Processing and Characterization of Nano-biocomposites Based on Mater-Bi® with Layered Silicates

A. Terenzi[1], A. Iannoni[1], L. Torre[1], A. Jiménez*[,2] and J.M. Kenny[1]

[1]*University of Perugia, UdR INSTM, Loc. Pentima Bassa 21,05100 Terni, Italy*
[2]*University of Alicante, Analytical Chemistry, Nutrition and Food Sciences Department, P.O. Box 99, 03080 Alicante, Spain*

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ABSTRACT: The development of new nano-biocomposites has been one of the main research areas of interest in polymer science in recent years, since they can combine the intrinsic biodegradable nature of matrices with the ability to modify their properties by the addition of selected nano-reinforcements. In this work, the addition of mineral nanoclays (montmorillonites and sepiolites) to a commercial starch-based matrix is proposed. A complete study on their processing by melt-intercalation techniques and further evaluation of the main properties of nano-biocomposites has been carried out. The results reported show an important influence of the nano-biocomposites morphology on their final properties. In particular, the rheological and viscoelastic characteristics of these systems are very sensitive to the dispersion level of the nanofiller, but it is possible to assess that the material processing behaviour is not compromised by the presence of these nano-reinforcements. In general, both nanofillers had a positive influence in the materials final properties. Mechanical performance shows improvements in terms of elastic modulus, without important limitations in terms of ductility. Thermal properties are improved in terms of residual mass after degradation and low improvements are also observed in terms of oxygen barrier properties.

KEYWORDS: Nano-biocomposites, Mater-Bi®, nanoclays, melt intercalation, characterisation

1 INTRODUCTION

One of the main environmental drawbacks caused by the widespread use of plastics for massive applications, such as food packaging, is their usual short lifetime, resulting in an important increase in the generation of plastic waste. There are many methods normally used to manage plastic products at the end of their shelf-life, such as incineration energy production, recycling and, finally, landfill disposal, which is the least desirable solution. All these methods for plastics waste management have several disadvantages and provide only partial solutions. Some of these problems stem from the low quality of some recycled products, an important contribution to global pollution and warming due to incineration and the accumulation of residues in landfill sites, with the inherent related problems of public health concerns and maintenance costs [1, 2]. Therefore, in recent years the interest in environmental issues related to plastics waste management has rapidly grown, and this fact has been one of the key issues driving researchers to develop environmentally-friendly polymers able to be used as replacements in the the main consumer-used commodities. One of the main lines of investigation followed in the last decade has been the development of biodegradable polymers obtained from renewable resources [3–7].

According to an early work by Doi and Fukuda in 1994 [8], biopolymers can be completely degraded by enzymatic action of living organisms (bacteria, fungi, yeasts), and the end-products of this action are CO_2, H_2O and biomass under aerobic conditions, or hydrocarbons, methane and biomass under anaerobic conditions. It is therefore clear that these materials are very interesting from an environmental point of view, since their by-products show very low environmental impact, and the raw materials used in their production are renewable with a lower impact on resource depletion than plastics obtained from fossil fuels. In

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Corresponding author: alfjimenez@ua.es

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the category of biopolymers obtained from renewable resources, those based on starch are one of the most promising families due to a good combination of being relatively low cost and their final properties, similar in most cases to those of commodities. However, there are still some loss of properties in the use of biodegradable polymers, such as thermal resistance, mechanical performance, and barrier properties, that limit their use in food packaging [4, 9–16].

Some approaches have been tested to overcome such disadvantages, one of the most successful being the proposed hybrid organic-inorganic systems, where the inorganic phase is in the nanometric scale [17, 18]. In these studies an important influence of the nanoparticles on the final properties was observed, such as thermal, fire resistant, mechanical, and barrier properties. In particular, many studies have focused on the use of layered silicates as nanofillers [9–22]. In general, the key factor to achieving a real improvement in the biopolymer's final properties is the compatibility between the matrix and nano-reinforcements, in particular the dispersion level of the nanofiller into the polymer structure. In the case of silicate nanofillers, only intercalated or exfoliated structures would result in real improvements in the nanocomposites' properties [23, 24].

The aim of this work is to analyse the influence of nanofillers, particularly nanoclays, on the final properties and rheological characteristics of a starch-poly(ε-caprolactone) (PCL) copolymer (Mater-Bi® NF-01U). This matrix was selected since it is commercially available and shows a good quality/cost ratio. In this work, montmorillonites and sepiolites, both pure and organo-modified, have been used as nano-reinforcements. The nanocomposites processing has been carried out by using melt-intercalation techniques; in fact, these technologies are very interesting from an industrial point of view since they allow the production of nanocomposites by using the usual processing equipment for thermoplastics manufacturing.

