Journal of Polymers and the Environment (2021) 29:3271–3287
https://doi.org/10.1007/s10924-021-02112-7

ORIGINAL PAPER

Effect of Alkaline Treatment and Coupling Agent on Thermal and Mechanical Properties of Macadamia Nutshell Residues Based PP Composites

Nycolle G. S. Silva[1] · Lucas I. C. O. Cortat[1] · Daniella R. Mulinari[1]

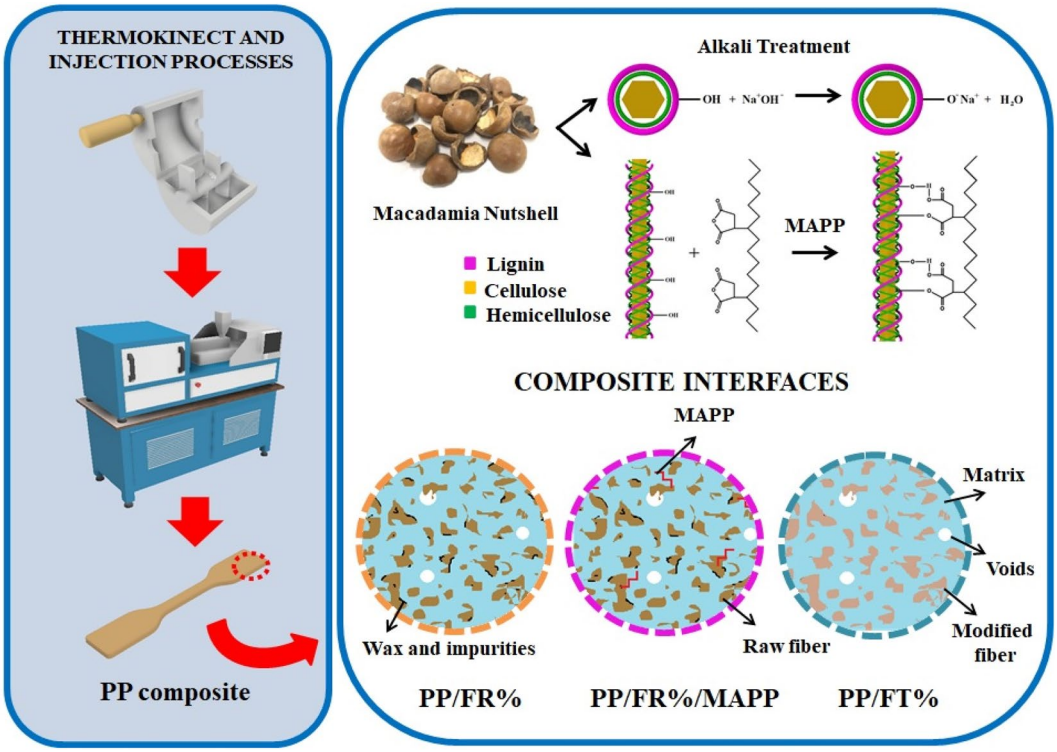
Accepted: 4 March 2021 / Published online: 18 March 2021

Abstract
The influence of alkaline treatment on the thermal and mechanical properties of polypropylene (PP) reinforced with fibers from macadamia nutshell (5 to 30 wt%) was studied. To improve the interaction between fiber and matrix, the fibers were submitted to an alkaline treatment, as well as a coupling agent (MAPP) was used. The composites were obtained in a thermokinetic mixer, milled, and injected. Then, the degradation temperature and the loss of mass of the composites, pure PP, and fibers were evaluated. The mechanical properties of the composites were also evaluated. The results indicated that the degradation peak of composites occurred at higher temperatures, which indicated that composite exhibited higher thermal stability at higher temperatures. The addition of raw and treated macadamia fibers to the PP increased the stiffness of the composites, as well as the use of a coupling agent when compared to the neat PP. However, the incorporation of 30 wt% treated fiber to the PP showed an enhancement of 67.5% in the tensile modulus. The morphological analysis enabled to evaluate the efficiency of the coupling agent and the treated fibers adhered to matrix. The response surface methodology (RSM) technique showed that the higher fiber content added to the PP enhanced the stiffness, and consequently reduced the impact strength of the materials.

