

Compatibilization of PHBV/PLA blends with diisocyanates

Jennifer González-Ausejo¹, Estefania Sánchez-Safont¹, José Maria Lagarón², Rafael Balart³, Luis Cabedo¹ and José Gámez-Pérez^{1*}

¹Polymer and Advanced Materials Group (PIMA), Universidad Jaume I, 12071 Castellon, Spain

²Novel Materials and Nanotechnology Group, IATA-CSIC, 46980 Paterna (Valencia), Spain

³Instituto de Tecnología de Materiales (ITM), Universidad Politécnica de Valencia, Campus de Alcoi, 03801 Alcoy (Alicante), Spain

*Correspondence to José Gámez Pérez (e-mail: gamez@uji.es)

ABSTRACT

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) was blended with poly(lactic acid) (PLA) using various reactive processing agents in order to decrease its brittleness and enhance its processability. Three diisocyanates, namely, hexamethylene diisocyanate (HMDI), poly(hexamethylene) diisocyanate (polyHMDI) and 1,4-phenylene diisocyanate (PDI), were used as compatibilizing agents. The morphology, thermomechanical properties and rheological behavior were investigated using scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), tensile tests, dynamo-mechanical thermal analysis in torsion mode (DMTA) and oscillatory rheometry with a parallel plate setup. The presence of the diisocyanates resulted in an enhanced polymer blend compatibility, thus leading to an improvement in the overall mechanical performance without affecting the thermal stability of the system. A slight reduction in PHBV crystallinity was observed with the incorporation of the diisocyanates. The addition of diisocyanates to the PHBV/PLA blend resulted in a notable increase in the final complex viscosity at low frequencies when compared with the same system without compatibilizers.

INTRODUCTION

Biopolymers have generated significant interest in recent years due to increasing awareness of environmental problems involving large amounts of discarded plastic. Most plastic items are produced from fossil fuels and they show very high degradation times (about 100-300 years), meaning that in the worst case scenario, they are left in the sea or waste landfills. In some cases, they are burned to recover some of the embodied energy, but their incineration produces an increased concentration of carbon dioxide in the atmosphere, while toxic gases are also released to the environment during the combustion cycle. This has led to an increased interest in the study of polymers derived from renewable resources, such as aliphatic biopolyesters, with the ability to completely biodegrade in composting conditions due to their hydrolysable backbone, thus alleviating the problem of landfill saturation ^{1,2}.

Among these biopolymers, there are two that are raising an increasing industrial interest, polylactic acid (PLA) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). PLA is a semicrystalline polymer which can present a relatively high strength and modulus, similar to that of PET and which shows an excellent thermoformability. However, its slow crystallization rate limits its potential applicability boundaries, such as permeability to gases and toughness, preventing its possible replacement of non-biodegradable polymers such as PET ³⁻⁵.

PHBV is a copolymer that presents similar crystallinity index that the homopolymer poly(hydroxybutyrate). The random valerate content in PHBV (below 25%) as a matter of fact, does not alter the usual PHB crystal structure and it shows similar properties as PHB, such as high tensile strength, high service temperature -similar to that of polypropylene (PP) ⁶- and barrier properties to oxygen close to that of the poly(ethylene terephthalate) (PET) ⁷. However, PHB practical application has been restricted by some other disadvantages such as thermal degradation (close to melting temperature) during processing and consequently a narrow processing window. The addition of valerate in PHBV decreases partially the melting point of the homopolymer, allowing its processing at slightly lower temperatures, thus decreasing thermal degradation. Even though this improvement, PHBV as well as PHB shows brittleness and a much higher cost compared to the fossil equivalents ⁷⁻¹¹.

Since polymer blending is a convenient approach to overcome the individual disadvantages of polymers and it allows for the production of new materials with improved properties ¹²⁻¹⁶, several researchers have reported the study of PHBV/PLA blends ¹⁷⁻²⁴ as a way to overcome some

limitations of PHBV. They claim that by decreasing the overall crystalline nature of the blend, brittleness, for instance, can be reduced. However, the resulting blends did not show the expected performance, being attributed to the lack of compatibility of these biopolyesters^{18–20}. A possible solution to this problem can be reached by increasing the interfacial adhesion, using a compatibilizer capable of reacting with the terminal groups of both PHBV and PLA during melt processing. This method, known as reactive blending, is very convenient due to its easy implementation on an industrial scale, using conventional polymer processing facilities. By blending PHBV with PLA, one should expect to decrease the processing temperature of PHBV, enlarge the processing window of PHBV for thermoforming by increasing the melt strength and also reduce the brittleness of the PHBV associated to secondary crystallization^{25,26}. Indeed, the use of such as compatibilizers may have another positive influence on the blends, acting as chain extender thermal stabilizers²⁷.

Recently, Zembouai *et al.*¹⁹ prepared blends based on PLA and PHBV by grafting maleic anhydride onto PHBV as a compatibilizing agent in combination with the addition of Cloisite 30B. Their results revealed that the morphology of the blend changed from co-continuous to a dispersed-type. This was attributed to the reduction of interfacial tension (increased interaction) among the interface between the blend components and the location of the clay in the blend. The blends exhibited enhanced mechanical properties with respect to the uncompatibilized PHBV/PLA blend, especially when PHBV was previously compatibilized.

Pivsa-Art *et al.*²⁸ studied the mechanical properties and biodegradation effect of PLA and PHBV blends with polyethylene glycol (PEG) as the compatibilizer, with molecular weights of 4000 and 6000 for biodegradable textile applications. It was found that the addition of PEG improved the tensile strength and Young's Modulus.

One group of reagents that could be used as compatibilizers in PHBV/PLA blends and have not yet been explored are diisocyanates. Isocyanates can react with either hydroxyl or carboxyl groups to form urethane linkages, as described in the literature (see refs.^{29–33} to mention a few). As Zeng noted out in his excellent review about compatibilization of PLA blends³³, isocyanates containing more than one isocyanate group can be used to compatibilize PLA blends with other polymers that contain hydroxyl or amino groups, since the isocyanates can react with terminal groups randomly thus generating copolymers of both blend components that can compatibilize the blend. The systems studied by Zeng in that work included PLA with biodegradable polyesters, polyamides and natural polymers.

Therefore, diisocyanates are promising reactive compatibilizers for blending PHBV with PLA which. To the best of our knowledge, have not been reported. In order to investigate their potential to improve the properties of PHBV/PLA blends in terms of their rheological and mechanical properties, three different diisocyanates have been tested with a fixed PHBV/PLA ratio of 75/25 in weight.

