

# Study of PHBV/PP mixtures: Preparation and physicochemical characterization

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## Abstract

*This research work consists in studying the structure-properties relationships of biopolymer mixtures based on poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and polypropylene (PP) elaborated by casting process according to the composition in terms of morphology, structure and thermal properties. The results showed a synergistic effect of glycerol addition on the thermal and morphological properties of the PHBV/PP blends.*

**Keywords:** Blend, Miscibility, Polymer, Plasticization.

## I. Introduction

Man has always used natural polymers (cotton, wool, hemp...) after as materials [1, 2]. However, since the discovery of polymerization and the production of synthetic polymers, they have become an essential part of our daily lives and it is now difficult to do without them. In a century the production of plastics has grown exponentially, this increased consumption has generated several problems: the rarefaction of the fossil resource because they are non-renewable and the pollution of the environment.

This is why materials from renewable resources are receiving increasing interest from the academic and industrial world. They are very varied in nature and often present interesting characteristics. However, some important properties of biobased polymers do not yet rival those of conventional petrochemical polymers such as polyethylene and polypropylene [3,4]. To be able to replace in the future a significant part of the polymers of fossil origin by biosourced polymers, multiple challenges are to be met. A great deal of research has been conducted over the past decade to develop more efficient materials from renewable resources, but there is still a long way to go before they can find their place in the competitive polymer market.

Among the class of biodegradable polymers derived from renewable resources, polyesters are undoubtedly those with the most promising future to replace polyolefin. Among them,

we can mention poly(hydroxyalkanoate) (PHA) or poly(lactic acid) (PLA) [5,6] which is produced on an industrial scale by companies such as Nature Works (USA) or PURAC Biomaterials (Holland). Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) or PHBV [7], produced by a wide variety of bacteria that store them as an intracellular energy reserve [8]. PHBV also has thermal and mechanical properties comparable to conventional thermoplastics such as polypropylene (PP). However, their cost is still too high and some of their properties are still too weak to replace petroleum-based polymers.

Polymer blending is an approach that allows the development of new materials with desired properties. Making these blends from existing polymers is less expensive than developing a new polymer. Moreover, the processes are generally quite simple (extrusion, internal mixer, injection...). Polymer blends are interesting because their properties depend on the parent polymers, properties that can therefore be varied with the blend composition [9, 10].

It is in this context that the subject of this work was born, the study of PHBV/PP mixtures prepared by solvent way (casting) on a whole range of composition and the highlighting of the various structure-properties relations. Morphological and structural characterization and thermal properties of mixtures will be addressed.

## II. Material and methods

### II.1. Materials

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) PHBV was supplied by Natureplast under the trade name PHI002 with a melt flow index (MFI) of g/10 min (190 °C/2.16 kg) (ISO 1133) and a melting temperature of 170–176 °C (values from supplier datasheets). Isotactic polypropylene (PP500P ©) used in this study as matrix was provided by SABIC (Saudi Arabia) with a melt flow index (MFI) of 3 g/10 min (230°C/2.16 kg) (ASTMD-1238) and a density of 0.9 g/cm<sup>3</sup> (values from supplier datasheets). Glycerol (M, 92.09g/mol, density, 1.26 g/cm<sup>3</sup>), chloroform (M, 119.38g/mol, density, 1.47 g/cm<sup>3</sup>), and xylene (M, 106.17, density, 0.86 g/cm<sup>3</sup>), which are provided by Sigma-Aldrich (St. Louis, USA).

### II.2. Composites processing

Different formulations of PHBV/PP were prepared by casting solution. The formulation contain PHBV is mixed in chloroform which is a good solvent for PHBV and the PP formulation is mixed in xylene. These two solutions are placed in a mechanical shaker for three hours at 62°C for PHBV and two hours at 140 °C for a PP. After mixing the two solutions PHBV and PP at room temperature for 10 minutes under stirring adds to this 1 ml of glycerol. The solutions without and with plasticizer, is deposited on petri dishes so that the solvent is evaporated. The films should be left in the open air for three days before placing in the oven at a temperature of 40°C for 24 hours.

The different formulations used are summarized in the Table 1.

