Research article

Manufacturing and characterization of highly environmentally-friendly composites with polylactide matrix and mango kernel seed flour

Jaume Gomez-Caturla^{1*}, Diego Lascano¹⁰, Nestor Montanes¹⁰, Rafael Balart¹⁰, Franco Dominici²⁰, Debora Puglia²⁰, Luigi Torre²⁰

¹Technological Institute of Materials (ITM), Universitat Politècnica de València (UPV), Plaza Ferrándiz y Carbonell 1, 03801 Alcoy, Spain

²Dipartimento di Ingegneria Civile ed Ambientale, University of Perugia, UdR INSTM, Strada di Pentima 4, 05100 Terni (TR) Italy

Received 7 July 2022; accepted in revised form 5 October 2022

Abstract. This work reports on the development of polylactide (PLA)/mango kernel seed flour (MKSF) composites combined with tributyrin (TBN) and triacetin (TCN) as plasticizers. Thus, wood plastic composites (WPC) are obtained by extrusion and injection-molding processes. The solubility, mechanical, morphological, thermal, colorimetric, water absorbance, flowability, and disintegrability properties are evaluated. The ductility of the PLA+MKSF composite is improved by the plasticizing effect of TBN and TCN (10 phr (parts per hundred resin) each). Elongation at break is increased from 4.4 up to 9.5 and 8.3%, respectively. The theoretical solubility analysis supports the good miscibility between PLA with TBN and TCN (relative energy difference (RED) values of 0.86 and 0.73, respectively) deduced from the mechanical performance. Field emission scanning electron microscopy (FESEM) images also corroborate the mechanical findings, where a decrease in the presence of voids in the PLA matrix suggests certain compatibility between MKSF and TBN, and TCN. Differential scanning calorimetry (DSC) and dynamic-mechanical-thermal analysis (DMTA) results show that the plasticizers decrease the glass transition temperature and the melting temperature of PLA, thus improving its ductility. Thermogravimetric analysis (TGA) results indicate that the thermal stability of the composite is slightly decreased due to the relatively high volatility of the plasticizers, while MKSF does not affect this matter. The composites exhibit excellent biodegradability, presenting more than 90% of disintegration in compost soil conditions in 12 weeks. Finally, MKSF provided the composites with a wood-like dark brown color and with high water absorbance.

Keywords: polymer composites, biodegradable polymers, mechanical properties, thermal properties, plasticizer

1. Introduction

Wood-plastic composites (WPC) have risen as an alternative for products made of wood. Those materials have a visual appearance similar to that of wood. The main difference is that they are composed of a thermoplastic polymeric matrix (such as polyethylene and polypropylene, among others), which is loaded with fillers from the wood industry (sawdust, fibres, flour) [1, 2]. In the first approach, the manufacturing

*Corresponding author, e-mail: jaugoca@epsa.upv.es © BME-PT of WPC implies the incorporation of wood-based elements. However, in the last years, other fillers have been proposed as alternatives for wood-derived fillers, either lignocellulosic fillers or mineral fillers (talc, calcium carbonate, among others), or agroforestry waste flours [3, 4]. The latter have gained quite a popularity due to the significant amount of generated waste (skin, calyx, seeds) [5–7]. As a result of their low cost and abundance, the incorporation

of fillers from food byproducts and agroforestry wastes has become a technical and viable solution in the plastics industry. Moreover, the materials obtained from them possess balanced properties and advantageous environmental efficiency [8]. The use of biofillers presents several advantages, such as facilitating or accelerating the disintegration of material; reducing the amount of used polymer, and the revalorization of a lignocellulosic waste, all these promoting the transition from a traditional linear economy to a circular economy and thus, remarkably reducing the carbon footprint [9, 10]. Rojas-Lema et al. [11] used wastes from persimmon peel to manufacture composite materials with a biopolyethylene matrix. Moreover, they studied the effect of silanization treatments and esterification with palmitic acid to enhance compatibilization between the filler and the polymer matrix. They reported interesting results compared to the conventional use of a maleic anhydride-grafted copolymer of polyethylene as a reference compatibilizer. It was also proved that this waste provided additional features to composites with polyethylene. In particular, it was observed that the persimmon peel wastes gave tremendous antioxidant activity to the polyethylene matrix. The compatibility between the polymeric matrix and the filler was also increased. The esterification with palmitic chloride treatment improved the hydrophobic behaviour of the materials, diminishing their water absorption capacity.

Tropical crops like mango have become one of the preferred products for consumers in the European market. This is because this fruit is considered exotic, has attractive colours, delicious flavour, and a comfortable odour [12]. Moreover, it presents a high nutritional value as it contains a large number of macronutrients (carbohydrates, proteins, lipids) and micronutrients (vitamins A, B, C, folic acid, and minerals), which help to prevent degenerative diseases [13]. The greatest producers in 2019 were Asia, accounting for 71.5% of the global market, followed by Africa (16%), America (12.3%), and finally Oceania, with 0.1% of the global production, according to the Food and Agriculture Organization of the United Nations. Even though the composition of mango fruit varies depending on its species, the flesh includes typically between 33-85 wt% of the total mass, resulting in a waste of 7-24 wt% of mango peel and 9-40 wt% of the kernel. The kernel contains 6-16 wt% of mango oil [14]. It has been reported that the kernel possesses a large amount of carbohydrates and proteins (58–80 and 6–13 wt%, respectively), apart from containing oleic and stearic acids [15] and polyphenols [16].

The search to reduce the use of petrochemical polymers in the composite fabrication sector has made the development and use of renewable and biodegradable materials gain popularity in the last few years [17]. Polylactic acid (PLA) is one of the most widely used polymer matrices in environmentally friendly materials. This is because PLA monomers are obtained from the fermentation of starch-rich compounds, so the products are biodegradable in controlled compost soil conditions [18, 19].

PLA-based composites present several limitations provoked by PLA's low impact strength and toughness and, subsequently, high fragility [20]. One of the most common techniques to overcome this inconvenience is mixing PLA with more flexible polymers and/or incorporating additives (plasticizers) [21, 22]. Lascano et al. [21] developed a binary blend using PLA and poly (butylene succinate-co-adipate) (PBSA). It was observed that the ductile behaviour of the blend improved, increasing the elongation at break and impact strength from 9.23% and 2.48 kJ/m² for neat PLA, respectively, to 56% and 5.75 kJ/m^2 for the blend with 30 wt% of PBSA. Several natural-origin plasticizers are being utilized due to their low toxicity. Among those plasticizers are lactic acid, lactic acid oligomers (OLA), vegetal oils (VO), citrate esters, tributyrin, triacetin, and so on. Montes et al. [23] developed a blend made of poly(lactic acid)/ poly(3-hydroxybutyrate) utilizing tributyrin as a plasticizer to produce completely natural films for food packaging applications. They observed that the incorporation of 15 wt% tributyrin increased the ductile properties of the material apart from presenting good water vapour barrier properties and certain transparency. Crystallinity was also increased. Coltelli et al. [24] studied the behavior of composites based on PLA and polyhydroxybutyrate plasticized with triacetin. They observed that PLA biodegradability improved thanks to the disintegration of the amorphous phase.

This work aims to develop a completely natural composite based on a polylactic acid (PLA) matrix and mango kernel seed flour (MKSF) as a biobased filler. To overcome the low intrinsic toughness of the PLA matrix, two bio-derived plasticizers were used, namely glycerol tributyrate (tributyrin) and glycerol triacetate (triacetin). There is little literature regarding the use of mango kernel flour as a filler for polylactide. Additionally, TBN and TCN have not been widely used for plasticizing PLA wood plastic composites and never have been used in a PLA/MKSF composite. The effects of both plasticizers and the MKSF filler were evaluated through standard mechanical, thermal, and thermomechanical tests, morphology characterization, water absorption, and disintegrability under controlled compost soil characterization.

