

# Miscibility of Poly(hydroxybutyrate)/Poly(vinyl alcohol) Melt Blends Plasticized With Glycerol

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**Abstract:** Poly(hydroxybutyrate)/poly(vinyl alcohol) (PHB/PVA) blends plasticized with glycerol were prepared by melt blending of PHB and glycerol plasticized PVA. The PHB/PVA-glycerol compositions were 90:10, 75:25 and 50:50 w/w, being the concentration of glycerol in the PVA mixture of 10 wt %. The blends were characterized by infrared spectroscopy, dynamic-mechanical thermal analysis, and scanning electron microscope of the fragile fractured surface. The results showed one single phase blend, indicating miscibility corroborated by the presence of a single glass transition temperature. The blending method proved to be an efficient way to tune PHB properties keeping its biodegradable nature since both PVA and glycerol are fully biodegradable materials.

**Keywords:** Blend miscibility; melt processing; poly(hydroxybutyrate); poly(vinyl alcohol)

## 1 Introduction

Poly (hydroxybutyrate) (PHB) is a biodegradable polymer derived from renewable resources with mechanical properties is usually compared to polypropylene. This polymer has been considered to have great potential for several applications; however, it has some drawbacks that limit its use, being the most relevant its brittleness and narrow processing window [1-3]. These limitations have been circumvented by different strategies such as blending with other polymers [1], by chemical modification (which include the grafting of plasticizers) by reactive extrusion [4,5], and the addition of plasticizers [6,7]. From the practical and economical point of view, the blends are more attractive in relation to the methods that involve the chemical modification of PHB or the use of plasticizer that can be exudates or extracted if PHB is used, for example, in packaging.

An interesting material for blends with PHB is poly (vinyl alcohol) (PVA), which is a biodegradable synthetic polymer obtained by the conversion of polyvinyl acetate by its hydrolysis. PVA characteristics are dependent fundamentally on the degree of polymerization and on the degree of hydrolysis [8]. PVA has good mechanical properties and is soluble in water. Huang et al. [9] showed by FTIR analysis that PHB/PVA blends they produced are miscible in any proportion of the components when prepared by solution in 1,1,1,3,3,3-hexafluoro-2-propanol. The system is very complex since both polymers are semi-crystalline. Melt blends of PHB/PVA are described only in few studies. One of these studies describes melt blends of PHB/PVA prepared by extrusion in a single-screw extruder [10,11], where the authors used PVA with 27 and 8.2 wt % of residual acetate groups and molar mass of 38,000 and 64,000 g.mol<sup>-1</sup> in the absence of plasticizers.

Here we investigated PHB/PVA blends prepared by melting using a new strategy in which PVA was previously plasticized with glycerol by solution blending in water. The plasticizer was used since PVA is usually very difficult to be processed in its absence, occurring degradation and poor mixing due to the high viscosity when processed in the absence of any plasticizer. The materials were characterized by

infrared spectroscopy, scanning electron microscopy and dynamic-mechanical thermal analysis. The results showed the ternary system PHB/PVA/Glycerol is miscible.

## **2 Experimental**

### **2.1 Materials**

Poly (hydroxybutyrate) (PHB) from Biocycle® (PHB Industrial S.A.) with molar mass  $M_w \sim 500,000 \text{ g.mol}^{-1}$ , determined by GPC and valerate content of 4% and poly(vinyl alcohol) (PVA) from Sigma-Aldrich with  $M_w 9,000 \text{ g.mol}^{-1}$  and a hydrolysis degree of 80% were used. As plasticizer, it was used reagent grade glycerol from Synth- Brazil.

### **2.2 Blend Preparation**

Plasticized PVA was obtained by solution blending [12] from a solution of glycerol and PVA with 20 wt % PVA and glycerol amount to give a final PVA/glycerol mixture with the proportion 90:10. The mixture was spread in a container and dried at 50°C in an air circulating oven and in following dried at 50°C for 24 hours in a vacuum oven. The resulting material was ground in the presence of liquid nitrogen in an IKA- model A11 mill (Germany), before extrusion.

For PHB/PVA blends, plasticized PVA was manually mixed with PHB (both in powder form) and the mixture extruded in a 16 mm L/D 26 single screw extruder with a Maddock-type mixer, from AX-Plásticos- Brazil. The temperature profile from feeding to die for PHB was 155°C, 169°C and 170°C and for PHB/PVA blends was 145°C, 150°C and 155°C. The PHB/PVA-glycerol blend compositions were 90:10, 75:25 and 50:50 w/w.