**Table 1.** Samples used in this study

Formulations	PHBV/PP (%)	PHBV (g)	PP (g)	Xylene (ml)	Chloroform (ml)
PHBV <sub>100</sub>	-	1	-	-	100
PP <sub>100</sub>	-	-	1	100	-
PHBV <sub>80</sub> PP <sub>20</sub>	80/20	0.8	0.2	20	80
PHBV <sub>70</sub> /PP <sub>30</sub>	70/30	0.7	0.3	30	70
PHBV <sub>60</sub> /PP <sub>40</sub>	60/40	0.6	0.4	40	60
PHBV <sub>50</sub> /PP <sub>50</sub>	50/50	0.5	0.5	60	40

### II.3. Techniques

#### 2.3.1. Microstructural analysis

Shimadzu FTIR 8400S model in the range of 4000–500 cm<sup>-1</sup> measured fourier transform infrared (FTIR) spectra. The equipment was operated in absorbance mode with four scans at a resolution of 4 cm<sup>-1</sup>. Thin films of different samples, which were between 60 and 80 lm in thickness, were prepared by compression moulding at 180 °C for 2 min.

#### 2.3.2. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to monitor the fracture surface of the composites after the samples were frozen in liquid nitrogen. The SEM analysis was performed using an FEI CONTA 200 system.

#### 2.3.3. Thermogravimetric analysis (TGA)

TGA experiments were carried out on a Setaram TG-DTA 92–10 thermal analyzer, using a scanning rate of 10 °C min<sup>-1</sup> under nitrogen in the temperature range starting from 25 °C to 700 °C.

#### 2.3.4. Differential scanning calorimetric analysis (DSC)

The DSC measurements were conducted using a DSC-LINSEIS differential scanning calorimeter with nitrogen as the purge gas. Samples of approximately 5–10 mg were analysed in the temperature range of 25–200 °C with a heating rate of 20 °C.

The crystallinity index of PHBV, PP and PHBV/PP mixtures can be determined from the following equations:

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times \frac{100}{\phi}$$

Where,  $\phi$  is the mass fraction of the dispersed phase in the mixtures, is the enthalpy of fusion (J/g) calculated from the peak of fusion in the DSC curve and is the heat of fusion for fully crystalline PHBV (146.6 J/g) [11], and for fully crystalline PP (209 J/g) [12].

## III. Results and discussion

### III.1. Evolution of the chemical structure by IRTF spectroscopy

Changes in chemical structure in PP/PHBV mixtures were evaluated by FTIR spectroscopy (Figure 1). From the spectra of virgin PHBV (Figure 1 (a)) we observe a band at 2946 cm<sup>-1</sup> attributed respectively to the asymmetric and symmetric elongation of C-H in the CH<sub>3</sub> methyl group, the deformation and symmetry of the CH<sub>3</sub> group causes an absorption for respective wave numbers of 1453 and 1379 and 1303 cm<sup>-1</sup>. An intense and neat band at 1725 cm<sup>-1</sup> is attributed to the elongation of the C=O carbonyl groups of the crystalline parts in PHBV [13]. The C-O-C elongation absorption bands are located between 800, 1000 cm<sup>-1</sup>, and the band at 1218 cm<sup>-1</sup> is assigned to the vibration of the methylene (CH<sub>2</sub>) group [14].

Concerning the spectrum of pure PP (Figure 1 (a)) reveals also the presence of several absorption bands we cite :

A large band with a peak centered at 2938 cm<sup>-1</sup> attributed to the asymmetric elongation vibration of the CH<sub>3</sub> group.

A very large band with peaks at 2925 and 2784 cm<sup>-1</sup> corresponding to the asymmetric elongation vibrations of CH<sub>2</sub>, CH<sub>3</sub> groups. A series of peaks between 1502 and 1342 cm<sup>-1</sup>

corresponding to the symmetric deformation of CH<sub>3</sub> group and shear deformation of CH<sub>2</sub> group. A series of peaks between 1200 and 1000 cm<sup>-1</sup> characteristic of elongation deformations of C-C and C-H bonds [15].

On the spectra of PP/PHBV mixtures at different compositions (Figure 1 (b)) show the characteristic bands of both homopolymers (PP and PHBV) without any change which indicates the absence of any interaction between these two materials [16,17].

The spectra of the PP/PHBV mixtures plasticized with glycerol (Figure 1 (c)) reveal bands positioned at 990, 910 and 844 cm<sup>-1</sup> attributed to the absorbance of the epoxy group, a band relative to the C=O group at 1734 cm<sup>-1</sup> but the intensity of the bands increases steadily, in addition to the bands characteristic of polypropylene.