2. Materials and methods 2.1. Materials

Bio-based PLA Purapol L130 grade (min. 99% of L-isomer) was supplied by Corbion Purac (The Netherlands, Amsterdam), with a density of 1.24 g/cm^3 , a melt flow index of 16 g/10 min (measured at a temperature of 210 °C and a load of 2.16 kg) and a melting temperature of 175 °C.

Flour extracted from mango kernel from *Mangifera indica L*. species was used as a filler. The mango seed was dried at 65 °C for a week. The mango kernel was extracted and submitted to a milling process in a Retsch Gmbh model ZM 1000 ultracentrifugal mill (Haan, Germany) with a sieve size of 25 μ m and a rotation speed of 12 000 rpm. Figure 1 shows the morphology and histogram (size distribution) of the mango kernel seed flour particles (MKSF), which present an average particle diameter size of 18– 20 μ m.

Glycerol tributyrate (tributyrin) from ACROS Organics[™] and distributed by Thermo Fisher Scientific (Geel, Belgium) (Product Code: A11830.0B) and glycerol triacetate (triacetin) from Sigma Aldrich



Figure 1. FESEM image of mango kernel seed flour (MKSF) particles at 150×with a marker scale of 20 μm.

(Madrid, Spain) (Product Code: 90240) were used as plasticizers. Tributyrin is 97% pure, with a density of 1.0335 g/ml and a melting point of -75 °C. Triacetin presents a purity of 99%, a density of 1.16 g/ml, and a melting point of 3 °C.

2.2. Manufacturing of PLA-MKSF composites

Prior to processing, PLA pellets and MKSF particles were dried in an air circulating oven at 65 °C for 12 hours to eliminate humidity. The compounds were formulated with a constant MKSF weight percentage of 30 wt%. Plasticizers (tributyrin and triacetin) were added directly in the extrusion process, always maintaining 10 phr (parts by weight of plasticizer per one hundred parts by weight of the PLA/ MKSF base composition taking the work of Pawlak et al. [25]). The compounds were named using the code PLA-MKSF/XX, where XX refers to the used plasticizer, TBN for tributyrin, and TCN for triacetin. These formulations were placed in a ziplock bag for the initial mixing. Then, they were submitted to an extrusion process in a co-rotating twin-screw extruder from Dupra S.L. (Alicante, Spain). The extrusion temperature profile was 160-170-180-190 °C with a rotating speed of 20 rpm. Then, the extruded filaments were pelletized in an air-knife unit. Finally, an injection-moulding process was carried out using a Meteor 270/75 from Mateu & Solé (Barcelona, Spain). Standardized tensile test and impact strength test specimens were obtained. The injection-moulding temperature profile was 170-175-180-190 °C from the hopper to the injection nozzle, with an injection time of 5 s and a cooling time of 60 s.

2.3. Characterization of PLA-MKSF composites

2.3.1. Theoretical miscibility between PLA and the plasticizers

When studying the interaction between a polymer and a plasticizer, the solubility of both components is very useful information to consider before initiating all the experimental setups. The general solubility parameter (δ) for each component can be calculated, according to the method of van Krevelen and te Nijenhuis [26], Equation (1), which takes into account the contributions of the dispersion forces (δ_d), polar forces (δ_p), and hydrogen bonding (δ_h):

$$\delta = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{1}$$

Each one of the contributions can be calculated by Equations (2), (3), and (4):

$$\delta_d = \frac{\sum F_{\rm di}}{V} \tag{2}$$

$$\delta_{\rm d} = \frac{\sqrt{\sum F_{\rm pi}^2}}{V} \tag{3}$$

$$\delta_{\rm h} = \sqrt{\frac{\sum E_{\rm hi}}{V}} \tag{4}$$

where F_{di} is the dispersive force contribution of the chemical groups present in the molecule, F_{pi} is the polar force contribution of the chemical groups present in the molecule, E_{hi} is the hydrogen cohesive energy contribution of the chemical groups in the molecule, and V is the molar volume of the molecule.

Considering the chemical structure and the group contribution of neat PLA and both plasticizers (tributyrin and triacetin), Table 1 gathers all the solubility components and the solubility parameter. Moreover, the parameter R_a was also calculated, which indicates the distance that exists between the solubility coordinates of the plasticizers and the ones of PLA. If R_a is zero, it is indicative of good miscibility between the polymer and the plasticizer. So, the solubility between both materials becomes poorer as the parameter R_a (the distance) increases until it surpasses a certain threshold, from which both polymer and plasticizer become incompatible. This distance relates to the polymer radius, R_0 , which defines a spherical solubility region of a polymer. The center of this sphere is determined by the three solubility contributions δ_d , δ_p , and δ_h . R_a is calculated Equation (5):

elements are in the threshold of good miscibility, while values superior to 1 are indicative of poor miscibility between both elements.

$$RED = \frac{R_{\rm a}}{R_0} \tag{6}$$

As it can be observed in Table 1, both tributyrin and triacetin have good miscibility for PLA, as their *RED* value is smaller than the unity, with both plasticizers exhibiting *RED* values of 0.86 and 0.73, respectively.

2.3.2. Mechanical characterization

The mechanical characterization of neat PLA and PLA-MKSF composites was carried out through tensile, impact strength, and hardness (Shore D) tests. Tensile tests were done following the ISO 527 using a universal testing machine ELIB 30 from Ibertest (Madrid, Spain), equipped with a cell load of 5 kN and a crosshead speed of 5 mm/min. Young modulus, tensile strength, and elongation at break were obtained with this test. Five specimens were tested, and their results were averaged.

The impact strength was determined through the Charpy test, using a Charpy pendulum with an energy of 6 J, from Metrotec S.A. (San Sebastian, Spain) on injection moulded rectangular unnotched samples with dimensions $80 \times 10 \times 4$ mm following ISO 179. Finally, Shore D hardness was measured using a durometer model 673-D from J. Bot S.A. (Barcelona, Spain), according to ISO 868. At least five samples were tested for each composite, and their corresponding parameters were averaged.

$$R_{\rm a} = \sqrt{4 \cdot \left(\delta_{\rm d_{plast}} - \delta_{\rm d_{PLA}}\right)^2 + \left(\delta_{\rm p_{plast}} - \delta_{\rm p_{PLA}}\right)^2 + \left(\delta_{\rm h_{plast}} - \delta_{\rm h_{PLA}}\right)^2} \tag{5}$$

Additionally, the relative energy difference (*RED*) was also calculated. This parameter indicates the ratio between R_a and the solubility sphere radius of neat PLA, R_0 , which is 10.7 MPa^{1/2} (Equation (6)) [27]. The lower the *RED* parameter is, the better the affinity between the polymer and the plasticizer. When the *RED* value is close to 1, it means that both

2.3.3. Morphology characterization

Morphology of fractured Charpy test samples was studied by field emission scanning electron microscopy (FESEM) using a ZEISS ULTRA 55 microscope from Oxford Instruments (Abingdon, United Kingdom). The samples were sputtered with a goldpalladium alloy in an EMITECH sputter coating

Table 1. Theoretical solubility parameters of PLA with tributyrin and triacetin plasticizers.

Material	δ _d [MPa ^{1/2}]	$\frac{\delta_p}{[MPa^{1/2}]}$	$\frac{\delta_h}{[MPa^{1/2}]}$	δ [MPa ^{1/2}]	R _a [MPa ^{1/2}]	<i>RED</i> [-]
PLA	15.33	8.44	10.98	20.66	-	
Tributyrin (TBN)	15.96	1.67	4.89	16.78	9.19	0.86
Triacetin (TCN)	16.21	2.60	6.10	17.51	7.81	0.73

SC7620 from Quorum Technologies, Ltd. (East Sussex, UK). The microscope was operated with an acceleration voltage of 1.5 kV.

