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# Poly(3-Hydroxybutyrate-co-3-Hydroxyvalerate)/Polylactide Blends: Thermal Stability, Flammability and Thermo-Mechanical Behavior

Idris Zembouai · Stéphane Bruzaud · Mustapha Kaci · Aida Benhamida · Yves-Marie Corre · Yves Grohens · Aurélie Taguet · José-Marie Lopez-Cuesta

**Abstract** Blends of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and polylactide (PLA) with different PHBV/PLA weight ratios (100/0, 75/25, 50/50, 25/75, 0/100) were prepared by melt compounding. Their mutual contributions in terms of thermal stability, flammability resistance, mechanical properties and rheological behavior were investigated. The study showed that the increase in PLA content in PHBV/PLA blends leads to enhanced properties. Consequently, thermal stability and flammability resistance were improved. Further, the rheological measurements indicated an increase in storage modulus and loss modulus of PHBV matrix by addition of PLA.

**Keywords** Polyhydroxyalkanoate (PHA) · Polylactide (PLA) · Blends · Thermal stability · Flammability

## Introduction

Society is nowadays faced to environmental concerns about fossil fuel-based polymers. They are not

environmentally friendly, not only due to the use of oil and gas as fossil raw materials for the production, but also due to their slow degradation rates under typical disposal conditions and the subsequent solid waste problems [1, 2]. During the last decade, significant attention has been focused on both biobased and biodegradable polymers.

Among all these polymers, polylactide (PLA) is one of the biobased and biodegradable polymers that can be used as promising alternative to the petroleum-based commodity materials, because it can be derived from renewable resources, such as corn, potato and other agricultural products [3, 4]. PLA is linear aliphatic thermoplastic polyester with excellent properties comparable to many petroleum-based plastics [5]. PLA has good mechanical properties, thermal plasticity, high degree of transparency and biocompatibility. However, some of its properties, like flexural properties, gas permeability and heat distortion temperature, are too low for widespread applications.

Polyhydroxyalkanoates (PHA) produced by bacterial fermentation or other microorganisms are also fully biodegradable polyesters with a wide array of properties that range from stiff thermoplastics to elastomers [6–9]. PHA has been studied extensively for some years as replacements or substitutes for current mainstream petrochemical plastics. The plastic-like properties and biodegradability of PHA make them attractive as potential replacements for non-degradable polyethylene and polypropylene, as well as biodegradable and biocompatible biomaterials for implant purposes [10]. PHA can be also used in both biomedical and pharmaceutical industrial applications due to their biocompatibility and non-toxic properties [11]. Nevertheless, the processability and the brittleness of some PHA remains the major problem in applications [12].

Many methods have been developed to increase the properties of biopolymers, such as random and block

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copolymerization, chemical modification or incorporation of numerous filler, which modulate both the biodegradation rate and the mechanical properties of the final products. Polymer blends have attracted more attention in the last decades since physical blending is another effective and simple way to prepare biodegradable composites with different morphologies and physical characteristics [13, 14]. The blending of polymers is a useful way of obtaining new materials with improved properties, less costly than chemical modifications or synthesis of tailor-made copolymers. The physical and mechanical properties of blends can be easily modified by choosing the polymers and varying the composition of the blend [15–17]. Thus, one of the improvement methods for physical and mechanical properties of PHA is to blend PHA with other polymers, including biopolymers and conventional petroleum-based polymers [18–21]. Most of the studies on PHA and PLA blends that have been reported in the literature concern blends prepared using solvent casting technique [14]. More recently, some studies have been carried out to prepare blends based on different PHA using melt compounding [22–27].

In a previous work, very recently published and dealing with the morphology of PHBV/PLA blends obtained by melt mixing [28], we have shown that blends of PHBV/PLA are not miscible and form a biphasic system over the whole composition range. The rheology of PHBV/PLA blends investigated in the dynamic mode reveals that PHBV exhibits a very impressive increase in complex viscosity with increasing the PLA content. In the PHBV/PLA blend and that at medium and high frequencies mixture, dynamic viscosity follows the mixing law. In terms of barrier properties, PHBV provides better water and oxygen barrier properties to PHBV/PLA blends acting as an efficient barrier promoter for PLA, even at quite low ratio.

In this paper which is a continuation of the previous work, the objective is to report some experimental data on blends of PHBV and PLA prepared by melt mixing through a comprehensive study of the thermal stability, flammability properties and thermo-mechanical behavior. The influence of each component on the other is evaluated and the structure/property relationships are studied at various PHBV/PLA blend compositions involving 75/25, 50/50 and 25/75 wt%, respectively.

## Experimental Section

### Materials Used

Poly lactide was supplied in pellets form by Nature Works under the trade name 7001D. The polymer is a semi-crystalline one having the following main properties:

density = 1.25 g cm<sup>-3</sup>, MFI = 6 g/10 min (210 °C, 2.16 kg), T<sub>g</sub> = 60 °C and T<sub>m</sub> = 160 °C.

