

## Understanding External Plasticization of Melt Extruded PHBV–Wheat Straw Fibers Biodegradable Composites for Food Packaging

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**ABSTRACT:** The objective of this work is to get further knowledge on the external plasticization mechanisms of melt extruded polyhydroxyl-3-butyrate-*co*-3-valerate (PHBV) when combined with wheat straw fibers (WSF). Different types of biodegradable substances, all authorized for food contact according to the European regulation, i.e., acetyltributyl citrate (ATBC), glycerol triacetate (GTA) and (PEG) at different molecular weights, were tested at different percentages (5, 10 and 20 wt %). Thermal and mechanical characterization of PHBV/plasticizer blends showed that a significant plasticizing effect was obtained using hydrophobic substances such as ATBC and GTA, with an increase of the elongation at break from 1.8% up to about 6% for an additive content of 10 wt %. However, the incorporation of WSF in plasticized PHBV led to a dramatic decrease in the elongation at break of composites, neutralizing the increase of this parameter by the addition of the plasticizers. The stress at break of plasticized films was also significantly decreased by the introduction of fibers. Such a loss of ductility was mainly explained by the occurrence of microscopic defects in the materials induced by the presence of fibers and to a poor adhesion at the fiber/matrix interface.   2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41611.

**KEYWORDS:** biopolymers and renewable polymers; composites; packaging; plasticizer; structure; property relations

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### INTRODUCTION

Numerous biocomposite materials, based on the combination of both bio-sourced and biodegradable polymer matrices with natural fillers, have been developed during the last decade in response to environmental concerns, to reach independence from price-climbing and declining availability of oil resources, and/or to develop specific new functionalities. In the case of food packaging applications, which represent the largest tonnages for plastics, R&D efforts focus on designing materials from non-food and low cost resources to answer specifications in terms of food quality and safety preservation, economic competitiveness and sustainability.<sup>1</sup>

Among the promising polymer matrices, bacterial aliphatic copolyesters, such as polyhydroxyl-3-butyrate-*co*-3-valerate (PHBV), are fully biodegradable materials<sup>2,3</sup> that can be produced from food industry by-products.<sup>4</sup> PHBV is easily process-able using either extrusion or injection processes.<sup>5–7</sup> However, PHBV processing costs are still high (3–5   kg<sup>–1</sup>)<sup>8</sup> for food packaging applications, and its high barrier properties are inadequate for fresh

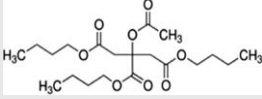
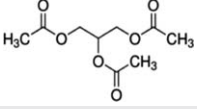
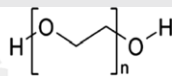
foods such as cheese, fruits or vegetables, which require respiring packaging. An example of strategy already investigated to make PHBV more competitive and to open its window of applications by modulating its functional properties was to produce composite materials by adding low cost lignocellulosic fibers obtained by grinding of agro-industrial by-products, e.g. wheat straw.<sup>5,9,10</sup> It was shown that the introduction of increasing amounts of wheat straw fibers (WSF) with different sizes led to a new range of PHBV-based composites with tunable properties, especially water vapour permeability, which could fulfil the requirements of respiring fresh food products.<sup>9</sup> The drawback of these composites is a more pronounced brittleness, mainly attributed to the poor interfacial adhesion between the hydrophilic fibers and the hydrophobic matrix which was highlighted by scanning electron microscopy (SEM) observations of cryo-fractured surfaces.<sup>5,9</sup>

To overcome this problem, external plasticization of the matrix by the introduction of low molecular weight plasticizers appeared as an alternative to soften the PHBV matrix. Plasticizers are generally used to improve polymer processing and

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**Table I.** Chemicals Used for PHBV Plasticization: Family's Substance, Substance Name and Abbreviation, Chemical Structure, Molecular Weight, Log *P*, and Thermal Properties [Melting Temperature (*T<sub>m</sub>*) and Ebullition Temperature (*T<sub>b</sub>*)]

Family's substance	Substance name	Chemical structure	Molecular weight (g mol <sup>-1</sup> )	Log <i>P</i>	Thermal properties	
					<i>T<sub>m</sub></i> (°C)	<i>T<sub>b</sub></i> (°C)
Citrates	Acetyltributyl citrate, ATBC		402	6.5	-59	343
Acylglycerols	Glycerol triacetate, GTA		218	-0.52	-78	258
Polyethers	Poly(ethylene glycol), PEG		400	-4.8	4-8	250
			1000	-	35-40	250
			4000	-	58-61	250

impact properties.<sup>11</sup> In the case of semi-crystalline polymers, an efficient plasticizer is expected not only to reduce the glass transition temperature (*T<sub>g</sub>*) of the amorphous phase by increasing the free volume, but also to depress the melting point of the crystalline phase. The use of different substances as suitable plasticizers for PHB and PHBV have been studied, like vegetable oils (e.g. soybean oil), triethyl citrate (TEC),<sup>12</sup> acetyl tributyl citrate (ATBC),<sup>13,14</sup> polyethylene glycol (PEG),<sup>15-17</sup> glycerol triacetate (GTA),<sup>18,19</sup> fatty alcohols with or without glycerol fatty esters.<sup>20</sup> In addition to the depression in *T<sub>g</sub>* values with respect to the neat polymer, the external plasticization generally leads to decreasing stiffness and increasing elongation at break of PHAs.<sup>12,15-19</sup> Most of these studies<sup>12,14-17,19</sup> focused on materials prepared by solvent casting, with no information on the external plasticization efficiency of PHBV in the case of materials prepared by a thermo-mechanical process, which is the most conventional method for shaping plastics at industrial scale.

In this context, the objective of the present paper is to get further knowledge on the external plasticization mechanisms of PHBV shaped by melt extrusion in combination or not with WSFs. With the aim to develop biodegradable materials for food packaging applications, the tested plasticizers for PHBV were selected among those biodegradable and authorized for food contact according to the European regulation, as well as among those already used to plasticize polyesters. Since blends were prepared by melt extrusion at high temperature, such substances were also selected based on their thermal resistance at the working temperatures to minimize loss of plasticizer by evaporation and degradation during material processing. Hence, the following substances were studied as PHBV plasticizers: acetyltributyl citrate (ATBC), GTA, and PEG at different molecular weights. Effective plasticization of the polymer was evaluated by thermal and mechanical characterization of the blends obtained. WSFs were then incorporated in plasticized PHBV matrix at a content of 20 wt %. Mechanical properties of biocomposites were discussed in relation to their morphology and structure at the molecular and microscopic scales.

## EXPERIMENTAL

### Materials

PHBV (3% HV) in the form of pellets (ENMAT Injection Molding Grade Y1000P) was provided by Tianan Biologic Material (China). As reported by the manufacturer, PHBV contains less than 0.5% of nucleating agents (boron nitride) and antioxidants (Irganox 1010). Such copolymer was used as polymeric matrix for plasticized and composite materials preparation.

