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Mechanical Recycling of Poly(3-Hydroxybutyrate-co-3-Hydroxyvalerate)/Polylactide Based Blends

Idris Zembouai · Stéphane Bruzaud ·
Mustapha Kaci · Aida Benhamida ·
Yves-Marie Corre · Yves Grohens

Abstract The effects of recycling cycles (up to six repeated cycles) on the structure and properties of neat poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), neat polylactide (PLA) and PHBV/PLA: 50/50 (wt%) blends elaborated by melt molding process were investigated. The changes in the chemical structure, the morphology and the thermal, mechanical and rheological properties of the recycled materials were studied. The reduction of molecular weights of both PHBV and PLA showed the predominance of chain scission mechanism as a result of degradation inducing an enhancement of PHBV chain mobility, as also revealed by the increasing of the PHBV crystallinity measured using differential scanning calorimetry and wide angle X-ray scattering. Nevertheless, all these effects were significantly smaller for neat PLA and PHBV–PLA blends compared to those of neat PHBV. Contrary to PLA, PHBV seems to be relatively more sensitive to the thermomechanical degradation and the presence of PLA in the PHBV–PLA blend tends to partially prevent the degradation of PHBV. Mechanical results evidenced the great recyclability of PHBV/PLA blends, even after six reprocessing cycles, since the values of mechanical characteristics remain more or less constant compared to the initial ones revealing the preservation of the material mechanical properties. A stabilizing effect of

PLA on the recyclability of PHBV–PLA blends was highlighted and it can be concluded that the incorporation of PLA in PHBV/PLA blends might be a promising route to extend the PHBV applications.

Keywords Poly(3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) · Polylactide (PLA) · Blends · Recyclability · Properties

Introduction

Biopolymers have generated great interest in this decade due to rapid growth in consumer awareness and stricter government regulation of municipal waste [1–3]. Biodegradable polymers derived from renewable resources have attracted increasing attention due to the great demand in biomedical field, including resorbable sutures, drug delivery systems, tissue scaffolds [4] and also for food packaging applications [5, 6]. Polyhydroxyalkanoates (PHA) [7, 8] and polylactide (PLA) [9–11] have received even more attention in view of sustainability. The interest in polymer blends is constantly increasing because this is an opportunity to finely adjust the functional properties of these materials [12–14]. This process was explored as an alternative economical way of achieving novel materials with desired properties [15–19]. Polymer recycling is one of the most important subjects of the current industry, besides producing biodegradable polymers, to increase the proportion of environment friendly materials. In the United States alone, recycling is done for more than 2 billion pounds of polymers [20]. However, the reprocessing and the recycling of polymers induce adverse effects on the final properties due to the degradation caused by mechanical shear forces coupled to thermal effects [21]. Zaverl and

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al. [20] studied the recyclability of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) with multiple melt processing (five cycles), using a twin screw extrusion followed by injection molding. The authors showed that the molecular weight of the polymer does not drastically decrease; however, a drop was observed after the third cycle, and set value of thermal decomposition decreased very slightly. In other hand, the recycling of PLA was studied by Duigou et al. [21] and Zenkiewicz et al. [22] which observed a less decrease in the mechanical properties, associated to a decrease in the onset temperature of the polymers after ten extrusion processes. A slight decrease of the mechanical properties was observed after several mold injection processes according to the nature of the polymer. Pillin et al. [23] studied the thermo-mechanical effects of recycling PLA on the mechanical properties, noting a reduction of stress and strain at break, whereas Young's modulus remained relatively constant.

In previous works, we focused on the study of the morphology and rheological properties of PHBV-PLA blends obtained by melt mixing [12] and a comprehensive study of the thermal stability, flammability properties and thermo-mechanical behavior of these blends was carried out [13]. The effect of compatibilizer and Cloisite 30B on the functional properties of PHBV/PLA blends was also studied [14]. The increase of the interest on PHA/PLA blends makes it of primary importance to assess its behavior upon recycling.

In this paper, which is a continuation of the previous works, the objective is to report the recycling effect on the properties of PHBV/PLA: 50/50 (wt%) blends elaborated by melt molding process up to six repeated processing cycles. The changes in the chemical structure, the morphology and the thermal, mechanical and rheological properties of the recycled materials were studied.

Experimental Section

Materials Used

PLA was supplied in pellets form by NatureWorks under the trade name 7001D. The polymer is a semi crystalline one having the following main properties: density = 1.25 g cm^{-3} , MFI = 6 g/10 min (210 °C, 2.16 kg), $T_g = 60 \text{ °C}$ and $T_m = 160 \text{ °C}$.

PHBV was manufactured by Tianan Biological Materials Co. Ltd. (China) and commercialized in pellets form under the trade name ENMAT Y1000P. According to the manufacturer, PHBV has the following properties: density = 1.25 g cm^{-3} , $T_g = 8 \text{ °C}$ and $T_m = 165 \text{ °C}$. This grade has been comprehensively characterized in a recent paper [7].

Sample Preparation and Recycling

PHBV and PLA pellets were dried under vacuum at 60 °C for 48 h prior to extrusion. They were then extruded with PHBV/PLA blend with weight ratios (50/50). Compounding was achieved in a single screw extruder at 30 rpm and the following temperature profile: 175/180/180 and 180 °C in the nozzle. The resulting material was granulated. Further a set of six passes were performed under the same processing conditions. Compounded pellets were also dried under vacuum at 60 °C for 48 h. Injection molding was then carried out on a Battenfeld HM 80-210 S Unilog B6 machine. Temperature profile was kept as follows: 175/180/180/180 and 180 °C in the nozzle to produce samples for mechanical tests. Parameters were kept constant at different cycles.

Characterization Methods

Differential Scanning Calorimetry (DSC)

DSC analyzes were performed on weighted samples of about 10 mg, using a Mettler-Toledo DSC-882 equipment. The samples were subjected to two heating and cooling ramps starting from -40 °C up to 200 °C and down to -40 °C with a scanning rate of 10 °C min^{-1} under nitrogen atmosphere. In the first run, the samples were heated from -40 to 200 °C at a heating rate of 10 °C min^{-1} . After being kept at 200 °C for 2 min, the samples were rapidly quenched to -40 °C . In the second run, they were heated at a rate of 10 °C min^{-1} to 200 °C .

