Biodegradable Blends Prepared from Poly(3-hydroxybutyrate) and Wood/cellulose Fibers

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In this study, blends of biodegradable matrix as poly(3-hydroxybutyrate) (PHB) and fibers provided by renewable resources were prepared by a melt blending method. Improvement of the compatibility between fibers and polymer was studied using coupling agents: maleic anhydride (MA) respectively, succinic anhydride (SA). Mixtures with two types of fibers were investigated in terms of microscopy, torque, density, tensile strength, melting temperature and contact angle. It is found that the mechanical properties of PHB with cellulose fibers blends were better than PHB and wood fibers.

Keywords: polyhydroxybuthyrate, wood fiber, cellulose fiber, coupling agent, blend

The new researches are focused on producing of biodegradable plastics/materials. Poly-3-hydroxybutyrate (PHB) is 100% biodegradable (after a few weeks in soil and other environments) and can be produced from renewable resources. PHB is highly crystalline, brittle and the price is very high. To reduce the quantities of polymeric material required, incorporating filler or fibers with biopolymers is an effective method of reducing effective end-product costs. The biopolymeric matrix is also ecofriendly [1].

In recent years, the use of natural fibers as filler in the manufacture of fiber-biopolymers composites has been of great interest to many researchers. Natural fibers are biodegradable and so can be suitably blended with PHB without losing their biodegradable properties.

PHB biocomposites with wood fiber [2], flax [3, 4], recycled cellulose fiber [1], pineapple fiber [5] and other natural fibers [6-12] have been reported.

These fibers have many advantages, such as low density, high specific strength and modulus, ease of fiber surface modification and wide availability. The main disadvantages of natural fibers in blends are the lower processing temperatures allowable, incompatibility between hydrophilic natural fibers and hydrophobic polymers and potential moisture absorption of the fibers [13-14]. This also leads to a weak interfacial bonding with the polymer matrix leading to the segregation of the two materials during polymerisation, affecting the mechanical properties. The leak of interfacial interactions leads to porosity, internal strains and environment degradation.

Therefore, modification of the fiber and/or polymer matrix is a main area for obtaining good composite properties [15].

Evidences showed tensile and flexural strength were increased by improving interfacial adhesion through fiber surfaces modification [16], fiber surfaces treatment by plasticizer [17, 18] and silane [3, 19]. The modification of wood fiber surfaces has been the subject of a number of reviews and texts [20-23].

In order to improve the affinity and adhesion between wood fibers and thermoplastic matrices in production, chemical coupling agents have been employed [19, 24, 25]. Coupling agents are substances that are used in small quantities to treat a surface so that bonding occurs between

it and other surfaces, e.g., wood and thermoplastics [26]. Coupling agents in wood fiber composite normally have bi- or multifunctional groups in their molecular structure. These functional groups, such as urethane structure (-N=C=O) of isocyanates, [-(CO) O-] of maleic anhydrides (MA), respectively succinic anhydrides (SA) and (Cl-) of dichlorotriazine derivatives, interact with the polar groups [mainly hydroxyl groups (-OH)] of cellulose and lignin to form covalent or hydrogen bonding [27].

Anhydrides such as MA and SA are popular coupling agents in wood fiber composite. SA and PHB have two functional groups, i.e., carboxylate groups (-COO-), which can link wood fiber through esterification or hydrogen bonding. But MA is an α, β-unsaturated carbonyl compound, containing one carbon-carbon double bond (C=C) and two carboxylate groups (-COO-). This conjugated structure greatly increases the graft reactivity of the carbon-carbon double bond on the heterocyclic ring with the polymer matrix through the conjugate addition under a radical initiator [28] resulting in crosslinking or strong adhesion at the interface. However the molecular chain of MA is much shorter than that of PHB matrix and wood fibers.
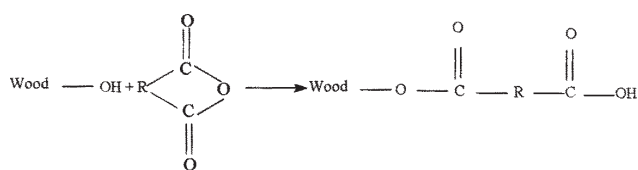

Fig.1. Esterification reactions for wood fiber reacted with maleic anhydride (when R is –HC=CH) or succinic anhydride (when R is –CH2– CH2–)

The esterification reactions of MA and SA with wood are shown in figure 1.