2 EXPERIMENTAL

Mater-Bi® NF-01U was kindly supplied by Novamont (Terni, Italy) and it was used as the biopolymer matrix. Commercial montmorillonites, i.e., Dellite HPS (natural) and Dellite 43B (modified) by Laviosa Chimica Mineraria SpA (Livorno, Italy), and PRG4 (natural) and PRG1 (modified) sepiolites from Tolsa (Madrid, Spain) were used in this study.

Materials were processed by melt intercalation by using a twin counter-rotating screw extruder BAUSANO MD30 (Torino, Italy) up to 3 extrusion cycles. Two nanofiller contents were used in all cases, i.e., 3 wt% and 5 wt%. Materials were analysed after one and three extrusion steps in order to evaluate the influence of the processing and morphology of the nano-biocomposites on their final properties. In particular, shear conditions and mixing time in the extruder were optimised as it was performed in previous works that demonstrated that higher shear resulted in better dispersion of the nanofiller in the biopolymer matrices [23, 24]. Table 1 shows the nanocomposites used in this work and their corresponding codes.

The temperature profiles in the extruder were in the range 120°C–145°C with a screw speed of 30 rpm. These experimental conditions were selected in agreement with results from preliminary thermogravimetry (TGA) and differential scanning calorimetry (DSC) analyses to ensure that processing was carried out at temperatures higher than softening and lower than degradation. Samples for testing were produced by injection moulding with a SANDRETTO micro 30 injection moulder (Torino, Italy). Injection temperature was fixed at 135°C, pressure was 150 MPa, while

Table 1 Materials tested in this study.

Materials	Code
Mater-Bi 1extr.	M-1
Mater-Bi 3extr.	M-3
Mater-Bi+3%HPS 1extr.	3-HPS-1
Mater-Bi+3%HPS 3extr.	3-HPS-3
Mater-Bi+5%HPS 1extr.	5-HPS-1
Mater-Bi+5%HPS 3extr.	5-HPS-3
Mater-Bi+3%43B 1extr	3-43B-1
Mater-Bi+3%43B 3extr.	3-43B-3
Mater-Bi+5%43B 1extr.	5-43B-1
Mater-Bi+5%43B 3extr.	5-43B-3
Mater-Bi+3%PRG4 1extr.	3-PR4-1
Mater-Bi+3%PRG4 3extr.	3-PR4-3
Mater-Bi+5%PRG4 1extr.	5-PR4-1
Mater-Bi+5%PRG4 3extr.	5-PR4-3
Mater-Bi+3%PRG1 1extr.	3-PR1-1
Mater-Bi+3%PRG1 3extr.	3-PR1-3
Mater-Bi+5%PRG1 1extr.	5-PR1-1
Mater-Bi+5%PRG1 3extr.	5-PR1-3

the flow rate was 35 cm^3 s^{-1}, pressure 140 MPa, time 8 s, and the cooling time with closed mould was 30 s.

Dynamic TGA tests were performed in a Mettler Toledo SDTA 851e analyser (Schwarzenbach, Switzerland) at six different heating rates from 2°C min^{-1} to 30°C min^{-1} starting from 30°C up to 600°C. Tests were conducted in Nitrogen atmosphere (50 mL min^{-1} gas flow) to avoid oxidative degradation. TGA data and kinetic parameters for degradation processes were analysed by following the Friedman [25] classical approach.

Fourier transformed infrared spectroscopy (FTIR) tests were carried out by using a Perkin-Elmer infrared spectrometer (PerkinElmer Spain, S.L., Madrid, Spain). Attenuated total reflectance (ATR) infrared spectra were obtained in the 4000–600 cm^{-1} region, using 128 scans and 4 cm^{-1} resolution. A blank spectrum was obtained before each measurement to compensate the humidity effect and the presence of carbon dioxide in the air by spectra subtraction. Films with average thickness 270 ± 10 mm were used in this study.

Mechanical properties were analysed by tensile testing following ASTM D638M standard; the elastic modulus, yield strength and yield strain were determined for all materials. Tests were performed at room temperature with an electronic dynamometer LLOYD LR30k model (West Sussex, UK) with load cell 30 kN and crosshead speed 5 mm min^{-1}.

Rheological tests were carried out with a strain controlled rotational rheometer Rheometric Scientific ARES (TA Instruments, New Castle, DE, USA). Parallel plate geometry with a gap of 2 mm was selected in order to minimize the wall effects due to the interaction between the testing tools and nanoparticles. Dynamic tests were performed at 140°C with frequency range from 0.01 rad s^{-1}. to 100 rad s^{-1}. The strain was fixed at 0.3% in order to make measurements in the linear viscoelastic region of these materials. For the determination of the linear viscoelastic region, preliminary strain, sweep tests on the materials were carried out.

3 RESULTS AND DISCUSSION

Results of TGA tests for pure Mater-Bi® after one and three extrusion steps for different heating rates are reported in Figure 1, where differential thermogravimetric curves are also shown. It is noticeable that the performance of the matrix in terms of high temperature behaviour was not significantly affected by the processing conditions and heating rates. This is evidence that the repeated extrusion cycles did not lead to significant degradation of this material, despite the succesive temperature changes.