2.3.4. Thermal characterization

The main thermal transitions of the PLA-MKSF composites were evaluated through differential scanning calorimetry (DSC) in a DSC 821 from Mettler-Toledo Inc. (Schwerzenbach, Switzerland). Samples weighed about 5-8 mg and were placed in 40 µl aluminium crucibles. The samples were subjected to a thermal cycle divided into three steps: a first heating cycle from 30 to $180 \,^{\circ}$ C was followed by a cooling cycle down to $-50 \,^{\circ}$ C and, finally, a second heating stage from -50 up to 220 °C was scheduled. The heating and cooling stages were run at a rate of 10 °C/min in a nitrogen atmosphere (66 ml/min). Parameters such as the glass transition temperature $(T_{\rm g})$, the cold crystallization peak temperature $(T_{\rm cc})$ and enthalpy (ΔH_{cc}), the melt peak temperature (T_{m}) and enthalpy (ΔH_m) were obtained from the second heating stage. Moreover, the degree of crystallinity $(X_{c} [\%])$ was calculated Equation (7):

$$X_{\rm c} \left[\%\right] = \frac{\left|\Delta H_{\rm m}\right| - \left|\Delta H_{\rm cc}\right|}{\left|\Delta H_{\rm m}^{0}\right| \cdot (1 - w)} \cdot 100 \tag{7}$$

where $\Delta H_{\rm m}^0$ is a theoretical value representing the theoretical melt enthalpy of a fully crystalline PLA polymer, *i.e.* 93.7 J/g as reported in the literature [28], and 1 - w is the weight fraction of PLA.

To evaluate the thermal stability and thermal degradation of the PLA-MKSF composites and MKSF at high temperatures, thermogravimetric analysis (TGA) was carried out on a TGA1000 thermobalance from Linseis (Selb, Germany). Samples of 15–20 mg were used, which were placed in standard alumina crucibles (70 µl). The heating cycle was established from 30 to 700 °C with a heating rate of 10 °C/min, with a nitrogen atmosphere (66 ml/min). The onset degradation temperature was estimated at a mass loss of 5% ($T_{5\%}$) in the corresponding TGA curve, while the maximum degradation rate temperature (T_{max}) was obtained from the first derivative thermogravimetric (DTG) curve.

2.3.5. Thermomechanical characterization

Dynamical mechanical thermal analysis (DMTA) was carried out in a DMA1 dynamic analyzer from Mettler-Toledo (Schwerzenbach, Switzerland), working in single cantilever flexural conditions. Rectangular samples with dimensions $20 \times 6 \times 2.7$ mm were subjected to a dynamic temperature sweep from -50 to 140 °C at a constant heating rate of 2 °C/min. The selected frequency was 1 Hz, and the maximum flexural deformation or cantilever deflection was set to 10 µm.

2.3.6. Water uptake characterization

Water uptake of neat PLA and PLA-MKSF composites was characterized following ISO 62:2008. Rectangular samples of dimensions 80×10×4 mm were sunk in distilled water at room temperature for nine weeks up to saturation. The samples were extracted from the distilled water, dried with absorbent paper, and weighed; the specimens were then again immersed in the distilled water. The weighting process was made on an analytical balance model AG245 provided by Mettler-Toledo (Schwerzenbach, Switzerland) with an accuracy of 0.001 g. This process was repeated every week under the same conditions; measurements were taken in triplicate to ensure reliable results. The percentage of water absorption was calculated using Equation (8):

Water absorption [%] =
$$\frac{W_{\rm t} - W_0}{W_0} \cdot 100$$
 (8)

where $W_t[g]$ is the weight of the dry sample at any time, and $W_0[g]$ is the weight of the initial dry sample.

2.3.7. Disintegration in controlled compost soil

The degree of disintegration under composting conditions of PLA samples and PLA-MKFS composites was studied at a temperature of 58 °C and relative humidity of 55% according to ISO 20200. Samples of dimensions $25 \times 2 \times 1$ mm were placed inside a textile mesh to facilitate their removal. Then they were buried in a controlled compost soil made of organic solids 45%, vegetable solids 40, 30% water content, and pH between 6 and 7. Samples were periodically extracted from the compost and cleaned with distilled water. Then they were dried and weighted with an analytical balance model AG245 from Mettler-Toledo (Schwerzenbach, Switzerland) with an accuracy of 0.001 g. The percentage of weight loss was calculated using Equation (9):

Weight loss [%] =
$$\frac{W_0 - W_t}{W_0} \cdot 100$$
 (9)

where W_0 is the initial dry weight of the sample and W_t is the weight of the sample after t burial time. All assays were carried out in triplicate to ensure accuracy and reliability.

2.3.8. Melt flow index

The melt flow index (MFI) of neat PLA and PLA-MKSF composites was determined using MFI equipment from Metrotec S.A. (San Sebastian, Spain), equipped with a 1 mm diameter nozzle. Measurements were taken using a temperature of 190 °C and an applied load of 2.16 kg, following ISO 1133. MFI measurements were done in triplicate for each composition.

2.3.9. Surface wettability and colour measurement

The wettability of the PLA and the PLA-MKSF composites was estimated by water contact angle (WCA) measurements. To this, an Easy drop FM140 goniometer supplied by Krüss equipment (Hamburg, Germany) was used. The test was carried out at room temperature with water droplets of approximately ~15 μ l randomly deposited on the sample surface. The WCA was measured eight times for each droplet for each formulation, and the average values were provided.

The effect of MKSF on the colour of the PLA matrix was analysed with a colorimeter model KONICA CM-3600d Colorflex-DIFF2 from Hunter Associates Laboratory (Reston, Virginia, USA). The instrument was calibrated considering the standard white tile and a mirror unit for black. The CIELab colour scale (coordinates L^* , a^* and b^*) was recorded. L^* refers to lightness, a^* stands for the colour coordinate between red and green, and b^* represents the colour coordinate between yellow and blue. The total colour difference (ΔE^*_{ab}) was calculated by Equation (10):

$$\Delta E_{ab}^{*} = \sqrt{(\Delta L^{*})^{2} + (\Delta a^{*})^{2} + (\Delta b^{*})^{2}}$$
(10)

where ΔL^* , Δa^* , and Δb^* are the differences between the CIELab colour coordinates of the samples and the reference colour.

3. Results

3.1. Mechanical characterization

Table 2 summarises the main values of the tensile test parameters, impact strength, and Shore D hardness of neat PLA and PLA-MKSF composites. In the case of neat PLA, high values of elastic modulus (E_t) and tensile strength (σ_t) are obtained (3848 MPa and 40.1 MPa, respectively), while a low percentage of elongation at break (ε_b) is obtained (4.7%). These properties are typical of PLA, being a rigid and brittle material [21]. The incorporation of MKSF leads to an increase in the stiffness and brittleness of the material. This is demonstrated by the high elastic modulus values reported, which are 35% higher than the values of neat PLA. It is also verified by a decrease in tensile strength and elongation at break of 40 and 35%, respectively, related to neat PLA. This provokes a highly brittle behavior in PLA-MKSF composites. This behaviour can be related to the low interaction between the MKSF and the surrounding PLA matrix, which generates a stress concentration effect, provoking a detriment of mechanical properties [29].