✉ Daniella R. Mulinari
dmulinari@hotmail.com; daniella.mulinari@fat.uerj.br

[1] Departament of Mechanical and Energy, Universidade do Estado do Rio de Janeiro, Rodovia Presidente Dutra km 298, Polo Industrial. Resende, Rio de Janeiro 27537-000, Brazil

Graphic Abstract



Keywords Macadamia nutshell · PP · Alkaline treatment · Thermal properties · Mechanical properties

Introduction

In recent decades, global policies have encouraged the use of agricultural waste because this is believed to lead to expansion of environmental awareness and sustainable development [1–4].

Agricultural wastes are defined as the residues left from the growing and processing of raw agricultural products such as fruits, vegetables, meat, poultry, dairy products, and crops. These wastes are currently used for many applications through the '3R' strategy of waste management [3]. Besides, these agricultural wastes are left in the field, serving as soil protection or as a nutrient-providing fertilizer [5]. However, even with this practice, a high quantity of residues is burned or dumped in landfills, resulting in soil and air pollution [6]. Therefore, several applications to which these wastes can be used, such as adsorbents in the elimination of heavy metals, anaerobic digestion, pyrolysis, direct combustion, animal feed, and reinforce in polymeric composites.

The composition of agricultural waste will depend on the system and the type of agricultural activities and they can be in the form of liquids, slurries, or solids. Agricultural waste, otherwise called agro-waste, is comprised of animal waste (manure, animal carcasses), food processing waste (only 20% of maize is preserved and 80% is waste), crop waste (corn stalks, sugarcane bagasse, drops and culls from fruits and vegetables, prunings) and hazardous and toxic agricultural waste (pesticides, insecticides, and herbicides, etc.) [5].

The Macadamia nutshell is very interesting, which is a genus of flowering plants in the family of Proteaceae, with seven native species in Australia. The shells consist of 70% by weight of the macadamia nuts and are considered as agricultural solid waste. Brazil is among the countries with the greatest potential for the production of this nut in the world, where only the company Tribeca-RJ accounts for 15% of production in Brazil [7]. The main reasons for the increase in Brazilian production were the entry of small processors with a focus on the domestic market and the launch of macadamia products by large industries in the areas of baking, chocolates, and ice creams. In addition to food consumption, their oil has been used in the production of cosmetics such as shampoo, soap, and moisturizer [2, 8]. Due to the increase in the macadamia nut production, waste disposal can be burned as a wood substitute in coffee roasting, ground to produce organic waste for gardening, used for mulch in the nut tree

orchards, or used for chicken litter that, after the use, returns to the orchard to be used as fertilizer [8].

Besides, macadamia nutshell is hard and brittle. Having a biological structure, it is highly optimized and efficient in terms of strength and toughness due to its ecological evolution and selection. Thus, the re-use of macadamia nutshell acts as a solution for a waste generation, which allows the recycling of this residue and generates interest in economic, technological, and environmental terms [2, 8–10].

An interesting application of this waste is its use as reinforcement in polymeric matrices for natural fiber-polymer composites due to advantages compared to synthetic materials. Cipriano et al. [7] investigated the influence of fibers chemical treatment in polypropylene composites reinforced with macadamia nutshell fibers (5 and 10 wt%). Dong and Davies [8] studied flexural properties of macadamia nutshell particle reinforced polyester composites and evaluated the process-induced voids. Sesana et al. [9] related a high mechanical resistance of macadamia nutshell and reported and reported a potential use as filler for replacing synthetic fibers. Song et al. [10] evaluated poly(lactic acid)/macadamia composites filaments and noted that PLA-10% macadamia nutshell presented the best mechanical properties.