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) was manufactured by Tianan Biological Materials Co. Ltd. (China) and commercialized in pellets form under the grade name ENMAT Y 1000P. According to the manufacturer, PHBV has the following properties: density = 1.25 g cm<sup>-3</sup>, T<sub>g</sub> = 8 °C and T<sub>m</sub> = 165 °C. This grade has been comprehensively characterized in a recent paper [12].

### Sample Preparation of PHBV/PLA Blends

Prior to use, all materials were dried under vacuum at 60 °C for 24 h. Drying is necessary to minimize the hydrolytic degradation of the polymers during melt processing in the extruder. PHBV/PLA blends were prepared by melt mixing in a Brabender Plasticorder mixer (model W 50 EHT) using the following characteristics: chamber volume of 55 cm<sup>3</sup>, sample weight of 40–70 g, maximum torque of 200 N and maximum temperature equal to 500 °C. The different PHBV/PLA blend compositions are presented in Table 1.

The processing parameters were mixing temperature, screw speed and residence time, equal to 180 °C, 50 rpm and 8 min, respectively. The resulting materials were grinded into pellets. Prior to compression molding, the pellets were dried over night under vacuum at 60 °C and compression molded in a Carver<sup>®</sup> hydraulic press at 180 °C under a pressure of 10 metric tons for 3 min to obtain films of about 200 μm thickness.

### Characterization Methods

#### Thermo-Gravimetric Analysis (TGA)

Thermo-gravimetric analysis experiments were carried out using a Perkin-Elmer thermal analyzer using a scanning rate of 10 °C min<sup>-1</sup> under nitrogen in the temperature range starting from 20 to 600 °C.

#### Pyrolysis Combustion Flow Calorimeter (PCFC)

Pyrolysis combustion flow calorimeter apparatus from FTT (UK) was used to pyrolyze (3 ± 1) mg of sample by heating

**Table 1** Code and composition of PHBV/PLA blends used

Samples	PHBV (wt%)	PLA (wt%)
PHBV	100	0
PHBV/PLA 75/25	75	25
PHBV/PLA 50/50	50	50
PHBV/PLA 25/75	25	75
PLA	0	100

up to 780 °C at a heating rate of 1 °C s<sup>-1</sup> under a nitrogen flow, and the gases produced during pyrolysis were sent into a combustor and burnt at a temperature of 900 °C in the presence of oxygen (20 %). PHRR and heat release rate (HRR) of samples were noted and each measurement was performed at least five times (up to ten times). The results were averaged with an error of less than 5 %, while the error on temperature of P<sub>HRR</sub> (T<sub>PHRR</sub>) measurement is less than 1 %. The gases produced at temperature of PHRR observed during the PCFC test were characterized.

### Tensile Testing

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<sup>-1</sup>. A MTS 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.

### Dynamic Mechanical Analysis (DMA)

The thermo-mechanical behaviour of polymer samples has been investigated using a dynamical mechanical analyser DMA 2980 from TA Instruments. A temperature scan from -40 up to 150 °C was performed at the rate of 3 °C min<sup>-1</sup> while a dynamic tensile test was performed at a frequency of 1 and 10 Hz with amplitude of 10 mm.

### 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. 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' and G'', 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 175 and 185 °C. All rheometrical data obtained were shown to be reproducible within ±5 %.

## Results and Discussion

### Thermal Degradation

The thermal stability of neat polymers and different blend compositions was investigated by TGA. As described in

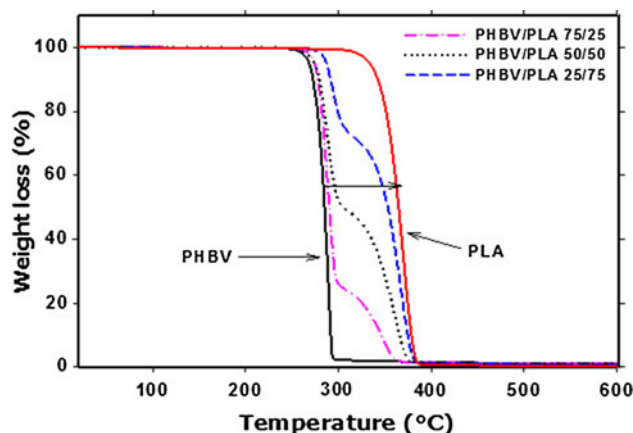


Fig. 1 TGA curves of PHBV, PLA and PHBV/PLA blends

Fig. 1, it can be observed that the degradation of each polymer occurred separately. As expected, PLA is more thermally stable than PHBV.

In general, the thermal weight-losses of PHBV and PLA were quite sensitive to temperature, with narrow decomposition temperature ranges [29]. The temperatures corresponding to the different stage of decomposition (5, 10 and 50 % for instance) for a polymer are essential for evaluating its thermal stability and are summarized in Table 2.