The systems were chosen looking for its applicability in thermoformed packaging applications. So, one of the diisocyanates was chosen among those approved for food contact applications hexamethylene diisocyanate (HMDI). Another diisocyanate worth to try was considered to be 1,4-phenylene diisocyanate (PDI), known to its high reactivity. Finally, to take advantage of the ability of the isocyanates to react with terminal groups of the polymer chains, a trifunctional isocyanate, poly(hexamethylene) diisocyanate (polyHMDI) was selected, with the aim of increasing the melt strength of the blend.

Even though isocyanates are known to be quite toxic, we are optimistic about their potential use as additives for compatibilizing blends, since they are used at very low contents ($\leq 1\%$) and they are submitted to an environment in which they are prompt to react to form polyurethanes (inside the extrusion barrel, with high temperature and high concentration of reactive species).

The ratio of PHBV/PLA 75/25 in wt. was selected since, according to literature, it presents the best compromise between barrier properties, maximum service temperature and deformation at rupture [3,31].

EXPERIMENTAL

Materials

PHBV with 3 mol.% hydroxyvalerate content was purchased from the Tianan Biologic Material Co. (Ningbo, P.R. China) in pellet form (ENMAT Y1000P). PLA IngeoTM Biopolymer commercial grade 2003D was supplied by the NatureWorks® Co. LLC, USA. The three compatibilizers used (hexamethylene diisocyanate, poly(hexamethylene) diisocyanate and 1,4-phenylene diisocyanate) were supplied by Sigma Aldrich.

Blend preparation

The PHBV and PLA used in this study were dried under vacuum at 80 °C for 2 h before use by a Piovan DPA 10 (Santa Maria di Sala VE, Italy), while the compatibilizers were used as received. The PHBV/PLA blends with 75:25 wt./wt., respectively, and different contents of compatibilizers were obtained by melt blending using an internal mixer (Rheomix 3000P ThermoHaake, Karlsruhe, Germany). To avoid degradation, the mixing time was kept under 4 min at a temperature of 180 °C and a rotor speed of 100 rpm. The mixer is supplied with software for displaying the variation of temperature (chamber and melt) and the torque during mixing. According to the melt temperature sensor during mixing, the melt temperature never reached 195 °C, which guaranteed that there was no severe thermal degradation during blending.

Films (0.2 mm thick) for scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and mechanical property analysis were obtained from the blends by melting in a hot-plate press (180 °C, 2 min for pre-melting, followed by 2 min at 3 bar). DMTA specimens with a thickness of 4 mm were obtained from injected bars, in a Meteor 270/75 injection molding machine (Mateu & Sole, Barcelona, Spain) with an injection temperature of 180 °C at the nozzle. For rheological measurements, discs (25 mm diameter and 2 mm thick) were obtained from the blends by melting in a hot-plate press at 180 °C and applying 300 bar for 2.5 min. All the samples were stored in a vacuum desiccator at ambient temperature for two weeks to allow full crystallization to take place³⁴.

Samples of both PHBV and PLA (referred to as neat PHBV and neat PLA, respectively) were processed under the same conditions as the blends, for the sake of comparison. The nomenclature used for the blends is as follows: PHBV/PLA for the systems with 75:25 wt./wt. without compatibilizer, and XY for the compatibilized blends, where X is the compatibilizer content and Y is the compatibilizer type: hexamethylene diisocyanate (HMDI), poly(hexamethylene diisocyanate) (polyHMDI) and 1,4-phenylene diisocyanate (PDI).

The compatibilizer content X was indicated as the estimated molar ration between the functional polymer reactive sites (alcohol and carboxylic acid end groups) and the compatibilizer ones (isocyanates), according to the available Mn and molecular weight data of polymers and isocyanates. For comparison purposes, these ratios were set equally at 1:1, 1:10 and 1:20 for the three isocyanates studied. Table 1 summarizes the detailed compositions of all the blends studied.

Characterization

The morphology of the cryofractured surfaces of the PHBV/PLA blends was evaluated by SEM using a JEOL 7001F. The samples were fractured in liquid nitrogen and subsequently coated by sputtering with a thin layer of Pt. The size of the dispersed phase observed in the SEM micrograph was evaluated, measuring the length of the spheres in microphotographs with ImageJ software (the number of spheres analysed was over 400 in all cases).

The thermal stability of the blends was investigated by means of TGA using a TG-STDA Mettler Toledo model TGA/SDTA851e/LF/1600. The samples were heated from 50 to 900 °C at a heating rate of 10 °C/min under nitrogen flow. The characteristic temperatures, $T_{5\%}$ and T_d , corresponded, respectively, to the initial decomposition temperature (5% weight loss) and to the maximum degradation rate temperature measured at the derivative thermogravimetric analysis (DTG) peak maximum.

DSC experiments were conducted using a DSC2 (Mettler Toledo) with an intracooler (Julabo modelo FT900). The weight of the DSC samples was typically 6 mg. Samples were first heated from -20 to 200 °C at 10 °C/min, kept for 1 min at 200 °C, cooled down to -20 °C at 10 °C/min, and then finally heated to 200 °C at 10 °C/min. The crystallization temperature (T_c), melting temperature (T_m) and melting enthalpy (ΔH_m) were determined from the cooling and second heating curve. T_m and ΔH_m were taken as the peak temperature and the area of the melting endotherm, respectively. By overlapping DSC scans of PLA, PHBV and PLA/PHBV blends, it could be deduced that PLA remains amorphous in the blends. Therefore, the net crystallinity (X_c) of the blends (after removing cold crystallization of PLA) corresponds solely to the PHBV phase and was calculated by the following expression:

$$X_c (\%) = \frac{\Delta H_m}{w \cdot \Delta H_m^0} \cdot 100 \quad (1)$$

where ΔH_m (J/g) is the melting enthalpy of the polymer matrix, ΔH_m^0 is the melting enthalpy of 100% crystalline PHBV (perfect crystal) (146 J/g) and w is the polymer weight fraction of PHBV in the blend³⁵. The DSC instrument was calibrated with an indium standard before use.

Tensile tests were carried out in a universal testing machine (Shimadzu AGS-X 500N) at a crosshead rate of 10 mm/min at room temperature. All samples were allowed to reach the

equilibrium under ambient conditions (25 °C and 50% R.H. for 24 hours before the testing). Tests were performed according to ASTM D638 with dumb-bell samples die-cut from approximately 200 µm thick films prepared by hot press. Five specimens of each sample were tested and the average results with standard deviation were reported.

Dynamic mechanical analysis (DMTA) experiments were conducted in an oscillatory rheometer AR G2 (TA Instruments, New Castle, EEUU) equipped with a clamp system for solid samples (torsion mode). Samples sizing 40 x 10 x 4 mm³ were subjected to a heating program from -20 to 130 °C with a heating rate of 2 °C/min at a constant frequency of 1 Hz. The maximum deformation (γ) was set to 0.1%.

