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Mechanical Characterization of Mango Peel Flour and Biopolypropylene Composites Compatibilized with PP-g-IA

J. Gomez-Caturla, L. Quiles-Carrillo, J. Ivorra-Martinez, D. Garcia-Garcia, R. Balart

***Abstract*—**The present work reports on the development of wood plastic composites based on biopolypropylene (BioPP) and mango peel flour (MPF) by extrusion and injection molding processes. PP-g-IA and dicumyl peroxide (DCP) have been used as a compatibilizer and as a free radical initiator for reactive extrusion, respectively. Mechanical and morphological properties have been characterized in order to study the compatibility of the blends. The obtained results showed that DCP and PP-g-IA improved the stiffness of BioPP in terms of elastic modulus. Moreover, they positively increased the tensile strength and elongation at break of the blends in comparison with the sample that only had BioPP and MPF on its composition, improving the affinity between both compounds. DCP and PP-g-IA even seem to have certain synergy, which was corroborated through Field Emission Scanning Electron Microscopy (FESEM) analysis. Images showed that the MPF particles had greater adhesion to the polymer matrix when PP-g-IA and DCP were added. This effect was more intense when both elements were added, observing an almost inexistent gap between MPF particles and the BioPP matrix.

***Keywords*—**Biopolypropylene, compatibilization, mango peel flour, wood plastic composite.

I. Introduction

IN recent years, society is becoming more aware about the environmental problems related to the extremely extended use of fossil based polymers, such as an increase in the carbon footprint and wastes ascribed to the production process of those polymers. This has led society and scientific communities to search for more environmentally friendly materials, such as wood plastic composites, which are comprised of a natural origin polymer and a natural organic filler. Biopolymers present very similar properties to their petrochemical equivalent [1].

Wood plastic composites (WPC) have become quite popular. When inserting natural fillers in polymer matrices, their cost is reduced and at the same time their mechanical, chemical and thermal properties are modified [2]. Their environmental value is also improved. There are several agroforestry and food industry wastes that have been studied as natural fillers for fabricating WPC, such as argan shell [3], almond shell flour [4], pomegranate peel [5], pinecone powder [6] or orange peel [7], among others. These fillers are introduced into polymeric matrices in order to obtain WPCs. In this sense, polypropylene (PP) is one of the most interesting polymers available. More importantly, the bio-based version is this propylene, BioPP, results more interesting due to its environmental added value.

BioPP is a semicrystalline thermoplastic polymer that presents good overall mechanical properties in terms of resistance and ductility and it can be obtained from biomethanol [8]. Being a polyolefin, it has a similar chemical structure to that of high-density polyethylene (HDPE), which is also highly non-polar. The hydrophobicity of this polymer is one of the main drawbacks when developing WPCs, as its affinity with polar lignocellulosic fillers, which are rich in hydroxyl groups, becomes very weak. This fact makes the resulting polymer/ filler blends to have poor mechanical properties due to a lack of compatibility and adhesion between the particles and the matrix.

There are several methods to improve the compatibility of natural lignocellulosic with hydrophobic polymers. Some of them include surface modification of the filler, such as acetylation or benzoylation, which block the hydroxyl groups in the filler [9]. Other methods imply the use of compatibilizing agents, normally copolymers, that are compatible both with the filler and the matrix. Some commonly used copolymers are polyolefins, most often polyethylene and PP, grafted with maleic anhydride functionalities, giving birth to PE-g-MA and PP-g-MA, respectively. Maleic anhydride (MA) increases the polarity of the non-polar polymers, making them more affine for lignocellulosic particles [10]. Itaconic acid (IA) compatibilizer has gained popularity recently, as it is an environmentally friendly alternative to MA. It can be obtained from citric acid and acts the same way as MA, increasing the polarity of non-polar polymers. Some studies have grafted PP with IA by reactive extrusion (REX) processes, using DCP as an initiator, in order to obtain PP-g-IA, which has proven to be an effective compatibilizer in PP/Clay nanocomposites [11] and in PP/EVOH blends [12].

Mango (*Mangifera indica L.*) is one of the most popular fruit crops, regarding worldwide production [13]. Such production means a great number of wastes, which include the peel, the stone, and the kernel. Mango kernel is a great source of starch [14], while mango peel contains a great number of phenolic compounds [15]. In terms of biorefinery and circular economy, mango is one of the most promising wastes to be used to develop new environmentally friendly WPC with additional interesting properties and at a reduced cost in comparison to pure biopolymers.