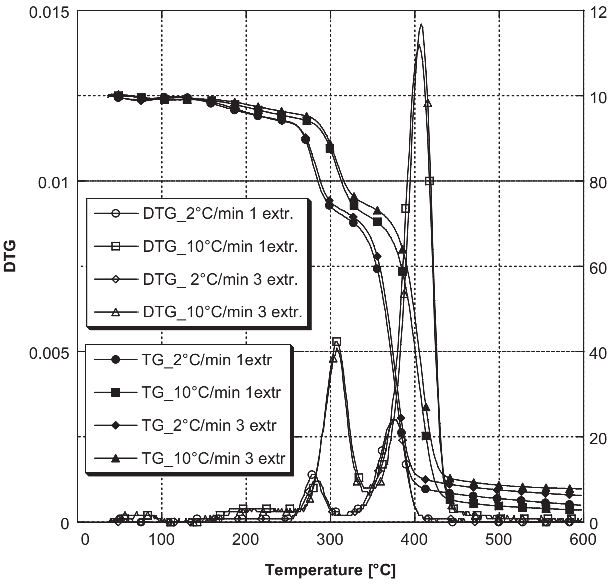

Figure 1 TGA curves of pure Mater-Bi® after one and three extrusion steps at different heating rates.

It can also be concluded from Figure 1 that the thermal degradation of the Mater-Bi® matrix is a complex process composed by two distinct steps evidenced by two peaks on the DTG curves. The first degradation step took place at around 300°C (maximum degradation rate), corresponding to the starch [26], and the second step with a maximum at around 410°C, corresponding to PCL thermal degradation under nitrogen, as has been previously reported [27]. The expected differences in degradation temperatures caused by the two heating rates used in the study (2°C min^{-1} and 10°C min^{-1}) are also observed, but this fact is not relevant.

The comparison of the DTG degradation curves for the pure matrix and the corresponding nano-biocomposites is reported in Figures 2a and 2b. These curves show the behaviour at high temperatures of composites with a nanofiller content of 5 wt%, but similar results were achieved for materials with 3 wt% nanofiller content. In general terms, it is observed that the thermal degradation process of Mater-Bi® is not significantly changed in the second step, i.e., the PCL degradation follows the same pattern with no influence from the presence of nanoclays. However, a significant variation in the degradation curve is noticed in the first degradation peak corresponding to starch, with a shift towards higher temperatures. This effect was observed for all nano-biocomposites, but the variation was lower for those with 43B, where differences in maxium degradation temperature were around 7°C compared with the increase of 12°C in the starch degradation peak obtained with the other nanofillers. This is a different behaviour than that reported by Alemdar *et al.* [28] for starch-cellulose nanofibers composites where no important differences in thermal

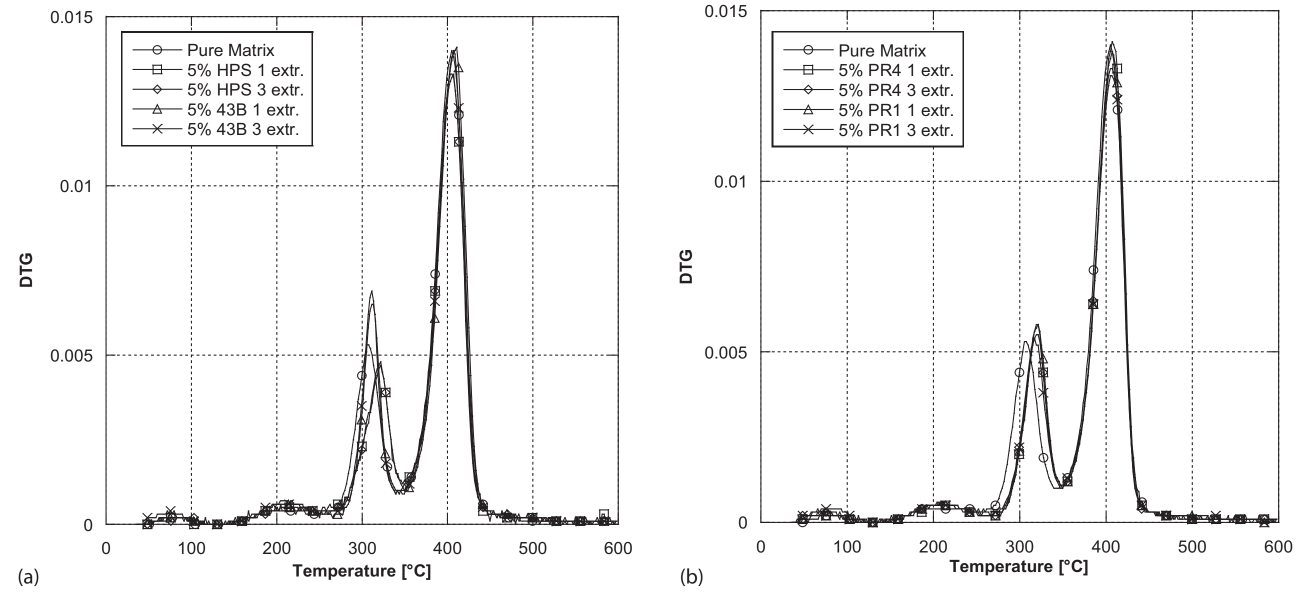

Figure 2 Comparison of thermal degradation DTG curves at 10°C min^{-1} of the pure matrix with (**a**) Montmorillonite-reinforced nano-biocomposites, and (**b**) Sepiolite-reinforced nano-biocomposites.