Chemicals used as plasticizers for PHBV were purchased from Sigma Aldrich (France) and were acetyl-tri-butyl citrate (ATBC), GTA, and PEG with three different molecular weights, i.e., 400 (PEG-400), 1000 (PEG-1000), and 4000 g mol<sup>-1</sup> (PEG-4000). Table I reports the chemical structure, molecular weight and thermal properties of the chemicals indicated above, as reported by manufacturer.

Native wheat straw (*T.aestivum* cv. Apache) was kindly provided by Fernand Meaux (St. Jean du Salès, Aveyron, France, harvested in 2007). WSFs with a median size (*d*<sub>50</sub>) of 469 μm (Berthet et al., unpublished results) were obtained from two successive grinding steps of native wheat straw. Native wheat straw (stored at room temperature (RT) and relative humidity and characterised by a moisture content of 8 wt % w.b.) was preliminary reduced using a cutting mill type SM2000 (Retsch, Germany) with a 4.0-mm sieve. Then, the 4 mm-particles previously dried during one night at 60°C were ground on a impact mill type 100 UPZ (Hosokawa Alpine, Germany), operated at 18,000 rpm and equipped with a 0.3 mm selection sieve (trapezoid holes), a 8-teeth rotor and an output recovery by cyclone.

### Preparation of Plasticized Composite Materials

Plasticized PHBV-based compounds were processed in a co-rotating twin-screw extruder Prism Eurolab 16XL (Termo Scientific, Germany) with a screw length to diameter ratio *L/D* = 40:1 (*D* = 15.6 mm). The extruder was assembled with an one-hole filament die of 3 mm in diameter. Before processing, PHBV copolymer was dried over night at 60°C, whereas

both powdery additives (PEG-1000, PEG-1500 and PEG-4000, see Table I) and WSFs were dried over night at 35°C. The desired plasticizer content (5, 10, or 20 wt %) was added during extrusion process using a syringe pump (KDS100, Kd Scientific) for liquid plasticizers (GTA, ATBC, PEG-400) and a gravimetric feeder (MiniTwin Feeder MT, Brabender) for those in the form of powder (PEG-1000, PEG-1500, PEG-4000). After extrusion, plasticized samples were cooled in a water bath and air-dried at RT before being cut using a Prism Eurolab pelletizer (Thermo Scientific). The pellets obtained were stored at 60°C for at least 12 h. Composite compounds were prepared by extrusion of the plasticized PHBV pellets together with the WSFs (20 wt %) that were fed to the extruder through the gravimetric feeder. The same procedure described above for plasticized PHBV (cooling, drying, cutting) was applied to the extruded composites.

Films (average thickness = 0.25 mm) were prepared by hot-pressing the pellets between two Teflon coated plates, at 170°C in a hydraulic press (PLM 10 T, Techmo, Nazelles, France). The samples were allowed to melt for 3 min, then a pressure of 150 bars was applied for 2 min. Finally, the samples were cooled at RT.

### Characterization of Materials

Differential Scanning Calorimetry (DSC) measurements were carried out using a DSC-Q100 (TA Instruments) apparatus, equipped with a liquid nitrogen cooling system (LNCS) accessory. The samples were initially heated up to above the melting temperature to cancel the previous thermal history, unless otherwise specified. Then, temperature was lowered and DSC heating scans were run at 20°C min<sup>-1</sup> in the temperature range -80°C/200°C in helium atmosphere. Quench cooling was applied between scans. Glass transition temperature ( $T_g$ ) was taken at half-height of heat capacity increment while the melting temperature ( $T_m$ ) was taken at the peak maximum of the melting endotherm.

Wide-angle X-ray diffraction measurements (WAXS) were recorded at RT with a PANalytical X'Pert PRO diffractometer equipped with an X'Celerator detector (for ultrafast data collection). A Cu anode was used as X-ray source ( $K_\alpha$  radiation:  $\lambda = 0.15418$  nm) and 1° divergence slit was employed to collect the data in the  $2\theta$  range from 3° to 60°. The degree of crystallinity ( $X_c$ ) was evaluated as the ratio between the crystalline diffraction area (obtained from the total area of the diffraction profile by subtracting the amorphous halo) and the total area of the diffraction profile.

The molecular weight of PHBV was evaluated by gel permeation chromatography (GPC). Samples were prepared by dissolving 25 mg of PHBV-based material in 5 mL of chloroform, in a closed tube, under stirring, at 50°C. Samples containing fibers were filtered on a 45  $\mu$ m-pores filter (VWR, filter paper, qualitative 413). Then, all samples were filtered on Macherey-Nagel CHROMAFIL syringe filter (O-20/15 MS type), with pores' size of 0.2  $\mu$ m. Molecular weight distributions were analysed by GPC with a differential refractive index detector (Waters 410) and a 600-mm column PL gel MixC 5 $\mu$ m. Chloroform was used as eluent at 1 mL min<sup>-1</sup> and 20  $\mu$ L of sample solution

were injected. Calibration of the GPC equipment was carried out with polystyrene standards.

Contact angles were measured at RT using a goniometre (Digidrop, GBX, France) equipped with a CCD camera (25 frames sec<sup>-1</sup>) and the GBX software (Windrop, GBX, France), on samples previously stored over silicagel. The dispersive ( $\gamma_s^d$ ) and polar ( $\gamma_s^p$ ) components of the solid surface tension were evaluated by applying the Owens-Wendt approach. For this purpose, four reference liquids were used: distilled water, diiodomethane (Acros organics, Geel, Belgium), ethylene glycol (Aldrich chemical, Milwaukee, USA) and glycerol (Merk, Darmstadt, Germany). To calculate the work of adhesion ( $W_{12}$ ) between the PHBV-based matrix ( $\gamma_1$ ) and the WSFs ( $\gamma_2$ ), the following harmonic-mean equation was used:

$$W_{12} = \frac{4\gamma_1^d\gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{4\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p} \quad (1)$$

Then, the interfacial tension ( $\gamma_{12}$ ) was calculated using eq. (4):

