



## A STUDY ON THE EFFECTS OF REPROCESSING CYCLES ON PHBV/PLA BLENDS

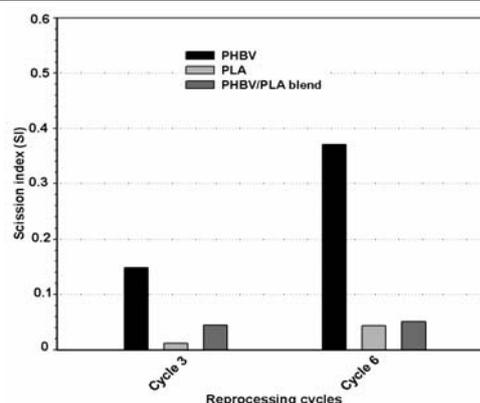
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In this paper some experimental results are reported on the effects of reprocessing cycles (up to 6 repeated cycles) on the properties of neat poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), neat polylactide (PLA) and blend of PHBV/PLA: 50/50 (w/w). The changes in thermal and rheological properties as well as in molecular weight of the recycled materials were investigated. The results showed a reduction in molecular weight for both neat PHBV and PLA and PHBV/PLA blend with reprocessing cycles due to chain scission mechanism responsible for the material degradation. Further, these effects were significantly smaller for PLA and PHBV/PLA blend compared to those of neat PHBV. The incorporation of PLA in PHBV/PLA blend may act as a stabilizer of the system and their wastes can support multiple processing cycles.



### INTRODUCTION

The use of polymer materials in a variety of fields has led to a generation of an increased amount of plastic wastes. Only a few amounts of these wastes are recycled, while the major part of municipal and industrial wastes is going to landfills.<sup>1</sup> Thus, the reuse and recycling of polymeric materials remains a worldwide challenge.<sup>2,3</sup> Consequently, polymer recycling is one of the most important subjects of the current industry.<sup>4</sup> In this respect, mechanical recycling as a favorable recycling method has been under attention for bioplastics.<sup>5</sup> One of the most common method to study the recyclability of polymer materials including bioplastics is to

simulate multiple processing and to find the durability or the service life by accelerated thermal and hydrothermal degradation.<sup>5</sup> Although several research papers have analyzed the effects of multiple processing on the structural, rheological and mechanical properties of the most common biopolymers (PLA, PHBV, PCL, etc.), there is however, a lack of data on the recycling ability of bioplastics blends such as PHBV/PLA system.<sup>6</sup> Therefore, the objective of this paper was to investigate the extent to which biopolymer blends based on PHBV and PLA: 50/50 (w/w) are reprocessable. Changes in molecular weight as well as in rheological and thermal properties were evaluated after each extrusion cycle.

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## RESULTS AND DISCUSSION

### 1. Thermogravimetric analysis

The thermal degradation behavior of neat PHBV, neat PLA and PHBV/PLA: 50/50 w/w blend is shown in Fig. 1a, b and c, respectively through TGA thermograms recorded for the first and the last reprocessing cycles, *i.e.* 6 repeated cycles. Further, Table 1 summarizes the values of decomposition temperatures at 5, 10 and 50 wt. % of loss as well as the final residue at 600°C. As reported,<sup>7</sup> PLA is more thermally stable than PHBV and subsequently, the thermal stability of PHBV/PLA blend is improved in the presence of PLA in the blend. According to the literature,<sup>8</sup> the thermal degradation of PHBV and PLA leads to polymer chains ended with carboxyl and vinyl groups. Carboxyl end groups of the polyester catalyze the hydrolysis reaction. The data reported in Table 1 indicate that for neat PHBV, the initial values of  $T_{5\%}$ ,  $T_{10\%}$  and  $T_{50\%}$  are about 272, 276 and 287°C, respectively. After 6 reprocessing cycles, the values remain almost unchanged. Similar trend is also observed for PLA, where the values of  $T_{5\%}$ ,  $T_{10\%}$  and  $T_{50\%}$  are approximately 335, 344 and 367°C, respectively. After multiple processing, the values are not significantly affected. For PHBV/PLA blend, the values of  $T_{5\%}$ ,  $T_{10\%}$  and  $T_{50\%}$  are intermediate between those of neat PHBV and PLA and remain almost stable after 6 processing cycles. Another thermal characteristic is the temperature corresponding to the maximum rate of weight loss, which is defined as the peak value of the first derivative curve obtained by 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 1. All neat polymers exhibit a single peak located at 290°C for PHBV, while for PLA, the value is

373°C, indicating that PLA and PHBV degrade in one step. DTG curves show double peaks for the whole PHBV/PLA blend samples showing two major weight loss steps.