### **2.3 Fourier Transform Infrared Spectroscopy**

FTIR analyzes were performed in a Perkin Elmer Spectrum 100 model FTIR, equipped with a total attenuated reflectance accessory (ATR) with diamond coated zinc selenide crystal. The samples films were 0.10 to 0.50 mm thickness.

### **2.4 Dynamical Mechanical Analysis**

DMTA analyzes were performed on a Perkin Elmer, DMA 8000 model. The samples were cut in the rectangular shape with dimensions of  $10.0 \times 6.0 \times 0.1$  (mm) and tested in the tensile mode with initial deformation of 5  $\mu\text{m}$ . The analyses were performed from -40°C to 180°C at a heating rate of 5 °C/min.

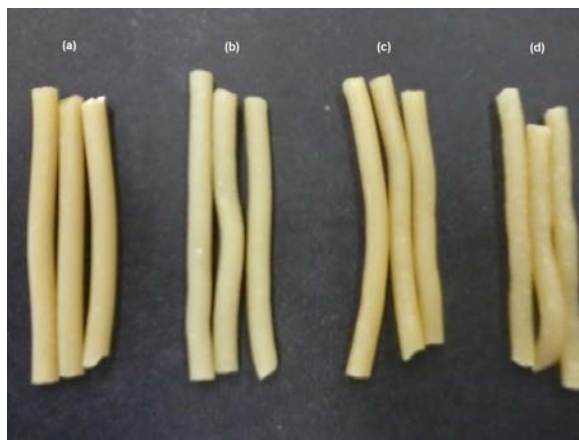
### **2.5 Scanning Electron Microscopy (SEM)**

SEM analyzes were performed on extruded samples from fragile fractured surface produced in liquid nitrogen. For the blend samples the fracture surface was extracted by immersion in water at 40°C under agitation for 24 hours for blends with 90% PHB, one hour for blends with 75% PHB and 30 minutes for blends with 50% PHB. The samples were vacuum dried and coated with platinum and analyzed in a Scanning Electron Microscopy Inspect F-50, FEI, Nederland.

## **3 Results and Discussions**

### **3.1 Melt blending of PHB/PVA**

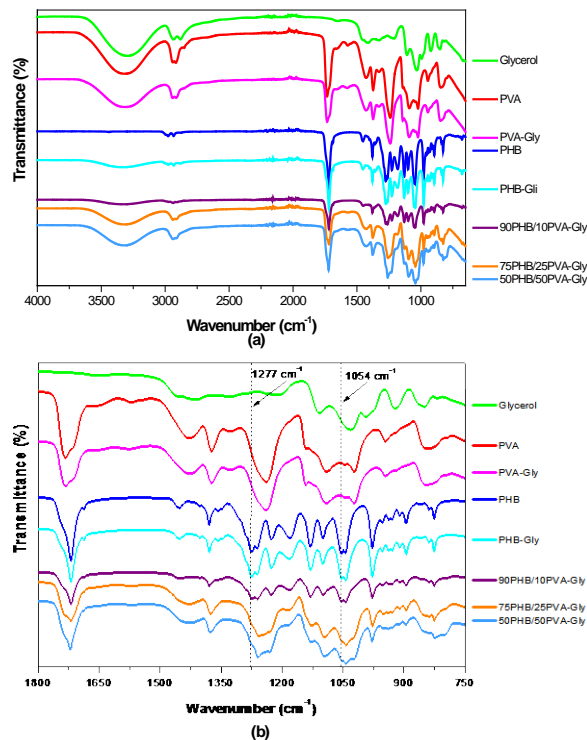
Fig. 1 shows the extruded samples of PHB and PHB/PVA blends with PVA-glycerol content varying from 10 to 50 wt%. The samples appearance is very similar and close to the pure PHB.