J. Gomez-Caturla*, L. Quiles-Carrillo, J. Ivorra-Martinez, D. Garcia-Garcia, and R. Balart are with the Technological Institute of Materials (ITM), Universitat Politècnica de Valencia (UPV) Plaza Ferrándiz y Carbonell 1, 03801 Alcoy, Spain (*corresponding author, e-mail: jaugoca@epsa.upv.es) luiquic1@epsa.upv.es, juaivmar@doctor.upv.es, dagarga4@epsa.upv.es, rbalart@mcm.upv.es

In the present work, the main objective is to develop a WPC based on a polymeric matrix of BioPP and MPF as filler. The main drawback of the study is to overcome the compatibility problems between the filler and the matrix, as BioPP is non-polar and MPF is a highly polar lignocellulosic component. In order to sort this problem out, PP grafted with IA has been produced by REX with DCP and used as a compatibilizer. Extrusion and injection molding processes have been used to make formulations of WPC with BioPP, MPF, DCP and PP-g-IA. The mechanical properties of the composites have been evaluated by means of the tensile test and impact strength test, and they have been verified by means of a morphological study by FESEM.

II. Materials and Methods

A. Materials

BioPP was supplied by Natureplast (Caen, France).

Osteen variety mangoes were purchased from Alcoy's local market, in Spain. Mangoes were first peeled and dried at 45 ºC for 48 hours in a dehumidifier (MCP Vacuum Casting System, Lubeck, Germany). Afterwards, the peels were grounded in a ZM 200 centrifugal mill (Düsseldorf, Germany) at 8000 rpm while being sieved through a 250 µm filter. Thus, MPF was obtained.

IA was supplied by Acros Organics (122810010) and DCP was supplied by Sigma Aldrich (1003031352).

B. Compatibilizer Production

In order to obtain PP-g-IA, IA was grafted onto BioPP following the methodology of Pesetskii et. al. [16]. BioPP and IA were first dried at 40 ºC for 48 hours in a dehumidifying dryer MDEO, DCP was used as initiator. Afterwards, IA and DCP were blended with BioPP at 1 and 0.2 wt.%, respectively. Then, the mixture was introduced in a twin-screw extruder from Construcciones mecánicas Duptra, S.L. (Alicante, Spain); with a diameter of 25 mm and a length-to-diameter ratio of 24. The temperature profile in the extruder was 175-195-195-195 ºC and the residence time was four minutes.

C. Extrusion and Injection of BioPP+MPF Composites

In order to remove the residual moisture, the prepared PP-g-IA, MPF and BioPP were dried at 40 ºC for 48 hours in a dehumidifying dryer MDEO. They were then blended according to the concentrations shown in Table I, and afterwards extruded in a twin-screw extruder from Construcciones Mecánicas Dupra, S.L. (Alicante, Spain). The profile temperature was 150-155-160-165 ºC. Finally, the materials were turned into pellets using an air knife unit.

TABLE I
Composition of the BioPP+MPF Composites

Symbol	BioPP (wt.%)	MPF (wt.%)	DCP (phr)	PP-g-IA (phr)
BioPP	100	0	0	0
BioPP+MPF	70	30	0	0
BioPP+MPF+PP-g-IA	70	30	0	3
BioPP+MPF+DCP	70	30	1	0
BioPP+MPF+PP-g-IA+DCP	70	30	1	3

The pellets were introduced into a Meteor 270/75 injection molding machine from Mateu & Solé (Barcelona, Spain) in order to obtain standard samples. The clamping force used was 75 tons, cavity filling and cooling times were 1 and 10 s, respectively; and the temperature profile from the hopper to the injection nozzle was 155-160-165-170 ºC.

D. Characterization of the Samples

1) Mechanical Characterization

The tensile properties of the composites were determined using a universal testing machine ELIB 50 from S.A.E Ibertest (Madrid, Spain). The cross-head speed was set to 5 mm/min and a 5-kN load cell was used following ISO 527-1:2012.

Impact strength was studied using a Charpy pendulum (1 J) from Metrotec S.A. (San Sebastián, Spain). Notched injection molded samples of dimensions 80 x 10 x 4 mm were used (V-notch with 0.25 mm radius) following ISO 179-1:2010. All experiments were performed at room temperature and at least 5 times.