In this context, synthetic fiber-polymer composites have excellent mechanical properties when compared to the natural fiber-polymer composites. However, natural fiber-polymer composites have low density, are typically biodegradable, and excellent strength/stiffness, which allows them to be widely used in several applications [10, 11]. The use of natural fibers from agro-industrial residues results in renewability and green characteristics that guarantee the sustainable use of priceless products. On the other hand, the processing of natural fiber-polymer composites is limited, due to the limited processing temperature of the fibers, the hydrophilic nature of the fibers, the dimensional instability due to the water absorption, and incompatibility between fiber/matrix [12–14]. This incompatibility between the fiber-matrix can cause poor interfacial adhesion, affecting the stress transfer of the matrix to the fibers, which harms the mechanical performance of the composite.

To improve adhesion, it is necessary to add coupling agents or to treat the fibers with coupling agents, or even promote chemical attacks on the fiber surface to give it a more irregular surface, facilitating adhesion to the polymeric matrix [15–17]. One of the chemical methods most used for the modification of natural fibers is the mercerization, sometimes referred to as alkaline treatment, which removes surface impurities, as well as the occurrence of fibrillation, obtaining a fibrous material with greater surface area and smaller diameter, producing an increase in the tensile strength of the fibers and the mechanical properties of the resulting composite. This method involves the modification of the structure and the chemical composition of fibers using an aqueous solution of sodium hydroxide (NaOH) [18–21]. The concentration, temperature, and time of action of the solution will depend on the characteristics of the fibers and their application. The type of alkali and its concentration influence the degree of swelling, and therefore, on the degree of transformation of the monoclinic crystalline lattice of cellulose I, presented by native cellulose, to cellulose II, which is a polymorph of cellulose I [22–24].

Opoku et al. [25] studied the effect of alkaline pretreatment and compatibilizer agent (MAPP) in the flax fiber-PP composites and obtained an increase of physical and mechanical properties (water absorption, tensile, and impact strength). However, their results showed that the incorporation of MAPP increased the negative effect of the fiber loading on flow behavior. Nayak et al. [26] investigated the effect of NaOH treatment of sisal fiber and the effect of other surface treatments such as silane, acetylation, strontium titanate ($SrTiO_3$), glycidyl methacrylate (GMA), and O-hydroxybenzene diazonium chloride (OBDC) with and without MAPP as compatibilizer. Their results confirmed that the alkali treatment or combination of alkali treatment and MAPP improves fiber-matrix interfacial adhesion such as mechanical and physical properties and that the optimum mechanical performance was obtained for the composite with 30 wt% of alkali-treated fiber and 5 wt% of MAPP. However, it was observed that the incorporation of Si, GMA, and OBDC to the composite improved mechanical and thermal properties. Akhatar et al. [20] evaluated the influence of alkaline treatment and fiber loading on the physical and mechanical of kenaf/polypropylene composites. Results demonstrated that the alkaline treatment on surface fiber improved the physical, morphological, and mechanical properties of composites due to the compatibility of kenaf-PP. However, variations in tensile and flexural properties depend on the treatment and kenaf fiber contents. Alharbi et al. [21] studied the effects of chemical composition, alkaline pretreatment, and particle size on mechanical, thermal, and structural properties of binderless lignocellulosic biopolymers prepared by hot-pressing raw micro fibrillated *Phoenix dactylifera* and *Cocos nucifera* fibers and leaves. By mechanical and thermal properties, the optimum results were observed for biopolymers pre-treated with 1 wt% NaOH, except for coconut leaf-based biopolymers. Results were correlated to chemical composition and particle size of milled lignocellulosic biomass. Vidyashri et al. [27] reported the influence of alkaline and $KMnO_4$ chemical treatments on epoxy/sugarcane bagasse composite and observed an improvement in the roughness of fibers surface, in thermal stability, and tensile properties.