Several changes were observed in the spectra of the plasticized mixtures, the most important being:

- The appearance of a new band in the 3261 cm<sup>-1</sup> region which can be attributed to bound hydroxyl groups (-OH). This intensity is more pronounced for the PHBV<sub>60</sub> /PP<sub>40</sub> formulation.

- Increase of the intensity of the 1724 cm<sup>-1</sup> band of the carbonyl group (C=O) of the PHBV<sub>60</sub> /PP<sub>40</sub> formulation.

All these changes confirm the existence of interaction between the functions of the groups of the PP/PHBV mixture and the plasticizer (glycerol).

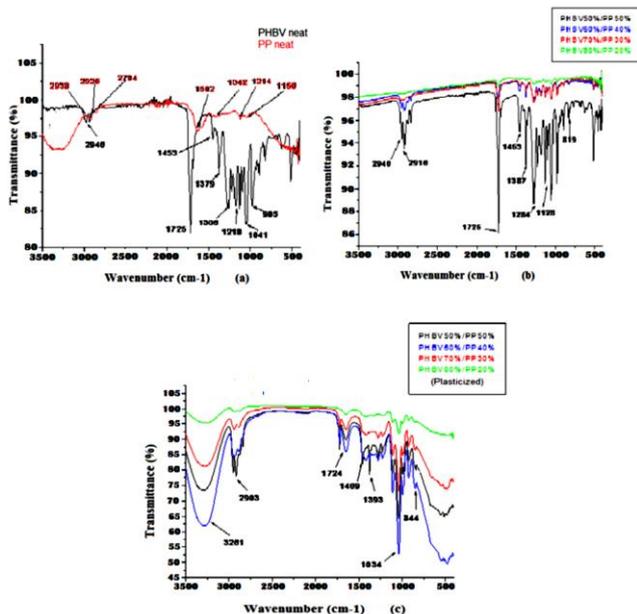


Figure 1. FTIR spectra of the Virgin PHBV, PP (a), PHBV/PP (b) before plasticized and PHBV/PP (c) after plasticized.

### III.2 Microscopic observations

SEM is used to characterize the dispersion state of PP in the PHBV matrix and evaluate the degree of miscibility between the two polymers (Figure 2).

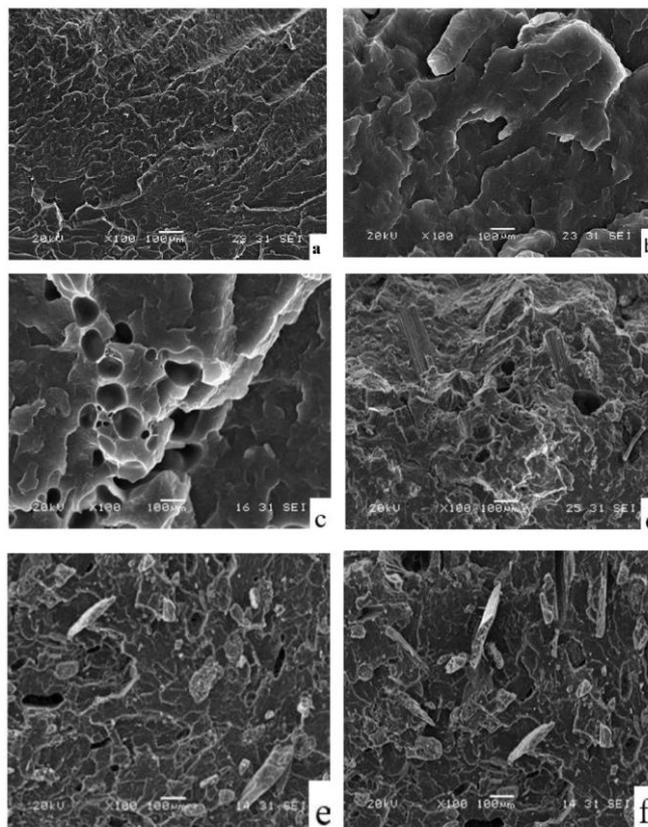


Figure 2. SEM Micrographs of fractured surfaces (a, b, c, d, e and f) for formulations: (a) virgin PHBV, (b) virgin PP, (c) PHBV 80/20, (d) PP/PHBV 70/30, (e) PP/PHBV 60/40 and (f) PP/PHBV 50/50 before plasticized.