Rheological Measurements. Oscillatory shear measurements were performed using an oscillatory rheometer AR G2 (TA Instruments, New Castle, EEUU) equipped with parallel plates of 25 mm diameter using a gap of 1.5 mm. Sample disks were vacuum dried at 60 °C for 24 h before testing. Strain sweep viscoelastic tests were first performed at a fixed angular frequency of 1 Hz in order to determine the extent of the linear regime, then, frequency sweep experiments were carried out at a fixed strain in the linear regime in order to determine the linear viscoelastic moduli, G' (storage modulus) and G'' (loss modulus), as well as the complex viscosity η^* . The angular frequencies were swept from 100 to 0.01 Hz with five points per decade at temperatures of 180 °C.

RESULTS AND DISCUSSION

Morphology

The morphology of the blends can be related with the degree of compatibility of their components. The morphology of the PHBV/PLA blends is clearly affected by the presence of the diisocyanates, as observed SEM.

Fig. 1 presents the SEM micrographs of all the PHBV/PLA blends studied as a function of diisocyanate type and content, as well as the histograms of the size for the dispersed phase. The SEM morphology observed for the PHBV/PLA blend without any compatibilizer (Fig. 1a) shows spheres of PLA (1.15 µm average diameter) evenly dispersed in the PHBV matrix. The neat separation between the phases and the presence of a detachment phenomenon is an evidence that indicates that the two phases are not compatible. Indeed, several authors have also reported the poor compatibility of PHBV/PLA blends with similar PHBV/PLA ratios^{18–20}.

The addition of diisocyanates produces a compatibilization effect that can be clearly observed with a reduction of the particle diameter of the dispersed PLA phase. Figs. 1b, 1e and 1h show that the addition of HMDI reduces the PLA particle size to average diameter values ranging from 0.84 to 0.88 μm . However, even though the differences in particle size may not be very pronounced as the HMDI content increases, at a 1:10 molar ratio and above, two populations of sphere sizes can be identified, showing a significantly higher ratio of entities with less than 0.7 μm . Furthermore, an increase in the amount of particles that are not detached can be observed for a 1:20 HMDI molar ratio (Fig. 1h), indicating better compatibility.

Regarding the effect of polyHMDI on the blends, there is a remarkable decrease in PLA domain size with increasing polyHMDI content, as seen in Figs. 1c, 1f and 1i, with average particle diameters of 0.95, 0.66 and 0.45 μm , respectively. This reduction in domain size is clearly seen in the corresponding histogram (Fig. 1l). Indeed, it can be observed that higher concentrations of polyHMDI seems to improve the adhesion between the phases decreasing the amount of detached particles, thus indicating higher compatibilization between both biopolymers¹⁹.

As well as polyHMDI, the use of PDI leads to a noticeable reduction in the size of PLA domains for all the contents studied in this work (Figs. 1d, 1g and 1j), with the average diameters being about 0.83, 0.58 and 0.57 μm for 1:1, 1:10 and 1:20 molar ratios, respectively. Although no differences in the morphology and domain size of PLA are observed at 1:20 with respect to a 1:10 molar ratios of PDI (Fig. 1m), detached PLA particles in SEM micrographs are significantly reduced with the highest PDI content. This observation would be in agreement with an increase in the interfacial adhesion and compatibility between both phases, promoted by PDI.

Thermal properties

In order to study the effect of compatibilizer content and type on the thermal stability of PHBV/PLA blends, TGA experiments were carried out. The mass loss and the DTG versus temperature for the neat PHBV, neat PLA and PHBV/PLA blends (with and without compatibilizers) were recorded and the values of the onset degradation temperature ($T_{5\%}$) and maximum degradation rate temperature (T_d) were calculated for all samples studied. Table 2 summarises all the parameters obtained.

The PHBV/PLA blends exhibit a two-stage mass loss step, with an onset degradation temperature ($T_{5\%}$) at about 275 $^{\circ}\text{C}$. The first step is characterised by a maximum mass loss rate (T_{d1}) at about

288 °C and another (T_{d2}) at around 350 °C. The first one is related to the thermal degradation of PHBV, which consists of a single weight loss step between 240 and 320 °C, corresponding to a random chain scission reaction³⁶. The second step is a consequence of the thermal degradation of PLA that takes place by the cleavage of bonds on the backbone to form cyclic oligomers, lactide and carbon monoxide as products³⁷.

The thermal decomposition process of the blends containing the diisocyanates did not show significant variations with respect to the uncompatibilized blend in $T_{5\%}$, with the exception of 10polyHMDI which showed a decrease in $T_{5\%}$ of about 3 °C. Regarding the maximum degradation rate temperatures, T_{d1} corresponding to the PHBV remained unchanged, whereas T_{d2} shifted to lower temperatures with increasing addition of diisocyanates. It is worthwhile highlighting the values of 326 and 322 °C for 1:20 molar ratios of polyHMDI and PDI, respectively. This behavior, which is also seen in other PLA/diisocyanates systems, can be attributed to the reaction of the remaining diisocyanates with the PLA chains and/or their degradation products³⁸.

Even though the maximum degradation rate temperature corresponding to the PLA fraction of the blends is reduced, the effect of diisocyanates on the overall thermal stability of the compounds, from a practical point of view, led by the PHBV matrix, is negligible.

In order to establish if the addition of diisocyanates alters the crystallization behavior of PHBV/PLA blends, DSC measurements were performed for samples with and without compatibilizers. Representative DSC curves of cooling and heating scans, after removal of the thermal history, are displayed in Fig. 2. Table 2 summarises the main parameters, crystallization and melting temperatures, crystallization enthalpies and degrees of crystallinity for all the samples studied in this work.

As shown in Fig. 2, the PHBV/PLA blends exhibit a mixed behavior corresponding to their blend ratio. In the blends, two peaks (a melting peak around 172 °C and a crystallization peak around 122 °C) can be related with the typical PHBV thermal behavior (neat PHBV in Table 2). Also, the PLA melting signal can be appreciated as small shoulders in the blend thermograms, although the endothermic cold crystallization peak of PLA (present in the neat PLA at 112.6 °C) cannot be easily determined.

After analysing the resulting DSC thermograms for the compatibilized blends, it can be noted that the T_c of PHBV was significantly shifted to lower temperatures (Fig. 2b) when the diisocyanates

were incorporated in the PHBV/PLA blends. This shift in T_c is more pronounced as the diisocyanate content is increased. Since the PHBV used in this study contains boron nitride, as nucleating agent, the resulting decrease in T_c can be attributed to the reaction products of the diisocyanates with PHBV and PLA, which would be able to hinder the crystallization of PHBV, and some side reactions of the isocyanates with the boron nitride particles, which would decrease the nucleating effect on PHBV. SEM micrographs of uncompatibilized blends and compatibilized ones show that boron nitride particles are detached in the first ones, but show some polymer stuck to them in the presence of compatibilizers (Fig. 3).