As expected, the incorporation of tributyrin (TBN) and triacetin (TCN) improves the ductile behaviour of PLA-MKSF composites. In the case of PLA-MKSF/TBN, a decrease in the tensile modulus and tensile strength of 37 and 58% can be observed, respectively. An increase in elongation at break can also be observed up to 9.5%, thus, demonstrating the plasticizing effect of tributyrin. Even though impact strength is lower than neat PLA, the PLA-MKSF composite plasticized with tributyrin has a higher impact strength than the unplasticized PLA-MKSF composite. This effect was also reported by other studies [30], with tributyrin as a plasticizer in a PLA/PHB blend. In general, it was observed how the

Table 2. Mechanical properties of PLA, PLA-MKSF composites obtained from tensile tests (elastic modulus – E_t , tensile strength – σ_t , elongation at break – ε_b), Shore D, impact strength.

Code		Tensile		Impost strongth	
	Elastic modulus, <i>E</i> t [MPa]	Strength, σ _t [MPa]	Elongation at break, ε _b [%]	Shore D hardness	[kJ/m ²]
PLA	3848±245	40.1±3.7	4.7±0.5	63.8±1.3	33.6±3.6
PLA-MKSF	5219±27	23.9±0.9	4.4±0.6	60.8±1.3	21.7±1.5
PLA-MKSF/TBN	2424±193	16.9±0.5	9.5±0.6	61.0±1.3	27.7±1.6
PLA- MKSF/TCN	2995±199	18.7±0.6	8.3±0.7	61.7±1.2	33.1±3.1

incorporation of tributyrin provoked a reduction of the tensile strength and elastic modulus in all formulations. However, no significant changes were observed in the elongation at break.

As it occurs with the composites with TBN, the incorporation of triacetin is quite notorious regarding ductile properties. On the one hand, a decrease in the elastic modulus and tensile strength of 22 and 33% with respect to neat PLA is observed. Additionally, an increase of 77% in elongation at break is observed. In spite of this, the impact strength of the material remains quite high, with a value of 33.1 kJ/m², comparable to the impact strength of neat PLA but with a noticeable difference since ductile properties have been improved. This effect can be related to the excellent miscibility that TCN has with the PLA matrix, as it was stated in the theoretical solubility section. This phenomenon, together with the compatibility of TCN with MKSF (composed mainly of polysaccharides and protein), enhances the general plasticization effect [31]. Some studies have reported that the plasticizer embeds the surface of lignocellulosic



particles, thus making the particles slide all over the matrix [32].

Regarding Shore D hardness, it can be observed that the incorporation of MKSF provokes a slight decrease in hardness from 63.8 down to 60.8. Different plasticizers (TBN and TCN) do not significantly affect the hardness, despite a little increase. These results are similar to those reported by Gonzalez *et al.* [33], who observed that the use of maleinized linseed oil (MLO) plasticizer did not alter the hardness of the matrix.

These results are in accordance with the estimated miscibility between neat PLA and tributyrin and triacetin. As the theoretical study showed good compatibility between the plasticizers and the polymer, which has been demonstrated by the good mechanical response in both cases.

3.2. Morphological characterization.

Figure 2 shows the morphology of the fracture surface of impact test samples of each one of the developed composites observed by FESEM at 1000× magnification. Figure 2a corresponds to neat PLA,





Figure 2. FESEM image of mango kernel seed flour (MKSF) particles at 1000× with a marker scale of 10 μm. a) PLA, b) PLA-MKSF, c) PLA-MKSF/TBN, d) PLA-MKSF/TCN.

which shows the typical morphology of a brittle polymer. This behaviour is detected by a smooth and flat surface, with the presence of little microcracks [21]. This perfectly matches the mechanical results observed in the previous section, where PLA exhibited an extremely low ductility (low elongation at break). In the case of Figure 2b, the morphology of PLA with the incorporation of MKSF is shown. The presence of MKSF particles is clearly seen all over the matrix, where the adhesion of the particles is undoubtedly poor, as evidenced by the presence of voids (white arrows) in the matrix surface. Pulledout MKSF particles generate those voids during impact fracture due to the poor compatibility between PLA and MKSF [34]. Figures 2c and 2d show the FESEM morphology of the composites with tributyrin and triacetin, respectively. The concentration of voids in the PLA matrix has been observed to be reduced with respect to the unplasticized PLA/MKSF composite. This indicates an increase in the affinity between PLA and MKSF microparticles, thanks to the addition of both plasticizers, which possess ester groups that enhance interaction with MKSF through hydrogen bonds [20]. Additionally, the gap (yellow arrows) between the MKSF particles and the surrounding PLA matrix is smaller than in the unplasticized composite. This fact corroborates the increased ductile properties observed in the mechanical characterization section, especially by using triacetin, which provided an elongation at break of 9.5%.

3.3. Thermal properties of PLA-MKSF composites

Differential scanning calorimetry (DSC) was used in order to study the thermal properties of the PLA-MKSF composites. Figure 3 gathers the thermograms that correspond to the second heating cycle of neat PLA and each one of the PLA-MKSF composites. At the same time, Table 3 summarizes the main thermal parameters extracted from these thermograms. Neat PLA shows a glass transition temperature at about 62 °C, which is a typical value for this polymer, as observed by Petchwattana *et al.* [20]. The addition of MKSF into the polymer matrix decreases this value by approximately 1 °C, indicating almost negligible plasticization.

On the other hand, adding tributyrin and triacetin decreases this temperature to 40.6 and 46.4 °C, respectively. This remarkable decrease is ascribed to increased chain mobility of the amorphous phase of PLA induced by both plasticizers [20]. The addition of triacetin and tributyrin also plays a key role in the cold crystallization process. The cold crystallization peak temperature of neat PLA is located at 115.3 °C. In contrast, the addition of MKSF decreases it down to 109 °C, but, once again, the incorporation of tributyrin and triacetin plasticizers moves the cold crystallization peak temperature down to such low values of 89 and 98 °C, respectively. This decrease in cold crystallization is also ascribed to the increase in PLA chain mobility, which provokes polymer chains to rearrange more quickly to a packed structure in the presence of plasticizers. Pure PLA exhibits a melting temperature of approximately 167°C, which is increased by the presence of MKSF up to 169 °C. This effect is typical in rigid lignocellulosic fillers, as they



Figure 3. Differential scanning calorimetry (DSC) thermograms of neat PLA and plasticized and unplasticized PLA-MKSF composites.

Table 3. Glass transition temperature (T_g) , cold crystallization peak temperature (T_{cc}) , cold crystallization enthalpy (ΔH_{cc}) , melting temperature (T_m) , melting enthalpy (ΔH_m) , and crystallinity X_c of the PLA-MKSF composites, obtained by differential scanning calorimetry (DSC).

Code	<i>T</i> g [°C]	<i>T</i> _{cc} [°C]	ΔH_{cc} [J/g]	<i>T</i> _m [°C]	ΔH_{m} [J/g]	X _c [%]
PLA	62.4±1.2	115.3±3.5	0.7±0.1	167.1±0.2	10.1±0.1	10.1±0.5
PLA-MKSF	61.3±1.5	109.5±4.1	24.6±0.4	169.1±0.4	30.3±1.2	8.7±0.2
PLA-MKSF/TBN	40.6±2.1	88.9±3.6	19.1±1.1	164.1±1.0	30.4±1.7	17.3±0.1
PLA-MKSF/TCN	46.4±1.7	98.2±2.7	24.7±0.5	165.0±1.2	29.3±1.2	7.1±0.3

are more thermally stable than neat PLA, thus delaying the melting phenomenon.

Similarly, the addition of plasticizers follows an analogous trend to the glass transition and cold crystallization temperatures. Tributyrin and triacetin decrease $T_{\rm m}$ to 164 and 165 °C, respectively, due to higher segmental mobility [20]. Finally, the crystallinity of PLA did not suffer significant changes, presenting a value of around 10%, except for the sample with tributyrin, which showed a crystallinity of 17.3%. This increase is related to the aforementioned enhanced chain mobility, which accelerates the crystallization rate of PLA, allowing it to crystallize at a lower $T_{\rm cc}$ and then present a higher crystalline region.