According to Table 2, the degradation temperatures at 5, 10 and 50 % loss shift to higher values, i.e. 332, 341 and 362 °C for the neat PLA in comparison with those of the neat PHBV which are 268, 272 and 284 °C, respectively. PHBV and PLA thermally degrade to produce polymeric chains terminated with carboxyl and vinyl groups [30] and carboxyl end groups of polyester catalyze hydrolysis reaction. The thermal degradation of PLA takes place by the cleavage of bond on the backbone to form also cyclic oligomer, lactide and carbon monoxide as products [31]. Mc Neill and Leiper [32] suggested that degradation of PLA takes place by a back-biting ester interchange reaction in a non-radical mechanism, involving the OH chain ends. The mechanism of thermal degradation in PHBV follows a

Table 2 Decomposition temperatures at 5, 10, 50 % weight loss and char yields at 600 °C of PHBV, PLA and PHBV/PLA blends

Samples	T <sub>5 %</sub> (°C)	T <sub>10 %</sub> (°C)	T <sub>50 %</sub> (°C)	Char yield (%)
PHBV	268	272	284	1.2
PHBV/PLA 75/25	273	278	290	1.2
PHBV/PLA 50/50	275	279	305	1.1
PHBV/PLA 25/75	287	291	353	0.9
PLA	332	341	362	0.3

random chain scission at ester groups, involving a  $\beta$ -hydrogen elimination process (six membered ring ester decomposition process) to form substituted olefins and oligomers [33].

All the decomposition temperatures of the blends are between those of PLA and PHBV. The thermal stability of the blends is regularly improved by the addition of PLA into the blend. This phenomenon is attributed to the higher thermal stability of PLA. Note that all samples have more or less 1 wt% residue at 600 °C suggesting that very small quantity of additives is present in both polymers. Particularly, this PHBV grade could contain mineral fillers as nucleating agents and stabilizers [12].

Another important thermal characteristic is the temperature corresponding to the maximum rate of weight loss, which is defined as the peak value of the first derivative of curve obtained in TGA (DTG). The difference in thermal decomposition behavior of the samples can be seen more clearly from the DTG curves (not shown here) and their corresponding decomposition temperature values ( $T_{max}$ ) are listed in Table 3.

All neat polymers exhibit a single peak located at 285 °C for PHBV and 366 °C for PLA, indicating that the PLA and PHB degraded in only one step. As it can be seen, the DTG curves show double peaks for the whole of PHBV/PLA blend samples showing two major weight loss steps. According to Table 3, the  $T_{max}$  value of the PHBV fraction contained in blends slightly shifts to higher temperature, i.e. from 287 °C for PHBV/PLA 75/25 up to 291 °C for PHBV/PLA 25/75. On the contrary, the  $T_{max}$  value of the PLA content in the blends tends to regularly decrease up to 347 °C for PHBV/PLA 75/25.

### PCFC Analysis

Pyrolysis combustion flow calorimeter has been used for assessing the flammability of PHBV/PLA blends compared to the neat polymers. Heat release capacity (HRC) and total heat release (THR) obtained by PCFC, are related to the char yield and the heat of complete combustion of the volatiles.

**Table 3** Decomposition temperatures of PHBV, PLA and PHBV/PLA blends obtained from DTG

Samples	$T_{max}$ (°C)
PHBV	285
PHBV/PLA 75/25	287 347
PHBV/PLA 50/50	290 359
PHBV/PLA 25/75	291 364
PLA	366

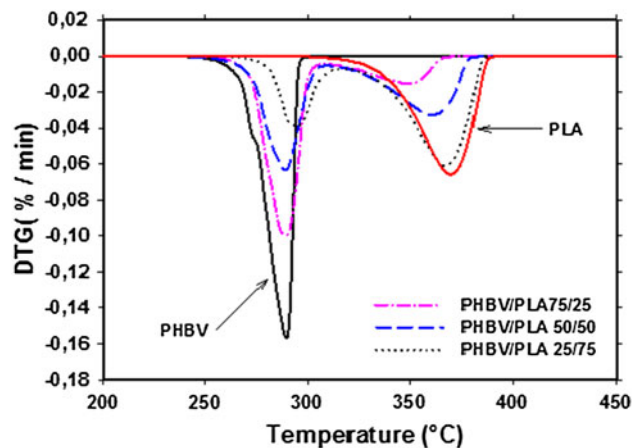
Here, the heat release evolution during sample pyrolysis in PCFC test is presented with the mass loss rate during pyrolysis in TG analysis. TG analysis was carried out under  $N_2$  at heating rates of  $10\text{ °C min}^{-1}$ . All results obtained from PCFC tests are summarized in Table 4. The HRR curves observed in PCFC test are correlated with the derivative weight curves from TG analysis at heating of  $10\text{ °C min}^{-1}$ , as demonstrated in Fig. 2.

It may signify that the weight loss observed from the pyrolysis in the TGA temperature range could be related to the release of combustible gas in PCFC test. The temperature at the maximum HRR was shifted to higher temperatures than the peak degradation in TGA, presumably because of higher heating rate in PCFC test. Two peaks are observed for PHBV/PLA blend comparatively to pure polymer. This can be related to the volatilization of each polymer occurred separately. Figure 3 shows that HRC decreases with increasing content PLA in the blend.

This indicates that PLA releases less heat than PHBV. The value of HRC of PHBV decreases almost linearly by about 10.4, 28.2 and 49.9 % by addition of 25, 50 and 75 wt% of PLA, respectively. The value of THR decreases similarly by about 6.8, 13.1 and 19.1 % by addition of 25, 50 and 75 wt% of PLA, respectively.