The degree of crystallinity (X_c) for the compatibilized blends, as shown in Table 2, remained similar to those observed for the uncompatibilized PHBV/PLA blend. Nevertheless, this value is about 3-4% lower than the neat PHBV, indicating that the addition of PLA in the PHBV matrix is responsible for such a slight decrease in its crystallinity. Regarding the melting peak temperature of PHBV (T_m) in blends with diisocyanates, it could be observed a drop around 2 °C with respect to neat PHBV or PHBV/PLA.

As mentioned before, isocyanates can combine with terminal alcohol and carboxylic acids. Since terminal groups of PHBV and PLA are alcohol and carboxylic acids, we expect that random reaction will make block copolymers of PLA and PHBV, thus providing a way of compatibilizing both polymers. Indeed, the secondary amines resulting in urethane groups can react with other isocyanates, providing a cross-linking point. In all cases, these species are excluded from crystal lattices, so they would tend to decrease a priori the crystallinity ratio of PHBV. In the case of PolyHMDI, since it is a trifunctional isocyanate, cross-linking is highly expected providing an explanation on why 1:1 ratio of HMDI does not alter the PHBV ability to crystallize, whereas 1:1 polyHMDI does. PDI, on the other hand, is a very reactive diisocyanate, so it may have had an influence on the particle size by starting the compatibilization of the blend sooner in the extrusion barrel, increasing the melt viscosity and making a more effective mixture during the reactive blending.

It is interesting to note that the composition 1:1 HMDI behaves differently from the rest of compatibilized blends, showing a slight increase in crystallinity index and not presenting a variation in T_c with respect to neat PHBV nor the uncompatibilized blend. This may be a consequence of the relative low amount of diisocyanate added, not making crosslinking points as in the case of polyHMDI. Also, there is another case that calls the attention, which is the melting behaviour of 10polyHMDI, which shows a broader melting signal at higher temperatures, suggesting that it has a

larger population of thicker lamellae compared to the rest of the compatibilized blends (Fig. 2a). These findings correlate well with their mechanical properties, analysed subsequently.

Mechanical properties

For the purpose of studying the effect of compatibilizer content and type on the mechanical properties of PHBV/PLA blends, tensile tests to rupture were conducted on specimens obtained from hot-pressed films. The Young's modulus, tensile strength and elongation at break for all the samples were assessed and the values obtained are summarised as a function of compatibilizer content in Fig. 4.

In Fig. 4a it can be seen that the addition of 25 wt.% of PLA to PHBV does not significantly affect the average values of the Young's modulus nor the strength at break of neat PHBV. Only a slight decrease in the elongation at break is observed in Fig. 4b.

The role of the compatibilizer in the PHBV/PLA blends is more complex. It can be clearly observed in Fig. 4b that the compatibilizer produces a significant increase in the elongation at break with respect to the uncompatibilized PHBV/PLA blend. However, increasing the compatibilizing content does not produce clear trends for the tensile properties.

It is interesting to highlight the tensile behavior of the 10polyHMDI composition, which shows an increase in tensile strength of 35%, as well as an increase of 53% in the elongation at break with respect to the uncompatibilized blend. Another interesting result can be found in the 1HMDI blend, where a very small amount of compatibilizer produced the highest increase in the elongation at break. This special mechanical behavior observed for 10polyHMDI and 1HMDI can be related to the peculiarities described in the DSC results.

The viscoelastic behavior and compatibilization degree of the PHBV/PLA blends were studied by DMTA, analysing their storage modulus (G') and $\tan(\delta)$ curves in a temperature range from -10 to 130 °C. The most representative curves (neat PHBV, PHBV/PLA, 1:20 molar ratio of HMDI, polyHMDI and PDI) are shown in Fig. 5.

The glass transition temperature of a polymer blend is one of the most important criteria to assess polymer miscibility, and can be directly related with the main peak value of $\tan(\delta)$. Neat PHBV and neat PLA exhibit single peaks of $\tan(\delta)$ at around 17 and 64 °C, respectively, (PLA curve not shown in Fig. 5) and the PHBV/PLA blend exhibits both peaks without a change in the position

with respect to the pure polymers. In the presence of diisocyanates, the $\tan(\delta)$ peaks (and subsequently, the T_g values) corresponding to the PHBV-rich and PLA-rich phases are shifted toward each other, indicating a compatibilization effect.

Specifically, it can be seen that the T_g of PHBV is less distinguishable as the compatibilizer content increases. The peak corresponding to the T_g of PHBV is more accentuated in the polyHMDI and PDI compatibilized blends, as can be seen in Fig. 5. This suggests a greater increase in the miscibility between PLA and PHBV in presence of these two compatibilizers, implying that there is more interfacial interaction, which is in total agreement with the SEM observations. This behavior was also reported by Zembouai *et al.* for PHBV/PLA nanocomposites by grafting maleic anhydride onto PHBV as a compatibilizing agent in combination with the addition of Cloisite 30B¹⁹.

The storage modulus (G') decreases with increasing temperature and it shows a drastic drop in modulus around the glass transition temperature range. In the case of the blends, the evolution of the G' shows intermediate behavior between the neat PHBV and PLA blends. The moduli of the PHBV/PLA blends do not change below the T_g of PLA with respect to neat PHBV. When the temperature is raised over the PLA T_g , the storage modulus of the blends decreases due to the lower intrinsic modulus of PLA at that temperature, in comparison to neat PHBV.

As the temperature rises, the reduction in the storage modulus of the blends with respect to neat PHBV is more evident, as seen in Fig. 5. In the case of the blend compatibilized with polyHMDI, the decrease in storage modulus is the highest. From this observation, it can be deduced that blending with PLA could provide a way to improve the thermoforming of PHBV. In fact, one of the limitations of thermoforming PHBV is due to its high crystallinity, which makes it very stiff until its melting point and very fluid afterwards, resulting in a very narrow temperature processing window. By blending with PLA, this range can be broadened towards lower temperatures, thus improving its thermoformability.

Rheological behavior

To evaluate the effect of the compatibilizer (type and amount) on the rheological properties of PHBV/PLA blends, dynamic oscillatory shear measurements were carried out as a function of frequency at 180 °C. All rheological measurements were driven from high to low frequencies. Fig. 6 shows the variation of the storage modulus (G'), loss modulus (G'') and complex viscosity (η^*)

versus frequency for neat PHBV and PHBV/PLA blends, with and without compatibilizers at their different contents.

The storage modulus (G') and the loss modulus (G'') typically increase with frequency, and the difference between G' and G'' values for all the specimens decreases at high frequencies (Figs. 6a, 6c and 6e). This is directly related to the viscoelastic properties of polymers with two overlapped responses: on the one hand, an immediate and non-time dependent elastic response and on the other hand, a time-dependent viscous response. At high frequencies, both PHBV and PLA offer a more elastic response and the viscous contribution is lower. Alternatively, at lower frequencies, viscous phenomena (time dependent) are allowed to a greater extent.