degradation patterns were observed. As previously indicated for the neat polymer matrix, the repeated extrusion cycles showed no influence in the thermal degradation of the nano-biocomposites.

Another effect clearly visible in these nano-biocomposites is the increase in the residual mass at 600°C. It is important to highlight that this effect is not only due to the addition of the inorganic nanoclay. In fact, as shown in Table 2, the difference between the residual mass obtained after thermal degradation of the neat matrix and nano-biocomposites is around 10% in all cases, always higher than the nanofiller content. This behaviour can be considered as the result of interactions between nanoclays and the polymer matrix leading to a higher carbonaceous residual mass.

By observing the data in Table 2, it is remarkable that the residual mass is affected by both the typology of the nanofillers (montmorillonite or sepiolite) and by the number of extrusion cycles. This last effect could be caused by the improvement in the dispersion level of the nano-biocomposites after repeated processing leading to a higher thermal stability. It is important to highlight that no significant differences in the residual mass after degradation are observed for the natural and modified nanoclays, giving an indication of the good compatibility between all these materials with the Mater-Bi® matrix.

The apparent activation energies (E_a) for both degradation steps were calculated by using the classical approach developed by Friedman [25]. The results are summarised in Table 3. The effect of nanofillers was not very strong in terms of apparent activation energies. It is observed that montmorillonites and sepiolites had more influence on kinetic parameters during the first degradation process. In fact, just some improvement in the second step was only achieved with the higher nanofiller content and the maximum dispersion level. During the first degradation process, corresponding to starch, a positive contribution in the increase of E_a can be observed even at the lower content of all nanoclays even after just one extrusion step, outlining the good compatibility in all cases, even with no chemical modification of the nanoclay. Similar results were observed

Table 2 Residual mass of the materials in TGA tests.

Materials	Residual weight [%]
Pure Mater-Bi®	2.6 ± 0.2
5 HPS 1	10.7 ± 0.2
5 HPS 3	12.6 ± 0.3
5 43B 1	10.5 ± 0.1
5 43B 3	11.5 ± 0.3
5 PR4 1	12.0 ± 0.3
5 PR4 3	10.6 ± 0.1
5 PR1 1	10.1 ± 0.2
5 PR1 3	11.4 ± 0.2

Table 3 Apparent activation energies of all materials calculated according to the Friedman method.

	Ea Friedman [kJ mol-1]	
Materials	**1st Peak**	**2nd Peak**
M 1	41,6	67,1
M 3	42,5	67,4
3 HPS 1	51,5	67,8
3 HPS 3	49,1	66,3
5 HPS 1	48,8	65,2
5 HPS 3	47,1	63,8
3 43B 1	45,0	63,5
3 43B 3	42,5	62,1
5 43B 1	44,1	65,7
5 43B 3	53,1	68,5
3 PR4 1	44,8	63,9
3 PR4 3	46,7	62,6
5 PR4 1	45,2	62,4
5 PR4 3	53,2	64,7
3 PR1 1	45,3	62,2
3 PR1 3	44,7	62,5
5 PR1 1	44,6	63,2
5 PR1 3	46,8	62,7

in previous studies on poly(lactic acid)-based nano-biocomposites [29]. The increase in the thermal stability of the nano-biocomposites, regardless of their composition, suggests a delay in the beginning of their thermal degradation. This effect could be caused by the presence of clay acting as a physical barrier for the heat transmission during the first stages of the process, and consequently retarding the starting point of thermal degradation in the case of nano-biocomposites when compared to the neat Mater-Bi® matrix.

The results of the FTIR analysis performed on all nano-biocomposites are summarised in Figures 3 and 4.

A general analysis of these data indicates that the main absorption peaks of the pure matrix are not significantly altered by the presence of nanofillers, and consequently it could be concluded that the presence of mineral nano-reinforcements did not imply strong chemical modifications in the biopolymer chain. As expected, an intense peak at 1709 cm^{-1} assigned to the presence of the C=O bonds in the matrix structure is observed. No significant changes in the wavenumber and relative intensity of this peak are noticed for nano-biocomposites, and consequently no important variations on the matrix structure are observed after the addition of nanoclays.