Scanning Electron Microscopy (SEM)

Morphologies were observed with a Jeol JSM-6031 scanning electron microscope to examine the fracture surface of the samples. The neck region for the broken specimens fractured in liquid nitrogen is parallel to the draw direction in order to reveal the internal morphology. Prior to observation, the fracture surfaces were coated with a thin gold layer by means of a polaron sputtering apparatus.

Wide Angle X-Ray Scattering (WAXS)

The WAXS measurements were performed at room temperature using advance diffractometer equipment (BRUKER AXS D8), operating at the $\text{CuK}\alpha$ radiation (wavelength $\lambda = 0.154 \text{ nm}$) for 40 kV and 40 mA. The 2θ scan range was used from 2 to 40° at a scan speed of 40 step s^{-1} .

Rheological Measurements

Oscillatory shear measurements were performed using a controlled stress Rheometer (Rheometer Anton Paar MCR

301) equipped with parallel disks of 25 mm diameter. Sample disks were vacuum dried at 60 °C for 24 h prior to testing. Samples were characterized at 175 °C for PHBV and 180 °C for PLA and PHBV/PLA blend. All rheometrical data were shown to be reproducible within ± 5 %.

Mechanical Properties

The static tensile tests were carried out in a laboratory where the temperature was 23 °C and the humidity was 48 % according to ISO 527 using a MTS Synergie RT1000 testing apparatus. The loading speed was 1 mm min⁻¹. AMTS extensometer was used with a nominal gauge length of 25 mm. The tests were carried out at least five times for each material and the results were averaged arithmetically. Izod notched impact testing was done with a Testing Machine according to ASTM D-256 standard. Due to high standard deviations, at least 10 samples were tested.

Dynamic Mechanical Analysis (DMA)

The thermo-mechanical behaviour of polymers samples has been investigated using a dynamical mechanical analyzer DMA 2980 from TA Instruments. The specimen was a thin rectangular strip with dimensions around 30 × 6 × 2 (mm)³ prepared from the compression molded. A temperature scan from -40 °C up to 150 °C was performed at the rate of 3 °C min⁻¹ while a dynamic tensile test was performed at a frequency of 1 Hz with amplitude of 10 μm.

Molecular Weight Measurement

Size exclusion chromatography (SEC) was used to determine the evolution of molecular weight. The apparatus is equipped with a set of three columns: two ResiPore and one PL gel Mixed C (Polymer Labs.). The detection system is composed of a refractometer and a UV detector. Chloroform was used as eluant with a flow rate of 0.8 mL min⁻¹. The elution profiles were analyzed by the Empower SEC module software (Waters). Calculations are based on calibration curves obtained from polystyrene standards ranging from 200 g mol⁻¹ up to 6 × 10⁶. The weight-average molecular weight and number-average molecular weight \overline{M}_n are obtained from the SEC analysis. The polydispersity index (PI) was calculated as $\overline{M}_w/\overline{M}_n$. Moreover, the average number of random chain scissions per unit mass (n_t) is calculated according to the following Eq. (1) [3]:

$$n_t = \frac{1}{\overline{Mn}_t} - \frac{1}{\overline{Mn}_0} \quad (1)$$

in which n_t represents the number of chain scission at a given processing cycle, while $\overline{Mn}(t_0)$ and $\overline{Mn}(t)$ are the number average molecular weight of samples after the initial and a given processing cycles, respectively.

Results and Discussion

Molecular Weight Changes

The changes in weight average molecular weight (\overline{M}_w), number average molecular weight (\overline{M}_n) and polydispersity index ($\overline{M}_w/\overline{M}_n$) taking place during reprocessing are shown in Table 1, which provides the values of \overline{M}_w and \overline{M}_n for one, three and six processing cycles for PHBV, PLA and PHBV/PLA blend. It is observed that \overline{M}_w of PHBV decreases when the cycle number increases, which is synonymous of the occurrence of polymer degradation [24, 25]. Indeed, after three and six cycles, \overline{M}_n of PHBV is reduced by almost 13 and 27 %, respectively. The significant decrease in both \overline{M}_w and \overline{M}_n of PHBV, associated to an increased polydispersity index, confirms the predominance of chain scission mechanism as a result of degradation [26]. The changes in \overline{M}_w and \overline{M}_n are in agreement with the enhancement of PHBV chain mobility, explaining the increasing of crystallinity (see later). The same phenomenon was reported by Zaverl et al. [20], when the reprocessing cycles reduce the molecular weight of PHBV due to chain scissions. This finding is also consistent with rheological data indicating a large reduction in the complex viscosity of PHBV with increasing the number of reprocessing cycles [20]. Nevertheless, a smaller decrease is observed for \overline{M}_n and of PLA compared to those of PHBV. The \overline{M}_n value of PLA is only reduced by 1.2 and 4.2 % after three and six cycles, respectively. Similar trend is also observed for \overline{M}_w which slightly shifts toward smaller

Table 1 Changes of molecular weight after reprocessing cycles

Samples	\overline{M}_w (g mol ⁻¹)	\overline{M}_n (g mol ⁻¹)	$\overline{M}_w/\overline{M}_n$
PHBV 1	404,020	299,410	1.35
PHBV 3	364,260	260,630	1.39
PHBV 6	311,480	218,500	1.42
PLA 1	262,320	187,990	1.39
PLA 3	260,810	185,780	1.40
PLA 6	248,840	180,170	1.38
PHBV/PLA 1	319,270	220,770	1.44
PHBV/PLA 3	315,740	211,470	1.49
PHBV/PLA 6	304,150	210,070	1.44