2) Morphology Characterization

In order to study the morphology of the materials, the fractured surface of each one of the samples was observed by FESEM in a ZEISS ULTRA 55 microscope supplied by Oxford Instruments (Abingdon, United Kingdom). The samples were first sputtered with a gold-palladium allow in an EMITECH sputter coating SC7620 model from Quorum Technologies, Ltd. (East Sussex, UK). The acceleration voltage was 2 kV.

III. Results

A. Mechanical Properties

The mechanical properties of BioPP+MPF composites were studied in order to evaluate the effect of PP-g-IA, DCP and MPF in the mechanical performance of BioPP and to analyses the compatibilizing effect of both PP-g-IA and DCP. In this sense, Fig. 1 gathers the variability of the elastic modulus and tensile strength (Fig. 1 (a)), elongation at break (Fig. 1 (b)) and impact strength (Fig. 1 (c)).

Regarding tensile properties, neat BioPP shows values of elastic modulus, tensile strength and elongation at break of around 1950, 18 MPa and 40%, respectively. These are typical values for this polymer, and are indicative of a ductile behavior, but with certain resistance and stiffness when compared to other more ductile polymers such as polyethylene [3]. The values obtained are similar to the ones obtained by Zhou et al. [17]. When MPF particles are introduced into the matrix it can be clearly seen how all tensile values considerably diminish. Elastic modulus and tensile strength go down to 1750 and 12 MPa, while elongation at break decreases to 16%. These general poor mechanical properties are probably due to a very bad compatibility between BioPP and MPF. This is because of the difference in polarity between both components. BioPP is a practically non-polar polymer, as its structure is only formed by C-H bonds, with very little difference in electronegativity [18]. On the other hand, MPF is a lignocellulosic filler, that possesses cellulose, hemicellulose, pectin, lignin and general phenolic

compounds [15], with hydroxyl groups that give it high polarity. Thus, both elements present low affinity for each other, as BioPP lacks functional groups to react with MPF. In this sense, Haq et al. [19] observed a similar effect in composites of mango wood powder and virgin PP. Yadav et al. [20] also observed this trend In PP composites with wood flour. The addition of PP-g-IA into the blend improves all tensile properties compared to the previous sample. Elastic modulus and tensile strength increase up to 2250 and 13.5 MPa, respectively. Elongation at break improves up to 19%. This increase seems to indicate that PP-g-IA acts as an effective compatibilizer between BioPP and MPF, improving the adhesion of the particles into the matrix and increasing their affinity. This is due to the reactivity that the IA functional group gives to BioPP, making it more affine for lignocellulosic particles. This phenomenon was also observed by Poletto [21], who increased the stiffness of PP with wood flour composites using PP-g-IA. Interestingly, the incorporation of DCP into the BioPP+MPF composites leads to a generally higher mechanical response of the composite compared to the PP-g-IA sample. Elastic modulus and tensile strength increase up to 2300 and 14 MPa, and elongation at break augments up to 28%, which is a 47% increase related to the BioPP+MPF+PP-g-IA sample. This improvement is mainly ascribed to the crosslinking effect of DCP, which helps to compatibilize the polymer chains with the MPF particles. This is because DCP induces free radical formation during REX on both components, which leads to a direct improvement in the cohesion of the blend and an increase in the general mechanical response. Kuruvilla et al. [22] reported how DCP was able to induce free radical reaction between low density polyethylene (LDPE) and cellulose fibers. Also, other studies reported an increase in tensile strength in polyethylene composites with pandanwangi fibers produced by REX with DCP, observing an increase in the tensile strength with the content in DCP [23]; thus, corroborating the positive effect of DCP over compatibilization and mechanical properties. Lastly, the sample with PP-g-IA and DCP in combination presents the best tensile properties, with an elastic modulus of 2350 MPa, a tensile strength of 14.5 MPa, and an elongation at break of almost 30%. These values are quite close to those of neat BioPP, and even this blend is superior in terms of elastic modulus, which stands for stiffness. It can be inferred that there is certain synergy between PP-g-IA and DCP that improves the compatibilization effect and increases the affinity and adhesion between the polymeric chains of PP and the lignocellulosic particles of MPF, obtaining better mechanical properties than using both compatibilizers on their own.