Two distinct bands at around 2920 and 2849 cm^{-1} are observed and they were assigned to the asymmetric and symmetric stretching vibrations of the methyl and methylene groups in the polymer structure. It is remarkable that the relative intensity of these bands for the pure biopolymer was higher after three extrusion processes, suggesting the possibility of a slight molecular rearrangement caused by the repeated processing steps. A similar behaviour was observed for peaks at 1409 and 1455 cm^{-1}, which were attributed to the bending vibrations of methyl groups.

Figure 5 shows the stress-strain properties for the pure matrix and the corresponding nano-biocomposites. In general, all these materials showed a ductile behaviour. Moreover these results indicate that the mechanical properties of the Mater-Bi® after one and three extrusion steps were very similar, indicating that no particular degradation of these materials occurred during processing.

The values of the elastic modulus, yield strength and yield strain for all nano-biocomposites are reported in Figure 6. As expected, the addition of both nanofillers to the biopolymer matrix had a positive effect on the elastic modulus, with increments of around 30% after the addition of 5 wt% of the modified montmorillonite. The nanofiller concentration plays an important role in the increase of the elastic modulus, with higher effects for additions of 5 wt%. Similar results were obtained by the addition of nanoclays to other biopolymers, such as poly(lactic acid), PLA, where increments in the elastic modulus were also reported [30]. Nevertheless, the increase in the elastic modulus obtained here after the addition of 5 wt% of nanoclays to starch-based polymers was lower than previous results obtained by Majdzadeh-Ardakani *et al.* [31], who reported increments higher than 50% in modulus after the addition of 5 wt% montmorillonites to thermoplastic starch. The unexpected low increase in the elastic modulus for Mater-Bi® nano-biocomposites could be attributed to the differences in crystallinity between starch and PCL in the biopolymer structure, resulting in a poor intercalation of the polymer inside the nanoclay layers leading to more heterogeneous materials.

The effects of the nanofillers addition on the yield strength (Fig. 6b) and yield strain (Fig. 6c) were generally low. In fact, the maximum improvement in yield strength was achieved for the addition of 5 wt% of the

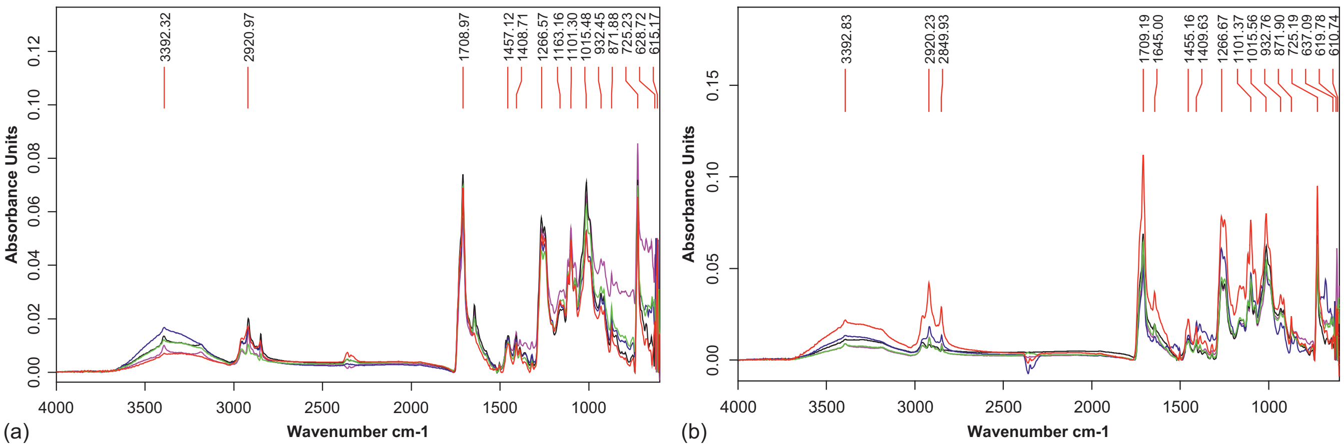

Figure 3 FTIR analysis in absorbance mode for the pure Mater-Bi® matrix (red) and nano-biocomposites with MMT 3 wt% (blue), MMT 5 wt% (magenta), modified MMT 3 wt% (green), and modified MMT 5 wt% (black); (**a**) after one extrusion, (**b**) after three extrusions.