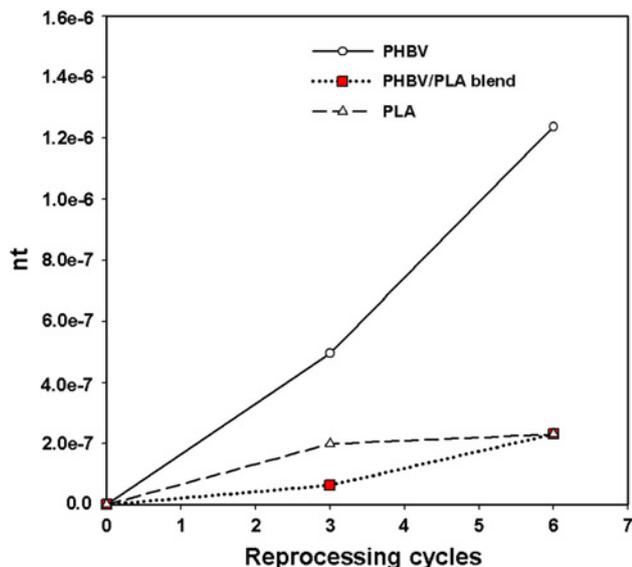


Fig. 1 Evolution of the average number of random chain scission (n_t) per unit mass for PHBV, PLA and PHBV/PLA blend as a function of cycles number

values. This relative stability in the molecular weights of PLA explains the constancy of the PLA crystallization enthalpy with the cycle number. For PHBV/PLA blend, the stability is relatively improved compared to the neat PHBV. After six cycles, \overline{M}_n of PHBV/PLA blend is only reduced by 4.8 %, due probably to the stabilizing effect of PLA in the blend.

Figure 1 represents the evolution of the average number of random chain scission (n_t) per unit mass for PHBV, PLA and PHBV/PLA blend as a function of cycle number and reveals a significant increase in the n_t value for PHBV after repeated reprocessing cycles. PHBV seems to be relatively sensitive to the thermomechanical degradation. On the contrary, only a slight increase in the n_t value is observed for PLA and for the blend PHBV/PLA, suggesting that the PLA presence prevents the degradation of PHBV based blend after repeated processing cycles. Further, the PLA incorporation in the PHBV/PLA blend clearly induces a better blend recyclability.

Calorimetric Properties

The DSC results of the thermal properties of different samples were reported in Tables 2, 3 and 4. The glass transition temperature (T_g), the crystallization temperature (T_c), the cold crystallization temperature (T_{cc}), the melting temperature (T_m), the crystallization enthalpy (ΔH_c), the cold crystallization enthalpy (ΔH_{cc}) and the melting enthalpy (ΔH_m) were determined from cooling and second heating scans for PHBV (Table 2), PLA (Table 3) and

Table 2 Thermal characteristics of PHBV as a function of number of reprocessing cycles obtained by DSC

Samples	$T_{cc,PHBV}$ (°C)	$\Delta H_{c,PHBV}$ (J/g)	$T_{g,PHBV}$ (°C)	$T_{m,PHBV}$ (°C)	$\Delta H_{m,PHBV}$ (J/g)
PHBV 1	117.1	93.4	1.1	172.2	101.4
PHBV 3	118.1	94.7	1.2	173.9	111.6
PHBV 6	120.1	100.1	1.6	171.7	112.0

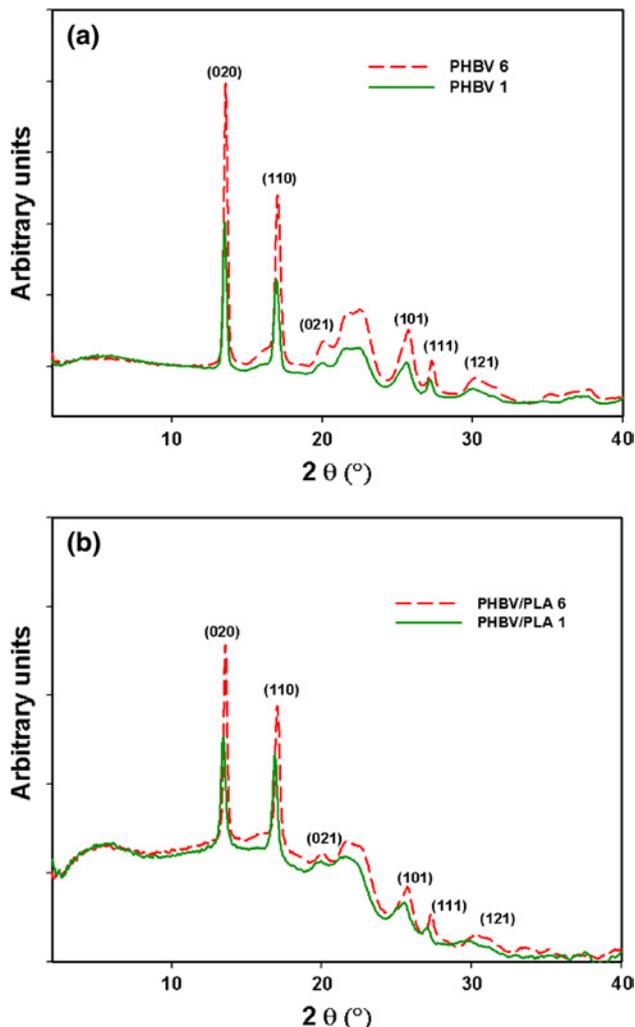
Table 3 Thermal characteristics of PLA as a function of number of reprocessing cycles obtained by DSC

Samples	$T_{cc,PLA}$ (°C)	$\Delta H_{cc,PLA}$ (J/g)	$T_{g,PLA}$ (°C)	$T_{m,PLA}$ (°C)	$\Delta H_{m,PLA}$ (J/g)
PLA 1	117.5	17.6	59.2	151.2	18.9
PLA 3	113.9	21.9	58.4	150.3	21.9
PLA 6	112.8	19.6	55.7	150.8	20.0