According to Table 1, the comparison of  $T_{max}$  value obtained in the first cycle and that after 6 repeated cycles for all samples show a decrease by approximately 2°C indicating that the recycled material is stable. Moreover, there is no noticeable change in the amount of residue at 600°C after 6 cycles.

### 2. Rheological properties

The recycling effect on the rheological properties of neat PHBV, neat PLA and blend of PHBV/PLA: 50/50 (w/w) was investigated up to 6 repeated extrusion cycles by dynamic shear measurements in molten state. The rheological measurements were started from high down to low frequencies which was checked to be within the linear viscoelastic domain. In this respect, Fig. 2a, b and c shows the loss modulus changes versus frequency for neat PHBV, neat PLA and PHBV/PLA: 50/50 w/w blend, respectively up to 6 repeated extrusion cycles. From Fig. 2a, the loss modulus of PHBV decreases significantly with the number of reprocessing cycles as a result of the thermo-mechanical degradation of the polymer by chain scission mechanism. In contrast, it is observed in Fig. 2b that the effect of multiple processing on the loss modulus of neat PLA is almost negligible. The stability of loss modulus indicates clearly that PLA is less sensitive to thermo-mechanical degradation compared to PHBV. For PHBV/PLA blend as shown in Fig. 2c, a relative stability of the loss modulus is also observed after recycling. This result suggests that the combination of PLA with PHBV is advantageous for PHBV/PLA blend regarding the stabilizing role of PLA.

Table 1

Values of decomposition temperature at 5, 10, and 50% of weight loss,  $T_{max}$  and char yields at 600°C for PHBV, PLA and PHBV/PLA: 50/50 (w/w) blend as a function of reprocessing cycles

Samples	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{max}$ (°C)	Char yield (wt. %)
PHBV 1	272.0	276.0	287.0	290.1	1.2
PHBV 6	270.0	274.5	286.0	289.0	1.2
PLA 1	335.3	343.6	366.6	372.6	0.3
PLA 6	336.0	343.5	365.0	370.1	0.4
PHBV/PLA 1	277.0	282.0	304.0	290.6 - 363.7	1.0
PHBV/PLA 6	278.0	281.0	302.0	288.0 - 361.6	1.0