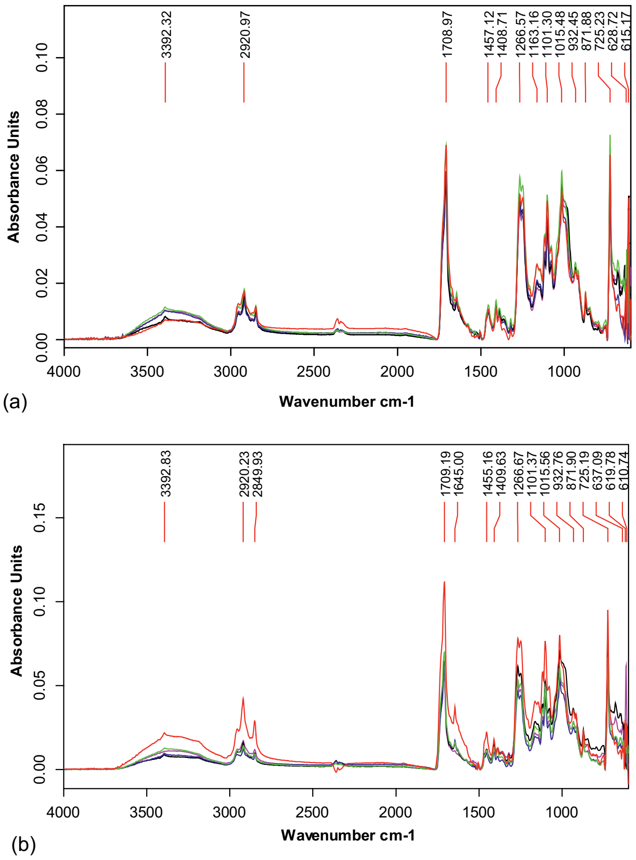

Figure 4 FTIR analysis in absorbance mode for the pure Mater-Bi® matrix (red) and nano-biocomposites with pure sepiolite 3 wt% (blue), pure sepiolite 5 wt% (magenta), modified sepiolite 3 wt% (green), modified sepiolite 5 wt% (black); (**a**) after one extrusion, (**b**) after three extrusions.

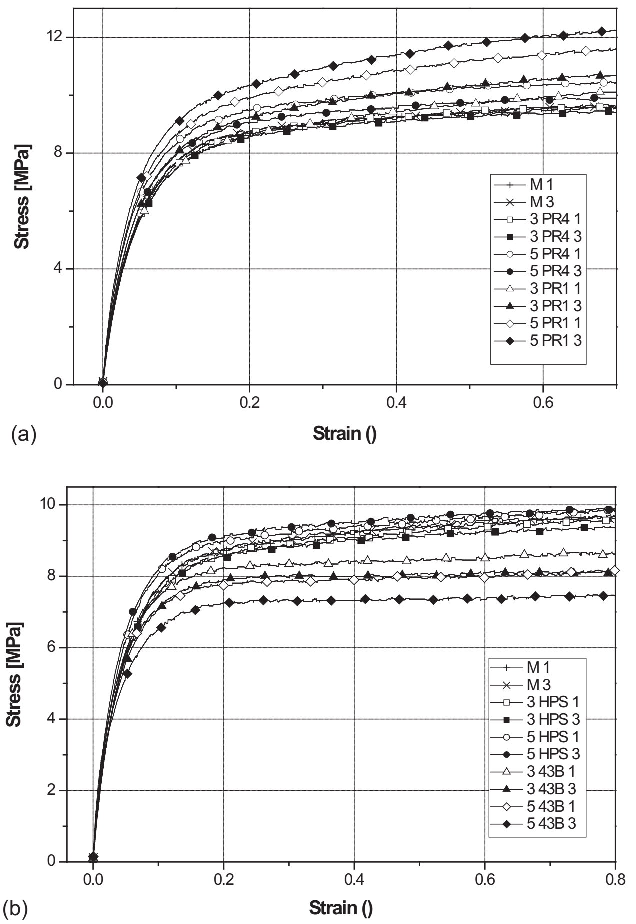

Figure 5 Stress-strain curves of nano-biocomposites: (**a**) montmorillonite; (**b**) sepiolite.