PHBV/PLA blend (Table 4) after one, three and six reprocessing cycles. The enthalpy of melting of PHBV increased from 101.4 J g⁻¹ after one cycle to 112 J g⁻¹ after six cycles. This can be explained by the reprocessing effect, which creates new nucleation sites. The crystal structures were affected by the multiple melt processing increasing the crystallinity of PHBV due probably to the reduction of the molecular weight of PHBV. Furthermore, it is observed an increase in the values of melting enthalpies relative to PHBV and PLA in PHBV/PLA blend with the number of reprocessing cycles. This can be interpreted by the increasing of crystallinity due to the recrystallisation of the molecule segments, which have been released by the polymer chain scissions induced by the thermo-mechanical degradation processes in the extruder. Concerning the melting enthalpy of PLA which slightly increases from 18.9 to 20 J g⁻¹ after sixth cycles, this small evolution may be attributed to a reduced mobility and consequently to a relative crystallization ability of PLA chains. In other hand, it was observed that T_g , T_m , T_c and T_{cc} values were also in the same range and were not drastically affected by the recycling, suggesting the great reprocessability of polymers. As the number of processing cycles increases, the crystallization enthalpy of PHBV and PHBV/PLA blend measured during cooling increases. The crystallization enthalpy of PHBV increases from 93.4 in the first cycle to 100.1 J g⁻¹ after the sixth one, while that of PLA remains relatively constant during all reprocessing cycles. The crystallization enthalpy of PHBV/PLA blend increases from 32.9 in the first cycle to 46.5 J g⁻¹ after the sixth one. This evolution of the crystallization enthalpy with the number of cycles is likely to be ascribed to a decrease of the molecular weight of PHBV which enhances the polymer chain mobility and increases crystallization kinetic.

Table 4 Thermal characteristics of PHBV/PLA blend as a function of number of reprocessing cycles obtained by DSC

Samples	$T_{c,PHBV}$ (°C)	$\Delta H_{c,PHBV}$ (J/g)	$T_{cc,PLA}$ (°C)	$\Delta H_{cc,PLA}$ (J/g)	$T_{g,PLA}$ (°C)	$T_{m,PLA}$ (°C)	$T_{m,PHBV}$ (°C)	$\Delta H_{m,PLA}$ (J/g)	$\Delta H_{m,PHBV}$ (J/g)
PHBV/PLA 1	117.4	32.9	122.3	2.0	57.1	152.6	173.3	4.3	40.4
PHBV/PLA 3	117.7	35.7	122.6	5.5	56.8	152.5	171.8	8.4	46.0
PHBV/PLA 6	118.6	46.5	123.7	4.7	55.4	151.2	171.4	11.1	53.2

**Fig. 2** WAXS patterns of **a** PHBV and **b** PHBV/PLA after one and six reprocessing cycles

Furthermore, no crystallization peak (T_c) is detected for PLA during cooling after six reprocessing cycles at the cooling rate of 10 °C/min, which is probably too fast to allow PLA crystallization.

WAXS Analysis

WAXS analysis was used to determine the changes in both the crystalline structure and the crystalline index of the polymers after six reprocessing cycles. Figure 2 shows

WAXS patterns of PHBV (Fig. 2a) and PHBV/PLA blend (Fig. 2b) after one and six reprocessing cycles. As described in a previous paper [12], the PHBV diagram reveals two strong diffraction peaks corresponding to the (020) and (110) planes of the orthorhombic unit cell, and small peaks assigned to the (021), (101), (111) and (121) planes. After six reprocessing cycles, no change is observed in the PHBV crystalline structure, but the peak intensity clearly increases. This is due to the enhancement of the crystallinity index after repeated reprocessing cycles, in agreement with the increase of PHBV chain mobility. The same comment can be made for the WAXS diagram of PHBV/PLA blend; the intensity of the different peaks increases after six reprocessing cycles. These results are in good agreement with the evolution of crystallization enthalpies observed by DSC analysis. Note that no characteristic peaks appear in the WAXS pattern of PLA because of its amorphous character.

Dynamic Mechanical Analysis

DMA gives very important information on the modulus values with respect to changes in the temperature during testing. As already reported in a previous work [13], neat PHBV shows high storage modulus compared to that of neat PLA and the blend presents intermediate storage modulus. DMA is also a useful analysis to evaluate the effect of recycling in the mechanical properties of PHBV, PLA and their blends. The evolution of the storage moduli according to the reprocessing cycles are plotted in Fig. 3. From Fig. 3a, the storage modulus of PHBV after the first cycle, presents below its T_g (1 °C) a value of 5,100 MPa, which decreases by about 8 % after six repeated reprocessing cycles. Beyond 1 °C, the values of storage modulus of PHBV at 25 °C decrease with the number of cycles as follows: 2,230, 2,070 and 1,920 MPa for one, three and six reprocessing cycles, respectively. This indicates that PHBV could be recycled without significant degradation in the thermomechanical properties, as reported by Zaverl and al. [20]. For PLA, the storage modulus after the first cycle presents below PLA T_g (60 °C) a constant value equal to 2,500 MPa which decreases by about 20 % after six repeated reprocessing cycles (Fig. 3b). We also observed that the storage modulus of pure PLA drops after its glass transition temperature, meanwhile the storage modulus of