In order to assess the thermal degradation behaviour of the composites, a thermogravimetric (TGA) analysis was carried out. Figure 4 shows the thermogravimetric (TGA) and first derivative (DTG) curves of the studied composites, whereas Table 4 gathers the main thermal parameters related to this analysis. Neat PLA exhibits a single-step degradation curve, typical of this polyester. Its onset degradation temperature $(T_{5\%})$ is drastically reduced from 365 °C down to 273 °C due to the incorporation of MKSF. This is due to the earlier decomposition of low molecular weight hemicellulose in the mango kernel seed flour [20]. A similar trend occurs with the maximum degradation rate temperature extracted from the first derivative diagram, as it decreases from 404.5 down to 322.6 °C for PLA-MKSF. This is ascribed to the inherent lower thermal degradation stability of the lignocellulosic particles of MKSF, namely hemicellulose, cellulose, lignin, and pectin [35]. This phenomenon is clearly observed in the TGA dia-

Table 4. Main thermal degradation parameters of the PLA-MKSF composites: onset degradation temperature at a mass loss of 5 wt% ($T_{5\%}$), maximum degradation rate temperature (T_{deg}), and the residual mass at 700 °C.

Code	T _{5%} [°C]	<i>T</i> _{deg} [°C]	Residual mass [%]
PLA	365.2±2.5	404.5±3.1	0.2±0.1
PLA-MKSF	272.7±1.2	321.1±1.3	0.2±0.2
PLA-MKSF/TBN	216.4±2.0	324.7±3.3	0.1±0.2
PLA-MKSF/TCN	204.1±1.1	321.2±1.1	0.1±0.2

grams, where the PLA mass decreases far later than in the rest of the samples. The TGA curves of the samples with tributyrin and triacetin show a two-step degradation process, which is ascribed to the initial degradation (plasticizer removal) of both plasticizers, which are more volatile than the PLA matrix [36]. In this case, the onset degradation temperature is further decreased to 218 and 203 °C for tributyrin and triacetin, respectively. This demonstrates the results observed in DSC, as both plasticizers reduce the interaction between polymer chains and increase their mobility, thus diminishing thermal stability. The maximum degradation rate temperature is also reduced to 325 and 322 °C, respectively, a decrease of approximately 20% relative to neat PLA. The residual mass of PLA-MKSF composites increases due to a higher tendency of MKSF for char formation than PLA.

3.4. Thermomechanical characterization

To assess the mechanical properties of the composites in dynamic thermal conditions, DMTA was carried out. This analysis also allows a more detailed evaluation of the glass transitions of polymers. Figure 5 shows the dynamic-mechanical thermal analysis



Figure 4. Thermal degradation of PLA-MKSF composites, a) thermogravimetric (TGA), and b) first derivative (DTG) of neat PLA, plasticized and unplasticized PLA-MKSF composites.



Figure 5. Plot evolution of a) the storage modulus (E') and b) the dynamic damping factor (tan δ) of the PLA-MKSF composites.

(DMTA) curves for all the PLA-MKSF composites, namely the evolution of the storage modulus (E') and the dynamic damping factor $(\tan \delta)$. At the same time, Table 5 gathers the main thermomechanical parameters to be analyzed. Figure 5a shows the variation of the storage modulus, which slowly decreases in the whole temperature range until a sudden drop is detected. This drop occurs between 60 and 70 °C for neat PLA and PLA-MKSF, and between 40 and 50 °C for the plasticized PLA-MKSF composites. Those drops are related to the α -relaxation of PLA chains once the glass transition region is surpassed [37]. This is due to the plasticizing effect of TBN and TCN, which increases the mobility of PLA chains, thus reducing their stiffness in comparison with neat PLA. These changes in rigidity are registered in Table 5, where there is a significant difference between the storage modulus at 5 and 70 °C, which goes down from 1500-1700 MPa to values of 8-50 MPa, respectively. Figure 5b allows observing more precisely the glass transition temperature of the materials, which is indicated by a peak in the evolution of the dynamic damping factor $(\tan \delta)$ with temperature. The glass transition temperature of neat PLA is located at approximately 65 °C, as already

 Table 5. Main dynamic-mechanical parameters of the PLA MKSF composites.

Code	E' at 5°C [MPa]	<i>E'</i> at 70 °C [MPa]	<i>Т</i> _g [°С]
PLA	1690.6±33.80	8.37±0.13	65.26±0.97
PLA-MKSF	1569.4±29.81	16.9±0.32	63.13±1.39
PLA-MKSF/TBN	1579.0±27.01	54.1±1.14	43.36±0.65
PLA-MKSF/TCN	1704.9±30.68	45.9±0.92	44.43±0.71

observed in DSC. Adding MKSF does not provoke significant changes in its T_{g} , with an average value of 63 °C. On the other hand, adding the TBN and TCN plasticizers reduces the glass transition temperature to 43 and 44 °C, respectively. This is again due to the chain mobility enhancement phenomenon that both plasticizers provide. This result proves the successful plasticization of PLA and demonstrates the increase in elongation at break reported in the mechanical properties section. After the glass transition process, there is a slight rise of E' in the plasticized samples and the PLA+MKSF composite, which can also be observed in the tan δ graph, around 80 °C. This rise is due to crystallization, as an increase in chain mobility favors the formation of crystals after the T_{g} [38]. This crystal formation slightly increases the stiffness of the composites, which is why E' increases a little bit at high temperatures (75 to 100 °C). This is in accordance with the DSC results, where a cold crystallization peak was recorded for the PLA+MKSF, and the TBN and TCN plasticized samples in the 75–100 °C temperature range.

3.5. Melt flow index (MFI)

Figure 6 gathers the melt flow index (MFI) for neat PLA and the PLA-MKSF composites developed in this work, measured at 190 °C with a load mass of 2.16 kg. Neat PLA presents an MFI of approximately 17 g/10 min, similar to that provided in the technical data sheet. Once the MKSF is incorporated into the PLA matrix, the melt flow index increases up to about 18 g/10 min. A similar effect was observed by Pantyukhov *et al.* [39] in polyethylene composites with lignocellulosic fibres as fillers. As expected, the



Figure 6. Melt flow index (MFI) of neat PLA and PLA-MKSF composites.

addition of tributyrin and triacetin drastically increased the MFI of the composites. This is ascribed to the enhanced chain mobility that both plasticizers provide to PLA-MKSF composites. Thus, the PLA polymer chain entanglement becomes poorer, positively affecting the composite's flowability. The measured MFI values for PLA-MKSF/TBN and PLA-MKSF/TCN are 42.5 g/10 min and 32.5 g/10 min, respectively. This indicates that the plasticizing effect of tributyrin is stronger than that of triacetin, as it has also been demonstrated in its mechanical and thermal properties.

3.6. Visual appearance and water contact angle characterization

Visual appearance is an essential factor regarding the product's perception by the consumer. Figure 7 shows the visual appearance of PLA-MKSF composites. At first sight, it can be seen that only the neat PLA sample shows certain transparency due to the semicrystalline nature of the polyester [40]. The incorporation of MKSF leads the samples to turn completely opaque with characteristic dark brown colours, which are especially attractive from the point of view of wood-plastic composites. Meanwhile, Table 6 gathers the $L^*a^*b^*$ colour coordinates. Neat PLA exhibited a luminance of 36.8, which is reduced to values close to

Table 6. Main colour parameters of the PLA-MKSF composites in terms of the CieLab colour space $(L^*a^*b^*)$ and the colour difference ΔE^*_{ab} .