**Figure 1:** PHB/PVA blends obtained by melting in different compositions; (a) pure PHB, (b) 90PHB/10PVA-Gly, (c) 75PHB/25PVA-Gly and (d) 50PHB/50PVA-Gly

### 3.2 Fourier Transform Infrared Spectroscopy (FTIR)

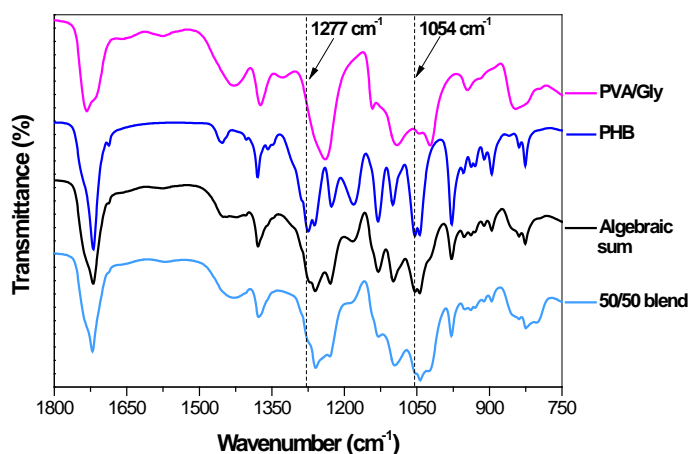
Fig. 2 shows the infrared spectra of the materials used (PHB, PVA, and glycerol) and of the PHB/PVA-glycerol blends. The FTIR spectrum for glycerol shows the stretching from O-H at about  $3297\text{ cm}^{-1}$ , the stretching from C-H groups at  $2810\text{--}2950\text{ cm}^{-1}$  and the absorption corresponding to the C-O-H groups in the region of  $1400\text{ to }1420\text{ cm}^{-1}$  [13]. For PHB and PVA [14-16] absorptions from O-H were observed at  $1021\text{ cm}^{-1}$ ,  $\text{-CH}_2$  in the interval from  $1417\text{ to }1461\text{ cm}^{-1}$  and C-H vibrations at  $830\text{ cm}^{-1}$ . In addition, both PVA and PHB showed typical carbonyl bands around  $1730\text{ cm}^{-1}$ . For a better visualization, the regions from  $750\text{ to }1800\text{ cm}^{-1}$  is shown in Fig. 2(b).



**Figure 2:** (a) Infrared spectra of pure materials, plasticized PHB and PVA and for the blends PHB/PVA-glycerol, (b) FTIR spectrum extended in the region between  $750\text{ and }1800\text{ cm}^{-1}$

Shifts of infrared absorption bands may indicate miscibility in polymer blends [17] due to specific interactions between chemical groups. In order to verify PHB/PVA miscibility, a more detailed observation of the blends spectra in comparison with the plasticized pure polymers was performed in Fig. 2(b). It was observed two bands displacements at 1277 and 1054  $\text{cm}^{-1}$  from PHB. These bands correspond to C-O vibration of PHB. For PVA, corresponding to the C-O stretch and to O-H bond.

In order to identify infrared band shift, Fig. 3 shows the spectra of the blend components (PHB and PVA-Glycerol), the curve obtained by adding algebraically the individual spectrum of the components and the spectrum of the 50PHB/50PVA-Gly. It is possible to observe several differences, as for example at 1277 and 1054  $\text{cm}^{-1}$  when comparing the spectrum generated by the algebraic sum of the spectra of PHB and PVA and of the 1:1 blend, evidencing specific interactions between the blend components which is an indication of miscibility.