**Table 4** HRC, THR and EHC from PCFC tests of PHBV, PLA and PHBV/PLA blends

Samples	HRC ( $J\text{ g}^{-1}\text{ K}^{-1}$ )	THR ( $kJ\text{ g}^{-1}$ )	Char at 600 °C (%)	EHC ( $kJ\text{ g}^{-1}$ )
PHBV	798	19.2	1.3	19.4
PHBV/PLA 75/25	715	17.9	1.0	18.1
PHBV/PLA 50/50	573	16.7	0.8	16.8
PHBV/PLA 25/75	471	15.5	0.6	15.5
PLA	444	15.4	0.3	15.5



**Fig. 2** HRR curve of a PLA, b PHBV, c PHBV/PLA 50/50 and d PHBV/PLA 25/75 and its relation to their derive curves of TG degradation at heating rate of  $10\text{ °C min}^{-1}$

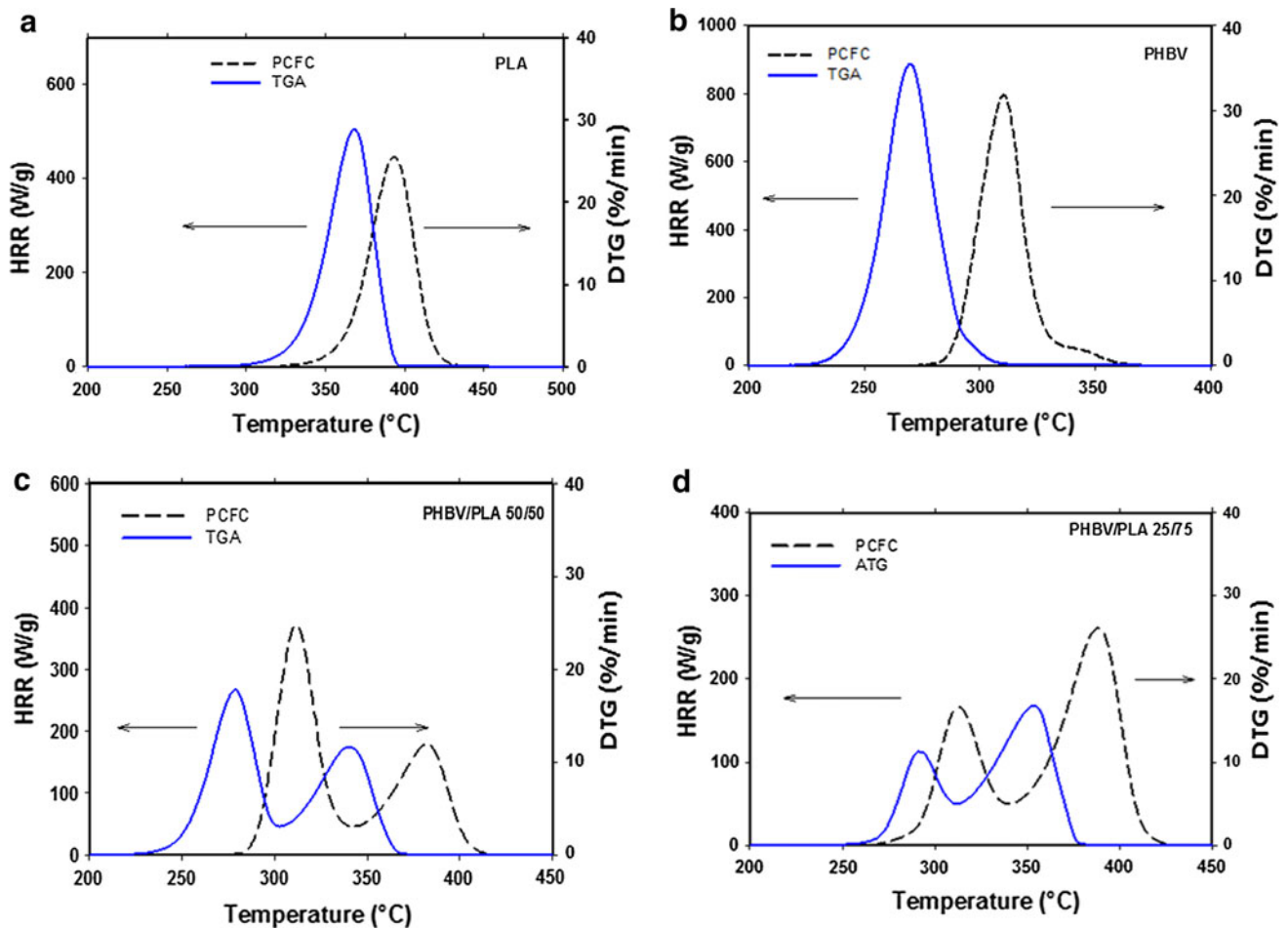


Fig. 3 HRC for PHBV, PLA and PHBV/PLA blend as a function of PLA content in the blend

### Mechanical Properties

The mechanical properties of PHBV/PLA blends as well as of neat components were investigated using tensile tests following the aforementioned protocol. Tensile measurements are reported in Table 5 and highlight the mechanical characteristics of PHBV, PLA and their blends.