Another interesting method is chemical grafting using maleic anhydride, which is one of the most popular, not only for modifying the fiber surface but also for entangling with the polymer matrix obtaining better interfacial bonding resulting in better mechanical properties of the composites

[28]. This compatibilizer must have at least two different co-monomers in its structure, where each one is compatible with each mixed homopolymer to increase the compatibility between fiber-matrix [29]. Chauhan et al. [30] investigated the effect of m-TMI-g-PP as a coupling agent in bamboo fiber-PP composites and revealed a continuous increase in tensile strength, flexural strength, and modulus of elasticity with higher fiber content. Besides, SEM images of the fracture surface showed effective wetting of the bamboo and polypropylene fiber. Arsad et al. [31] prepared green composites reinforced with kenaf fiber treated with NaOH, recycled PP/recycled PA6 as a copolymer**,** and MAPP as compatibilizer. During the increase of fiber loading**,** it was observed a decrease followed by an increase in tensile strength and flexural strength, an increase in elastic modulus**,** and a decrease in the impact strength due to the higher hardness of the material. Furthermore, the best kenaf fiber composition to produce green potential composite was the content of 30 wt%. On the other hand, Balasundar et al. [32] studied physical, mechanical, morphological, and chemical characteristics of pistachio nutshell for bio filler application and reported from surface roughness data that this nut does not require any treatment, also presenting good structural and thermal properties and can be considered as a potential filler for replacing synthetic fibers.

Among polymers matrices, polypropylene (PP) is a polyolefin with wide extensive use in various applications like automobile, electronic, and domestic appliance industries. Besides, PP presents a low melting point, resistance to many chemicals, hydrophobic character, good stiffness, and strength and it is relatively cheap [19, 28, 33, 34]. One of its further advantages is that its properties can be modified by filler and fibers to improve its stiffness, strength, dimensional stability, or impact strength.

This study proposed the use of macadamia nutshell residues in different contents (5, 10, 15, 20, 25, and 30 wt%), using polypropylene (PP) as a polymeric matrix. The effect of surface treatment and compatibility agents on thermal and mechanical properties were evaluated.

Materials and Methods

Materials

To obtain the natural fibers-polymer composites, the fibers from the macadamia nutshell residues were supplied by Tribeca, located at Fazenda Santa Marta, Piraí/RJ, and polypropylene (PP) was provided as pellets by BRASKEM (H503). Fibers were then ground in a mill and sieved to obtain samples that passed through 35 mesh screens. The compatibilizer used was maleic anhydride grafted polypropylene (MAPP) Epolene 43P provided by Westlake Chemical Corporation with a molecular weight of 9100 g/mol and acidity index of 45 mg KOH/g.

Fiber Treatment

Macadamia fibers were oven-dried for 24 h at 100 °C. Following, to modify the fibers surface, an alkaline treatment process was used, immersing the raw fibers in NaOH solution (4% m/v) to 70 °C and maintained at this temperature for 1 h. Then, they were filtered in a vacuum filter and washed with distilled water until neutral pH, as can be shown in Fig. 1.

Characterization

The morphology of the raw and treated fibers was analyzed by Scanning electron microscopy (SEM), by using a microscope HITACHI model TR-3000 (HITACHI Ldt., Tokyo, Japan), with tungsten filament operating at 5 kV, a low-vacuum technique was employed, and a secondary electron detector. Samples were dispersed on brass support and fixed with a double face 3 M tape. To determine the diameter and length of fibers a histogram with Gauss fit function was plotted in the mathematical software OriginPro 8.5.