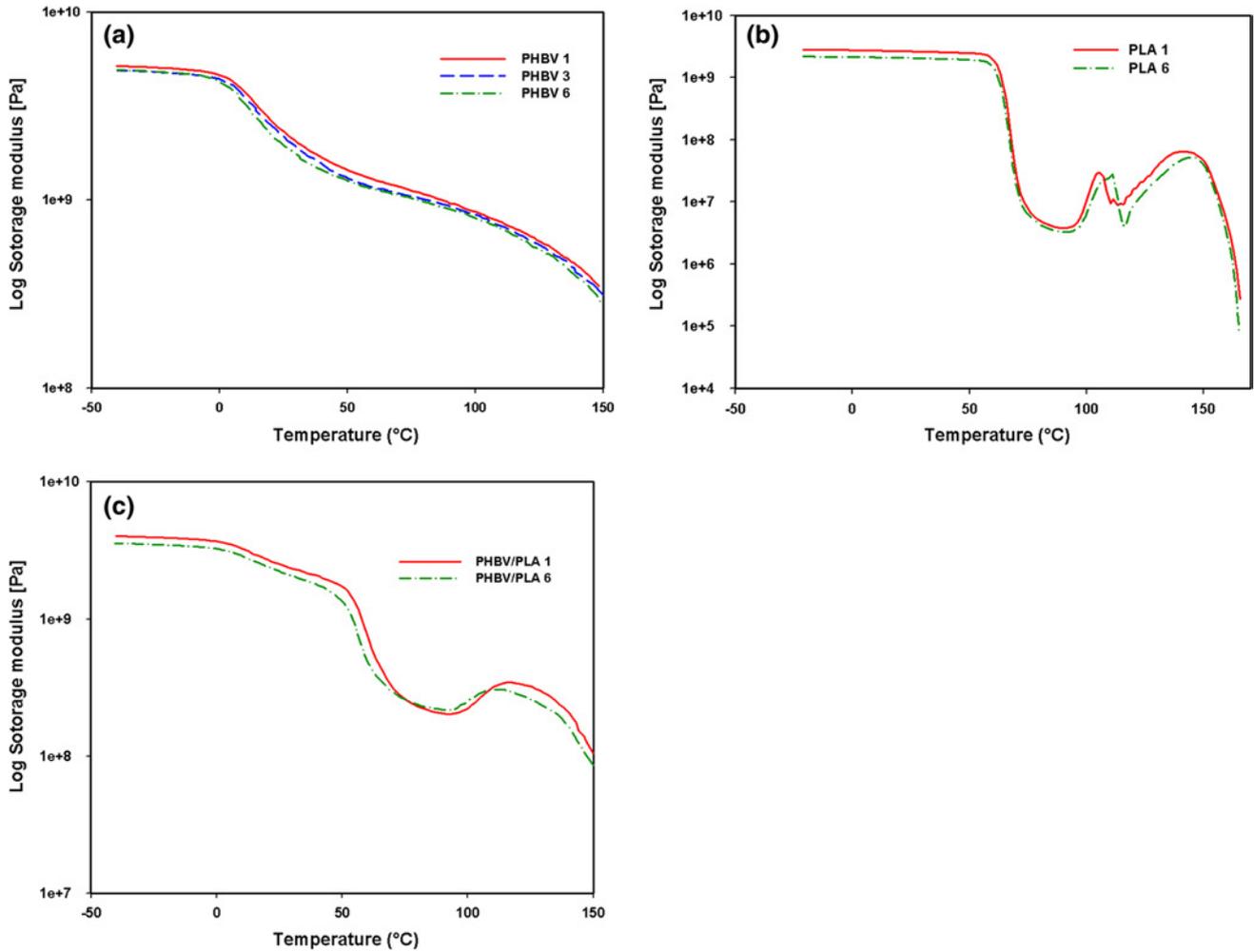


Fig. 3 DMA storage modulus for **a** PHBV, **b** PLA and **c** PHBV/PLA blend submitted to several reprocessing cycles

PLA after six cycles firstly drops and then slightly increases after 100 °C due probably to recrystallization of PLA. Moreover, the PLA storage modulus dramatically drops after the melting temperature. The curve demonstrates that PLA exhibits glassy, glass transition, cold crystallization and liquid flow behaviors. In addition, the storage modulus values of PLA were not really affected by the repeated processing cycles suggesting the ability of PLA to be recycled. For PHBV/PLA blend (Fig. 3c), the storage modulus at cycle 1 decreases at PHBV T_g and a second decrease is observed around 60 °C corresponding to PLA T_g . The recrystallization observed above 110 °C may explain the increase in storage modulus of PHBV/PLA blends. After six repeated cycles, the storage modulus of PHBV/PLA blend decreases by about 9 % at 25 °C and the decrease is almost in the same order for the other temperature ranges. Mechanical results obtained using DMA highlight the great recyclability of PHBV/PLA blends, even after six reprocessing cycles.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) is employed to investigate the effect of the repeated reprocessing cycles on the morphology of polymers and their blends. Two SEM images illustrating the morphology of samples after one and six cycles are shown for PHBV, PLA and PHBV/PLA blend (Fig. 4).

The SEM micrographs of PLA after the first and 6 cycles (Fig. 4a, b, respectively) show a regular and smooth surface compared to that of PHBV due to the amorphous character of PLA. The SEM micrographs of PHBV after one and six cycles corresponding to Fig. 4c, d, respectively point out a significant homogeneity for both samples. It can be clearly seen that the fractured surfaces are almost identical, although a few surface irregularities appear after six reprocessing cycles. This is probably due to the increase of the PHBV crystallinity with the number of cycles. The observation in the PHBV/PLA blend of a two phase-system