The hydroxyl groups of wood are most often the reactive sites. The MA-modified natural fiber showed much lower reactivity than the natural fiber SA modified. This was probably due to the higher activation energy for reaction of MA compared to SA.

The aims of the research reported here were to obtain blends based on PHB and wood/cellulose fibers, to determine the effect of filler type on improving mechanical,

Table 1

COMPOSITION OF EVALUATED FORMULATIONS (% vol.)

Formulation [a]	Mixture	Filler content	Resin content
B	PHB	0	100
BRMA-5	PHB-Cellulose Fiber 5% -MA	5	94
BRMA-10	PHB-Cellulose Fiber 10% -MA	10	89
BRMA-20	PHB-Cellulose Fiber 20% - MA	20	79
BLMA-5	PHB-WF 5% - MA	5	94
BLMA-10	PHB-WF 10% - MA	10	89
BLMA-20	PHB-WF 20% - MA	20	79
BRSA-5	PHB-Cellulose Fiber 5% - SA	5	94
BRSA-10	PHB-Cellulose Fiber 10% - SA	10	89
BRSA-20	PHB-Cellulose Fiber 20% - SA	20	79
BLSA-5	PHB-WF 5% - SA	5	94
BLSA-10	PHB-WF 10% - SA	10	89
BLSA-20	PHB-WF 20% - SA	20	79

[a] B = pure PHB; R = Cellulose Fiber; WF = Wood Fiber; MA = maleic anhydride; SA = succinic anhydride

thermal and rheological characteristics of the formulations performed.

Improving compatibility between fiber and PHB was studied using coupling agents like maleic anhydride (MA) and succinic anhydride (SA). The study shows also the effect of fiber content on properties of blends.

Experimental part
Materials

Poly(3-hydroxybutyrate)(PHB), type P226 was used as the polymer matrix. The material has a density of 1.17 g/cm^3 and melting point of 173 ^{0}C. Prior blending, PHB was dried in the oven at 80 ^{0}C, for 2 h.

Cellulose fibers type EFC 1000 were supplied by CARTIF, Spania. The properties of the fibers are: water content = 4.5 ± 0.1(%); wax = 0.9 %; lignin = 28.7 ± 0.1%; holocellulose = 87.3 ± 1.3 %; free –OH content on the surface = 322 ± 14 mg KOH/g and aspect ratio = 6.7.

Wood fibers type LSL 200/150, were supplied by CARTIF, Spania. These show the following properties: water content = 8.7 ± 0.1 %; free –OH content on the surface = 230 ± 15 mg KOH/g and aspect ratio = 5.4.

The fibers were used as the discontinuous phase in the mixtures. All fibers with sizes of 200 μm, were untreated.

Coupling agents as maleic anhydride (MA) and succinic anhydride (SA)had both purity ≥ 99%.

The fibers were treated with 7 % (weight) of MA, respectively SA. Prior to surface modified and blending, the fibers were dried in the oven for at least 4 h at 105 ^{0}C to ensure that moisture content was below 0.5 %. The fibers treated were then oven-dried at 105 ^{0}C for 6 h.

PHB and wood/cellulose fibers treated were initially weighed and melted according to the various fiber contents indicated in table 1. The composition of each formulation is also shown.

Methods

The formulations were prepared using a BRABENDER Plastograph, under a mixing temperature of 180 ^{0}C for 10 min and a rotation speed of screws of 40/70 rpm.

Preparation of test specimens

After blending, the samples were pressed into thin plates by a laboratory press type POLYSTAT 200 at the following conditions: temperature: 160 ^{0}C, pressing time: 5 min and pressure of 200 bar. Plates with the thickness of 1 mm were obtained.

Conditioning

Prior to performing mechanical measurements, the specimens were conditioned at (50 ±5) % relative humidity for at least 40 h at (23 ±1) ^{0}C, in a humidity-controlled room type BTH80/-20 according to ISO 291.

Characterization
Blend morphology

Specimens were analyzed with optical microscope (BX 41 OLYMPUS Live view digital SLR camera E-330 with special software Quick Photo Micro 2.3).

The micrographs of samples were taken at X20 magnification to identify the dispersion of fibers in polymer matrix.