The physical structures of the fibers were evaluated by X-ray diffraction using a Shimadzu diffractometer, (model XDR-6100, Kyoto, Japan). The measuring conditions were: CuKa radiation with graphite monochromator, 30 kV voltage, and 40 mA electric current. The patterns were obtained in 10°–50° angular intervals with 0.05 steps and 1 s of counting time. The crystallinity index (CI) was calculated by using Eq. (1), where I_{002} is the maximum intensity of the I_{002} lattice reflection, and I_{101} is the maximum intensity of X-ray scattering broadband, due to the amorphous region of the sample. This method was developed by Segal et al. [24], and it has been widely used for the study of natural fibers.

$$CI = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} \times 100 \quad (1)$$

where CI – Percentage of crystallinity index; Ic represents the maximum intensity of crystalline region peak and I_{am} represents the intensity of amorphous region, calculated as the minimum height of the valley between the crystalline peaks.

The chemical structures of the fibers were analyzed by Fourier transformed infrared (FTIR) spectroscopy with attenuated total reflectance (ATR) diamond accessory conducted on a Frontier 94,942 (PerkinElmer Inc., Waltham, Massachusetts, USA) equipment. The analysis was performed in a transmittance mode with 64 scans, in a range of 4500–400 cm^{-1}, at the resolution of 4 cm^{-1}.

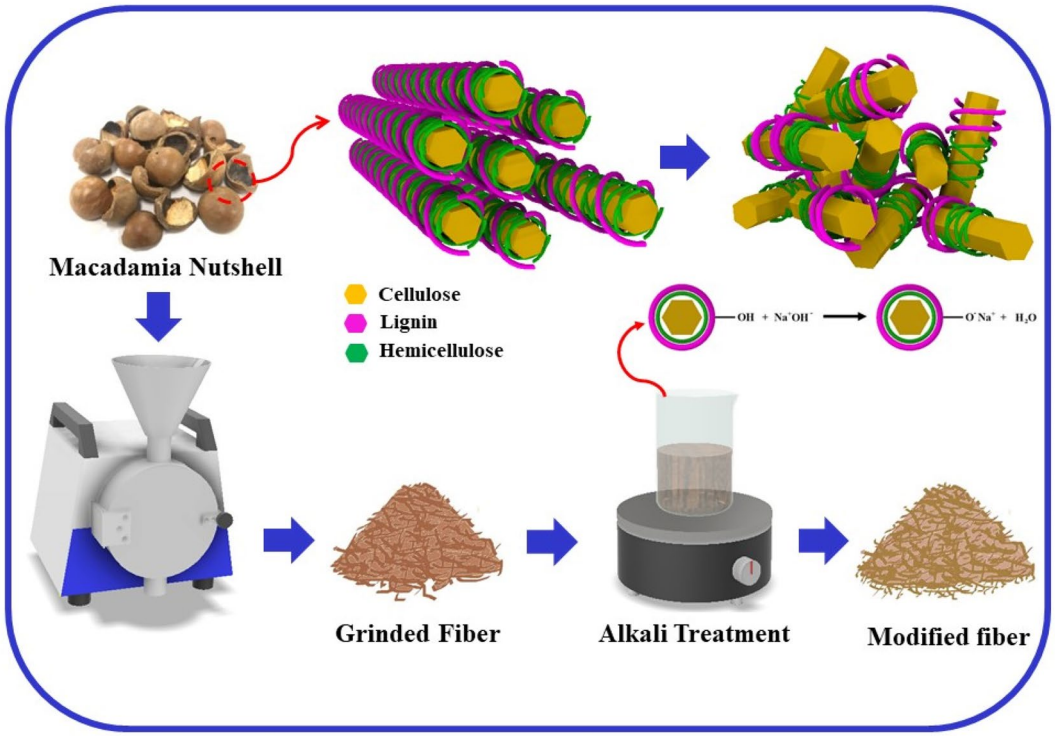


Fig. 1 Scheme of the alkaline treatment in the raw fibers from macadamia nutshell