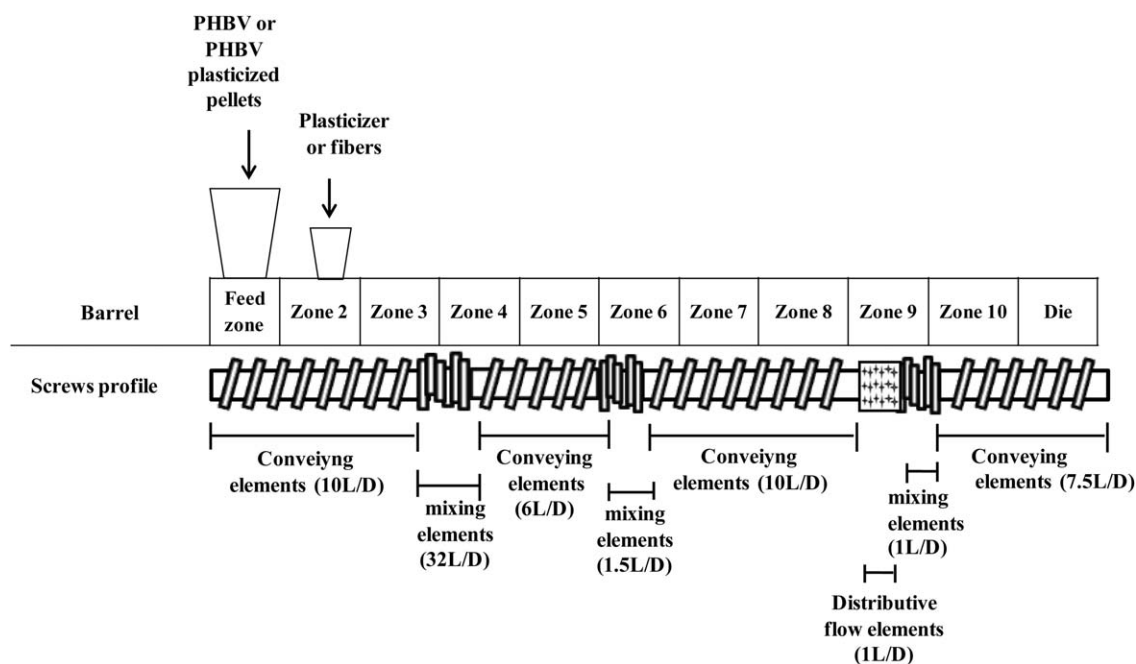
$$\gamma_{12} = \gamma_1 + \gamma_2 - W_{12} \quad (2)$$

Stress-strain measurements were performed at RT on dog-bone shaped specimens (4-mm wide) die-cut from both hot-pressed sheets (0.25-mm thick) using a tensile testing machine (Zwick BZ2.5/TN1S, France). Ten specimens of each sample were tested at a cross head speed of 10 mm min<sup>-1</sup> and a initial gage length of 40 mm. Average values and standard deviations are reported for the stress and strain at break ( $\sigma_b$  and  $\varepsilon_b$ ) and for the tensile Young's modulus ( $E$ ). Before tensile testing, samples were conditioned at RT for 48 h over P<sub>2</sub>O<sub>5</sub> under vacuum, to let PHBV develop a constant crystallinity degree.

Scanning electron microscopy (SEM) observations of cryo-fractured film surfaces were performed using a scanning electron microscope (SEM S-4500, Hitachi, Japan) with an acceleration voltage of 2 kV and a detector for secondary electrons. Films were previously frozen under liquid nitrogen, then manually fractured, mounted, and coated with gold/palladium on an ion sputter coater.

## RESULTS AND DISCUSSION

The first part of this work will focus on investigating and understanding mechanisms of external plasticization of melt processed PHBV. Three percentages (5, 10, and 20 wt %) of five substances will be tested, i.e., ATBC, GTA, and PEG with molecular weights of either 400, 1000, or 4000 g mol<sup>-1</sup> (Table I). The way the processing conditions were optimized by testing different extruder settings will be presented. The accent will be then put on deciphering results obtained from DSC analysis and tensile tests, allowing to conclude on the efficiency of external plasticization of PHBV. Based on tensile test results, one plasticizer percentage (10 wt %) was selected as suitable amount for the development of PHBV plasticized samples. In a second part, two plasticizers will be selected among previously tested formulations with the aim to further study the impact of the incorporation of WSF on the mechanical properties of plasticized materials in relation to their morphology and structure at the molecular and microscopic scales. The effect of plasticizer polarity on the reinforcing effect of WSF on PHBV matrix will be



**Figure 1.** Representation of the extruder settings used for the preparation of PHBV-based compounds.

also investigated by appositely selecting two substances with different polarity. A fiber content of 20 wt % will be used in the present study. Indeed, It has been shown in a preliminary study that given the objective to decrease the final cost of the material by using the highest possible fiber content, a filler content of 20 wt % was an optimal fiber content in terms of process-ability.<sup>9</sup>

#### Plasticization of PHBV

Unlike alternative methods to prepare blends at laboratory scale like solvent casting, melt processing is the conventional method for producing plastics in industry due to its large-scale applicability. In a first step, the processing conditions used to prepare plasticized PHBV-based blends were optimized by testing different extruder settings. At this stage, a special attention was given to the impact of additives on the polymer molecular weight. An efficient external plasticization is known to cause a decrease of polymer glass transition temperature ( $T_g$ ) as the consequence of the enhancement of the free volume (the volume fraction not occupied by the macromolecules), conferring further molecular mobility to the amorphous phase. This effect generally leads to melting point depression in plasticized samples.<sup>14,18,21,22</sup> Thus, to investigate if the additives used effectively act as plasticizers for PHBV, DSC analysis and tensile tests were performed on plasticized samples.

**Optimization of the Processing Conditions.** Different extruder settings were tested to obtain the optimal processing conditions. Temperature profile, screw speed, and feed position were varied until an extruded wire visible homogeneous and with a good melt strength was obtained. Figure 1 represents feed positions and one of the two screw profiles used, while Table II reports the temperature profile applied to extrude each sample. All PHBV samples were processed by assembling the screws as represented in Figure 1 and by setting the speed at 500 rpm, except in the case of the use of solid plasticizers like PEG-1000 and

PEG-4000 for which different extruder settings were used. Indeed, by applying the same temperature profile used for PEG-400, a high speed (900 rpm) was required to prevent accumulation of the plasticizer at the surface of the extruded polymer. Thus, in order not to expose the polymer to excessive shearing, which can cause macromolecular chain scission, the ten-zone heating profile was increased (Table II) and the speed was lowered at 300 rpm. Furthermore, the screws were assembled with reverse screw elements just after the mixing elements (1.5 L/D) to improve polymer and plasticizer mixing. To check if the mixing of PHBV and plasticizers could be improved, selected blends of PHBV containing 10 wt % of plasticizer were re-processed in the same correspondent conditions. Comparison of thermal and mechanical behaviour of samples subjected to either one or two extrusion cycles did not show significant differences, demonstrating that the conditions described above provided optimal mixing.

It is worth noting that extrusion of ATBC and GTA with the polymer required less effort such as a lower temperature profile to obtain an optimal mixing with respect to PEG processing. These observations can be indicative of a better miscibility of the hydrophobic additives (ATBC and GTA) with the hydrophobic polymeric matrix. Furthermore, as PEG molecular weight increases, the miscibility with the polymer decreases, as indicated by the higher temperatures and the different screw profile (Figure 1, Table II) applied.