Melting temperatures

Melting temperatures were determined using a differential scanning calorimeter (METTLER TOLEDO, DSC 823e). The sample sizes were approx. 5-7 mg, and the samples were sealed in 40μL aluminum crucibles. The measurement was done in a range from 20-200°C with a 10°C/min temperature rate.

Density

The density was calculated from the resulting volume (length x width x thickness) and the sample mass.

Tensile strength

Measurements of tensile strength were performed on a DINAMOMETER FP 10, according to ISO 527-3. A minimum of five samples was tested and the results were averaged. The tensile strength is the maximum load divided by the original cross sectional area. The specimens of the previous conditioned samples were used and the measurements were conducted at a 500 mm/min crosshead speed.

Contact angle measurements

Contact angle measurements were carried out at room temperature using the sessile drop technique, with the equipment type CAM 101 with a high-speed digital video camera type C200-HS KSV Finlanda to record the drop image. Water at room temperature was used for this purpose. Sessile drops were deposited using a Hamilton syringe of 5 μL directly on the surface films.

Results and discussion
Blend morphology

The micrographs of blends with different fibers volume percentage are shown in figure 2. Morphology of the polymer blends plays an important role in the properties of the final product, especially their mechanical properties depend on it.

The results showed that the fillers were found to be well distributed in BRSA-5 (b), BRSA-10 (c), BRSA-20 (d), BRMA-10 (f), BRMA-20 (g), BLSA-5 (h), BLSA-10 (i), BLSA (j), BLMA-5 (k), BLMA-10 (l), BLMA-20 (m) blends. BRMA-5 (e) is evidence to see an uneven distribution of Retenmaier cellulose fibers because of poor melt homogeneity.

In PHB/Cellulose fibers blends, the maximum size of filler is 200 μm, whereas in the PHB/Wood fibers blends it became 130 μm.

Torque measurements

All the blends showed lower torque than PHB (sample code B). Torque value of blends decreased with increasing filler content and mixing time, and approached a stable value when the mixing time was greater than 8 min, suggesting that good mixing had occurred after this time.

Initially, the torque responses of BLMA and BRMA blends were significantly lower than those of BLSA and BRSA blends at the same filler content (5, 10 and 20 %). Then,
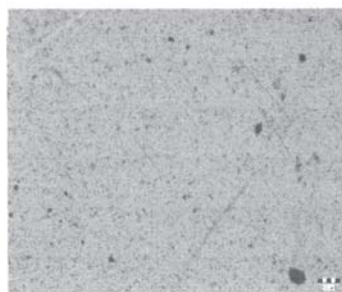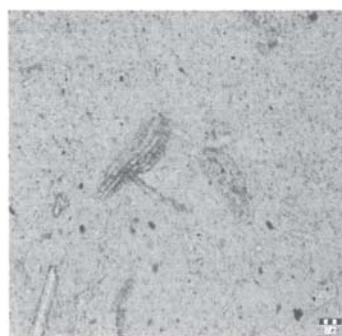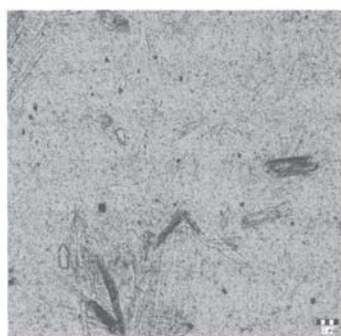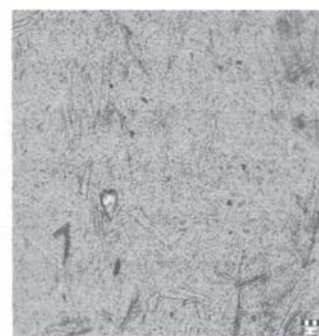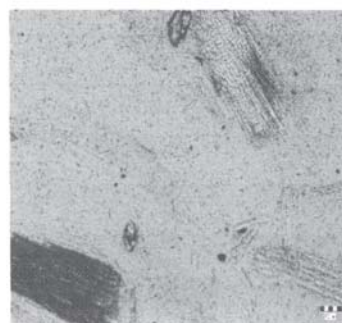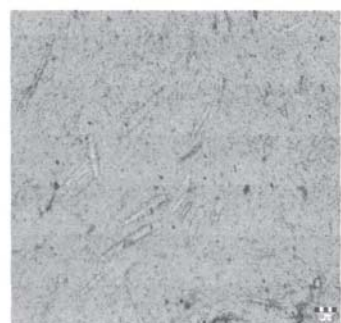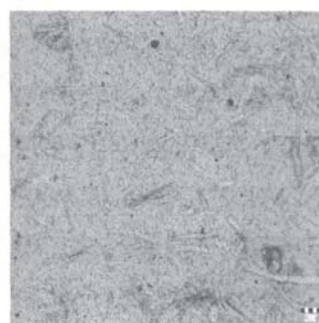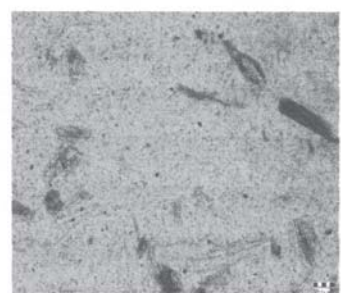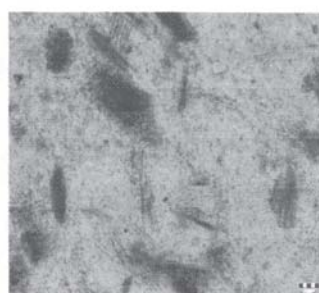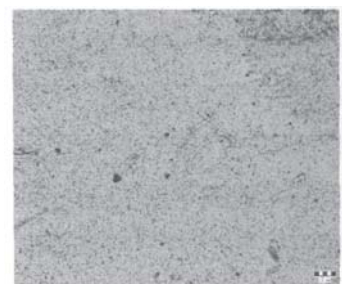