Preparation of PP Composites

The raw and treated fibers were mixed with polypropylene (PP) in a thermokinetic mixer model MH-50H, 48 A (MH Equipamentos Ltda., Guarulhos, SP, Brazil) at a high-speed rate rotation (5250 rpm) for 53 s, in which fibers were responsible for 5 to 30 wt% of the composition. The composites were then milled in a granulator mill (brand Plastimax, 3.7 kW, Caxias do Sul, RS, Brazil) and dried at 50 ºC for 2 h. When the coupling agent was used, the proportion of PP was 78 wt% and the coupling agent was 2 wt% (Table 1). The composites injection was conducted in a digital injector (model IHM-BC-06, AX Plásticos Máquinas Técnicas Ltda., Diadema, SP, Brazil), using four heating zones in the injection unit: (i) First zone (material entrance) – 185 °C; (ii) Second zone (intermediate heating) – 190 °C; (iii) Third zone (intermediate heating) – 195 °C; (iv) Fourth zone (injector nozzle) – 50 °C.

Thermal Characterization of the Composites

The thermal stability of the composites was examined by performing the thermogravimetric analysis (TGA). This test method computes the weight loss incurred in the materials with the action of the temperature in a controlled atmosphere. Measurements were made by subjecting the material to a temperature range of 25–600 °C. TGA was conducted a

Table 1 Compositions in wt% of composites

Samples	PP	FR	FT	MAPP
PP	100	–	–	–
PP/5%FR	95	5	–	–
PP/10%FR	90	10	–	–
PP/15%FR	85	15	–	–
PP/20%FR	80	20	–	–
PP/25%FR	75	25	–	–
PP/30%FR	70	30	–	–
PP/5%FR/MAPP	93	5	–	2
PP/10%FR/MAPP	88	10	–	2
PP/15%FR/MAPP	83	15	–	2
PP/20%FR/MAPP	78	20	–	2
PP/25%FR/MAPP	73	25	–	2
PP/30%FR/MAPP	68	30	–	2
PP/5%FT	95	–	5	–
PP/10%FT	90	–	10	–
PP/15%FT	85	–	15	–
PP/20%FT	80	–	20	–
PP/25%FT	75	–	25	–
PP/30%FT	70	–	30	–

FR raw fibers, *FT* treated fibers

Thermo analyzer TG/DTA 6200 series, model Exstar 6000 (Perkin Elmer® Inc, Boston, Massachusetts, USA), with a heating rate of 10 °C min^{-1} in a nitrogen atmosphere and specimen weight of 10 mg.

Mechanical Characterization

Five specimens were tested for each composite and PP pure. Tensile tests were carried out according to ASTM D638 using an EMIC testing machine, model DL2000, Instron Brasil Equipamentos Científicos Ltda, São José dos Pinhais, Paraná, Brazil), equipped with pneumatic claws with a load cell of 5 kN at a crosshead speed of 1.3 mm/min. The Young´s modulus was calculated from the linear region of the stress–strain data. Impact tests were performed on an EMIC brand Izod type equipment, with a 1.5 J pendulum with five specimens analyzed with dimensions in agreement with the ASTM D 256 standard.

Morphology

The fractured surface of the samples on composites from tensile and impact tests was examined through a scanning electron microscope (SEM) by using a microscope HITACHI model TR-3000 (HITACHI Ldt., Tokyo, Japan), with tungsten filament operating at 5 kV, employing a low-vacuum technique and a secondary electron detector. Samples were dispersed on brass support and fixed with a double face 3 M tape. The fracture surface of the samples on composites was also analyzed by Stereomicroscopy using ZEISS Axio Imager 2.