The incorporation of PLA leads to small changes in the rheological behavior. However, with the incorporation of the compatibilizer, an increase in the storage modulus (G') and loss modulus (G'') at low frequencies with respect to those of both neat PHBV and PHBV/PLA can be clearly seen. The different viscoelastic responses of these materials become even more substantial when the compatibilizer content increases, being most pronounced in the case of the addition of PDI as the compatibilizing agent.

Such an increase in the storage and loss modulus (G' and G'') at lower frequencies has been reported by several authors for PHBV/PLA systems. Zhao *et al.*³⁹ explained this behavior with the formation of entangled structures in the PHBV/PLA melts. These entanglements lead to highly reversible elastic deformation of melts, partially preventing the relaxation of the melt structures. Furthermore, they raise the possibility that the immiscible nature of PLA/PHBV blends might play a role in the evolution of G' curves at low frequencies. Zembouai *et al.*²¹ also found the same behavior for similar PHBV/PLA blends, also noting the immiscibility of both components⁵ and the droplet/matrix morphology⁴⁰ as the origin of the phenomenon.

A shoulder in G' , G'' and complex viscosity is observed in all the studied compositions, even neat PHBV. This shift in viscosity at low frequencies has been attributed to the presence of minerals in the PHBV (boron nitride), used as nucleating agents, which can act also as fillers⁵.

It can be appreciated that this shoulder shifts to higher frequencies when the diisocyanate content is increased, being most pronounced for the 1:20 molar ratio of compatibilizer (even at 1:10 in the case of PDI). Such a shift, which comes with an increase in complex viscosity at lower frequencies, is observed for 1:10 and 1:20 molar ratios of HMDI, polyHMDI and PDI. This behavior is most

enhanced with the addition of PDI with respect to the other two diisocyanates at an equal molar ratio. In agreement with the previous reasoning, an increase in the droplet/matrix surface would lead to such an increase in viscosity at low frequencies, such as that observed in Fig. 6, in good agreement with the previous SEM analysis.

This reasoning, however, is called into question by the same authors, arguing that rheological tests performed at 175 °C did not yield the same results as the ones performed at 185 °C²¹. They opened up the possibility that some unmelted PHBV particles could be responsible for the high values of viscosity at low frequencies. To discard this possibility in our experiments, samples were placed in DSC pans at the same temperature of their and our rheological measurements, that is at 175, 180 and 185 °C, for 5 min, which is the typical time lapse for the rheological tests. After that, controlled cooling showed that there were no self-seeding phenomenon at 185 or 180 °C, thus proving that complete melting took place and that the thermal history was erased at the rheometer. Samples kept at 175 °C showed some nucleating effect, with a shift of the crystallization peak to higher temperatures.

The possibility of reaching higher values of complex viscosity at low frequencies with high molar ratios of diisocyanate as the compatibilizer is also quite interesting from the processing point of view of PHBV. This result again opens the possibility of improving the thermoforming ability of PHBV, broadening the processing window towards higher temperatures, complementing the effects observed in DMTA analysis towards lower temperatures.

CONCLUSIONS

PHBV/PLA blends with three different compatibilizers (hexamethylene diisocyanate, (HMDI), poly(hexamethylene) diisocyanate (polyHMDI) and 1,4-phenylene diisocyanate (PDI)) were successfully obtained by melt blending.

Favourable morphologies were achieved during processing for the three compatibilizers, enhancing the miscibility between both polymers, as derived from SEM. The addition of diisocyanates within the range studied slightly decreases the overall crystallinity, and there was a slight variation in the melting temperature and a marked decrease in crystallization temperature. Nevertheless, no effect on the thermal stability of the compatibilized blends was observed with the addition of the diisocyanates.

The mechanical properties of such blends were characterised by an increase in elongation at break of PHBV/PLA blends through incorporation of HMDI, polyHMDI and PDI as compatibilizing agents.

The processability of PHBV can be facilitated with its blend with PLA and compatibilization with the studied diisocyanates, due to widening the processing window of PHBV, which should contribute to enhancing the thermoforming of PHBV, as concluded by DMTA and rheological results.

Therefore, the use of diisocyanate-type compatibilizers to improve the industrial processability of biopolymer blends may be a promising approach for extending their applications with a view to replacing commodity polymers. Further studies to assess the remaining isocyanate groups and thermoforming properties are requested to find practical applications for these formulations.

ACKNOWLEDGMENTS

Financial support for this research from Ministerio de Economía y Competitividad (project AGL2015-63855-C2-2-R), Generalitat Valenciana (GV/2014/123) and Pla de Promoció de la Investigació de la Universitat Jaume I (PREDOC/2012/32 and E-2015-22) is gratefully acknowledged. The authors are also grateful to Raquel Oliver and José Ortega for experimental support.

REFERENCES

- [1. Shah, A. A.; Kato, S.; Shintani, N.; Kamini, N. R.; Nakajima-Kambe, T. *Appl. Microbiol. Biotechnol.* 2014, 98, 3437–3447.
- [2. Mittal, V. *Nanocomposites with Biodegradable Polymers*; Oxford University Press, 2011.
- [3. Auras, R.; Lim, L. T.; Selke, S. E. M.; Tsuji, H. *Poly(Lactic Acid)*; Auras, R.; Lim, L.-T.; Selke, S. E. M.; Tsuji, H., Eds.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2010.
- [4. Gámez-Pérez, J.; Velazquez-Infante, J. C.; Franco-Urquiza, E.; Pages, P.; Carrasco, F.; Santana, O. O.; MasPOCH, M. L. *Express Polym. Lett.* 2011, 5, 82–91.
- [5. Gerard, T.; Budtova, T. *Eur. Polym. J.* 2012, 48, 1110–1117.
- [6. Bucci, D. Z.; Tavares, L. B. B.; Sell, I. *Polym. Test.* 2005, 24, 564–571.
- [7. Cava, D.; Gimenez, E.; Gavara, R.; Lagaron, J. M. *J. Plast. Film Sheeting* 2006, 22, 265–274.
- [8. Lagaron, J. M.; Lopez-Rubio, A. *Trends Food Sci. Technol.* 2011, 22, 611–617.
- [9. Rhim, J. W.; Park, H. M.; Ha, C. S. *Prog. Polym. Sci.* 2013, 38, 1629–1652.