Regarding impact strength, a considerable variation with respect to neat BioPP can be appreciated with the incorporation of MPF, PP-g-IA and DCP. Neat BioPP shows a value of approximately 10 kJ/m^2, which is indicative of a certain ductile polymer, while the rest of the samples are clearly inferior to this value, as it is presented in Fig. 1 (c). The BioPP+MPF sample shows an impact strength value of 2.8 kJ/m^2. Thus, it means that MPF strongly embrittled the material and made it more fragile. This is ascribed to the poor adhesion and dispersion of the particles in the polymer matrix, therefore forming aggregates that induce stress concentration points that reduce the toughness of the material.

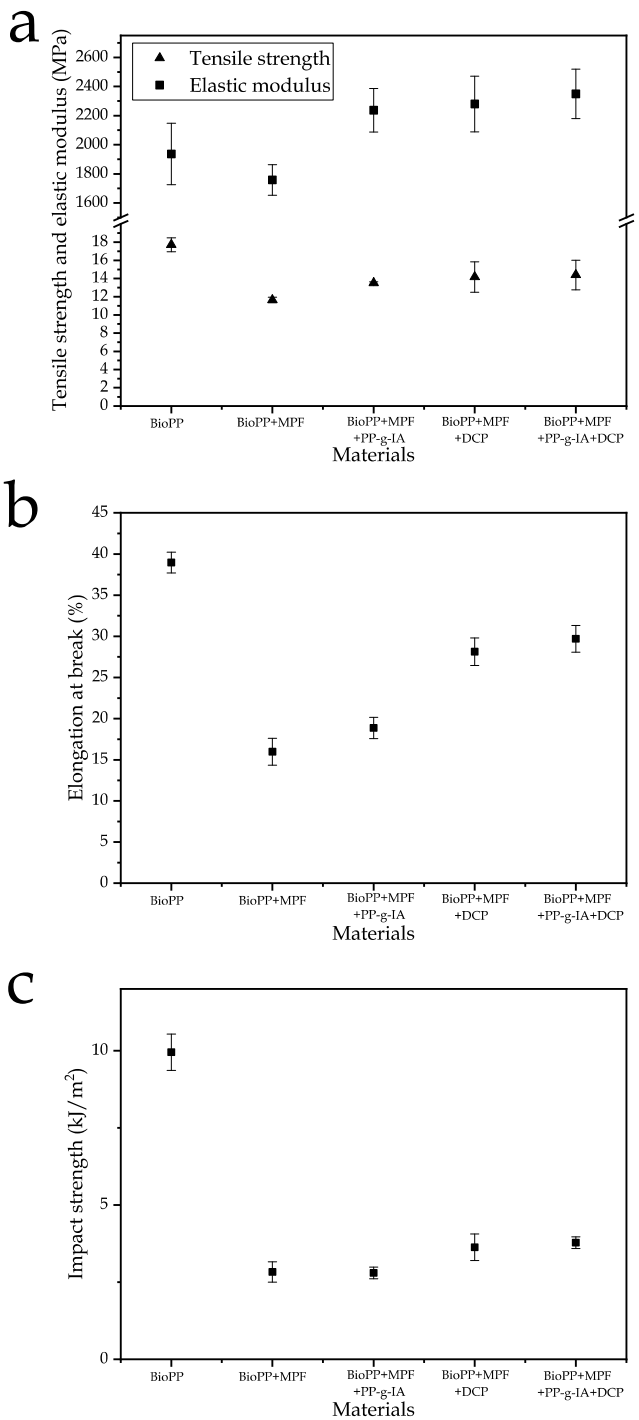

Fig. 1 Mechanical properties of the BioPP+MPF composites: (a) tensile strength and elastic modulus; (b) elongation at break; (c) impact strength

Quiles-Carrillo et al. [24] reported a clear decrease in impact strength of polylactide (PLA) when incorporating almond shell particles. The addition of PP-g-IA to the blend does not change impact strength, which means that in spite of improving the adhesion between BioPP and MPF, it does not prevent

lignocellulosic particles from aggregating. On the contrary, DCP does improve up to a certain point impact strength. Values of 3.6 and 3.8 kJ/ m^2 are obtained for the sample with DCP and the sample with DCP and PP-g-IA, respectively. This improvement is probably ascribed to the ability of DCP to induce free radical formation between BioPP and MPF, which increases both the adhesion of the particles into the matrix, and the dispersion of the particles all over the matrix, preventing the formation of aggregates up to a point. The study of Sari et al. [23] showed the ability of DCP to increase impact strength in pandanwangi fiber/PE composites.