All the extruded samples obtained were water-cooled, then cut in pellets and finally they were hot-pressed to obtain sample sheets (as described in “Preparation of plasticized composite materials” section). Upon samples storage, only in the case of PHBV formulated with either 20 wt % of PEG-400 or PEG-1000 exudation phenomena, i.e., migration of the plasticizer from the polymeric matrix surface resulting in a slimy sheet,

**Table II.** Temperature Profiles Used for the Extrusion of PHBV-Based Samples

Sample	Temperature (°C)									
	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Zone 8	Zone 9	Zone 10	Die
PHBV	180	180	180	170	170	160	160	160	150	140
PHBV/ATBC										
PHBV/GTA										
PHBV/PEG-400	180	180	180	180	180	180	170	170	160	160
PHBV/PEG-1000	190	190	180	180	180	180	170	170	170	160
PHBV/PEG-4000										
PHBV/WSF	180	180	180	170	170	160	160	160	160	150
Plasticized PHBV/WSF										

was observed, indicating that at this content the polymer was not fully compatible with those additives.

**Molecular Weight.** The impact of plasticizer addition (10 wt %) on the molecular weight of PHBV was evaluated by GPC (Table III). In the case of pure PHBV, the molecular weight was half decreased after the two shaping steps of extrusion and thermo-moulding (from 438,000 Da down to 219,300 Da). This molecular weight decrease was attributed to the sensitivity of PHBV towards thermal treatment as well as to hydrolysis reactions induced by the presence of potential residual water molecules.<sup>23</sup> However, even if such a decrease in the molecular weight of PHBV could induce changes in mechanical properties, it remains still high as compared to other conventional polymers. It is thus expected that such deterioration would not compromise the possibility of using thermally processed PHBV for food packaging applications. A similar decrease in the molecular weight of PHBV was noticed in the presence of hydrophobic ATBC and GTA plasticizers. In the case of PEG-400, an even more decrease in the polymer molecular weight was noticed (down to 164,000 Da), probably due to the fact that this highly hygroscopic substance brought to the system an

important quantity of free water available to induce hydrolysis reactions. However, it is worth noting that such a degradation of PHBV was not observed when either PEG-1000 or PEG-4000 were added, probably due to the sorption of residual water molecules by these hydrophilic substances, preventing their availability to react with PHBV.

**Thermal Properties.** The DSC curves (second heating scan, after sample quenching) of PHBV samples containing 10 wt % of plasticizer are shown in Figure 2. DSC results are reported in Table III, which also contains the degree of crystallinity ( $X_c$ , %) measured by WAXS analysis (Supporting Information Figure S1). A depression of PHBV glass transition temperature, as well as of its melting point was observed for the polymer blended with ATBC, GTA and PEG-400 (Table III). This behaviour indicates that these three additives act as plasticizers for the biopolyester, even the most hydrophilic ones such as PEG-400, by increasing the mobility of polymer chains in the amorphous phase. The strongest  $T_g$  reduction was observed for PHBV plasticized using ATBC ( $T_g = -14^\circ\text{C}$ ), suggesting that such apolar substance displayed the highest affinity towards PHBV, as already found in previous studies for citrate esters in other

**Table III.** Glass Transition Temperature ( $T_g$ ), Glass Transition Range ( $\Delta T_g$ ), Melting Temperature ( $T_m$ ), Crystallinity ( $X_c$ ), Molecular Weight ( $M_w$ ), and Dispersity ( $I_p$ ) of PHBV-Based Films Containing 10 wt % of Plasticizer (ATBC, GTA, PEG-400, PEG-1000, PEG-4000) and Composite Films Based on Plasticized PHBV (ATBC or PEG-400, 10 wt %) and WSF (20 wt %).

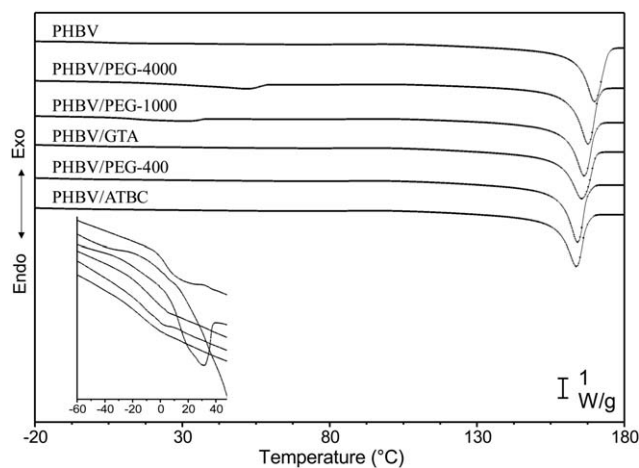
Sample	$T_g^a$ (°C)	$\Delta T_g$ (°C)	$\Delta C_p$ (J/g°C)	$T_m$ (°C)	$\Delta H_m^b$ (J/g)	$X_c^c$ (%)	$M_w^d$ (g mol <sup>-1</sup> )	$I_p$
PHBV (pellets as received)	-	-	-	-	-	-	438,000	2.5
PHBV	3	12	0.30	170	82	66	219,300	2.1
PHBV/ATBC	-14	29	0.41	164	86	68	227,000	2.0
PHBV/GTA	-8	23	0.38	166	89	67	225,900	2.5
PHBV/PEG-400	-12	24	0.45	164	91	67	164,000	2.0
PHBV/PEG-1000	-	-	-	166	87	64	348,400	1.3
PHBV/PEG-4000	-	-	-	168	85	65	404,800	1.3
PHBV/WSF	3	12	0.32	169	70	-	170,000	2.0
PHBV/ATBC/WSF	-14	28	0.42	163	94	57	222,000	1.6
PHBV/PEG-400/WSF	-12	23	0.41	161	95	-	74,500	1.9

<sup>a</sup> Typical standard deviation value of 1 to 2°C.

<sup>b</sup> Melting enthalpy normalized to PHBV weight fraction in the blend.

<sup>c</sup> Percentage of crystallinity ( $\pm 10$ ) determined by WAXS.

<sup>d</sup> Typical variation coefficient from 1 to 2%.



**Figure 2.** DSC curves (second heating scan after quench) of plasticized PHBV samples containing 10 wt % of plasticizer.

polyesters such as PHB<sup>22</sup> or PLA.<sup>14,23</sup> Such results were confirmed by contact angle measurements highlighting a highest affinity of PHBV for ATBC (contact angle value of  $43 \pm 4^\circ$ ) than for PEG-400 (contact angle value of  $73 \pm 2^\circ$ ) (Table IV). In the case of PHBV/PEG-400 blend, the reduction in  $T_g$  was probably linked not only to the addition of the plasticizer but also to the PHBV breakdown products, resulting from the previously observed PHBV hydrolysis, that could also act as plasticizers because of their low molecular weight.<sup>23</sup> Furthermore, the detection of only one  $T_g$  in the PHBV blends with ATBC, GTA or PEG-400 suggested a complete miscibility of the samples at 10 wt % of plasticizer content.