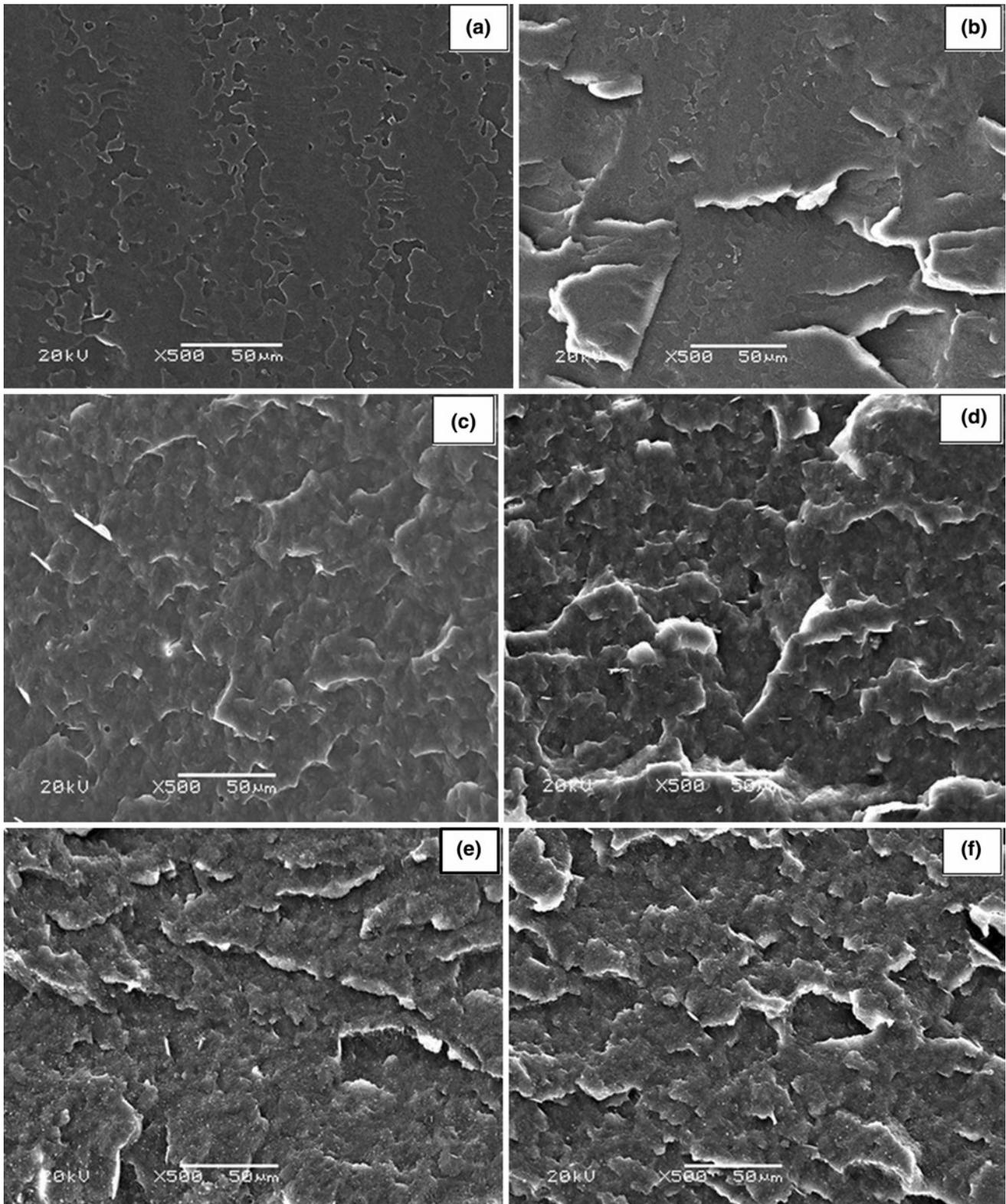


Fig. 4 SEM micrographs of fractured surface of PLA (**a** cycle 1 and **b** cycle 6), of PHBV (**c** cycle 1 and **d** cycle 6) and of PHBV/PLA blend (**e** cycle 1 and **f** cycle 6)

evidences a clear biphasic morphology with the rougher surface after six cycles (Fig. 4f) compared to the first cycle (Fig. 4e). SEM images allow us to confirm DMA results since the morphology of different samples does not significantly affected by the reprocessing cycles leading to conclude that the degradation in these conditions can be considered as quite negligible.

Rheological Properties

We investigated the recycling effect of PHBV, PLA and PHBV/PLA blend up to six repeated processing cycles on the rheological properties using dynamic shear measurements in the molten state. Rheological measurements were checked to be within the linear viscoelastic domain for all the specimens. Figure 5 presents the complex viscosity changes after the first reprocessing cycle as a function of frequency after different recycling processes for PLA, PHBV and PHBV/PLA blend. It is observed from Fig. 5a that the PLA samples exhibit a non-Newtonian flow profile with a plateau at low frequencies and shear thinning behavior when the frequency increases for the different reprocessing cycles. The rheological curves of PLA samples show a very slight decrease in the complex viscosity with increasing the number of cycles. At 0.1 Hz, the complex viscosity values are 2,290, 1,970 and 1,610 Pa s after one, three and six cycles, respectively. This behavior may be explained by a slight decrease of molecular weight due to chain scission phenomena. Figure 5b shows the results of the effect of reprocessing cycles on the complex viscosity of PHBV. Dynamic frequency sweep tests were carried out from 100 down to 0.1 Hz in a few cases to 0.01 Hz (when it was possible). It can be noted that the complex viscosity of PHBV is drastically reduced. Indeed, at 0.1 Hz and after one cycle, the complex viscosity value is 1,720 Pa s and after only two reprocessing cycles, the viscosity decreases strongly to 1,370 Pa s. After six cycles, the material becomes very fluid with a viscosity of 239 Pa s. The strong decrease in the viscosity with increasing the number of reprocessing cycles can be correlated to a decrease in the polymer molecular weights [23, 25]. PHBV is prone to undergoing chain scission during the extrusion process and this effect is enhanced by multiple reprocessing cycles. In the Fig. 5c, the curves represent the effect of reprocessing cycles on the complex viscosity of PHBV/PLA blend. Comparing the complex viscosity of PHBV/PLA blend from first and sixth extrusion, the former presents higher viscosity because the latter was subjected to several reprocessing cycles. In this figure, regarding the evolution of the complex viscosity, it is possible to observe the stabilizing effect of PLA on the PHBV with a better stability of the PHBV/PLA blend after reprocessing compared to that of PHBV alone. The degradation seems to be

more pronounced for the neat PHBV than for the PHBV/PLA blend during various reprocessing cycles. Furthermore, in the rheological tests of the PHBV/PLA blend on the sixth extrusion cycle, we can go up to 0.01 Hz while in the case of PHBV it is limited to 0.1 Hz because the polymer becomes very fluid and the complex viscosity is not detectable after the second cycle. On the other hand, the variation of the complex viscosity shows that the addition of PLA to PHBV does not affect anymore the resulting viscosity after the fifth cycle. This result is of primary importance to stimulate recycling of PHBV/PLA blend and their next industrial uses. At low frequencies, it is clearly observed an increase of complex viscosity of PHBV/PLA blend, the origin of this increase is not really understood even if this increase in complex viscosity at low frequencies is a reproducible and known phenomenon for immiscible blends as reported elsewhere [15]. Several reasons can be at the origin of this phenomenon, which is well known for the droplets/matrix morphology [12, 13].

The loss modulus versus frequency for neat PLA, PHBV and PHBV/PLA blend after six repetitive cycles showed a very slight decrease of loss modulus of PLA after six cycles (Figures not shown here). As expected, it can be noted that the loss modulus of PHBV is drastically reduced after reprocessing cycles. Indeed, at 0.1 Hz and after the fourth cycle, the loss modulus presents a reduction of 54 % compared to the first cycle one, indicating a higher degradation rate of PHBV matrix and subsequently, a greater chain mobility with a molecular weight reduction (also shown by SEC). In the case of PHBV/PLA blend, a relative stability is always highlighted after recycling. At 0.1 Hz, after the fourth and fifth cycles, the loss modulus of PHBV/PLA blend is only reduced by 17 and 25 % compared to that of the first cycle, confirming the stabilizing role of PLA. PHBV/PLA blend after reprocessing preserves its viscoelastic properties, in comparison with neat PHBV. Finally, the reprocessing cycles favor the thermal degradation of PHBV while PLA is relatively resistant towards reprocessing.