B. Morphological Properties

The morphological properties of the composites are closely related to their mechanical response due to the dependence of the latter on the internal structure. Studying the morphology of the samples helps to support the mechanical property findings. In this context, Fig. 2 shows the FESEM images of fractured impact strength samples at 500X magnification.

Fig. 2 (a) is representative for the neat BioPP sample, which shows a characteristic rough and wrinkled surface of a ductile polymer [24], as it was observed in the mechanical properties section. Fig. 2 (b) corresponds to the BioPP+MPF sample. MPF particles can be clearly seen in the image, and it can be observed that there is little adhesion between the polymer matric and the lignocellulosic particles, due to the great gap that exists between both compounds, as well as some holes that are representative for particles that fell off after fracture. As it was commented in Subsection *A*, this is ascribed to the poor affinity between both elements due to a great difference in polarity. This morphological effect was also observed by Nagmouchi et al. [25] in olive stone flour (OSF)/PP composites, where there existed gaps between the particles and the matrix.

The incorporation of PP-g-IA into the blend is shown in Fig. 2 (c), and at first glance it can be seen how there are fewer holes all around the sample and that the gaps between the existing particles and the matrix are narrower than in the previous sample, which is indicative of an improvement in adhesion and affinity between BioPP and MPF, corroborating the results obtained in the mechanical section. This improvement is due to the dual functionality of PP-g-IA; PP chains interact by chemical affinity with BioPP, while IA functionality reacts with the hydroxyl groups in cellulose, hemicellulose, pectin, lignin and the phenolic compounds in MPF [26].

The sample with DCP is illustrated in Fig. 2 (d). It can be seen how in this case, the adhesion of the particles in the matrix is even greater than in the PP-g-IA sample, as it can be identified by the narrow gap between the fillers and the matrix and by the fact that the particles are embedded into the matrix. This is the reason why the mechanical properties of this sample were superior to the previous one, demonstrating how the crosslinking effect of DCP supports the increase in affinity of BioPP and MPF particles.

The final sample, BioPP+MPF+PP-g-IA+DCP is observed in Fig. 2 (e). In this case, it can be clearly seen how there are very few holes in the surface, the particles are almost completely embedded in the polymer matrix, and the gap between the particles and the surrounding matrix is almost inexistent. These facts are clear indicators about an increase in affinity between BioPP and MPF, and demonstrate the superior mechanical properties exhibited by this sample in tensile and impact tests, compared to the rest of the blends. Again, all this points out to a certain synergy between PP-g-IA and DCP.

All these results perfectly match the values and the mechanical behavior shown in Subsection *A*, thus demonstrating the positive effect that PP-g-IA and DCP exert over the affinity of the blends.

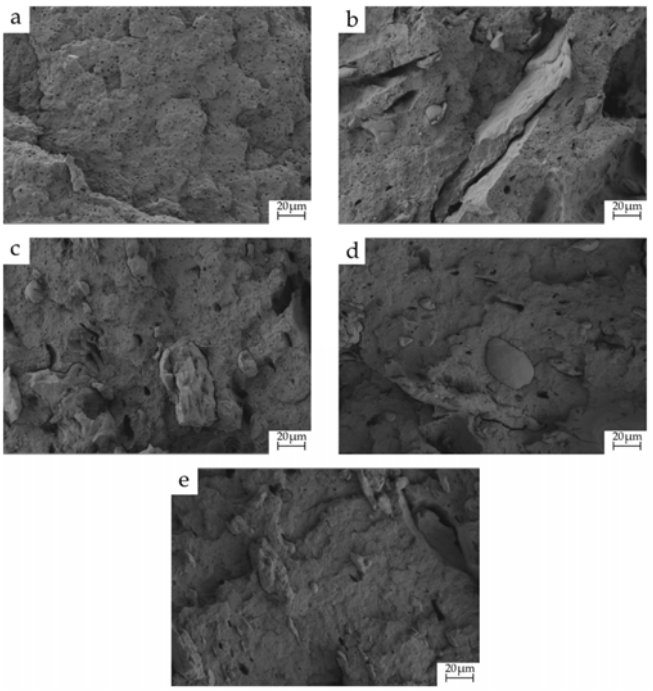

Fig. 2 FESEM images of the BioPP+MPF composites: (a) BioPP; (b) BioPP+MPF; (c) BioPP+MPF+PP-g-IA; (d) BioPP+MPF+DCP; (e) BioPP+MPF+PP-g-IA+DCP

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