Code	L*	<i>a</i> *	<i>b</i> *	ΔE_{ab}^{*}
PLA	36.8±0.3	-0.2±0.1	0.9±0.1	-
PLA-MKSF	25.8±0.3	3.1±0.1	3.5±0.1	11.7±0.3
PLA-MKSF/TBN	26.0±0.1	4.2±0.2	5.3±0.1	12.4±0.1
PLA-MKSF/TCN	26.9±0.3	4.0±0.1	5.4±0.2	11.6±0.3

26 for all the rest of the samples as a result of the incorporation of MKSF, which turns the samples into darker colours.

Regarding colour coordinates a^* and b^* , neat PLA displays very low values (-0.2 and 0.9, respectively) due to its characteristic white colour. Adding MKSF increases those values to 3.1 and 3.5, respectively. This was expected, as the observed dark brown colour is composed of red and yellow components. With the addition of tributyrin and triacetin, both values increase even more, as they provide a clearer tonality to the dark brown colour of the PLA-MKSF composite, as seen in Figure 7. The values of a^* and b^* for TBN and TCN are very close to 4 and 5, respectively, in both cases. Finally, the colour difference ΔE_{ab}^{*} is very similar for all three PLA-MKSF composites, giving values of approximately 12. That was expected, as the three samples presented very similar colours. A similar tonality was reported in previous work for a polypropylene matrix with mango peel wastes [41].

The water contact angle analysis gives information regarding the affinity and interaction of the studied materials with water. Figure 8 shows the contact angle of distilled water with the surface of each one of the PLA-MKSF composites developed in this study. As it can be observed, neat PLA presents a contact angle of 85°, which is characteristic of a hydrophobic polymer according to Vogler, who established the hydrophilic threshold at 65° [42]. Once MKSF is added to the polymer matrix, the contact angle considerably decreases to 75°, increasing the hydrophilicity of the polymer. This behaviour is ascribed to the polar groups contained in MKSF, mainly from



Figure 7. The visual appearance of the PLA-MKSF composites.



Figure 8. Water contact angle measurements of plasticized and unplasticized PLA-MKSF composites.

polysaccharides and proteins. Those molecules have a great capacity to form hydrogen bonds, thus increasing affinity towards the water and then enhancing hydrophilicity [43]. The addition of plasticizers into the PLA-MKSF composite reduces the affinity towards water, exhibiting contact angles of 78.5 and 82° for tributyrin and triacetin, respectively. Both plasticizers reduce the contact angle of neat PLA, as tributyrin and triacetin are certainly hydrophilic [44]. However, they increase the contact angle in relation to the PLA-MKSF sample. This could be due to the interaction of ester groups contained in both plasticizers with the hydroxyl groups in MKSF, thus reducing the availability of –OH functionalities in MKSF that can hydrogen-bond with water molecules.

3.7. Water uptake

The water uptake test evaluated the water absorption capacity of neat PLA and PLA-MKSF composites over 11 weeks. Figure 9 shows the evolution of the water absorption of the samples over 11 weeks in terms of the percentage of water mass absorbed in relation to the initial weight of the specimens. As expected, neat PLA presents the lowest water absorption profile, with maximum absorption of less than 1 wt%. This is the typical behaviour of a hydrophobic polymer; a similar profile was observed in previous works [37] for neat PLA. When MKSF is added into the PLA matrix, the water uptake of the composite drastically increases up to almost 12 wt% at 11 weeks of immersion in distilled water. This effect is ascribed to the presence of polar groups in the composite coming from starch, proteins, and lignin. Their characteristic



Figure 9. Water uptake evolution of the PLA-MKSF composites over 11 weeks.

functionalities provide the material with a great affinity for water, as observed in the contact angle measurements. Finally, adding tributyrin and triacetin also increases the water absorption compared with neat PLA up to 6.5 and 5 wt%, respectively. However, they decrease the water absorption capacity with respect to the PLA-MKSF composite. This decrease could be related to the interaction between carbonyl groups in both plasticizers and hydroxyl groups in MKSF, reducing the possible reaction with distilled water [45]. The sample with tributyrin seems to slightly decrease its mass over time from 4 weeks of immersion. This could be ascribed to the certain water solubility of the plasticizer in distilled water. The results presented here are in total accordance with the contact angle measurements, where tributyrin also presented a slightly higher affinity for water than triacetin.

3.8. Disintegration test

The disintegrability of the PLA-MKSF composites was assessed through the disintegration test. Figure 10 shows the disintegration profile of all the studied PLA-based samples in terms of mass loss. As can be observed, only neat PLA disintegrated at 100% (at 9 weeks). Nonetheless, the remaining specimens disintegrated up to 90% at 12 weeks, which is the objective for considering a material biocompostable [43]. Neat PLA exhibited the typical behaviour of a biodegradable polymer, fully disintegration at 9 weeks due to a hydrolytic degradation process. Once MKSF is added to the polymer matrix, the disintegration capacity decreases to 90% at 12 weeks of incubation time in compost soil.



Figure 10. Disintegration profile of the PLA-MKSF specimens over 12 weeks.

Moreover, the addition of plasticizers does not significantly vary tPlease check all of the figures and tables, carefully (axes, headings, designations, lowercase or capital letters, etc.).

Please check the equations, carefully.he disintegration process. This decrease in biodegradability could be ascribed to an increase in the crystallinity of the polymer, especially in the PLA-MKSF/TBN composite. The hydrolytic degradation process occurs more easily in the amorphous regions of the polymer. Thus, the higher the crystallinity, the lower the proportion of the amorphous phase in the polymer, providing more resistance against biodegradation [37]. Nonetheless, both plasticizers do increase the disintegrability rate during the first 8 weeks. This phenomenon could be ascribed to the hydrophilic nature of TBN and TCN, which makes water absorption and diffusion through the polymer bulk in the initial phase of disintegration to be faster. This results in higher hydrolysis in the polymer chains, leading to smaller molecules (monomers and short-chain oligomers) being available for microorganisms to attack [46]. In the last weeks, the samples with MKSF seem to have a disintegrability threshold, which could correspond to the MKSF fraction left in the samples, which does not fully disintegrate.

Figure 11 gathers images that record the visual aspect of the samples all over the test. As has been aforementioned, it is observed that neat PLA is entirely disintegrated after 9 weeks, while the rest of the specimens continue to degrade until week 12, when just little remnants are left (90% of biodegradation). Moreover, neat PLA started to decompose at week 2, as demonstrated by the macrocracks that

appear in the square sample in Figure 11. In contrast, the MKSF samples start their decomposition at week 4. Thus, the results herein presented are in total accordance with the disintegration profile shown in Figure 10.

4. Conclusions

This work shows the successful development of wood plastic composites based on a polyester PLA matrix with mango kernel seed flour (MKSF) as a reinforcing agent and tributyrin (TBN) and triacetin (TCN) as plasticizers. The addition of MKSF gave the composites a characteristic dark brown color, which could prove to be interesting in replacing wood-based materials for these wood-plastic composites. Regarding their mechanical response, tributyrin and triacetin improved the ductility of the polymer matrix, increasing the elongation at break from 4.4% for the PLA+MKSF sample to 9.5 and 8.3% for PLA+MKSF/TBN and PLA+MKSF/TCN, respectively. These results matched the theoretical solubility parameters of neat PLA and the plasticizers, which were also studied, showing good compatibility between PLA, TBN, and TCN (RED values of 0.86 and 0.73, respectively). FESEM results also supported the mechanical properties of the composites, as well as certain compatibility effects exerted by the plasticizers over the polymer matrix and the MKSF particles. The plasticizing effect was further verified by thermal analysis, where the glass transition temperature and melting temperatures were reduced in relation to neat PLA as a result of the increased chain mobility provided by both TBN and TCN. MKSF made the affinity for water of the composite drastically increase, as was observed by means of contact angle measurements and water uptake. Both plasticizers reduced this considerably large water absorption of PLA+MKSF thanks to their bonding with MKSF particles. The thermal degradation of the composites became faster as a result of the presence of both plasticizers, again attributed to the increased chain mobility of the polymer chains ascribed to the plasticizing effect. Finally, all the composites showed a positive response towards disintegration under compost soil conditions. Disintegrating over 90% of the total mass of the samples.

