$ by weight). In order to provide a more complete description of the properties and degradability of these systems, tests related with impact properties, vapour permeability and soil biodegradation are currently under investigation.

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