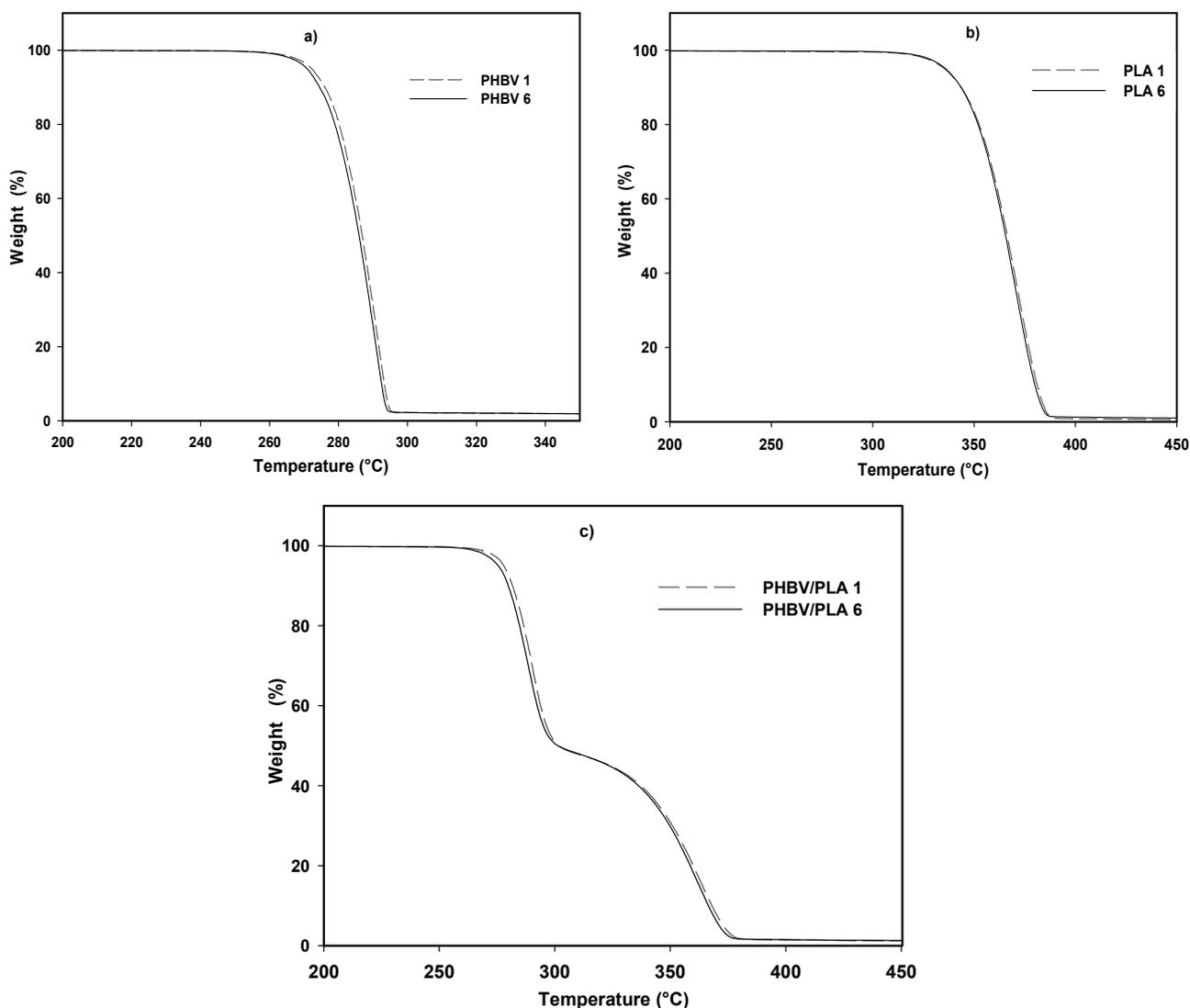


Fig. 1 –TGA curves for neat PHBV, neat PLA and PHBV/PLA: 50/50 (w/w) blend recorded after 1 and 6 processing cycles.

### 3. Molecular weight changes

The changes in the weight and number-average molecular weights taking place during reprocessing may be related to the extent of degradation of the materials. In this respect, Fig. 3 shows the variation of scission index (SI) versus reprocessing cycles for neat PHBV, neat PLA and PHBV/PLA: 50/50 (w/w) blend. It is observed a large increase in the SI values for neat PHBV with increasing the number of extrusion cycles in agreement with the rheological data. Indeed, the SI value for PHBV is almost 0.15 after 3 cycles and

this value increases to 0.37 after 6 cycles. This indicates clearly that recycling of PHBV induces chain scission. In contrast, only a slight increase in the SI value is observed for PLA after 6 cycles reaching 0.04. Similar behavior is also noted for PHBV/PLA blend. These results indicate that PLA may act as a stabilizer for the system PHBV/PLA during reprocessing and their wastes can support moderate recycling, which is a significant improvement on the environmental impact of these polymers.<sup>9</sup>