Fig. 2. The optical microscopy of the PHB/wood fiber and PHB/cellulose fiber blends
(a) PHB; (b) BRSA-5; (c) BRSA-10; (d) BRSA-20; (e) BRMA-5; (f) BRMA-10;
(g) BRMA-20; (h) BLSA-5; (i) BLSA-10;
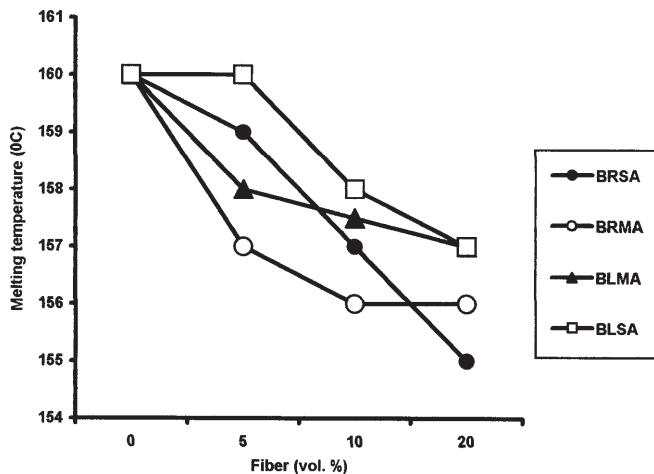(j) BLSA-20; (k) BLMA-5; (l) BLMA-10; (m) BLMA-20

Fig. 3. Melting temperature vs. fiber content for PHB/wood fiber and PHB/cellulose fiber blends

Fig. 4. Effect of filler content on densities for PHB/Wood fiber and PHB/Cellulose fiber blends

after 4 min, the improved rheological behavior of BLSA and BRSA blends is attributed to the conformational change of the wood fiber and cellulose fiber molecules [29] caused by formation It was reported that the melt viscosity of treated wood fibers also decreased with increasing molecular weight of the ester group [30]. Another possible cause is that wood fibers/cellulose fibers behave as filler within the molten PHB matrix.

The main contribution for the torque value is from the molten PHB. When the content of wood fibers and cellulose fibers increases, expansion and stretch of BLMA and BRMA matrices also increases, making movement of molten PHB easier at higher wood fibers contents, and resulting in the decrease in torque.

Final torque decreased with increasing filler content for BLSA and BRSA blends because the viscosity of molten wood fiber/cellulose fiber is lower than that of molten PHB.

Measurement of melting temperature (Tm)

Figure 3 shows the melting temperatures by differential scanning calorimetry (DSC) for PHB/Wood fiber and PHB/Cellulose fiber blends at different fiber contents (0, 5, 10 and 20 %).