All in all, these results prove that environmentally friendly wood plastic composites can be obtained from the combination of PLA, MKSF, TBN, and TCN, with enhanced ductility, good thermal stability,

Week	PLA	PLA-mKSF	PLA-MKSF/TBN	PLA-MKSF/TCM
0				
1				
2				
3			3	
4	K			
5			No.	2
6				

Figure 11. Evolution of the visual appearance of the samples $(25 \times 2 \times 1 \text{ mm})$ during the disintegration test.

Week	PLA	PLA-mKSF	PLA-MKSF/TBN	PLA-MKSF/TCM
7				
8		ġ		
9			N	12
10				
11		蒙		
12				

Figure 11. Evolution of the visual appearance of the samples (25×2×1 mm) during the disintegration test (continued).

and excellent biodegradability. Thus, they could be used in applications substituting wood-based products, as they present quite attractive dark brown colors.

References

 Azeez A. T.: A review of wood plastic composites effect on the environment. Journal of University of Babylon for Pure and Applied Sciences, 25, 360–367 (2017). [2] Siakeng R., Jawaid M., Asim M., Saba N., Sanjay M. R., Siengchin S., Fouad H.: Alkali treated coir/pineapple leaf fibres reinforced PLA hybrid composites: Evaluation of mechanical, morphological, thermal and physical properties. Express Polymer Letters, 14, 717–730 (2020).

https://doi.org/10.3144/expresspolymlett.2020.59

- [3] Mokhena T. C., Sadiku E. R., Mochane M. J., Ray S. S.: Mechanical properties of fire retardant wood-plastic composites: A review. Express Polymer Letters, 15, 744–780 (2021). https://doi.org/10.3144/expresspolymlett.2021.61
- [4] Akintayo O., Olajide J., Betiku O., Egoh A., Adegbesan O., Daramola O., Sadiku E., Desai D.: Poly(lactic acid)-silkworm silk fibre/fibroin bio-composites: A review of their processing, properties, and nascent applications. Express Polymer Letters, 14, 924–951 (2020). https://doi.org/10.3144/expresspolymlett.2020.76
- [5] Persic M., Mikulic-Petkovsek M., Slatnar A., Veberic R.: Chemical composition of apple fruit, juice and pomace and the correlation between phenolic content, enzymatic activity and browning. LWT-Food Science and Technology, 82, 23–31 (2017). https://doi.org/10.1016/j.lwt.2017.04.017
- [6] Mala T., Sadiq M. B., Anal A. K.: Optimization of thermosonication processing of pineapple juice to improve the quality attributes during storage. Journal of Food Measurement and Characterization, 15, 4325–4335 (2021).

https://doi.org/10.1007/s11694-021-01011-8

[7] Kringel D. H., Dias A. R. G., da Rosa Zavareze E., Gandra E. A.: Fruit wastes as promising sources of starch: Extraction, properties, and applications. Starch-Stärke, 72, 1900200 (2020).

https://doi.org/10.1002/star.201900200

[8] Haeldermans T., Samyn P., Cardinaels R., Vandamme D., Vanreppelen K., Cuypers A., Schreurs S.: Poly(lactic acid) bio-composites containing biochar particles: Effects of fillers and plasticizer on crystallization and thermal propertiess. Express Polymer Letters, 15, 343–360 (2021).

https://doi.org/10.3144/expresspolymlett.2021.30

- [9] Kalita N. K., Hazarika D., Kalamdhad A., Katiyar V.: Biodegradation of biopolymeric composites and blends under different environmental conditions: Approach towards end-of-life panacea for crop sustainability. Bioresource Technology Reports, 15, 100705 (2021). https://doi.org/10.1016/j.biteb.2021.100705
- [10] Rojas-Lema S., Ivorra-Martinez J., Lascano D., Garcia-Garcia D., Balart R.: Improved performance of environmentally friendly blends of biobased polyethylene and kraft lignin compatibilized by reactive extrusion with dicumyl peroxide. Macromolecular Materials and Engineering, **306**, 2100196 (2021). https://doi.org/10.1002/mame.202100196

[11] Rojas-Lema S., Lascano D., Ivorra-Martinez J., Gomez-Caturla J., Balart R., Garcia-Garcia D.: Manufacturing and characterization of high-density polyethylene composites with active fillers from persimmon peel flour with improved antioxidant activity and hydrophobicity. Macromolecular Materials and Engineering, 306, 2100430 (2021).

https://doi.org/10.1002/mame.202100430

[12] Tharanathan R. N., Yashoda H. M., Prabha T. N.: Mango (*Mangifera indica L.*), 'The king of fruits' – An overview. Food Reviews International, 22, 95–123 (2006).

https://doi.org/10.1080/87559120600574493

[13] Maldonado-Celis M. E., Yahia E. M., Bedoya R., Landázuri P., Loango N., Aguillón J., Restrepo B., Guerrero Ospina J. C.: Chemical composition of mango (*Mangifera indica L.*) fruit: Nutritional and phytochemical compounds. Frontiers in Plant Science, **10**, 1073 (2019).

https://doi.org/10.3389/fpls.2019.01073

- [14] Wadhwa M., Bakshi M.: Utilization of fruit and vegetable wastes as livestock feed and as substrates for generation of other value-added products. Rap Publication, Bangkok (2013).
- [15] Das P. C., Sattar S., Jony M. E., Islam M. N.: Rehydration kinetics of flour from dehydrated mango kernel. Food Research, 2, 474–480 (2018). https://doi.org/10.26656/fr.2017.2(5).210
- [16] Ribeiro S., Barbosa L., Queiroz J., Knödler M., Schieber A.: Phenolic compounds and antioxidant capacity of brazilian mango (*Mangifera indica L.*) varieties. Food chemistry, **110**, 620–626 (2008). https://doi.org/10.1016/j.foodchem.2008.02.067
- [17] Gao C., Zhang J., Zhang D., Dong Y., Wang S., Peng J., Liu Y.: Synthesis of bio-based waterborne polyesters as environmentally benign biodegradable material through regulation of unsaturated acid structure. European Polymer Journal, **156**, 110632 (2021). https://doi.org/10.1016/j.eurpolymj.2021.110632
- [18] Garcia-Garcia D., Carbonell-Verdu A., Arrieta M. P., López-Martínez J., Samper M. D.: Improvement of PLA film ductility by plasticization with epoxidized karanja oil. Polymer Degradation and Stability, 179, 109259 (2020).

https://doi.org/10.1016/j.polymdegradstab.2020.109259

- [19] Gürler N., Paşa S., Alma M. H., Temel H.: The fabrication of bilayer polylactic acid films from cross-linked starch as eco-friendly biodegradable materials: Synthesis, characterization, mechanical and physical properties. European Polymer Journal, **127**, 109588 (2020). <u>https://doi.org/10.1016/j.eurpolymj.2020.109588</u>
- [20] Petchwattana N., Naknaen P., Narupai B.: A circular economy use of waste wood sawdust for wood plastic composite production: Effect of bio-plasticiser on the toughness. International Journal of Sustainable Engineering, 13, 398–410 (2020).

https://doi.org/10.1080/19397038.2019.1688422

[21] Lascano D., Quiles-Carrillo L., Balart R., Boronat T., Montanes N.: Toughened poly(lactic acid) - PLA formulations by binary blends with poly(butylene succinate-co-adipate) - PBSA and their shape memory behaviour. Materials, 12, 622 (2019). https://doi.org/10.3390/ma12040622