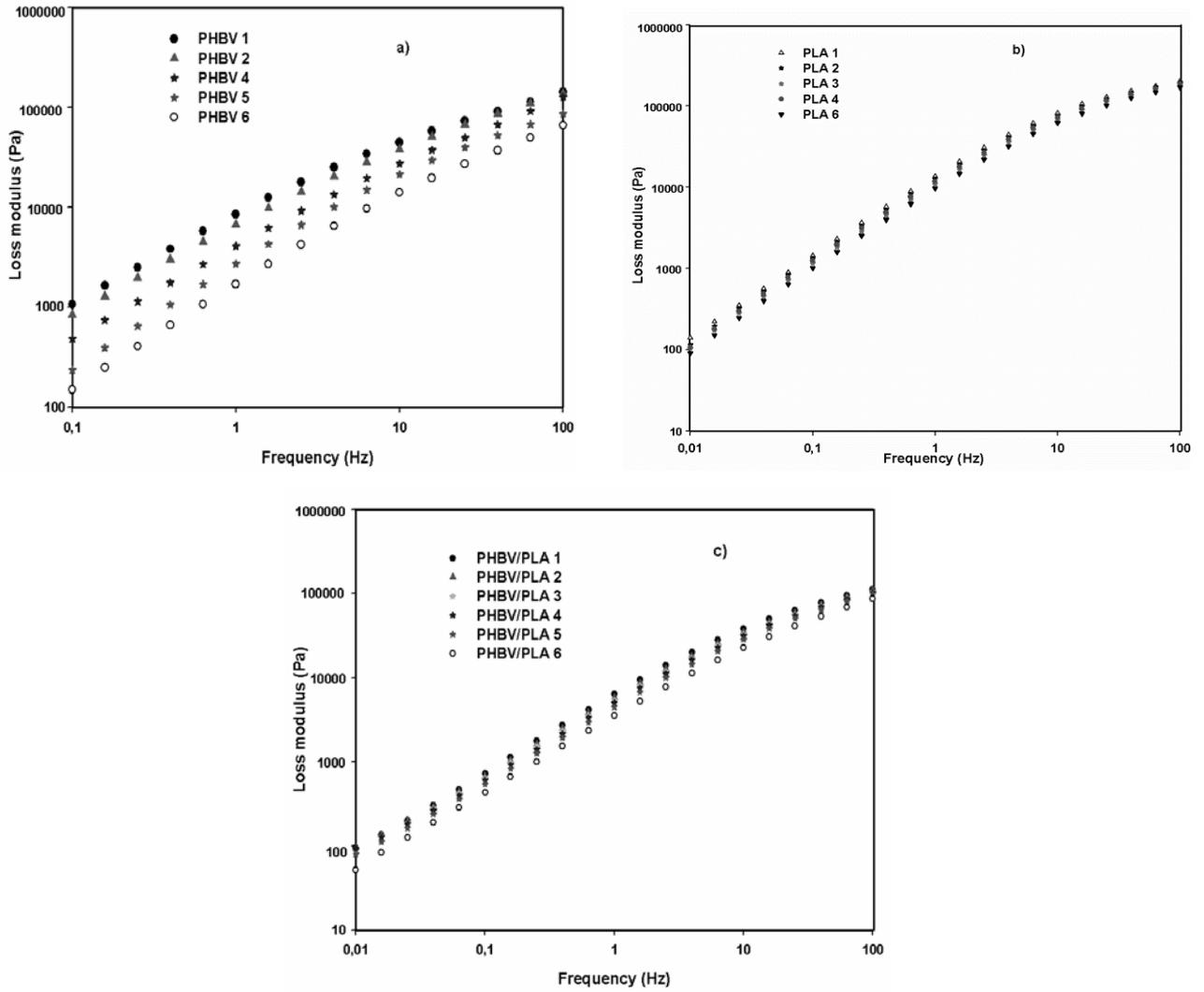


Fig. 2 – Loss modulus as a function of frequency for a): PHBV, b): PLA and c): PHBV/PLA: 50/50 (w/w) blend submitted to several processing cycles.