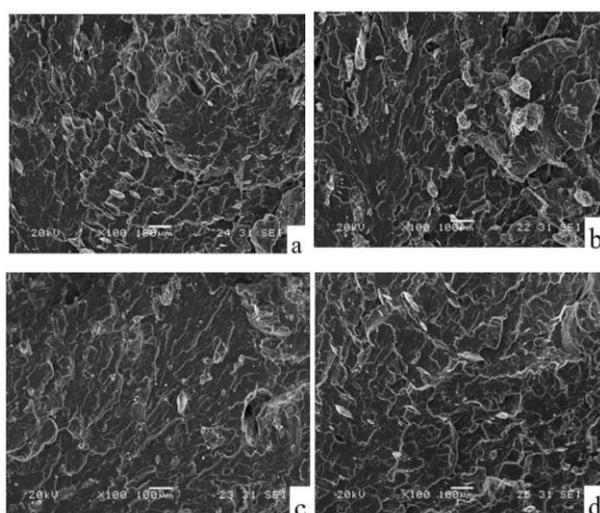
The micrographs of PHBV (Figure 2 (a)) and PP (Figure 2 (b)) show an irregular and rough fracture surface due to its crystal structure. The PHBV image shows white trace over the entire surface which is attributed to the presence of organic fillers in the commercial PHBV [18].

Figure 2 (c, d, e et f) shows the scanning electron microscopy images of the fractured surfaces of the different PP/PHBV blends. The micrographs in figure 2.(c et d) (20% et 30% by weight of PP) show spherical domains of the minor phase dispersed in the continuous phase (matrix) and the presence of void at the interface between the two phases. Moreover, the surfaces of the particles extracted from the matrix are smooth and without any visible roughness. All these characteristics are typical of immiscible mixtures. Similar images were obtained by Hoseini and al [19], Kim and al [9] for 75/25 LDPE/PLA blends, and 80/20 and 20/80 LLDPE/PLA blends. Such images have also been observed for many binary mixtures such as PE/PP [20], PE/PS [21], PE/collagen [22]. In general, a roughness of the particle surface is evidence of good interfacial adhesion between the particles and the matrix [22-24].

Micrographs of the 50/50 and 40/60 PP/PHBV blends (Figures 2.e-f) reveal co-continuous morphologies that result from coalescence of domains of the same phase. At these compositions, it becomes difficult to distinguish the dispersed phase from the matrix [10].

These morphologies consist of only two large polymer domains, in this case PP and PHBV, extending completely over the entire structure. However, it is also observed, in the co-continuous structure, that each continuous phase encompasses micro-domains of the other phase, i.e., sub-inclusions of the PP are present inside the PHBV and vice versa. The formation of these under-inclusions can be explained by the fact that, at phase inversion, a small amount of each phase is surrounded by the growing continuous phase [25].

Regarding the effect of glycerol addition on the morphology of PP/PHBV blends, the comparison of different micrographs show drastic changes in the morphology of the materials (Figures 3). With the incorporation of 1% of glycerol in PP/PHBV 80/20 and PP/PHBV 70/30, the size of the PP nodules is considerably reduced and the dispersed phase becomes more deformed and less discernible, as can be seen clearly in Figure 3(a e b). This effect is even more pronounced in PP/PHBV 60/40 (Figure 3 (c)) and 50/50 (Figure 3 (d)) mixtures, which reveals an almost homogeneous morphology at this magnification suggesting an improvement of the miscibility between the two mixture components. It can be inferred that the addition of glycerol acted synergistically to produce smaller nodules and a relatively uniform distribution of them within the PHBV matrix.



**Figure 3.** SEM Mmicrographs of fractured surfaces (a, b, c and d) after plasticized for formulations: (a) PP/PHBV 80/20, (b) PP/PHBV 70/30, (c) PP/PHBV 60/40 and (d) PP/PHBV 50/50.

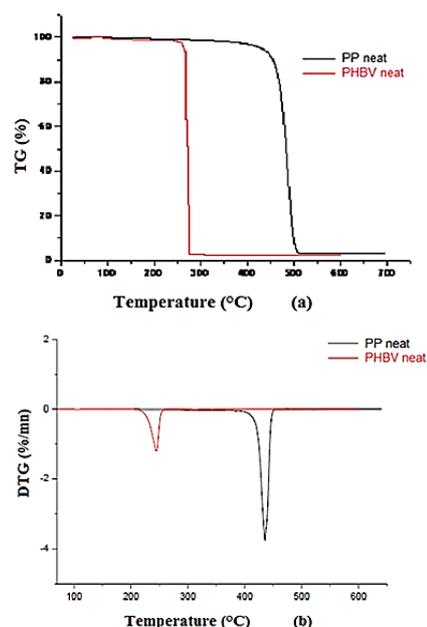
### III.3. Thermogravimetric analysis (TGA)