Neat PHBV features a brittle behavior with a relatively high modulus close to 2,600 MPa and an elongation at break of about 2 % whereas modulus and elongation at break of neat PLA indicate the values of 2,175 MPa and 5.5 %, respectively. For the PHBV/PLA blends, it can be seen that both stress and elongation at break regularly increase with the PLA content due to the amorphous phase of the blend. At the same time, the Young's modulus shows a noticeable and progressive decrease. For the PHBV/PLA 75/25 and 50/50 blends, the values of both tensile stress and elongation at break are lower than those of neat PLA. However, the mechanical results obtained for the PHBV/PLA 25/75 blend show an increase in the elongation at break compared to that of neat PLA (7 % for the PHBV/

Table 5 Tensile properties of PHBV, PLA and PHBV/PLA blends

Samples	Stress at break (MPa)	Elongation at break (%)	Young modulus (MPa)
PHBV	33.9 ± 2.0	1.5 ± 0.1	2593 ± 93
PHBV/PLA 75/25	37.3 ± 2.6	1.6 ± 0.2	2453 ± 24
PHBV/PLA 50/50	44.6 ± 2.3	4.7 ± 0.7	2357 ± 210
PHBV/PLA 25/75	45.1 ± 1.5	7.0 ± 1.3	2212 ± 103
PLA	55.7 ± 1.7	5.5 ± 1.2	2175 ± 113

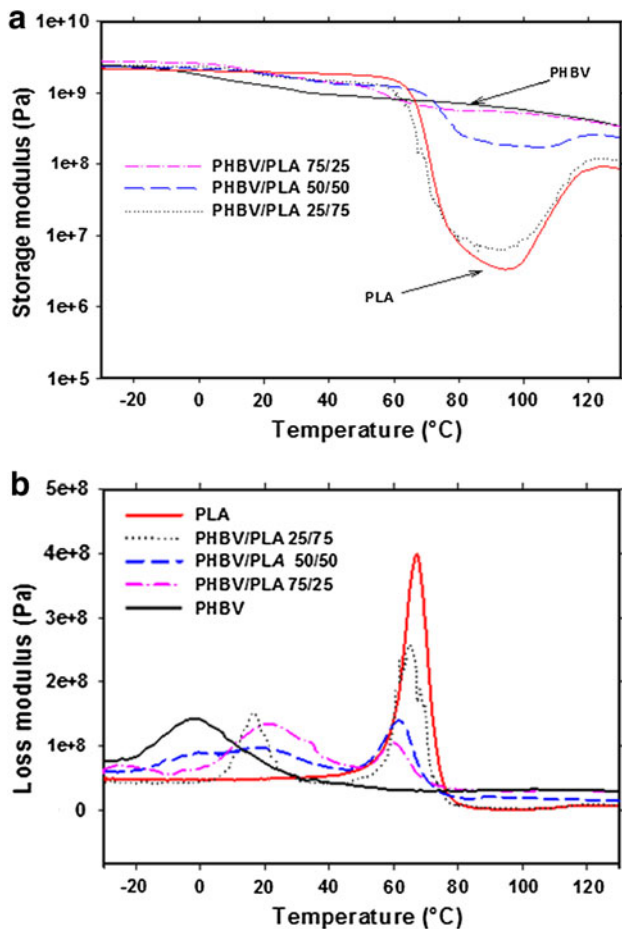
PLA 25/75 blend against 5.5 % for neat PLA). This slight improvement may be mainly attributed to the finely dispersed PHBV particles acting as a filler to enhance the PLA properties, as reported in a recent article [28]. It is known that large spherulitic material is more brittle than fine spherulite one. Similar effect has been reported by Zhang and Thomas [23] who indicated that when 25 % of PHB were added to PLA, the blends showed better mechanical

properties than neat PLA. This was explained as a result of the presence of amorphous PLA which significantly reduce the size of the PHB spherulites, well dispersed in the continuous amorphous PLA phase, especially at higher PLA content. Such behavior was also reported by Noda et al. [26] who indicated that when 10 % of PHA were added to PLA, the elongation at break of the blends was higher than that of the neat polymers due to the amorphous phase of the blend. Therefore, it can be concluded that blending leads to an enhancement in the mechanical properties of neat polymers.

### Dynamic Mechanical Properties

Dynamic mechanical analysis is a thermoanalytical technique to study the viscoelastic properties of the polymers. Figure 4a, b shows the temperature dependency of the dynamic storage modulus and loss modulus of neat PHBV, neat PLA and PHBV/PLA blends.