10. Javadi, A.; Pilla, S.; Gong, S.; Turng, L. S. *Handbook of Bioplastics and Biocomposites Engineering Applications*; Pilla, S., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2011.
11. Sridhar, V. *Express Polym. Lett.* 2013, 7, 320–328.
12. Ferri, J. M.; Fenollar, O.; Jorda-Vilaplana, A.; García-Sanoguera, D.; Balart, R. *Polym. Int.* 2016, 65, 453–463.
13. Martínez-Abad, A.; González-Ausejo, J.; Lagarón, J. M.; Cabedo, L. *Polym. Degrad. Stab.* 2016.
14. Cabedo, L.; Luis Feijoo, J.; Pilar Villanueva, M.; Lagarón, J. M.; Giménez, E. *Macromol. Symp.* 2006, 233, 191–197.
15. Arrieta, M. P.; López, J.; López, D.; Kenny, J. M.; Peponi, L. *Eur. Polym. J.* 2015, 73, 433–446.
16. Deng, Y.; Thomas, N. L. *Eur. Polym. J.* 2015, 71, 534–546.
17. Modi, S.; Koelling, K.; Vodovotz, Y. *Eur. Polym. J.* 2013, 49, 3681–3690.
18. Modi, S.; Koelling, K.; Vodovotz, Y. *J. Appl. Polym. Sci.* 2012, 124, 3074–3081.
19. Zembouai, I.; Bruzaud, S.; Kaci, M.; Benhamida, A.; Corre, Y.; Grohens, Y.; Lopez-Cuesta, J.-M. *Polym. Eng. Sci.* 2014, 54, 2239–2251.
20. Zembouai, I.; Kaci, M.; Bruzaud, S.; Benhamida, A.; Corre, Y.-M.; Grohens, Y. *Polym. Test.* 2013, 32, 842–851.
21. Zembouai, I.; Bruzaud, S.; Kaci, M.; Benhamida, A.; Corre, Y.-M.; Grohens, Y.; Taguet, A.; Lopez-Cuesta, J.-M. *J. Polym. Environ.* 2013, 22, 131–139.
22. Jost, V. *Chem. Biochem. Eng. Q.* 2015, 29, 221–246.
23. Liu, Q.; Wu, C.; Zhang, H.; Deng, B. *J. Appl. Polym. Sci.* 2015, 132, n/a – n/a.
24. Li, L.; Huang, W.; Wang, B.; Wei, W.; Gu, Q.; Chen, P. *Polymer (Guildf)*. 2015, 68, 183–194.
25. Li, J.; Lai, M. F.; Liu, J. J. *J. Appl. Polym. Sci.* 2004, 92, 2514–2521.
26. Bugnicourt, E. *Express Polym. Lett.* 2014, 8, 791–808.
27. Cailloux, J.; Santana, O. O.; Franco-Urquiza, E.; Bou, J. J.; Carrasco, F.; Gámez-Pérez, J.; Maspoch, M. L. *Express Polym. Lett.* 2012, 7, 304–318.
28. Pivsa-Art, S.; Srisawat, N.; O-Charoen, N.; Pavasupree, S.; Pivsa-Art, W.; Yamane, H.; Ohara, H. In *Annual Technical Conference - ANTEC, Conference Proceedings*; Society of Plastics Engineers, 2013; Vol. 2, pp. 1777–1779.
29. Gerard, T. *Express Polym. Lett.* 2014, 8, 609–617.
30. Raffa, P.; Coltelli, M.-B.; Savi, S.; Bianchi, S.; Castelvetro, V. *React. Funct. Polym.* 2012, 72, 50–60.
31. Torres, N.; Robin, J. J.; Boutevin, B. *J. Appl. Polym. Sci.* 2001, 79, 1816–1824.
32. Dogan, S. K.; Reyes, E. A.; Rastogi, S.; Ozkoc, G. *J. Appl. Polym. Sci.* 2014, 131, n/a – n/a.
33. Zeng, J.-B.; Li, K.-A.; Du, A.-K. *RSC Adv.* 2015, 5, 32546–32565.
34. Alata, H.; Aoyama, T.; Inoue, Y. *Macromolecules* 2007, 40, 4546–4551.

35. Sanchez-Garcia, M. D.; Lagaron, J. M. *J. Appl. Polym. Sci.* 2010, 118, 188–199.
36. Grassie, N.; Murray, E. J.; Holmes, P. A. *Polym. Degrad. Stab.* 1984, 6, 127–134.
37. Kopinke, F. D.; Mackenzie, K. J. *Anal. Appl. Pyrolysis* 1997, 40-41, 43–53.
38. Chen, B.-K.; Shen, C.-H.; Chen, A. F. *Polym. Bull.* 2012, 69, 313–322.
39. Zhao, H.; Cui, Z.; Sun, X.; Turng, L.-S.; Peng, X. *Ind. Eng. Chem. Res.* 2013, 52, 2569–2581.
40. Castro, M.; Carrot, C.; Prochazka, F. *Polymer (Guildf)*. 2004, 45, 4095–4104.

Figure Captions:

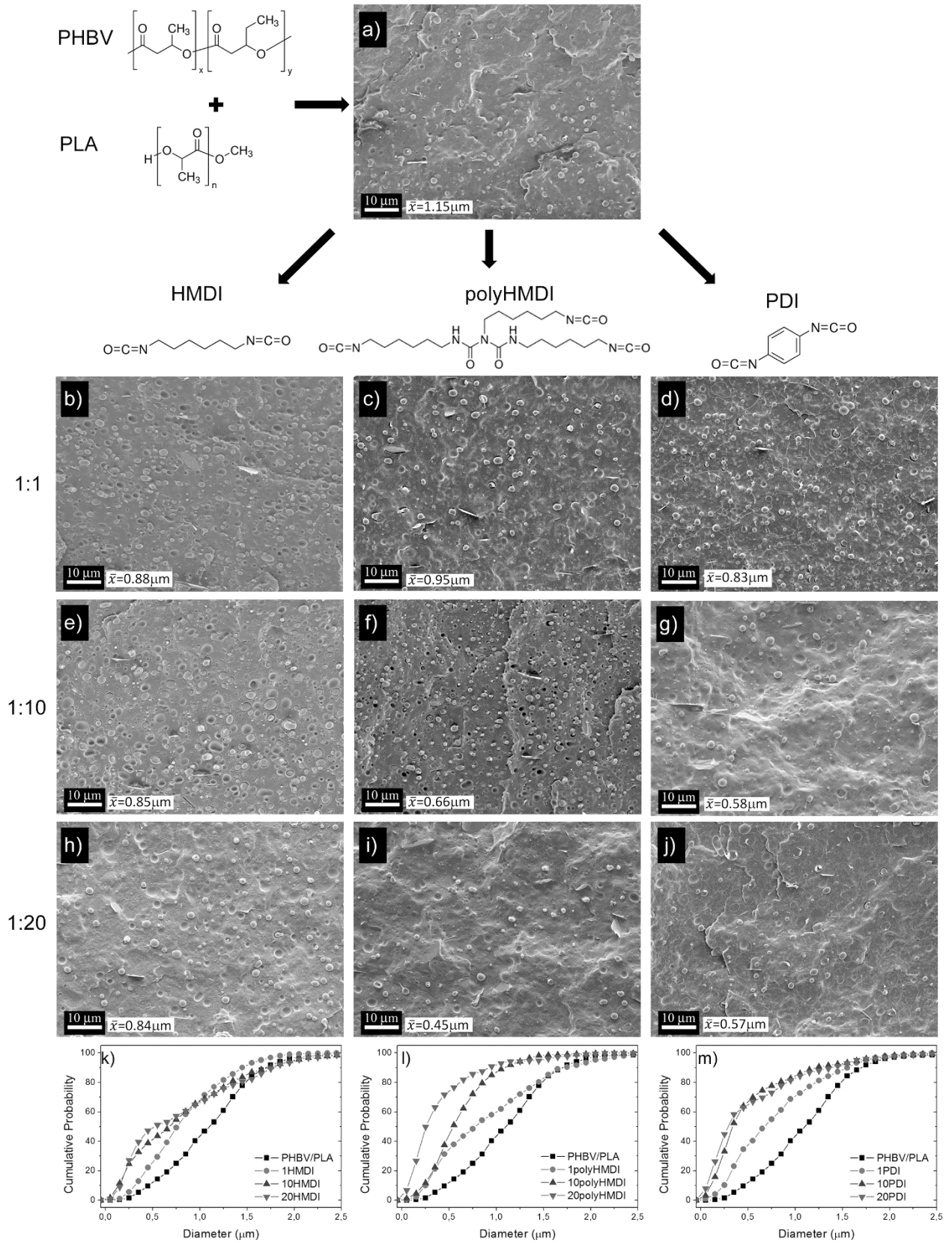


Fig. 1: SEM images of the fracture surfaces of PHBV/PLA blends with diisocyanates.

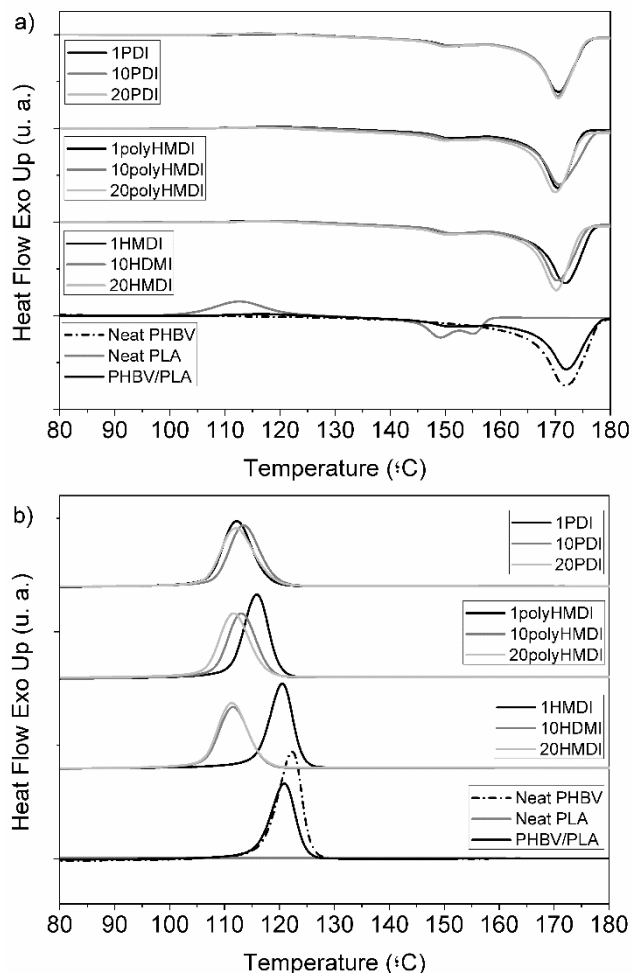


Fig. 2: DSC curves of neat PHBV, PHBV/PLA and PHBV/PLA blends with a 1:20 molar ratio of diisocyanates.

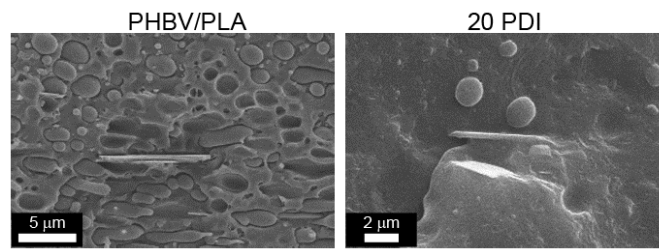


Fig. 3: SEM micrographs of boron nitride particles in PHBV/PLA blend and PHBV/PLA blend with a 1:20 molar ratio of PDI.

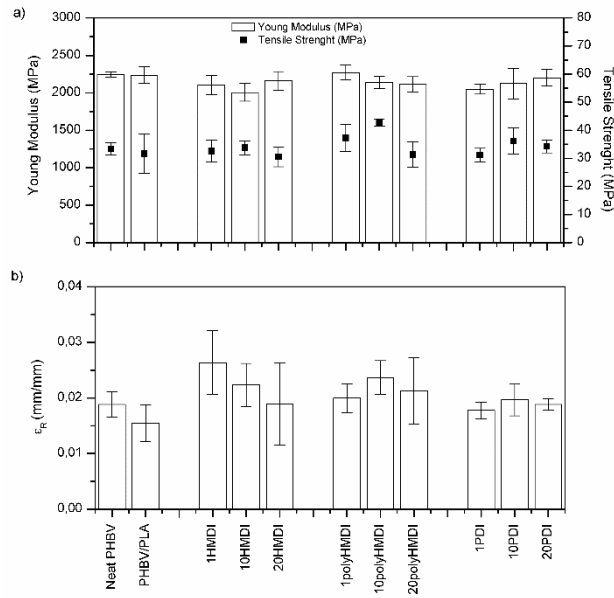


Fig. 4: Young's modulus (E), tensile strength (σ_y) and elongation at break (ϵ_R) of neat PHBV and PHBV/PLA blends with diisocyanates versus compatibilizer content.