Thermal stability is defined as the maximum temperature the material can withstand without irreversible mass loss. The thermogravimetric analysis allows to follow the variation of the mass of a sample according to the temperature and thus to reach the parameters of decomposition of a material. To facilitate reading, it is convenient to represent the derived curve (DTG) of the TGA. This curve makes it easier to identify mass loss phenomena since they appear as peaks. Figures 4 and 5 illustrate, respectively, the thermal decomposition curves (TG) and the curves of their first-order derivatives (DTG) for PP, PHBV and their mixture, the most important characteristic temperatures of the different materials are summarized in Table 2.

**Table 2.** TGA data for neat PHBV, PP and PHBV/PP blend

Formulations	Td (°C)	T <sub>50%</sub> (°C)	Tmax (°C)	Vmax (%/mn)	Residue rate (%)
PP <sub>100</sub>	421	434	440	3.41	0.85
PHBV <sub>100</sub>	262	272	280	1.17	1.35
PHBV <sub>60</sub> /PP <sub>40</sub>	185	270	270	3.2	1.25
PHBV <sub>50</sub> /PP <sub>50</sub>	200	285	272	2.8	0.96
PHBV <sub>60</sub> /PP <sub>40</sub> (plasticized)	240	250	255	1.9	0
PHBV <sub>50</sub> /PP <sub>50</sub> (plasticized)	240	260	268	1.65	0

In Figure 4(a) the loss of mass of PP and PHBV took place in a single regular step, to wait towards the end of very low masses which are of the order of 0.85 for PP and 1.35 for PHBV. These results are confirmed in figure 4(b) by the presence of a single peak in the corresponding DTG curve, these results are in agreement with that found in literature [26, 27].



**Figure 4.** Thermal degradation behavior of the neat PHBV and P : (a) TGA thermograms and (b) DTG thermograms.

Examining the results in Table 2, it can be noticed that PP shows more stability than PHBV where the difference between the corresponding temperatures at the onset of their degradation is about 80°C for PP ( $T_d = 421^\circ\text{C}$ ) and ( $T_d = 262^\circ\text{C}$ ) for PHBV. On the other hand, the decomposition of PP took place over a larger temperature range than that of PHBV, which indicates that the decomposition reaction of PHBV is more rapid than PP. Thus, thermal degradation of PHBV results in a greater loss of mass (96%) than PP (98%).

According to the literature [28-30], the thermal degradation of PP occurs by random chain cleavage and follows a radical mechanism. The main pyrolysis products are homologous series of alkenes, alkanes and dines [30]. However, the degradation of PHBV is more complex. Its degradation at temperatures above 200°C includes intermolecular transesterification reactions, which lead to the formation of cyclic and acrylic oligomers, as well as fragmentation, which leads to acetaldehyde and carbon dioxide.

Concerning PHBV/PP mixtures, thermogravimetric curves (Figure 5) show for all compositions, a degradation process in two steps, confirmed by DTG curves (Figure 5(b)) by the presence of two distinct peaks.

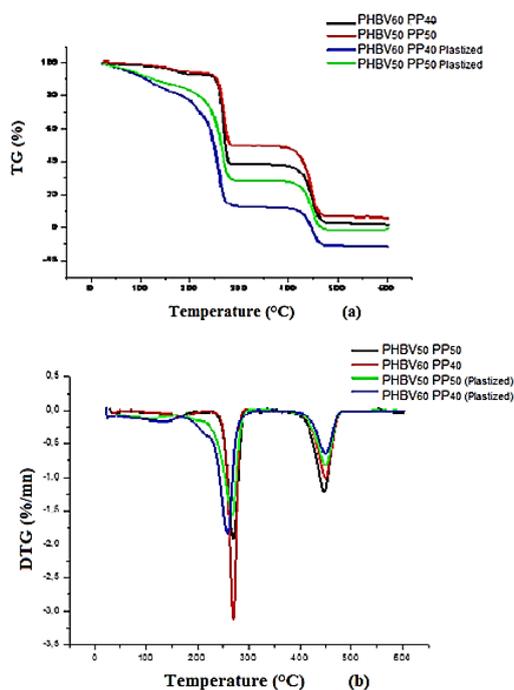


Figure 5. Thermal degradation behavior of the PHBV/PP blend before and after Plasticized: (a) TGA thermograms and (b) DTG thermograms.