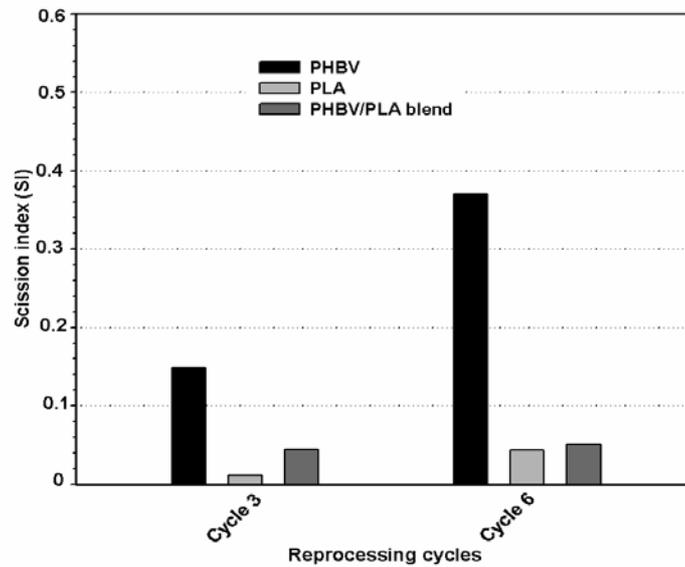


Fig. 3 – Evolution of scission index (SI) for PHBV, PLA and PHBV/PLA: 50/50 (w/w) blend as a function of reprocessing cycles.

## EXPERIMENTAL

### 1. 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 characteristics: 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.

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, the main properties of PHBV are: density = 1.25 g.cm<sup>-3</sup>, T<sub>g</sub> = 8°C and T<sub>m</sub> = 165 °C.

### 2. Sample preparation and reprocessing

Pellets of PHBV, PLA and PHBV/PLA: 50/50 (w/w) blend were dried under vacuum at 60 °C for 48 h prior to repeated extrusion cycles. Melt compounding was achieved in a single screw extruder at 30 rpm and temperature profile of 175/180/180 and 180°C in the nozzle. The resulted materials were 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.

### 3. Characterization methods

#### 3.1. Thermogravimetric analysis (TGA)

Thermogravimetric 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.

#### 3.2. Rheological measurements

Oscillatory shear measurements were performed using a controlled stress Rheometer (Rheometer Anton Paar MCR301) 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 rheological data were shown to be reproducible within ±5 % error.

#### 3.3. Molecular weight measurements

Sterical exclusion chromatography (SEC) was used to determine the evolution of molecular weight during the repeated processing cycles of the materials. 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 eluent with a flow rate of 0.8 mL/min. The elution profiles were analyzed by the Empower GPC module software (Waters). Calculations are based on calibration curves obtained from polystyrene standards ranging from 200 g/mol up to 6 ×10<sup>6</sup>. The weight-average molecular weight ( $\overline{M}_w$ ) and number-average molecular weight ( $\overline{M}_n$ ) are obtained from the SEC analysis. Polydispersity index (PI) was calculated as  $\overline{M}_w / \overline{M}_n$ . Moreover, the value of scission index (SI) was determined according to Eq. (1).<sup>10</sup>

$$SI = \frac{\overline{M}_n(t_0)}{\overline{M}_n(t)} - 1 \quad (1)$$

where, SI represents the scission index at a given processing cycle,  $\overline{M}_n(t_0)$  and  $\overline{M}_n(t)$  are the number-average molecular weight of samples after the initial cycle and a given processing cycle, respectively.

## CONCLUSIONS

The recyclability of PHBV, PLA and PHBV/PLA blend was studied by extrusion up to 6 cycles. The molecular weight changes as well as thermal and rheological properties were investigated. From the study, it can be concluded through TGA analysis that both neat polymers, i.e. PHBV and PLA and PHBV/PLA blend were thermally stable up to 6 repeated cycles. On the other hand, the loss modulus of PHBV decreased significantly with increasing the number of extrusion cycles due to thermo-mechanical degradation. In contrast, the loss modulus of neat PLA remained almost unchanged after 6 cycles. The addition of PLA to PHBV resulted in a relative stability of the loss modulus of PHBV-PLA blend during recycling, thus conferring the role of stabilizer to PLA in the blend material. This result is in a good agreement with the changes in the molecular weight of the blend material. Finally, PHBV/PLA blend exhibit interesting recycling properties compared to neat PHBV.

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