The viscoelastic curves show different relaxation zones which are related to the calorimetric transitions along the



**Fig. 4** a Dynamic storage modulus ( $E'$ ) and b loss modulus ( $E''$ ) of PHBV, PLA and PHBV/PLA blends

increasing temperature-axis. As shown in Fig. 4a, the storage modulus of neat PLA is almost constant below the transition temperature. At  $T_g$ , there is a sharp drop in  $G'$ , as expected for an amorphous polymer. For the neat PHBV, when the temperature is increased above  $-2^\circ\text{C}$ , the storage modulus decreases due to the occurrence of its glass transition. In general, the PHBV/PLA blends show higher storage modulus at temperatures below the glass transition of PHBV, while these curves gradually decrease in storage modulus from around  $15^\circ\text{C}$ , which is associated with the glass transition of PHBV, indicating an increase in glass transition of PHBV in the polymer blends. The storage modulus of PLA at room temperature is about 2.2 GPa, in agreement with the value for a glassy polymer. At  $T_g$ , the storage modulus of PLA decreases more than 1 order of magnitude, reaching a value below 300 MPa. It is also observed that the storage modulus of PHBV shows a lower value than that of PLA at room temperature. In the case of PHBV/PLA blends, the blends with high content of PLA shows a higher storage modulus above room temperature and increases with increasing content of PLA. However, below the  $T_g$  of PHBV, the blends with higher concentration of PHBV exhibit higher modulus. Above  $T_g$  of PLA, the PHBV shows a higher storage modulus. However, the storage modulus of the blend decreases by increasing the PLA content. Thus, it can be argued that above  $65^\circ\text{C}$ , the molecular mobility increases as the glassy PLA molecule changes to the rubbery state. An increase in the storage modulus above  $100^\circ\text{C}$  in neat PLA and blends of PHBV/PLA 25/75 and PHBV/PLA 50/50 may be due to recrystallization of PLA [34]. For the blend containing lower fraction of PLA, i.e. PHBV/PLA 75/25, it is obviously more difficult to observe the recrystallization of PLA in the DMA curve.

The loss modulus is the viscous response of the material. It is associated with the unrecoverable energy of dissipation by the material to the system and it is out of the phase component of the complex modulus. From the loss modulus curves in Fig. 4b, the glass transition temperature can be observed.  $T_g$  is usually interpreted as the peak of either the tan delta or the loss modulus curves obtained during the dynamic mechanical test. The values of  $T_g$  determined from DMA experiments are reported in Table 6.

Dynamic mechanical analysis is usually employed to assess the miscibility of the polymer blends [35]. As shown in Fig. 4b and Table 6, different values of  $T_g$  are observed for all blends confirming their immiscibility. In our case, a depression of the PLA glass transition is observed when PHBV content is increased. The gradual decrease in the peak intensity and broadening in the loss modulus peak of PLA indicates the change in dampening effect as the PHBV content in the blend increased [25]. On the contrary, a shift in  $T_g$  of PHBV toward the high temperature range is

**Table 6** Glass transition temperatures from DMA of PHBV, PLA and PHBV/PLA blends

Samples	$T_{g,PLA}$ (°C)	$T_{g,PHBV}$ (°C)
PHBV		1.2
PHBV/PLA 75/25	58.6	18.3
PHBV/PLA 50/50	61.3	16.7
PHBV/PLA 25/75	64.5	16.3
PLA	67.1	

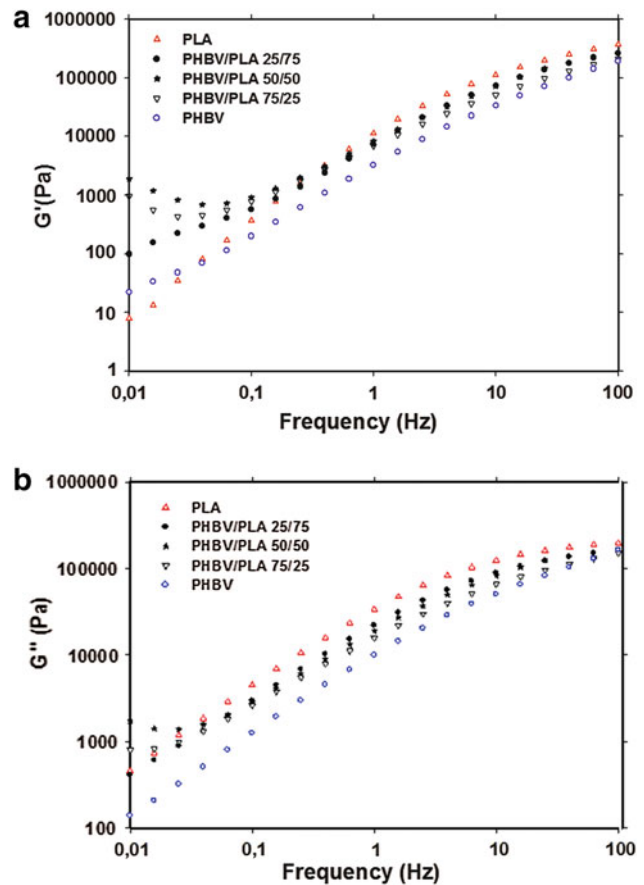
observed in presence of PLA indicating a mutual influence of each polymer toward the other.

### Rheological Analysis

In general, PHBV degradation is rapid above its melting temperature. This poses a major problem for the use of experimental data obtained in the rheological study. Indeed, the behavior of PHBV in the molten state is changing rapidly, which leads to lower modulus and viscosity. On the contrary, PLA shows a much better thermal stability [22]. In the present study, rheological tests were conducted at a temperature of 175 °C. It is important to indicate that this is the minimum temperature to perform rheological measurements on PHBV due to the fact that below this temperature, the polymer is not completely melted. According to our previous work [28], the results indicated that the complex viscosity of PHBV and PLA are both stable at low frequencies suggesting that no degradation has occurred in the polymers so that the thermal stability of PHBV and PLA was not affected.