A different behaviour was observed for both PHBV/PEG-1000 and PHBV/PEG-4000 blends. DSC curves of such samples display an endothermal baseline shift around  $-60^\circ\text{C}$  and a small endotherm located in a wide temperature range (from  $-20$  to  $40^\circ\text{C}$  for PHBV/PEG-1000 and up to  $60^\circ\text{C}$  for PHBV/PEG-4000) that are respectively associated with the glass transition and melting of PEG plasticizer (Figure 2). Such wide endotherms hide the glass transition of PHBV amorphous phase, preventing its measurement. The presence of such thermal events suggested that PEG-1000 and PEG-4000 blends were not completely miscible with the biopolyester and that a pure PEG crystalline phase separation occurs in these blends. A degree of miscibility was however attested by the slight melting point depression observed for these blends (Table III). Considering that PEG-400 forms a completely miscible blend (only one  $T_g$  detected), it is clear that misci-

bility decreases, as expected, with increasing molecular weight.

The normalized melting enthalpy values of PHBV in all plasticized blends (Table III), did not significantly change with respect to pure PHBV. This means that the polymer crystallized to the same extent in the blends as in the pure state. This behaviour was confirmed by WAXS analysis. Indeed, the degree of crystallinity ( $X_c$ ), calculated from X-ray diffractograms (Supporting Information Figure S1), of all plasticized samples were similar to that of pure PHBV (Table III).

The mentioned phenomenon of exudation during storage concerning PHBV blends with 20 wt % of either PEG-400 or PEG-1000 clearly reflects the poor compatibility of these plasticizers with PHBV. It can be supposed that at high content, the hydrophilic substances that display higher affinity for themselves than for the PHBV matrix, led to the formation of clusters that tend to more easily exude. This behaviour is clearly observable in the case of the liquid PEG-400 and the waxy PEG-1000 plasticizers that gave rise to slimy sheets upon storage; whereas no exudation, but phase segregation through crystallization of pure plasticizer as previously discussed, was observed for PEG-4000 which is solid at RT. The other chemicals (ATBC and GTA), which showed an efficient plasticization effect, i.e., good miscibility with PHBV through polymer-plasticizer interactions, did not provide any evidence of exudation over the range of tested plasticizer contents.

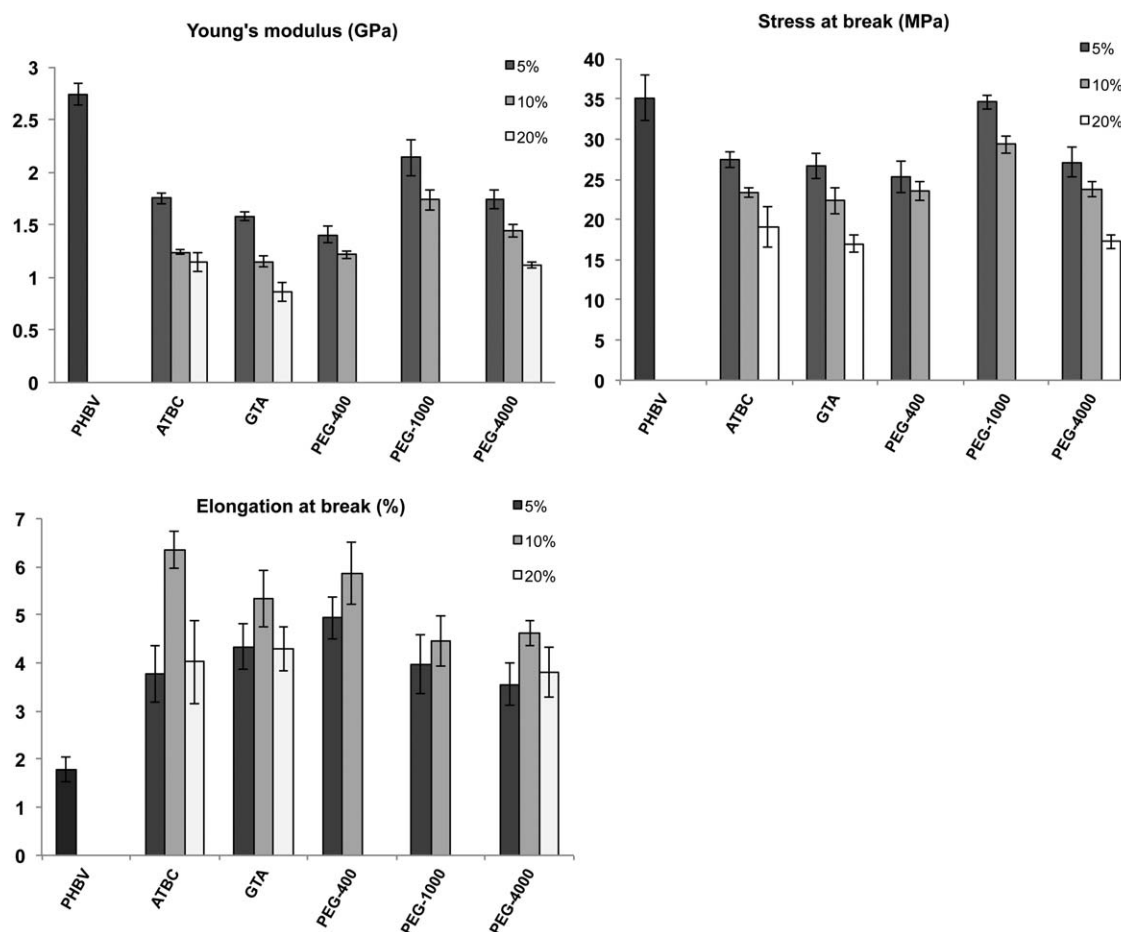
**Mechanical Properties.** The ultimate expected output of additive incorporation to PHBV was to reduce polymer brittleness. Mechanical properties of PHBV samples were assessed by tensile stress–strain measurements. Young's modulus ( $E$ ), tensile strength ( $\sigma_b$ ) and elongation to break ( $\epsilon_b$ ) of the melt processed PHBV with 5, 10 or 20 wt % of additive are shown on Figure 3. If compared to the neat matrix, a significant plasticizing effect was noticed for all the formulations, as highlighted by an increase in the strain at break together with a decrease in both the tensile strength and the Young's modulus (Figure 3). Even in the worst case (5 wt % of PEG-4000), the elongation at break was at least doubled, from  $1.8 \pm 0.3\%$  for the neat matrix up to  $3.6 \pm 0.4\%$  for the plasticized material.