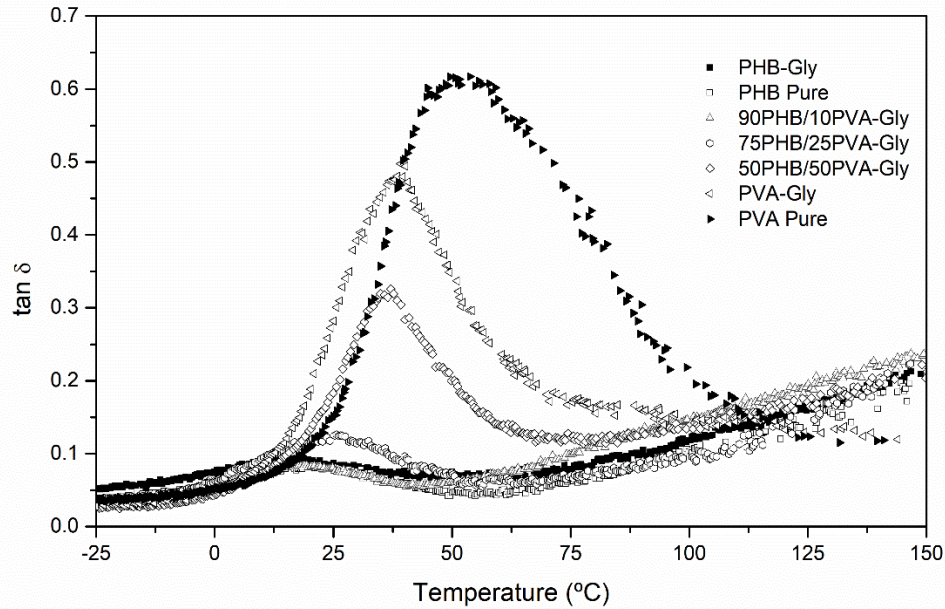


**Figure 3:** Spectra of the components of the mixture (PHB and PVA-Glycerol) and the algebraic sum of both (in black). Below is the spectrum of the blend with 50 wt % of PHB

The blends of PHB/PVA studied by Huang et al. by solution blending [9] also showed shift of the ester absorption at 1715  $\text{cm}^{-1}$  which was attributed to miscibility.

### 3.3 Dynamic-Mechanical Thermal Analysis (DMTA)

Fig. 4 shows the loss tangent ( $\tan \delta$ ) curves obtained by DMTA for the pure materials and for the blends. It is possible to observe a shift of  $\tan \delta$  peak which can be related to the glass transition temperature of the materials. It is possible to observe only a single  $T_g$  ( $\tan \delta$  max.) for all blends, which temperature is intermediate between the  $T_g$  of the pure polymers. This result confirms the miscible character of these blends. The  $T_g$  taken at the maximum in  $\tan \delta$  curves are presented in Tab. 1.



**Figure 4:** Curves of  $\tan \delta$  for the pure materials and for plasticized blends obtained by DMTA

**Table 1:** Values for  $T_g$  estimated from DMTA  $\tan \delta$  peak at its maximum

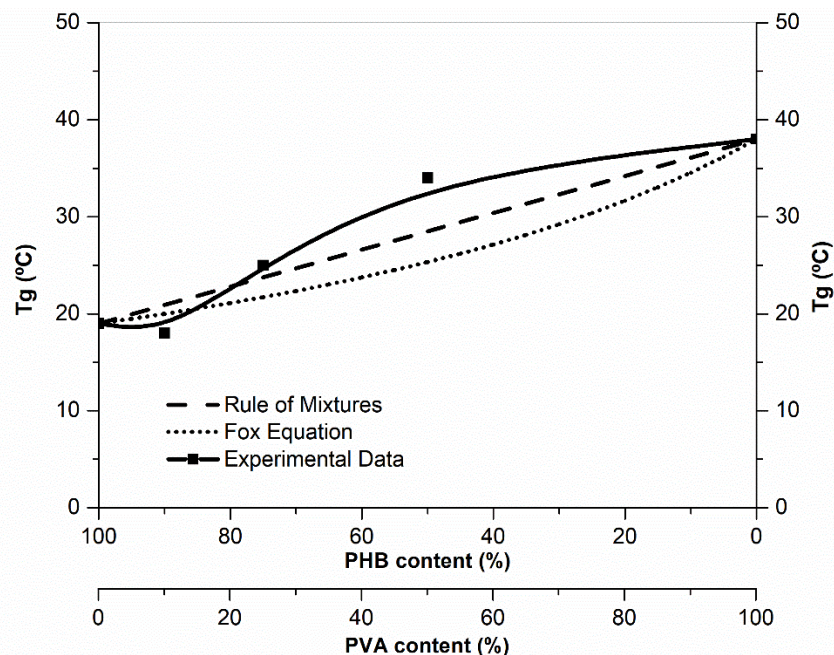
| Material        | $T_g$ DMTA (°C) |
|-----------------|-----------------|
| PHB-Gly         | 14              |
| PHB             | 19              |
| 90PHB/10PVA-Gly | 18              |
| 75PHB/25PVA-Gly | 25              |
| 50PHB/50PVA-Gly | 34              |
| PVA-Gly         | 38              |
| PVA             | 50              |