[22] Tejada-Oliveros R., Gomez-Caturla J., Sanchez-Nacher L., Montanes N., Quiles-Carrillo L.: Improved toughness of polylactide by binary blends with polycarbonate with glycidyl and maleic anhydride-based compatibilizers. Macromolecular Materials and Engineering, 306, 2100480 (2021).

https://doi.org/10.1002/mame.202100480

[23] Montes M. I., D'amico D. A., Manfredi L. B., Cyras V. P.: Effect of natural glyceryl tributyrate as plasticizer and compatibilizer on the performance of bio-based polylactic acid/poly(3-hydroxybutyrate) blends. Journal of Polymers and the Environment, 27, 1429-1438 (2019).

https://doi.org/10.1007/s10924-019-01425-y

- [24] Coltelli M-B., Mallegni N., Rizzo S., Fiori S., Signori F., Lazzeri A.: Compatibilization of poly(lactic acid) (PLA)/plasticized cellulose acetate extruded blends through the addition of reactively extruded comb copolymers. Molecules, 26, 2006 (2021). https://doi.org/10.3390/molecules26072006
- [25] Pawlak F., Aldas M., Parres F., López-Martínez J., Arrieta M. P.: Silane-functionalized sheep wool fibers from dairy industry waste for the development of plasticized PLA composites with maleinized linseed oil for injection-molded parts. Polymers, 12, 2523 (2020). https://doi.org/10.3390/polym12112523
- [26] van Krevelen D. W., te Nijenhuis K.: Properties of polymers: Their correlation with chemical structure; Their numerical estimation and prediction from additive group contributions. Elsevier, Amsterdam (2009).
- [27] Auras R. A., Lim L-T., Selke S. E., Tsuji H.: Poly(lactic acid): Synthesis, structures, properties, processing, and applications. Wiley, Amsterdam (2011).
- [28] Kangallı E., Bayraktar E.: Preparation and characterization of poly(lactic acid)/boron oxide nanocomposites: Thermal, mechanical, crystallization, and flammability properties. Journal of Applied Polymer Science, 139, e52521 (2022).

https://doi.org/10.1002/app.52521

- [29] Quiles-Carrillo L., Montanes N., Sammon C., Balart R., Torres-Giner S.: Compatibilization of highly sustainable polylactide/almond shell flour composites by reactive extrusion with maleinized linseed oil. Industrial Crops and Products, 111, 878-888 (2018). https://doi.org/10.1016/j.indcrop.2017.10.062
- [30] D'Amico D. A., Montes M. L. I., Manfredi L. B., Cyras V. P.: Fully bio-based and biodegradable polylactic acid/poly(3-hydroxybutirate) blends: Use of a common plasticizer as performance improvement strategy. Polymer Testing, 49, 22-28 (2016).

https://doi.org/10.1016/j.polymertesting.2015.11.004

[31] Murariu M., da Silva Ferreira A., Pluta M., Bonnaud L., Alexandre M., Dubois P.: Polylactide (PLA)-CaSO₄ composites toughened with low molecular weight and polymeric ester-like plasticizers and related performances. European Polymer Journal, 44, 3842-3852 (2008).

https://doi.org/10.1016/j.eurpolymj.2008.07.055

- [32] Herrera N., Mathew A. P., Oksman K.: Plasticized polylactic acid/cellulose nanocomposites prepared using melt-extrusion and liquid feeding: Mechanical, thermal and optical properties. Composites Science and Technology, 106, 149-155 (2015). https://doi.org/10.1016/j.compscitech.2014.11.012
- [33] Gonzalez L., Agüero A., Quiles-Carrillo L., Lascano D., Montanes N.: Optimization of the loading of an environmentally friendly compatibilizer derived from linseed oil in poly(lactic acid)/diatomaceous earth composites. Materials, 12, 1627 (2019). https://doi.org/10.3390/ma12101627
- [34] Liminana P., Garcia-Sanoguera D., Quiles-Carrillo L., Balart R., Montanes N.: Optimization of maleinized linseed oil loading as a biobased compatibilizer in poly (butylene succinate) composites with almond shell flour. Materials, 12, 685 (2019).

https://doi.org/10.3390/ma12050685 [35] Mwaurah P. W., Kumar S., Kumar N., Panghal A.,

- Attkan A. K., Singh V. K., Garg M. K.: Physicochemical characteristics, bioactive compounds and industrial applications of mango kernel and its products: A review. Comprehensive Reviews in Food Science and Food Safety, 19, 2421-2446 (2020). https://doi.org/10.1111/1541-4337.12598
- [36] Avolio R., Castaldo R., Avella M., Cocca M., Gentile G., Fiori S., Errico M. E.: PLA-based plasticized nanocomposites: Effect of polymer/plasticizer/filler interactions on the time evolution of properties. Composites Part B: Engineering, 152, 267-274 (2018). https://doi.org/10.1016/j.compositesb.2018.07.011
- [37] Terroba-Delicado E., Fiori S., Gomez-Caturla J., Montanes N., Sanchez-Nacher L., Torres-Giner S.: Valorization of liquor waste derived spent coffee grains for the development of injection-molded polylactide pieces of interest as disposable food packaging and serving materials. Foods, 11, 1162 (2022). https://doi.org/10.3390/foods11081162
- [38] Martin O., Avérous L.: Poly(lactic acid): Plasticization and properties of biodegradable multiphase systems. Polymer, 42, 6209-6219 (2001). https://doi.org/10.1016/S0032-3861(01)00086-6
- [39] Pantyukhov P., Kolesnikova N., Popov A.: Preparation, structure, and properties of biocomposites based on low-density polyethylene and lignocellulosic fillers. Polymer Composites, 37, 1461–1472 (2016). https://doi.org/10.1002/pc.23315

- [40] Nguyen T. L., Bedoui F., Mazeran P. E., Guigon M.: Mechanical investigation of confined amorphous phase in semicrystalline polymers: Case of PET and PLA. Polymer Engineering & Science, 55, 397–405 (2015). https://doi.org/10.1002/pen.23896
- [41] Gomez-Caturla J., Balart R., Ivorra-Martinez J., Garcia-Garcia D., Dominici F., Puglia D., Torre L.: Biopolypropylene-based wood plastic composites reinforced with mango peel flour and compatibilized with an environmentally friendly copolymer from itaconic acid. ACS Applied Polymer Materials, 4, 4398–4410 (2022). https://doi.org/10.1021/acsapm.2c00373
- [42] Vogler E. A.: Structure and reactivity of water at biomaterial surfaces. Advances in Colloid and Interface Science, 74, 69–117 (1998). https://doi.org/10.1016/S0001-8686(97)00040-7
- [43] Jorda-Reolid M., Gomez-Caturla J., Ivorra-Martinez J., Stefani P. M., Rojas-Lema S., Quiles-Carrillo L.: Upgrading argan shell wastes in wood plastic composites with biobased polyethylene matrix and different compatibilizers. Polymers, 13, 922 (2021). https://doi.org/10.3390/polym13060922

- [44] Zięba A., Drelinkiewicz A., Chmielarz P., Matachowski L., Stejskal J.: Transesterification of triacetin with methanol on various solid acid catalysts: A role of catalyst properties. Applied Catalysis A: General, 387, 13– 25 (2010). https://doi.org/10.1016/j.apcata.2010.07.060
- [45] Meskens F. A.: Methods for the preparation of acetals from alcohols or oxiranes and carbonyl compounds. Synthesis, **1981**, 501–522 (1981). https://doi.org/10.1055/s-1981-29507
- [46] Arrieta M. P., López J., Rayón E., Jiménez A.: Disintegrability under composting conditions of plasticized PLA–PHB blends. Polymer Degradation and Stability, 108, 307–318 (2014).

https://doi.org/10.1016/j.polymdegradstab.2014.01.034