Logically, the plasticizing effect was globally more pronounced for the lowest molecular weight molecules (ATBC, GTA and PEG-400). But surprisingly, no big difference was noticed as a function of plasticizer polarity, showing that the origin of the increase polymer chain mobility, i.e., either by external plasticization (in the cases of ATBC and GTA) or by polymer molecular weight

**Table IV.** Contact Angle Values ( $^\circ$ ) of Liquids of Reference on Composite Constituents

Sample	Water	Glycerol	Ethylene glycol	Diiodomethane	ATBC	PEG-400
WSF <sup>a</sup>	$33 \pm 5$	$91 \pm 2$	$48 \pm 4$	$48 \pm 3$	$24 \pm 1$	$54 \pm 2$
PHBV	$100 \pm 2$	$93 \pm 4$	$80 \pm 7$	$61 \pm 3$	$43 \pm 4$	$74 \pm 1$
PHBV/ATBC	$97 \pm 2$	$77 \pm 2$	$74 \pm 2$	$52 \pm 4$	-	-
PHBV/PEG-400	$73 \pm 5$	$58 \pm 5$	$75 \pm 1$	$32 \pm 25$	-	-

<sup>a</sup>From 26.



**Figure 3.** Tensile properties of plasticized PHBV samples with 5, 10, or 20% (w/w) of additive content. The error bars represent the standard deviation values.

decrease (in the case of PEG-400), did not matter. The highest elongation was obtained with the use of only 10 wt % of ATBC, which is the most apolar substance and which was demonstrated to display the best plasticizing effect with PHBV, with the achievement of  $6.4 \pm 0.4\%$  of elongation at break. Globally, analysing the tensile properties exhibited by blends with different plasticizer contents, the amount of 10 wt % allowed to obtain a good balance between decreasing of Young's modulus and tensile strength and increasing of elongation to break (Figure 3).

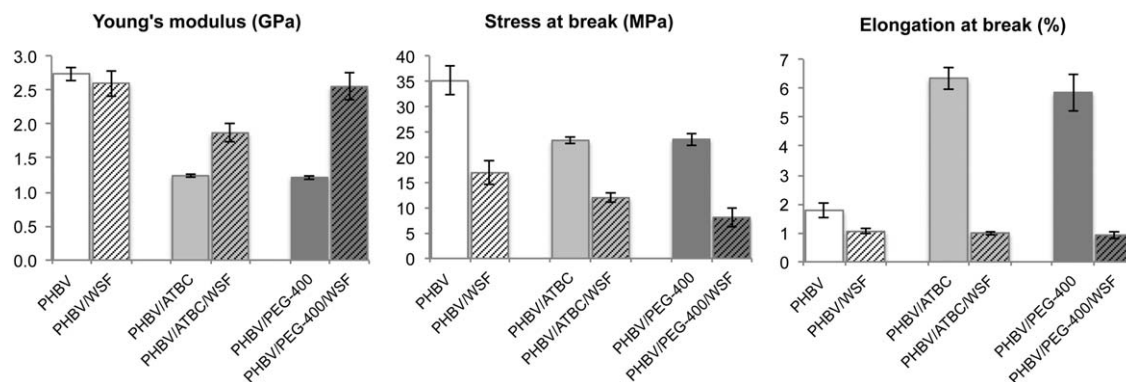
However, it is worth noting that the increase in PHBV ductility was not drastic, in agreement with previous results on commercial PHB and PHBV blended with plasticizers by either solvent casting<sup>12,14,16</sup> or extrusion processing.<sup>18</sup> Such a limited deformability improvement could be ascribed to the high degree of crystallinity of PHBV, resulting in a high proportion of amorphous zones that interact with crystalline zones and are consequently not easily accessible to the plasticizer, and therefore in a small proportion of "free" amorphous zones able to be plasticized. Furthermore, given that the glass transition temperature of virgin PHBV ( $3^\circ\text{C}$ ) is well below the testing temperature ( $20^\circ\text{C}$ ), the amorphous phase is already in a mobile state when evaluating the mechanical properties. Thus, the increase in the mobility of the PHBV amorphous phase achievable due to  $T_g$  lowering by external plasticization can be only limited. Both the

low "free" amorphous phase content and the  $T_g$  location with respect to the tensile test temperature, are likely explain the impossibility to induce dramatic changes in PHBV mechanical properties by external plasticization.

To conclude on this part, the efficiency of a plasticizer is dependant on its chemical structure, molecular weight and concentration. When comparing the thermal and mechanical behaviour of all samples, the best results were obtained by using 10 wt % of ATBC as plasticizer. For this reason, PHBV/ATBC blend was logically selected as plasticized matrix for the following development of composite materials. PEG-400, which is a strong hydrophilic substance, was also selected to investigate the impact of the polarity of the plasticizer on the reinforcing effect of (hydrophilic) WSFs on (hydrophobic) PHBV matrix.

#### Impact of WSFs on the Structure/Functional Properties Relationships of Plasticized PHBV-Based Materials

Composite films based on plasticized PHBV (PHBV/ATBC and PHBV/PEG, 90/10 w/w %) and 20 wt % of WSF were prepared by melt extrusion, following by thermo-pressing. PHBV-based composites were subjected to stress-strain measurements performed as previously described for plasticized samples and results are shown on Figure 4.



**Figure 4.** Mechanical properties of composite PHBV-based films filled with 20% (w/w) of WSFs. For comparison purposes, the corresponding PHBV-based matrix is also reported. The error bars represent the standard deviations.

In the case of non-plasticized materials, the introduction of WSF led to an increased brittleness of materials (significant decrease in both the strain and stress at break), together with a decreased toughness (decrease in the energy at break). Several concomitant phenomena have been validated to explain this effect: a poor adhesion at the fiber/matrix interface, preventing a good transfer of load from the continuous polymer phase to the dispersed fibers, the presence of macroscopic defects such as holes, and a degradation of the polymer molecular weight induced by the presence of WSFs. In parallel, the Young's modulus remained quite stable, mainly due to the similarity of PHBV and WSFs Young's modulus values.

The addition of high modulus fibers in plasticized PHBV significantly increased PHBV Young's modulus, leading to a rigidity similar to the one of non-plasticized materials. However, the elongation at break was dramatically decreased in the composites, neutralizing the increase of this parameter by the addition of the plasticizers. The stress at break of plasticized PHBV-WSF films was also significantly decreased with respect to the reference blends without WSF, with a decrease all the more pronounced in the case of materials plasticized with PEG-400.