Fig. 5 shows the plot of  $T_g$  (taken at the peak of  $\tan \delta$ ) as a function of blend composition with a curve marked with a solid line to guide the eye, and the curves estimated using the Rule of Mixtures and Fox equation [18] expressed respectively by Eqs. (1) and (2).

$$T_g = w_1 T_{g1} + w_2 T_{g2} \quad (1)$$

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (2)$$

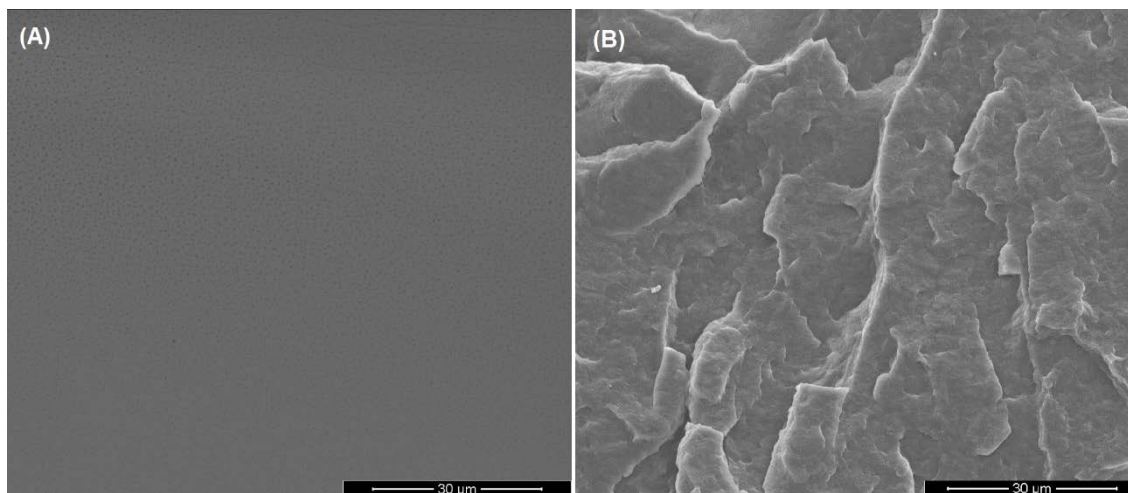
The experimental data do not fit very well the curves of the Fox equations and the Rule of Mixtures, however, its tendency is clearly of a miscible blend [19]. The deviation observed from Fox equation and the rule of the mixture is expected since the system is very complex due to the fact that hydrogen bonding dominates the interactions and also due to the presence of a third component, glycerol. Fox equation considers a mixture in which the components are distributed randomly with low or any interaction between them [18]. In addition, the studied system contains the polar glycerol and can be considered a ternary mixture. Despite the observed deviations from the classical equations used to predict the  $T_g$  of miscible binary blends, the results indicate miscibility between PHB and PVA in the presence of glycerol [19].



**Figure 5:** Plots of experimental data (■) with solid lines to guide the eye and curves obtained using the data of  $T_g$  for PHB and PVA-glycerol using the rule of mixtures (dash line) and Fox equation (dot line)