Mechanical Properties

The changes in the mechanical properties after the reprocessing cycles of PHBV, PLA and PHBV/PLA blend were also investigated using tensile tests. Tensile modulus, elongation at break and impact strength are reported versus reprocessing cycles in Figs. 6, 7 and 8, respectively. In Fig. 6, it is observed that the highest value of tensile modulus is obtained on PHBV after the first cycle and decreases from 4,346 to 3,859 MPa after six reprocessing cycles. This relatively small decrease of PHBV tensile modulus may be explained by the decrease in the molecular weight which is counter-balanced by an increase in

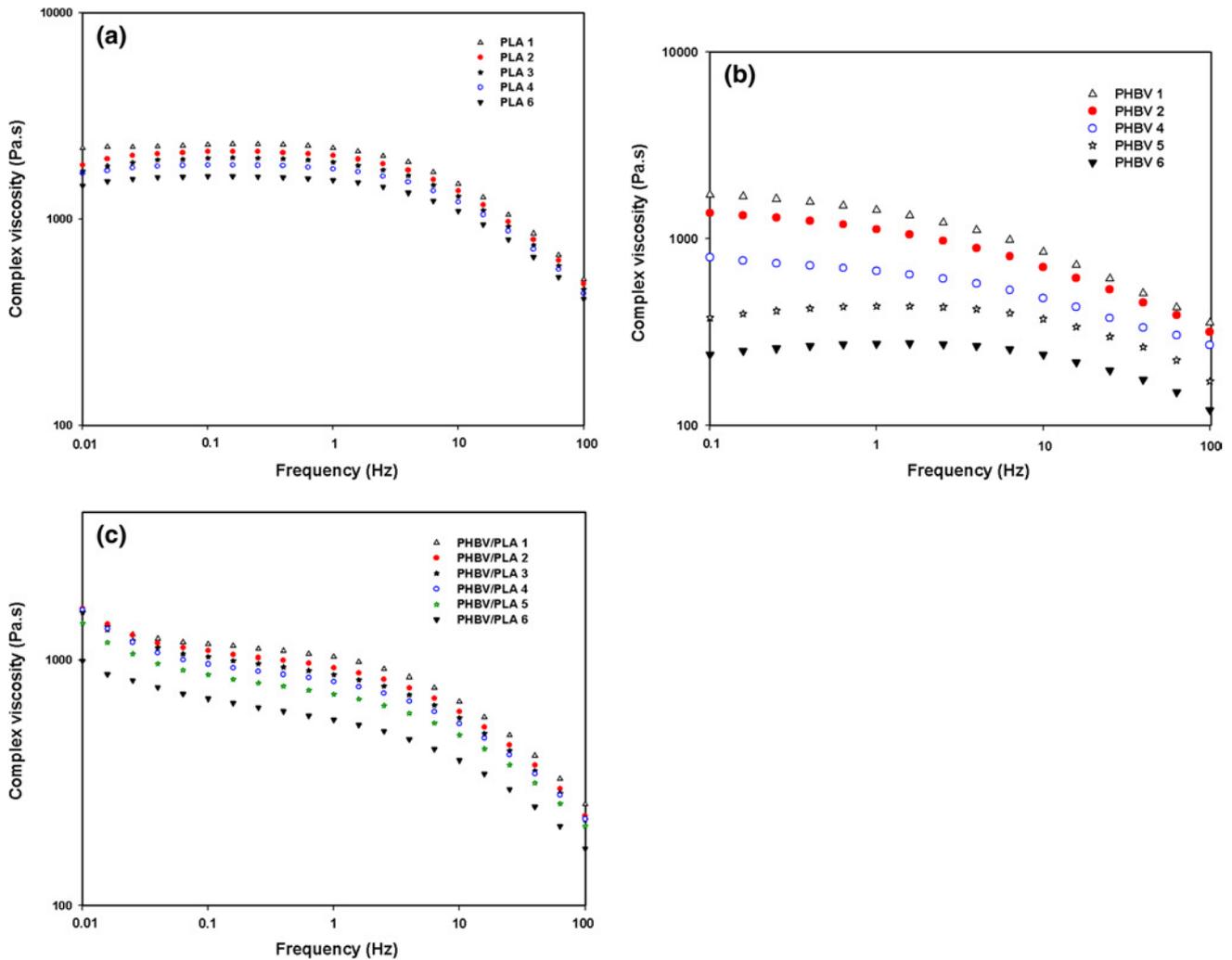


Fig. 5 Complex viscosity as a function of frequency for **a** PLA, **b** PHBV and **c** PHBV/PLA blend submitted to several reprocessing cycles

crystallinity. The tensile modulus of PLA decreases from 3,796 to 3,386 MPa after six cycles. The repeated cycles induce a small effect on the tensile modulus of PLA explained by the slight decrease of molecular weight. For PHBV/PLA blend, the tensile modulus after the first cycle is slightly higher than that of PLA, and decreases from 4,007 to 3,621 MPa after six reprocessing cycles. The difference observed between these values being not very significant, we can consider that the tensile modulus of PHBV/PLA blend remains relatively constant after six reprocessing cycles. The ductility measured as the strain at break versus reprocessing cycles is shown in Fig. 7 for PHBV, PLA and PHBV/PLA blend. The strain at break of PLA slightly decreases with the number of cycles. After six cycles, the strain at break of PLA decreases from 2.5 to 1.9 %; this phenomenon may be a consequence of the decrease of the chain length which favors the crack propagation above the elastic domain. The strain at break of

PHBV follows similar trend than that of PLA, even if the initial values are clearly different, and PHBV becomes a little more brittle after multiple processing cycles. The strain at break follows the same trend than that of the PHBV modulus, which is a consequence of the drop in the molecular weights. The strain at break of PHBV/PLA blend is intermediate between that of PHBV and that of PLA. The addition of PLA to PHBV increases the strain at break of blend. After six reprocessing cycles, the values of strain at break remain more or less constant compared to the initial ones revealing the retention of the mechanical properties of PHBV and PLA during reprocessing cycles.