According to previous literature, the following assumptions, that will be deeply discussed below, could be proposed to explain the decrease of both the elongation and the stress at break of plasticized PHBV when adding WSFs: (i) a decrease in the polymer molecular weight, induced by the conjugated presence of plasticizer and WSFs, (ii) a preferential localization of plasticizer at the fiber/matrix interface, (iii) the occurrence of macroscopic defects in the materials induced by the presence of WSFs, and (iv) a poor adhesion at the fiber/matrix interface, preventing a good transfer of load from the continuous polymer phase to the dispersed fibers. These different assumptions have been refuted or validated by structural and morphological analysis, from the molecular to the macroscopic scale.

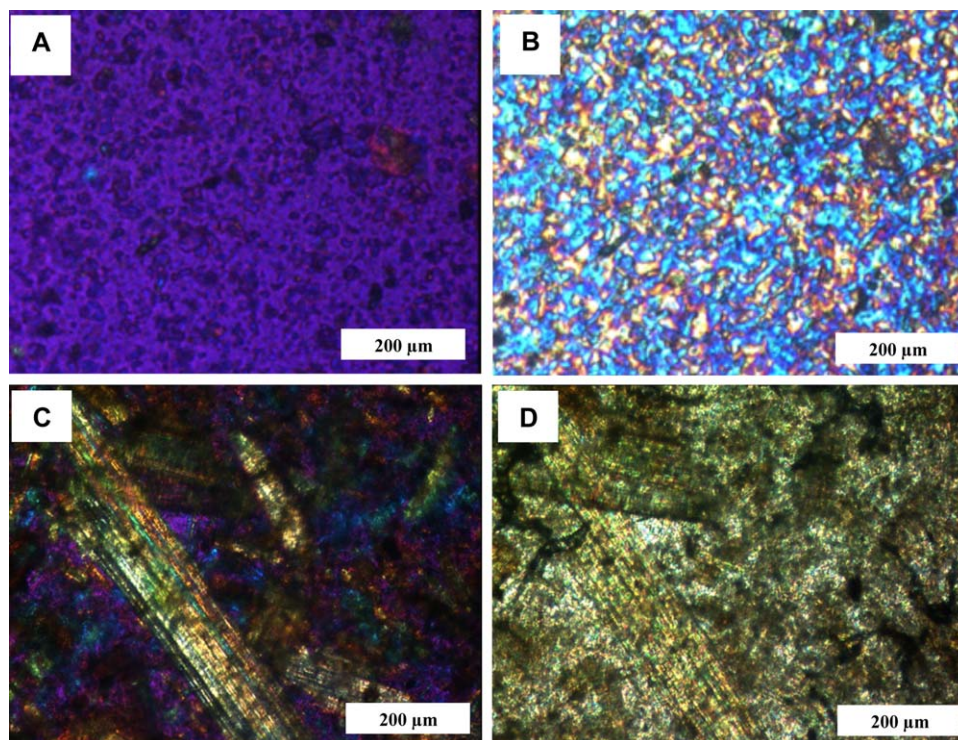
The first assumption proposed to explain the degradation in ultimate tensile properties, i.e., a decrease in the polymer molecular weight, has been checked by assessing the evolution of the PHBV molecular weight in plasticized composite materials by GPC (Table III). In the case of PHBV/WSF composites, the degradation of the molecular weight (from 220,000 Da

down to 170,000 Da) was attributed to mechanical friction phenomena induced by the presence of WSFs, as well as to hydrolysis and trans-esterification reactions that could be favoured by the presence of wheat straw degradation products, e.g., water, alcohols<sup>24</sup> and carboxylates.<sup>25</sup> In the case of materials plasticized with ATBC, no change in molecular weight was noticed after the addition of fibers, showing that ATBC allowed to «stabilise» the polymer, i.e., hindering PHBV degradation reactions that could be induced by the presence of WSFs. This phenomenon is more likely due to a decrease in the molten viscosity during the mixing step, thus limiting mechanical friction. In the case of PEG-400, the degradation of the polymer was all the more important in the presence of fibers, with the Mw decreasing down to 74,500 Da for PHBV-PEG-400/WSF composites (Table III). It can be concluded from this analysis that this first assumption, i.e., a decrease in PHBV molecular weight to explain the degradation in ultimate tensile properties, could only be validated in the case of PHBV/PEG-400/WSF systems, but not for PHBV/ATBC/WSF materials.

As already largely reported for plasticized materials filled with cellulose-based fibers, the second assumption proposed to explain the increased brittleness would be an «anti-plasticizing» effect of WSFs induced by a preferential migration of the plasticizer at the fiber/matrix interface, especially if the plasticizer displays a better affinity for the fibers than for the polymer matrix, as it is here the case. Indeed, for either ATBC or PEG-400, the contact angle values of the plasticizer with the WSFs is lower than the one with the PHBV matrix (Table IV). Such a phenomenon would be demonstrated by a significant increase of the  $T_g$  value as compared with the neat plasticized PHBV matrix. However, DSC analysis highlighted that  $T_g$  values for plasticized PHBV containing or not WSF did not significantly differ (Table III), thus allowing to conclude that this hypothesis does not hold true.

Morphological analysis by microscopic observations revealed that the degradation of ultimate properties induced by the incorporation of WSFs can also be due to the presence of micro-cracks in the materials (Figure 5). Figure 5 displays polarized optical microscopy (POM) pictures of the unfilled ATBC plasticized matrix (A et B) and the respective material





**Figure 5.** POM pictures of PHBV/ATBC (A et B) and PHBV/ATBC/WSF (C and D) materials at either the molten state (A and C) or the crystallized state (B and D). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

filled with 20 wt % of WSFs (C and D) at both the molten state (A and C) and the crystallized state (B and D). WSFs were quite easily identifiable, as some of their components appeared to be birefringent, cellulose crystals in all likelihood. The formation of cracks within the PHBV-based matrix was observed during the crystallization process (black lines on the pictures) for composite materials, but not for the neat matrix, even in the case of plasticized materials. These cracks were attributed to constraints generated by the presence of fillers within the semi-crystalline polymer matrix. Similar observations were done for materials plasticized with PEG-400.