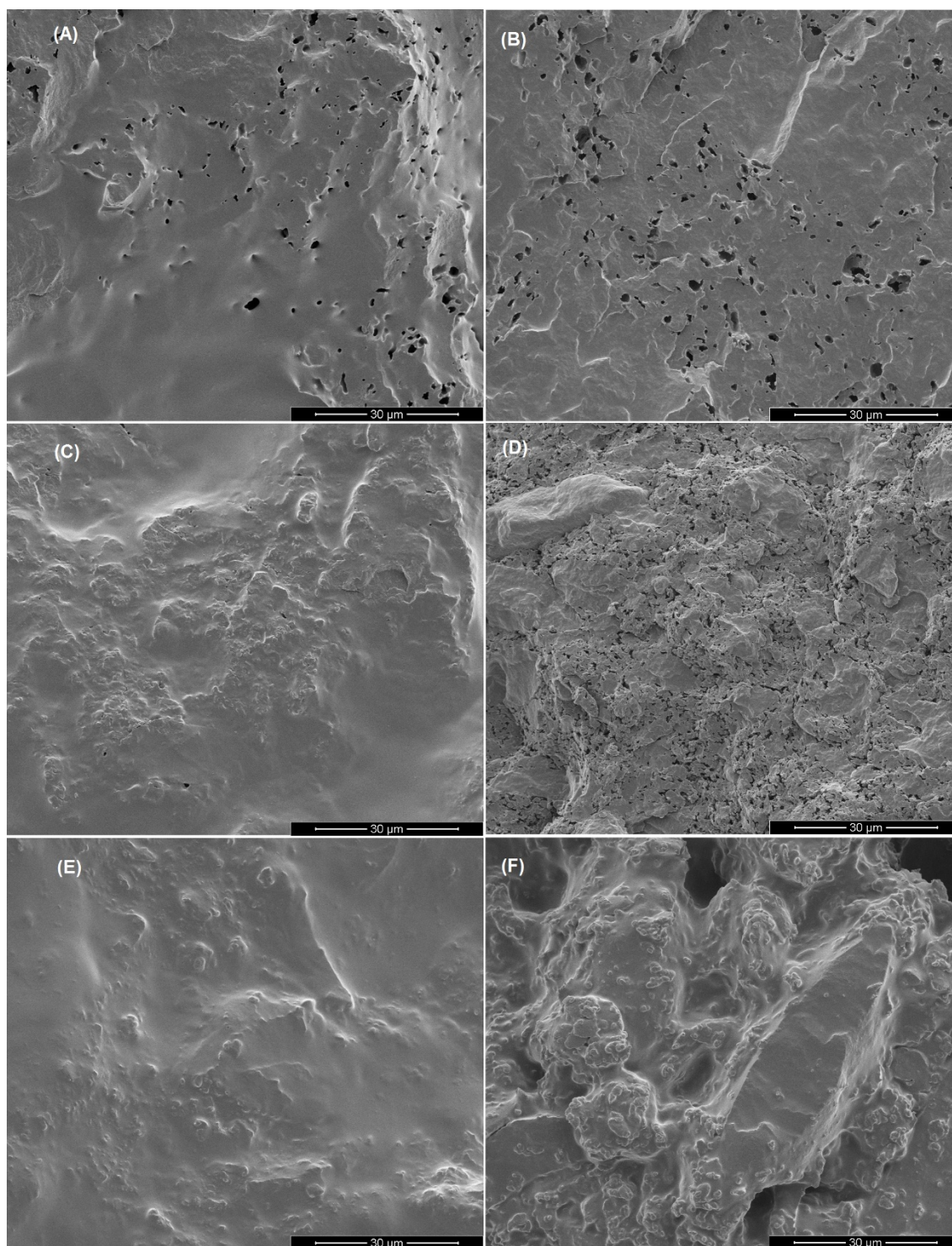
### 3.4 Scanning Electron Microscopy (SEM)

Fig. 6 shows the micrographs of PVA and PHB. The micrograph of the PVA shows a flat and uniform appearance. Micrographics of PHB showed the typical scaly surface of semicrystalline polymers.



**Figure 6:** Micrographs for the (a) PVA and (b) PHB

Figs. 7(a)-7(f) shows the micrographs of the blends (not extracted on the left and PVA extracted on the right).



**Figure 7** Micrographs of the blends containing 90% PHB (a and b), 75% PHB (c and d) and 50% (e and f) being un-extracted on the left and PVA extracted on the right

The rough and irregular surface of the fragile fracture surface showed in Fig. 7 could indicate phase separation or crystallization. One possible reason is partial miscibility which however was not detected by the DMA measurements.

The results of both FTIR and DMA corroborate the conclusion that the blends produced are miscible, despite the results of SEM. The low molar mass of PVA use could also contribute to miscibility unlike the high molar mass PVAs used in the works of Huang et al. [9] and Azuma [20].

#### 4 Conclusions

Glycerol plasticized PHB/PVA blends was obtained by melting blending. The blends were prepared by extrusion of plasticized PVA and PHB. The miscibility of the blends was confirmed by FTIR and DMTA. Band shifts in FTIR are indicative of intermolecular interactions and miscibility. The single  $T_g$  criterion was achieved in the DMTA analysis results. Despite the fact that  $T_g$  determined by means of DMTA indicate miscibility the values deviate from that expected by Fox equation and the Rule of Mixture. It was not possible to clearly observe the presence of distinct phases by SEM images of fragile fractured surface, however, the surface is not flat as expected for amorphous single phase blends.

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