Results

FTIR

From the spectra obtained by FTIR (Fig. 2), it can be observed that the NaOH treatment effectively modified the fiber composition. It was observed broadband appeared at 3347 cm^{-1}, which confirmed the presence of free OH groups in the cellulose molecules, while the bands that appeared between 2800 and 2900 cm^{-1} corresponded to C–H absorption bands [16]. Also, the appearance of the main spectral bands (1734, 1640, 1267, and 897 cm^{-1}) corresponding to the lignocellulosic components (cellulose, hemicellulose, pectin, and lignin) constituting the raw macadamia fibers was visible. After the alkaline treatment, a decrease in peak intensity around 3347 cm^{-1} was observed, referring to the stretching of the −OH bonds of polysaccharides and displacement to 3334 cm^{-1}, which is assigned to the change in the crystalline system. Partial removal of hemicellulose, lignin, and pectin by the decrease of the band at 1734 cm^{-1}

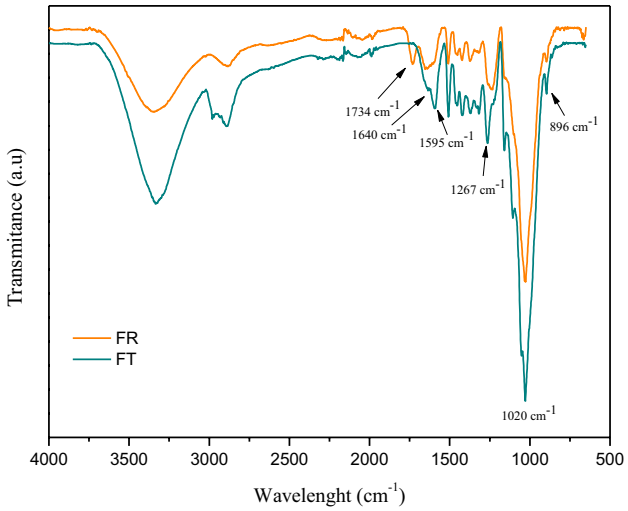


Fig. 2 FTIR spectra of raw and treated fibers

was also observed, which is related to C=O bonds of the aldehydic groups in the lignin and acetyl groups in the hemicellulose [20]. Peak intensity at 1640 cm^{-1} is related to the OH bending of absorbed water and its near-disappearance after the alkaline treatment due to the partial removal of lignin on the fiber surface and the absorption at 1595 cm^{-1} is relative to the vibration of C=C bonds of the aromatic rings, which decreased in intensity after the treatment [20, 35]. The peak intensity around 1267 cm^{-1} related to C–OH in a plane at C-6 was moved after the alkaline treatment, which is related to a crystal change from cellulose I to cellulose II [36]. Also, the peak intensity at 1020 cm^{-1}, which is atributted to the stretching vibration of the functional groups of hemicellulose and cellulose structure increased after the alkaline treatment due to the partial removal of lignin fraction [37].

SEM

The morphological changes were studied for the confirmation of the effects on the fiber surfaces, as can be seen in Fig. 3. Raw fibers possessed impurities that were removed after alkaline treatment, as shown in Fig. 3a–d. The alkaline treatment is considered an efficient method to promote the hemicellulose and lignin hydrolysis [38], this phenomenon characterizes the onset of a defibrillation process and can be attributed to removal of non-cellulosic compounds present in the middle lamella that bind the elementary fibers and also to the removal of oil, wax, and, impurities [16, 39]. Thus, after the chemical treatment, it was noticed that the cellular structures became more evident, the waxes were removed from the fibers surface, and an evident decrease in the average size of the diameter (~50%) and the size of the fibers, which showed a length average of 205 ± 84 µm for raw fiber