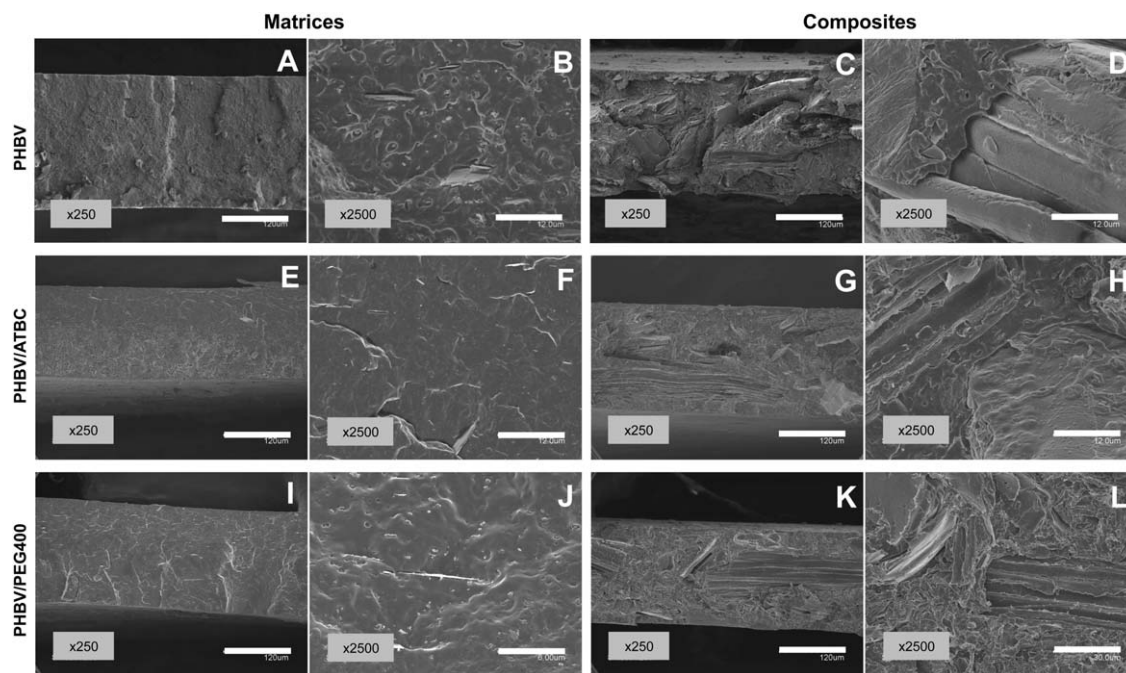
Finally, the last important phenomenon that could be responsible for mechanical failure would be a poor fiber/matrix interface, thus neutralizing the positive plasticizing effect. Table V presents the surface energy of each material constituents and the interfacial tension ( $\gamma_{12}$ ) between WSFs and the different PHBV-based matrices. Low values of interfacial tension are an indicative of a high compatibility between constituents, reflect-

ing that the affinity of WSFs will be better for PHBV/PEG-400 than for PHBV or PHBV/ATBC (Table V). Differences in theoretical adhesion deduced from contact angle measurements were further investigated by SEM observations of cryo-fractured surfaces of composite films (Figure 6). Some nicks and small platelets are visible on the cryo-fractured surface of the neat matrix. They are assumed to be boron nitride crystals, used as a nucleating agent in Tianan's PHBV. By contrast, composite materials displayed rough fractured surfaces due to the presence of WSFs. No significant difference was observable between non-plasticized composite materials or composite materials plasticized with either PEG400 or ATBC. In all the cases, no fibers aggregates were observed, but some pull-outs were clearly visible. At high magnification, interfacial gaps between the matrix and the fibers were also visible for all composites, even in the presence of plasticizers. Those observations highlighted a relatively poor adhesion between the fibers and the matrix, which was ascribed to the more hydrophilic nature of the fibers as

**Table V.** Solid Surface Tension of Composite Constituents [Dispersive Component ( $\gamma_S^d$ ), Polar Component ( $\gamma_S^p$ ) and Total Surface Tension ( $\gamma_S$ )], Theoretical Interfacial Tension ( $\gamma_{12}$ ) Between Wheat Straw Fibres and the Different PHBV-Based Matrices

Sample	$\gamma_S^d$ (mN m <sup>-1</sup> )	$\gamma_S^p$ (mN m <sup>-1</sup> )	$\gamma_S$ (mN m <sup>-1</sup> )	$\gamma_{12}$ (mN m <sup>-1</sup> )
WSF <sup>a</sup>	21.1 ± 4.5	23.4 ± 0.6	44.5 ± 0.5	-
PHBV	27.3 ± 3.1	0.5 ± 0.3	27.8 ± 3.1	22.7
PHBV/ATBC	31.7 ± 1.5	0.6 ± 0.2	32.3 ± 1.4	23.8
PHBV/PEG-400	34.4 ± 4.5	5.0 ± 1.3	39.4 ± 3.4	15.1

<sup>a</sup>From 26.



**Figure 6.** SEM pictures of cryo-fractured surfaces of PHBV, PHBV/ATBC and PHBV/PEG-400 films and of their respective composites filled with 20 wt % of WSFs.

compared to the hydrophobic matrix. This poor fiber/matrix adhesion would be in favour of the degradation of the mechanical properties.

## CONCLUSION

In this work, biodegradable and bio-based composites constituted of the bacterial copolyester PHBV as polymeric matrix and WSFs as fillers were developed for food packaging applications. Biodegradable and food contact substances, i.e., ATBC, GTA, and PEG at different molecular weights, were incorporated by melt extrusion to overcome the brittleness of materials. By exploring the useful melt processing conditions to prepare the materials, an optimal mixing of the components was achieved. The impact of external plasticization on the thermal and mechanical behaviour of PHBV was investigated, as well as the combined effect of the addition of WSFs.

Effective plasticization was assessed by PHBV glass transition depression observed for all blends analysed. The strongest  $T_g$  reduction was observed for PHBV plasticized using ATBC showing this plasticizer the best affinity with the polyester as confirmed by contact angle measurements. Mechanical properties results showed that external plasticization led to decrease polymer rigidity and to slightly improve PHBV flexibility. In particular, the use of 10 wt % of ATBC allowed to obtain a good balance between decreasing of Young's modulus and tensile strength and increasing of elongation at break, thus providing a good matrix material for the preparation of composites.

However, the incorporation of lignocellulosic fibers in the plasticized matrix led to an increase of PHBV Young's modulus and to a decrease of both elongation at break and tensile strength of

the polymer. Thereby, the increase of PHBV deformability through plasticization was neutralized by the addition of the WSFs. Those results suggest a relatively poor adhesion between the fibers and the matrix, which was ascribed to the more hydrophilic nature of the fibres as compared to the hydrophobic matrix. Indeed, when a good adhesion is established between the composite components, the load applied is transferred from the polymeric phase to the fibers causing a reinforcement of the material. The poor compatibility of PHBV with the WSFs was confirmed by SEM observations of cryo-fractured surfaces of composite films that revealed the presence of interfacial gaps between the matrix and the fibers. Further investigations aiming at overcoming the lack of adhesion at the fiber–matrix interface (e.g., surface chemical modification) could lead to the development of PHBV composites in which the fibers not only serve to lower polymer cost but also to improve PHBV mechanical properties. To conclude on the suitability of using PHBV/WSF biocomposites as food contact materials for food packaging applications, it should be first necessary to assess their chemical safety through both overall and specific migration tests, to produce composite trays at pilot scale and to compare their properties to benchmark products. These tasks have been planned in the frame of the European project EcoBioCAP ([www.ecobiocap.eu](http://www.ecobiocap.eu)) and will be the object of future publications.

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