The impact strength of PHBV, PLA and PHBV/PLA blend as a function of the number of reprocessing cycles is shown in Fig. 8. The impact strength decreases from 4.6 (for the first processed PHBV) to 3.6 J m⁻¹ (for the sixth processed PHBV). The reduction of impact resistance with reprocessing cycles seems also to be correlated with the

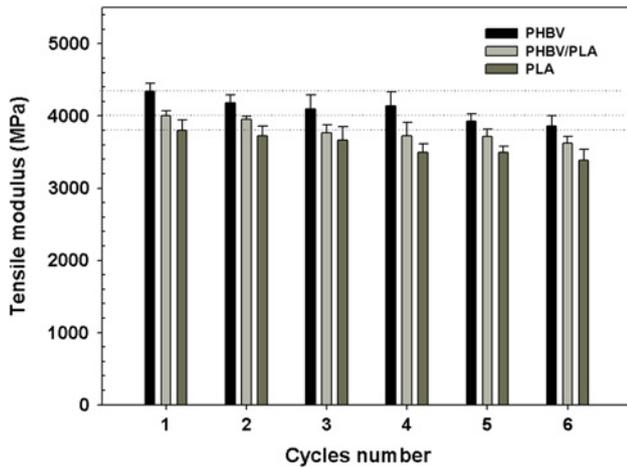


Fig. 6 Tensile modulus as a function of number of reprocessing cycles for PHBV, PLA and PHBV/PLA blend

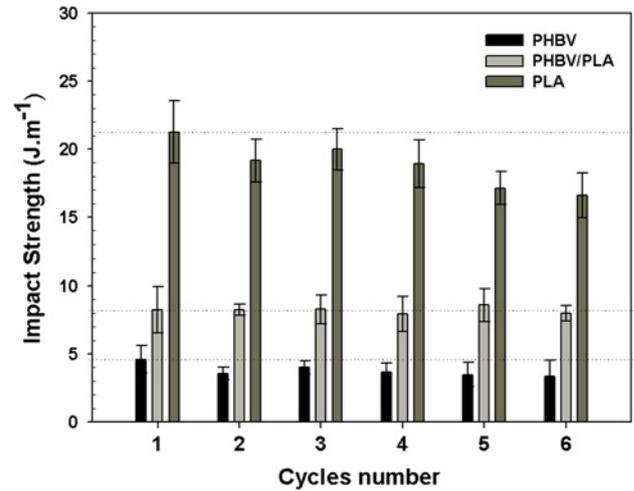


Fig. 8 Impact strength as a function of number of reprocessing cycles for PHBV, PLA and PHBV/PLA blend

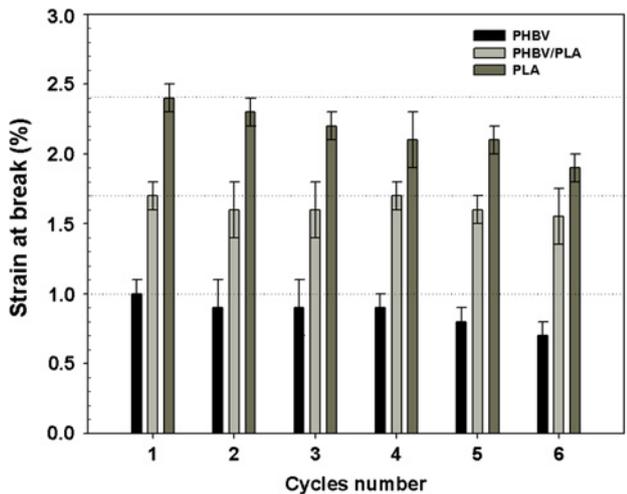


Fig. 7 Strain at break as a function of number of reprocessing cycles for PHBV, PLA and PHBV/PLA blend

evolution of molecular chain weights. Shorter molecular chain and broader chain length distribution result in poor chain entanglements, resulting in a decrease in toughness for the multiple processed PHBV. Other factors such as the defective sites in PHBV matrix should be invoked to account for the reduction in the impact resistance. The impact strength of PLA nearly remains constant until the fourth processing cycle; after this, a decrease in the impact strength is observed. The impact strength of PLA decreases from 21.2 (the first processed PLA) to 16.6 J m⁻¹ (the sixth processed PLA). The effects of processing cycles on the impact strength of PHBV/PLA blend have similar trend, as the average values were in the same range

showing almost identical values with only small fluctuations.

Conclusion

The recyclability of biopolymers like PHBV, PLA and PHBV/PLA blend was studied through repeated reprocessing cycles (up to 6). The changes induced by reprocessing in terms of morphology thermal, mechanical and rheological properties were investigated. Under the experimental conditions used, the following conclusions can be drawn:

The morphology and the structure of PHBV, PLA and PHBV/PLA are differently affected by repeated reprocessing cycles. Regarding their stability as a function of the cycle number, PLA is less sensitive to reprocessing cycles compared to PHBV which is significantly degraded. Indeed, a partial PHBV degradation occurs during reprocessing evidenced by a large decrease in the molecular weight and viscosity. This is consistent with SEC data indicating a significant decrease in the average molecular weight of the neat PHBV during reprocessing due to chain scission resulting from thermo-mechanical degradation. The DSC data also demonstrated that the enhancement of the PHBV chain mobility as a function of cycle number could be correlated with the molecular weight decrease. The whole results highlight that the thermo-mechanical PHBV degradation is significantly reduced in the presence of PLA. Consequently, the mechanical properties of PLA and PHBV/PLA blends are less affected after six cycles contrary to neat PHBV which exhibits a reduction in these properties.

Finally, the above results highlight the stabilizing effect of PLA on PHBV-based blends. This may constitute a promising way in order to minimize the degradability of PHBV and to enhance its recyclability.

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