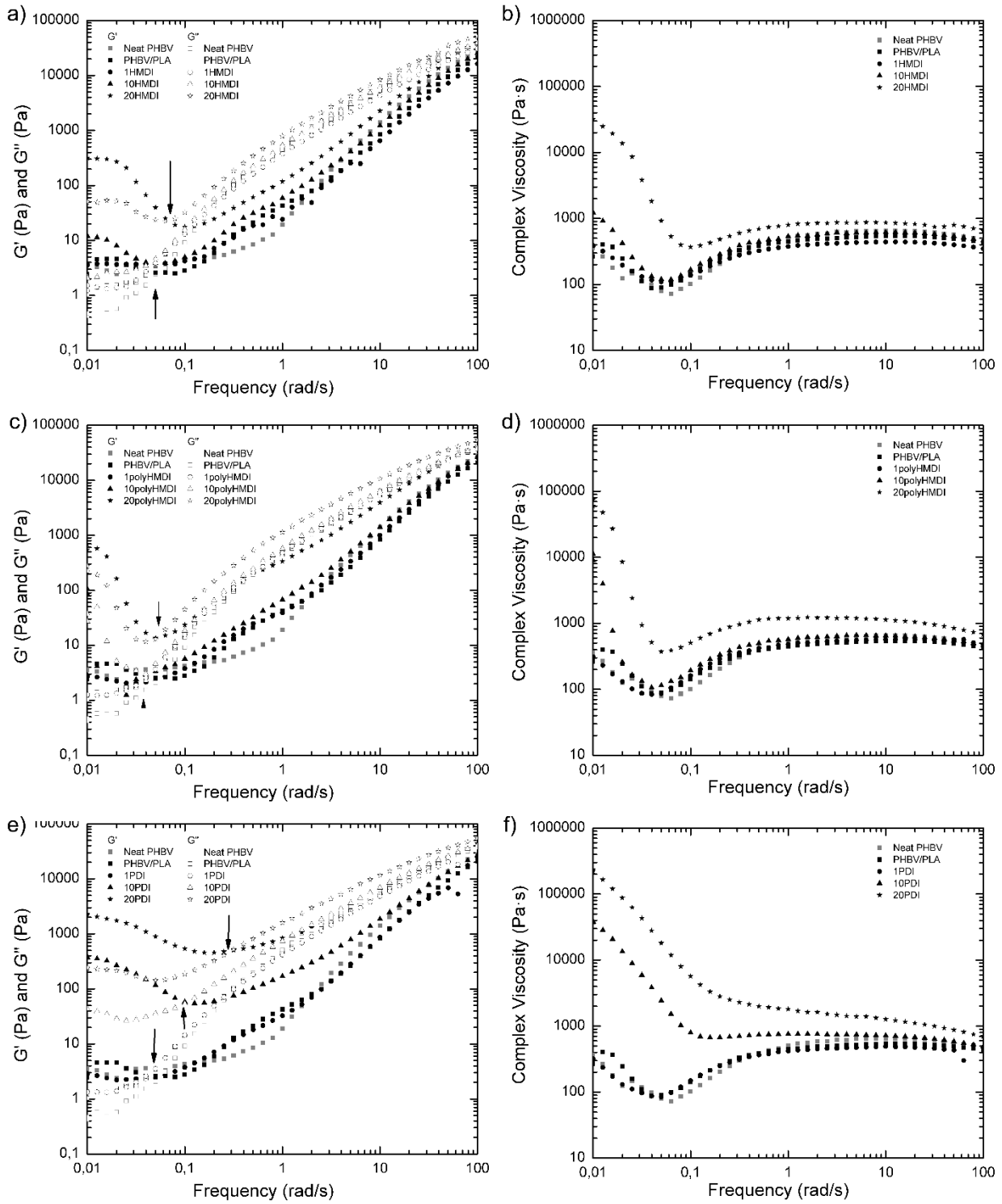


Fig. 5: a) Dynamic storage modulus (E') and b) delta tangent of PHBV, PHBV/PLA and PHBV/PLA blends with a 1:20 molar ratio of diisocyanates.

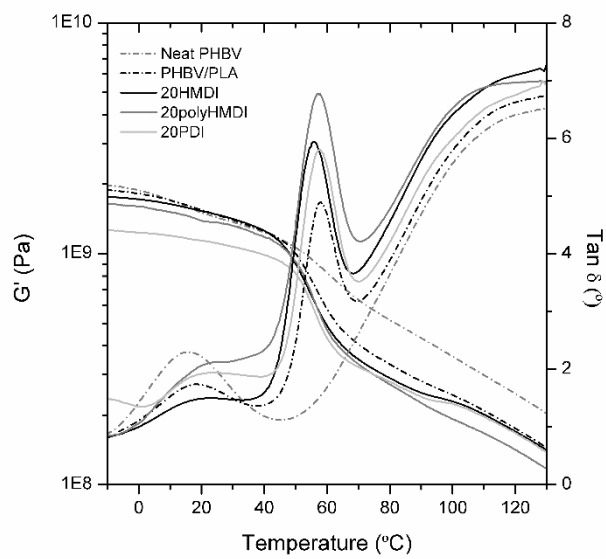


Fig. 6: Evolution of a) storage modulus (G'), b) loss modulus (G'') and c) complex viscosity of neat PHBV, PHBV/PLA and PHBV/PLA blends with diisocyanates at 180 °C under 1% dynamical shear strain.

Table Captions:

Table 1: Nomenclature of studied PHBV, PLA and PHBV/PLA blends.

SAMPLE	Weigh percentage		Molar ratio			Compatibilizer phr
	PHBV	PLA	HMDI	polyHMDI	PDI	
Neat PHBV	100					
Neat PLA		100				
PHBV/PLA	75	25				
1HMDI	75	25	1:1			0,06
10HMDI	75	25	1:10			0,63
20HMDI	75	25	1:20			1,26
1polyHMDI	75	25		1:1		0,11
10polyHMDI	75	25		1:10		1,14
20polyHMDI	75	25		1:20		2,27
1PDI	75	25			1:1	0,06
10PDI	75	25			1:10	0,60
20PDI	75	25			1:20	1,20

Table 2: DSC and TGA data of PHBV and PHBV/PLA blends with and without diisocyanates.

	T _m (°C)	X _c (%)	T _c (°C)	T _{5%} (°C)	T _{d1} (PHBV) (°C)	T _{d2} (PLA) (°C)
Neat PHBV	171,8±0,2	66,6±0,6	122,4±0,1	274±1	289±1	-
PHBV/PLA	172,05±0,1	63,3±2,3	120,9±0,1	275±1	288±2	350±1
1HMDI	171,7±0,0	68,7±0,4	120,5±0,1	275±2	289±1	350±1
10HMDI	170,2±0,3	63,6±0,4	111,7±0,1	274±1	288±1	338±2
20HMDI	170,2±0,2	63,1±4,9	111,2±0,2	274±2	289±1	346±1
1polyHMDI	170,6±0,2	63,0±6,2	115,9±0,1	275±1	288±2	350±1
10polyHMDI	170,7±0,0	63,2±2,7	113,0±0,1	272±1	287±1	338±1
20polyHMDI	170,0±0,2	62,3±2,5	111,5±0,2	274±2	286±2	326±2
1PDI	170,7±0,3	63,3±0,7	112,2±0,2	276±1	288±1	350±1
10PDI	170,5±0,0	62,9±1,6	113,4±0,0	276±1	290±2	349±1
20PDI	170,5±0,0	64,7±1,0	112,2±0,1	276±2	290±2	322±2