In contrast, Fig. 5a, b summarize the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) versus frequency sweeps of PHBV blended with PLA at 175 °C, respectively.

A dynamic frequency sweep tests were carried out to characterize the viscoelastic properties of PHBV/PLA blends at 175 °C. It is observed that, at high frequencies (1–100 Hz), both  $G'$  and  $G''$  of blends are higher than neat PHBV and these characteristics seem to increase with decreasing the PHBV content, suggesting that the blend moduli simply follow a mixing rule. At lower frequency (0.01 Hz), the blend displays more rubbery properties with increasing PLA content. This increased elasticity would result in more resistance of the polymer to flow when it is subjected to shear or extensional forces. The elastic modulus evolution of PLA, PHBV and the blend PHBV/PLA 25/75 shows a typical terminal behavior with a slope of around 1.72, 0.93 and 0.74 ( $R^2 = 0.99$ ) at low frequencies, respectively. For  $G''$ , the slope magnitude of PHBV, PLA and the blend PHBV/PLA 25/75 are 0.85, 0.99 and 0.96 ( $R^2 = 0.99$ ), respectively. For the blends PHBV/PLA 50/50 and 75/25, it is clearly observed an increase of  $G'$

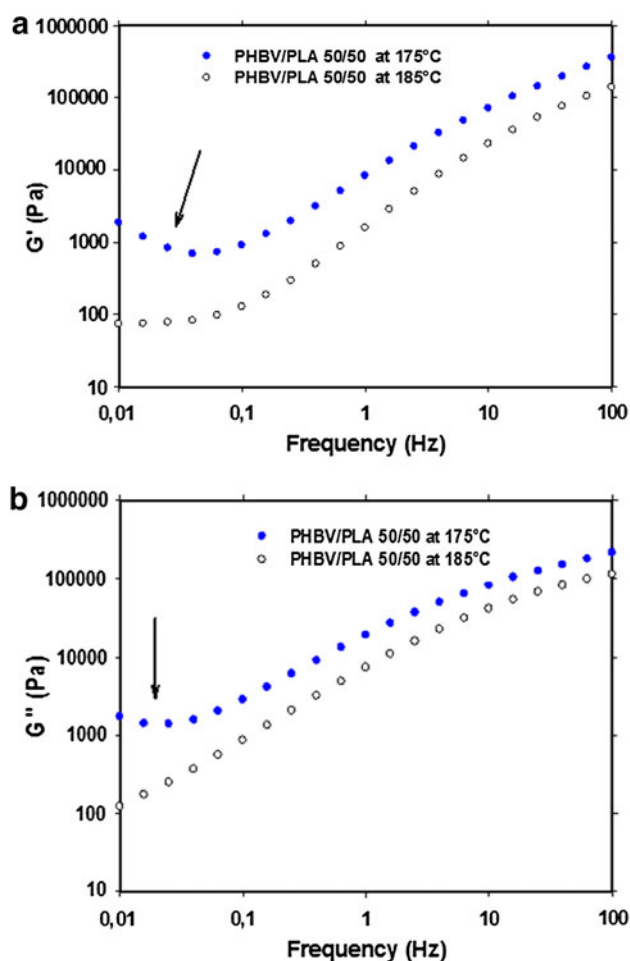


**Fig. 5** Evolution of **a** storage modulus ( $G'$ ) and **b** loss modulus ( $G''$ ) of PHBV, PLA and PHBV/PLA blends at 175 °C under 2 % of dynamical shear strain

and  $G''$  at low frequencies. The origin of this increase is not really understood even if this increase in  $G'$  at low frequencies is a reproducible and known phenomenon for immiscible blends as reported elsewhere [22]. Several reasons can be at the origin of this phenomenon, which is well known for the droplets/matrix morphology [36]. On the other hand, a shoulder on  $G'$  and  $G''$  would correspond to the additional elastic response originating from the surface of the droplets of the phase dispersed in the continuous matrix; another explanation may be proposed taking into account the presence of minerals in the PHBV used stabilizers, which can act as nanofillers [22]. When experiment temperature is more far from melting temperature of PHBV, this phenomenon can be also observed at 185 °C but this phenomenon is much less pronounced in this case than at 175 °C (Fig. 6a). Finally, when compared the temperature effect on viscoelastic behavior, the  $G'$  and  $G''$  values at 185 °C are lower than  $G'$  and  $G''$  values at 175 °C (Fig. 6a, b).

This strong difference in  $G'$  and  $G''$  could be due to thermal and mechanical degradation of the material when





**Fig. 6** Evolution of **a** storage modulus ( $G'$ ) and **b** loss modulus ( $G''$ ) of PHBV/PLA 50/50 at 175 and 185 °C under 2 % of dynamical shear strain

increasing temperature, which can significantly change the properties of the material.