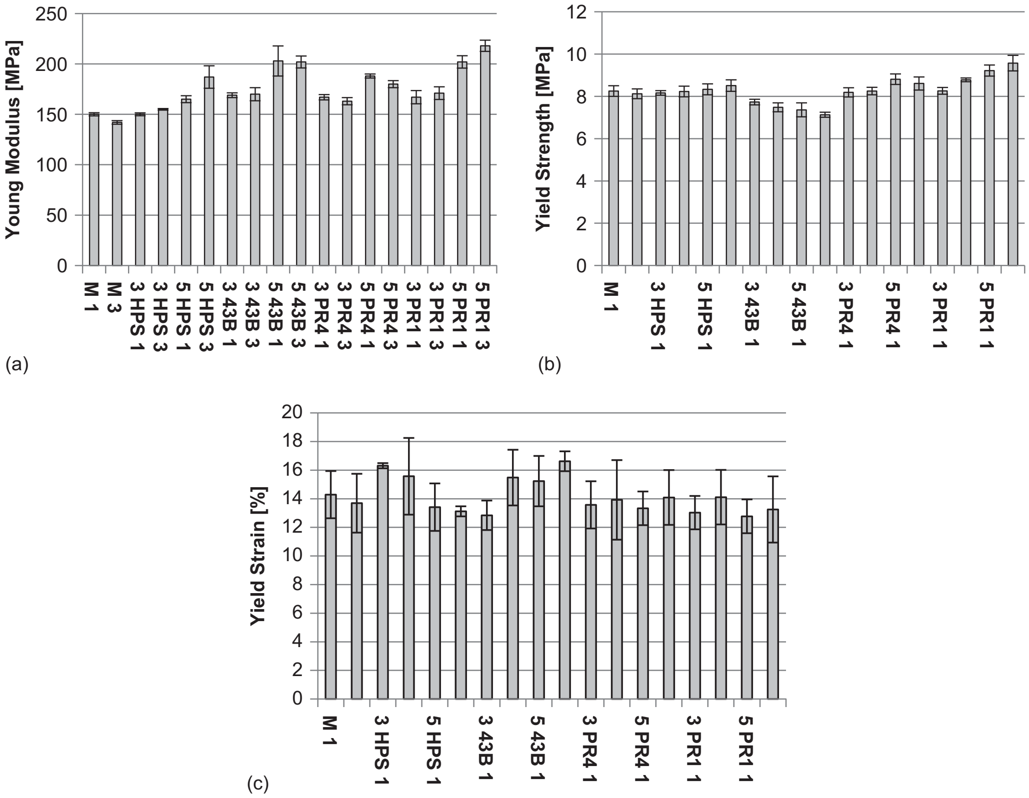

Figure 6 (**a**) Elastic modulus, (**b**) yield strength and (**c**) yield strain of the nano-biocomposites.

modified sepiolite, getting an increment of around 17%. Even the modified montmorillonite gave a negative contribution to the yield strength, and in this case both the nanoclay concentration and the number of extrusion steps played a negative role. The rest of the tested nanofillers showed a positive effect, but it was observed that sepiolites seemed to give a higher reinforcement than montmorillonites.

In summary, the results of these mechanical tests confirmed that the dispersion level and the compatibility of nanofillers with the Mater-Bi® matrix were relatively good, resulting in homogeneous nano-biocomposites. In fact, their general behaviour with unmodified nanofillers was good and modest improvements in all tensile parameters were observed. The modified nanofillers, indeed, showed a higher effect than the unmodified counterparts, but this effect was not regular in all the parameters analysed in this work.

The results of the rheological characterisation, in particular, the viscoelastic behaviour, for all nano-biocomposites are reported in Figure 7. Once again, it is observed that multiple extrusion steps had no noticeable effect on the matrix degradation; in fact, viscosities as well as storage modulus (G′) and loss modulus (G′′) do not show any remarkable difference in materials tested after one and three extrusions.

Several authors reported that some particular rheological behaviour, like shear thinning and solid-like viscosities in the low frequency region, are clear evidence of good dispersion level of the nanofiller through the polymer matrix [32–41]. In particular, it has been reported that the exfoliation or delamination of the nanocomposite structure could be correlated to the slope of the viscosity curves in the low frequency region [34, 35]. In our case, the dispersion level of compatibilised systems was higher than the dispersion level of pure montmorillonites in the Mater-Bi® matrices. In fact, the viscosities and viscoelastic moduli for systems reinforced with pure MMT showed similar values to those of pure matrix, while modified MMTs showed clear increments in G′ and G′′ values due to the presence of the modified inorganic nanofiller. This behaviour was particularly noticeable in the low frequency region with an increase in the slope of viscosity curves and by the tendency to reach a plateau in both viscoelastic moduli.

A general tendency was observed where viscosities at low frequencies were lower in systems reinforced with 5 wt% of pure MMT than those for systems with 3 wt% of modified MMT. This behaviour could be explained by the difficulties in the homogeneous dispersion for MMTs at 5 wt% in the