We found that for all blends performed, the BRSA blend shows the smallest Tm.

For BRMA-5, BRMA-10, BLMA-5, BLMA-10, BLMA-20, BRSA-5, BRSA-10, BRSA-20, BLSA-10 and BLSA-20 blends, a decrease in the melting temperature (by about 1-5 °C) was observed with increasing filler content. This is due to the lower melt viscosity of wood fibers/cellulose fibers compared to that of PHB. These results were in accordance with the corresponding torque measurements, which showed that these blends had a lower melt torque than PHB. Studying the behaviour of cellulose fibers blends with different coupling agents at melt is showing that the blends based on PHB, Rettenmeier fibers and SA present the lower melt temperature. This means that BRSA blends are processed more easily than BRMA blends. Also, between the blends based on PHB, wood fibers and different coupling agents, is no important difference of the melting temperature, only at 5% wood fiber content the BLMA mixture shows a decrease with 2 °C than BLSA-5 mixture.

For BLSA-5 blend it is obvious the same Tm as pure PHB. This was probably caused by the hydrophilic character of wood fiber which would lead to poor adhesion with the hydrophobic PHB or homogeneity of fiber with matrix. Therefore, difficulty in arranging the polymer chain, increases due to fibers prohibiting movement of the polymer segments. The researchers who studied the
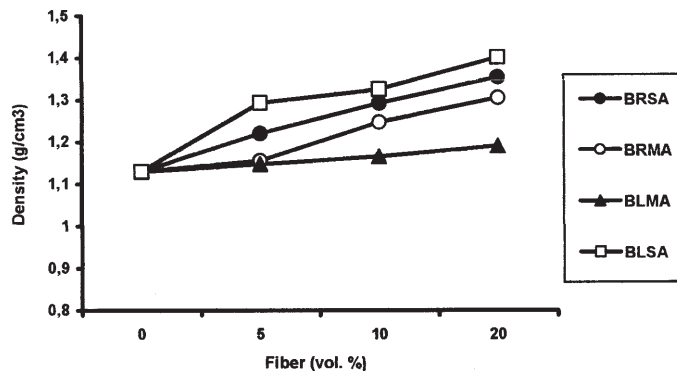
properties of wood fibers blended with polyethylene-octene elastomer, reported similar phenomena [30].

Densities of blends

Figure 4 shows the effect of fiber content on densities for PHB/wood fiber and PHB/cellulose fiber blends. The density values are important in order to know the weight of the blends to be produced as a design parameter.

It is obvious that density for all blends performed increased with increased fiber content. The higher density is observed for BLSA and BRSA blends. BLMA and BRMA blends show a decrease in density than BRSA and BLSA blends, for the same fiber content.

The increase in density of the PHB/fiber blends with the addition of fiber indicates a good dispersion of the polymer-based matrix material within the wood fibers.

Tensile strength

Figure 5 shows the effect of filler content on the tensile strength for PHB/wood fiber and PHB/cellulose fiber blends.
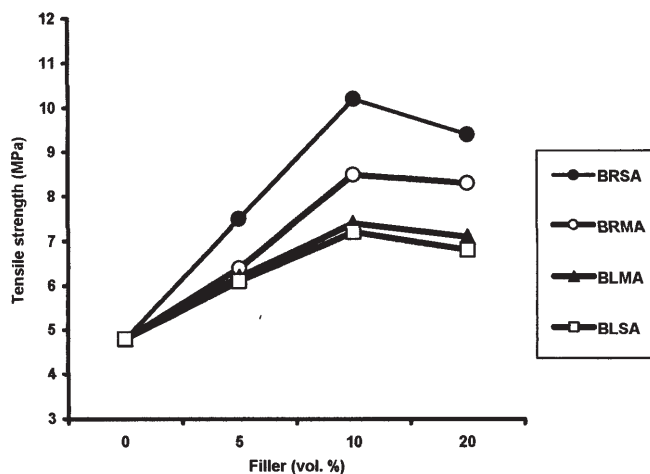

Fig. 5. Effect of filler on the tensile strength for PHB/wood fiber and PHB/cellulose fiber blends

The tensile strength indicates improvement of this property when cellulose fibers or wood fibers are incorporated. This property depends on the easeness of stress transfer between the phases present in the blend, higher stress transfer leading to higher strength.