The temperature of the first decomposition peak is close to the pure PHBV peak while the second peak is close to that of pure PP. Thus, the initial mass loss of the PHBV/PP mixture is

mainly due to the decomposition of PHBV while the second thermal degradation step is due to the decomposition of PP. Such findings were made during the thermal degradation of the studied mixtures by [31, 32], these authors suggest that the thermal degradation of each component of the studied mixtures occurs independently i.e. it is not affected by the presence of the other component. The negligible amounts of residual masses at 600 °C obtained after the second stage of decomposition, indicates a complete material degradation, although the residue beyond 600°C increases with the increase of the PHBV content.

The TGA and DTG curves of the plasticized formulations presented in figure 5 (a, b), we clearly observe that the thermal degradation profiles follow the same trend (two mass losses). According to the results of Table 2 we notice that the addition of plasticizer to the mixtures PHBV<sub>60</sub>/PP<sub>40</sub> and PHBV<sub>50</sub>/PP<sub>50</sub> leads to a decrease of the temperature of onset of degradation ( $T_d$ ), and this decrease increases with the increase of the quantity of PHBV. This is due to the flexibility of plasticized PHBV/PP blends which have a much lower decomposition temperature than non-plasticized PHBV/PP blends.

#### III.4. Differential scanning calorimetric analysis (DSC)

DSC was used to study the miscibility and possible interactions between PHBV and PP in the mixtures. The values of melting temperatures ( $T_m$ ) and crystallinity rate reported in Table 3.

It can be seen from the results in Table 3 that the values of the melting temperatures ( $T_m$ ) remain relatively unchanged regardless of the proportion of PP in the mixture.

Table 3. Results of melt temperature and crystallinity obtained by DSC

Formulations	Before plasticization		After plasticization	
	$T_r$ (°C)	X (%)	$T_r$ (°C)	X (%)
PP <sub>100%</sub> /PHBV <sub>0%</sub>	169.12	36.8	168.33	31.40
PP <sub>0%</sub> /PHBV <sub>100%</sub>	171.10	/	170.14	/
PP <sub>20%</sub> /PHBV <sub>80%</sub>	170.17	30.2	169.12	27.12
PP <sub>10%</sub> /PHBV <sub>70%</sub>	168.3	25.32	168.10	20.32
PP <sub>10%</sub> /PHBV <sub>50</sub>	168.8	19.11	167.22	15.33

Concerning the values of the crystallinity rate of each polymer decreases with the addition of the other polymer. This decrease can be attributed to the crystallization of PHBV is limited by the presence of PP; similar results have also been reported on the crystallization behavior of other PHBV-based blends [33, 34]. The effect of the addition of glycerol on the crystallinity of the two polymers in the blend, the results presented on Table 3. It is observed that the percentage of crystallinity tends to

decrease for both polymers. This may be due to the fact that glycerol has a significant influence on the flexibility of the PHBV/PP blend chains and on the intermolecular interactions, probably explained by a certain affinity between the two polymers [35].

#### IV. Conclusions

Mixtures based on PHBV and PP with and without plasticizer (glycerol), were prepared by casting solution.

The morphological study of the different samples, compared to PHBV alone and PP alone, showed that the PHBV/PP mixtures form a biphasic system over the entire compositional range.

The immiscibility between the two components of the mixtures was revealed using SEM analysis, which clearly showed the appearance of a co-continuous morphology for the PHBV<sub>50</sub>/PP<sub>50</sub> mixture while the other compositions of 80/20, 70/30 mixtures led to a dispersed morphology. The dispersion of the PP was significantly refined with the incorporation of the plasticizer (glycerol), due to increased interactions between the components.

Infrared spectroscopy (FTIR) of the unplasticized PHBV/PP mixtures showed the absence of any reaction in these mixtures while the spectra of the plasticized PHBV/PP mixtures showed the existence of interaction between the different constituents. Such interaction preventing reactions between the functional groups of the plasticizer.

Thermal properties (DSC) show that each of the two constituents (PHBV and PP) influences the crystallization of the other in the mixtures. The thermogravimetric analysis showed that the addition of plasticizer to the PHBV<sub>60</sub>/PP<sub>40</sub> and PHBV<sub>50</sub>/PP<sub>50</sub> mixtures leads to a decrease of the temperature of onset of degradation (Td), this decrease increases with the increase of the PHBV quantity.

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