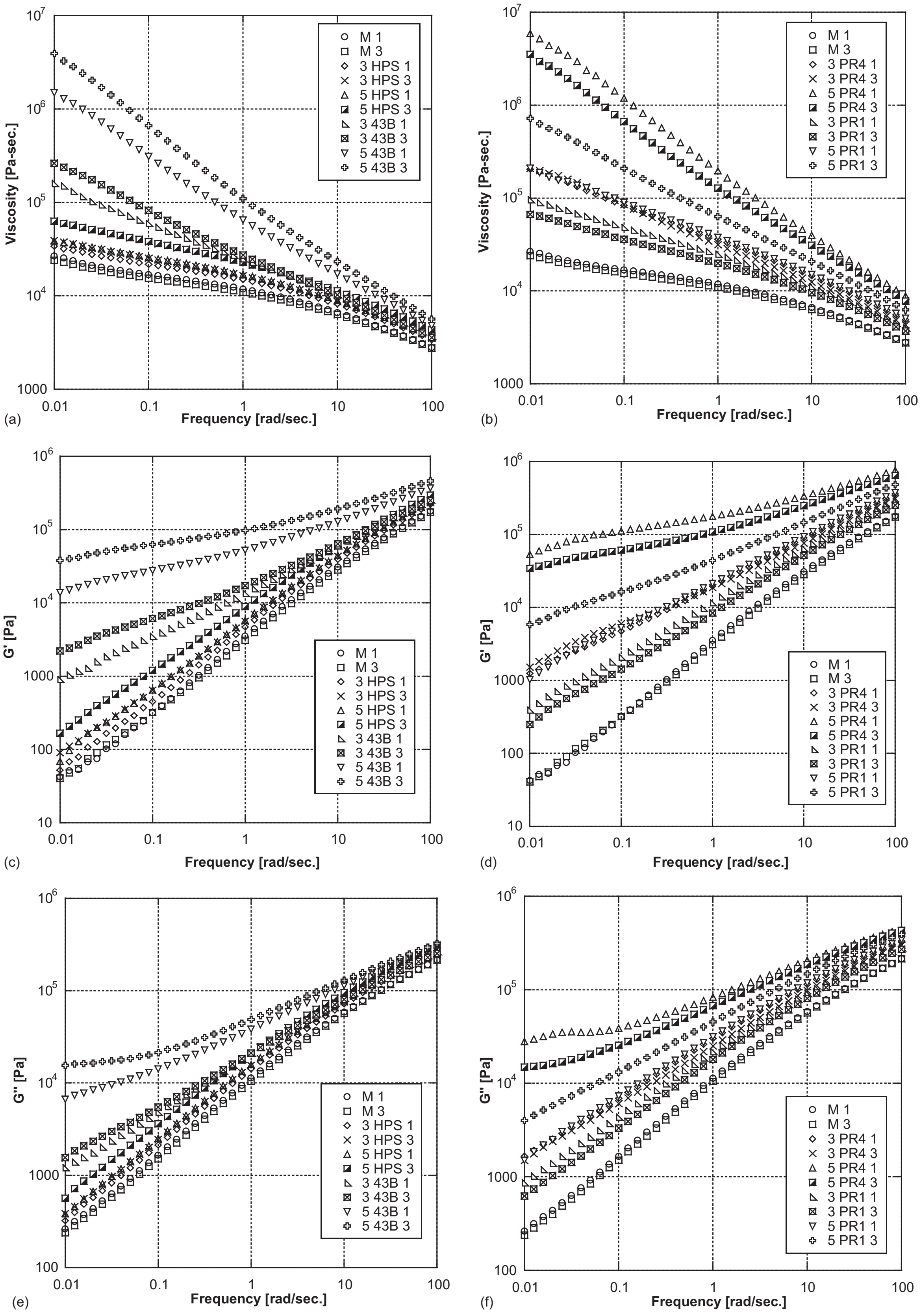

Figure 7 Complex viscosity, storage modulus (G′) and loss modulus (G′′) of the pure matrix: (**a**,**c**,**e**) MMT filled systems and (**b**,**d**,**f**) Sepiolite filled systems.

starch-based matrices, as has been reported by other authors. The positive contribution of the repeated extrusion steps for all the studied systems was also noticeable. In general, those systems after three extrusion steps showed higher viscosity and viscoelastic moduli than the corresponding materials after just one extrusion.

When considering the sepiolite-filled materials, significant modifications of the rheological behaviour, particularly the increase in shear thinning and solid-like behaviours at low frequencies, are observed in both, modified and unmodified nano-biocomposites. In this case it is also observed that these modifications are more pronounced in systems with pure sepiolite than in those with modified sepiolite.

In summary, from the processing point of view, these viscoelastic curves show that the presence of both nanofillers does not make it difficult to possibly process the materials in the molten state. In fact, the usual processing methods of thermoplastic polymers involve very high shear rates, and the results reported here show that both the viscosity and viscoelastic characteristics of nanocomposites at high shear rates are very similar to those of the pure matrix.

4 CONCLUSIONS

The addition of commercial nanoclays to commercial Mater-Bi® resulted in the formation of nano-biocomposites with potential to be used in different applications where the increase in mechanical and barrier properties would be an important issue. In general terms, a positive contribution of both nanofillers in the material mechanical and thermal properties was observed. The FTIR results showed that the addition of nanofillers did not result in chemical modifications of the matrix structure and crystallinity.

It was noticed that the compatibilisation treatment for both nanofillers had some effect in the material properties, this effect being less significant for the sepiolite systems. These results indicated that pure sepiolite shows the higher compatibility with the Mater-Bi® matrix. Finally, it is important to highlight that the rheological parameters are quite sensitive to the compatibility between matrix and nanofillers. Therefore, the processing of the studied nano-biocomposites is not compromised by the presence of nanofillers at contents lower than 5 wt%. In fact, the viscosity and viscoelastic parameters of the filled systems and of the pure matrix are quite similar at high shear rates.

In conclusion, nano-biocomposites based on a Mater-Bi® matrix with the addition of commercial nanoclays are potentially applicable materials in new biomaterial concepts for use in massive applications, considering their good mechanical and thermal properties, their wide processing window and their intrinsic biodegradable nature.

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