In all blends performed, tensile strength increase has been observed with increase of fiber content. This might be attributed to the decrease in melting temperature of mixtures with incorporation of cellulose/wood fibers. The stress transfer is more evident between PHB and cellulose
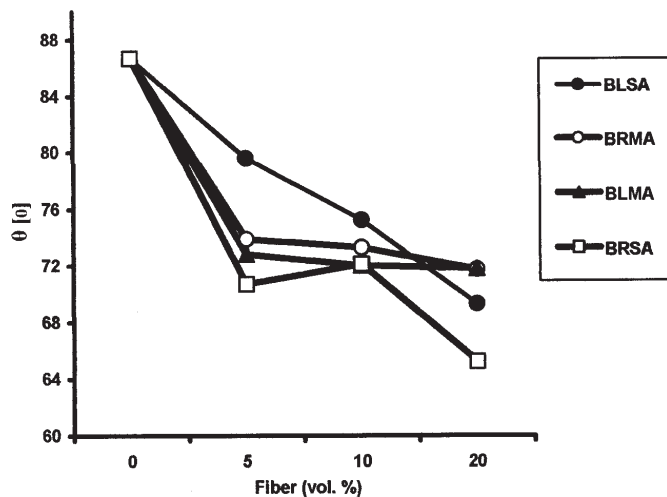
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Fig.6. Contact angle against filler content for PHB/ wood fiber and PHB/cellulose fiber blends

fibers than between PHB and wood fibers. It was reported that the acetic anhydride grafted PHB and blended with wood fibers improved the tensile strength of PHB/wood fibers [31]. The increased bonding between fiber and matrix effectively transfers the applied load to the fiber through the matrix, resulting high tensile strength.

For BRSA, BRMA, BLSA and BLMA blends, the tensile strength increased continuously and markedly as fiber content increased to a content of 10 %. The blends containing 20 vol. % wood fibers and cellulose fibers gave the lowest tensile strength at break because the higher filler content increased the phase size.

The decline in tensile strength is observed to a content of 20 % filler. This effect is due to the amount of glassy material present in the blends and this make them more brittle.

It is evident that the mechanical properties strongly depend on the dispersion and phase size of fiber in the polymer matrix.

Contact angle measurements

The variation of contact angle for blend compositions was given in the figure 6.

It can be observed that the blends possess smaller contact angle compared to neat PHB due to hydrophilic nature of fibers. The decrease of contact angle of water is prominent to BLSA-5, BLSA-10, BLSA-20, BRSA-5, BRSA-20, BLMA-5, BLMA-10, BLMA-20, BRMA-5, BRMA-10, BRMA-20 blends. Lowest contact angle shows BRSA-20 blends probably due to the ratio aspect of the cellulose fibers which is too lower than the wood fibers. The less affinity of the blends indicates the reduction in the hydrophilic nature of the blends due to the sizes of fibers.

For mixtures made in the laboratory there are observed two phenomena: the decrease of contact angle for BLSA, BLMA, BRMA, BRSA-5, BRSA-20 samples that is due to high hydrophilic character of fillers and on the other hand, the slowly increase of contact angle value for BRSA-10 may be due to homogeneity and to increase in surface roughness mixtures. Grundke and colab. [32] reported similar phenomena.

Conclusions

The properties of blends made from PHB reinforced with treated cellulose/wood fibers have been studied.

The results indicate that the cellulose fibers or wood fibers enhance the mechanical properties when these fillers are blended with PHB.

The torque measurements for all blends performed have shown that the viscosity of molten wood fiber/cellulose fiber is lower than that of molten PHB.

The melting temperature decreased with increasing filler content for all blends.

The blends containing PHB and cellulose fibers exhibit enhanced mechanical properties compared with those containing PHB and wood fibers, especially regarding tensile strength.

The results presented in this study suggest that cellulose fibers are superior to wood fibers in terms of physico-mechanical properties. The fineness and large aspect ratio cellulose fiber were probably the major reasons.

Due to large size of the cellulose fibers is observed lower values of contact angle compared with wood fibers. Moreover, the increasing in surface roughness of polymer surface has influence the contact angle.

This research has investigated only a few important issues of PHB polymers and natural fillers. The findings from this study will provide a framework for the future development of trials at laboratory and pilot scale in order to obtain items such as tomato yarn, packaging for agriculture by extrusion and molding injection technologies.

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