## Conclusion

The goal of this work was to investigate the thermal stability, flammability resistance and mechanical behavior of PHBV/PLA blends, obtained using melt mixing technique. The thermal stability in this work was evaluated by TGA and it was relatively improved by the addition of PLA to the blend. PCFC test showed that the blends present flammability properties that can be tuned by changing blend composition. Moreover, decomposition of each polymer in the blend seems to occur without interactions between them. Tensile results indicated that the stress at break for blends decreased with increasing PHBV content. A decrease in elastic modulus, as well as an increase in elongation at break, was seen for an increase in PLA

content in the blend. DMA analysis showed two different glass transition values of  $T_g$  for all the blends. This is an indication of the immiscibility of the blends; the specific variation of  $T_g$  with amount of polymers is an information that each polymer influences each other. The rheological measurements indicated an enhancement of storage modulus and loss modulus of PHBV matrix by addition of PLA. At high frequencies, both moduli seem to follow the mixing rule; at low frequencies there is a strange increase of  $G'$  for some blends that is not understood yet. More work is needed to better understand the specific viscoelastic behaviour observed at low frequencies.

It can be concluded that the production of blends based on PHBV and PLA can be an efficient and promising route to extend the applications as biodegradable materials, PHBV for instance, considering the possibility to finely tune their functional properties playing with the respective proportions of each component.

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## References

- Shah A, Hasan F, Hameed S (2008) *Biotechnol Adv* 26:246
- Mülhaupt R (2013) *Macromol Chem Phys* 214:159
- Gupta AP, Kumar V (2007) *Eur Polym J* 43:4053
- Lim LT, Auras R, Rubino M (2008) *Prog Polym Sci* 33:820
- Zaidi L, Bruzaud S, Bourmaud A, Médéric P, Kaci M, Grohens Y (2010) *J Appl Polym Sci* 116:1357
- Chardon S, Bruzaud S, Lignot B, Elain A, Sire O (2010) *Polym Test* 29:966
- Suriyamongkol P, Weselake R, Narine S, Moloney M (2007) *Biotechnol Adv* 25:148
- Sudesh K, Abe H, Doi Y (2000) *Prog Polym Sci* 25:1503
- Noda I, Green PR, Satkowski MM, Schechtman LA (2005) *Biomacromolecules* 6:580
- Chen G, Wu Q (2005) *Biomaterials* 26:6565
- Lee J, McCarthy S (2009) *J Polym Environ* 17:240
- Corre YM, Bruzaud S, Audic JL, Grohens Y (2012) *Polym Test* 31:226
- Peng S, An Y, Chen C, Fei B, Zhuang Y, Dong L (2003) *J Appl Polym Sci* 90:4054
- Imre B, Pukanszky B (2013) *Eur Polym J* 49:1215
- Tao J, Song C, Cao M, Hu D, Liu L, Liu N, Wang S (2009) *Polym Degrad Stab* 94:575
- Furukawa T, Sato H, Murakami R, Zhang J, Noda I, Ochiai S, Ozaki Y (2007) *Polymer* 48:1749
- El Hadi AM (2011) *Polym Eng Sci* 51:2191
- Na Y, He Y, Asakawa N, Yoshie N, Inoue Y (2002) *Macro molecules* 35:727
- Meredith JC, Amis EJ (2000) *Macromol Chem Phys* 201:733
- Gajria A, Dave V, Gross R, McCarthy S (1996) *Polymer* 37:437
- Corre YM, Bruzaud S, Grohens Y (2013) *Macromol Mater Eng*. doi:10.1002/mame.201200345

22. Gerard T, Budtova T (2012) *Eur Polym J* 48:1110
23. Zhang M, Thomas NL (2011) *Adv Polym Technol* 30:67
24. Modi S, Koelling K, Vodovotz Y (2012) *J Appl Polym Sci* 124:2074
25. Nanda MR, Misra M, Mohanty AK (2011) *Macromol Mater Eng* 296:719
26. Noda I, Satkowski MM, Dowrey AE, Marcott C (2004) *Macromol Biosci* 4:269
27. Zhao Q, Wang S, Kong M, Geng W, Li RKY, Song C, Kong D (2012) *J Biomed Mater Res B Appl Biomater* 100:23
28. Zembouai I, Kaci M, Bruzard S, Benhamida A, Corre YM, Grohens Y (2013) *Polym Test* 32:842
29. Abdelwahab MA, Flynn A, Chiou BS, Imam S, Orts W, Chiellini E (2012) *Polym Degrad Stab* 97:1822
30. Kopinke F, Remmler M, Mackenzie K (1996) *Polym Degrad Stab* 52:25
31. Mc Neill I, Leiper H (1985) *Polym Degrad Stab* 11:309
32. Mc Neill I, Leiper H (1985) *Polym Degrad Stab* 11:267
33. Kunioka M, Doi Y (1990) *Macromolecules* 23:1933
34. Badia JD, Strömberg E, Karlsson S, Ribes Greus A (2012) *Polym Degrad Stab* 97:670
35. He Y, Zhu B, Inoue Y (2004) *Prog Polym Sci* 29:1021
36. Castro M, Carrot C, Prochazka F (2004) *Polymer* 45:4095