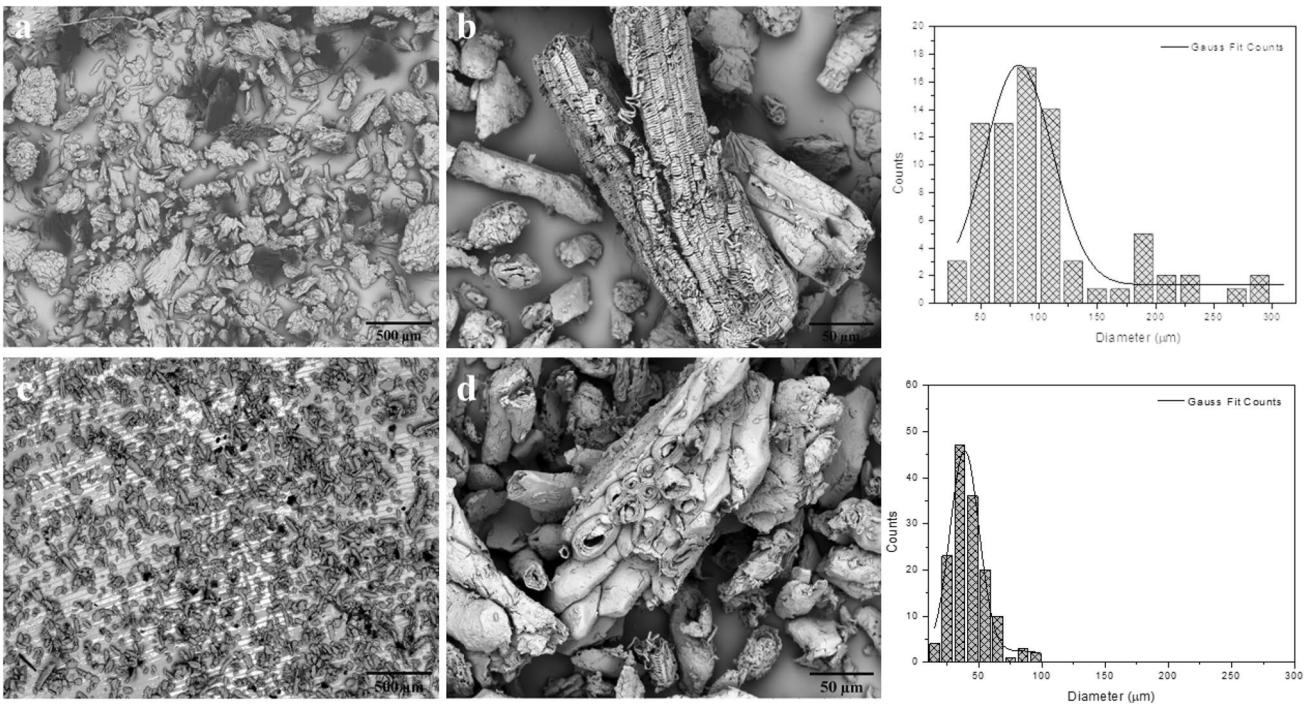


Fig. 3 SEM of fibers: raw fiber (**a**, **b**); treated fiber (**c**, **d**) and their respective diameter distribuition histograms

and 121 ± 44 µm for treated fiber, i.e., a 41% reduction in fiber length, as shown in Fig. 3a–d and their respective histograms. Zhou et al. [40] reported that the alkaline treatment makes the fiber surface rougher, improving the fiber-matrix interaction, because it increases the composite interfacial contact. [39]. Also, a reduction in fiber size, after the treatment was observed, favoring the fiber/matrix adhesion of the prepared composites. [20, 21].

XRD

Figure 4 shows the XRD of raw and treated fibers. A diffraction pattern of lignocellulosic fibers can be seen with 2θ peaks at 16°, 22° and 35° relayed to (110), (002), and (004) lattice planes, respectively, the peak valley at 2θ = 18° represented the diffraction intensity of amorphous cellulose I and the intensity at 2θ = 34.5° (004) corresponds to the alignment and direction of the cellulose II [22, 24]. Senthil et al. [41] characterized of *Musa paradisiaca L.* cellulosic natural fibers from agro-discarded blossom petal waste and observed two main peaks, the first one around 2θ = 17.87°, corresponds to the amorphous fraction (110) and the second peak corresponds to the crystallographic fraction (002) of cellulose I at 2θ = 22.01°, and a crystallinity index of 56.71%. According to Ganguli et al. [42], the pretreatments could convert native cellulose I into cellulose II, which is more crystalline. Also, a wide peak was observed at 22.6° in the treated peanut shell with NaOH and attributed

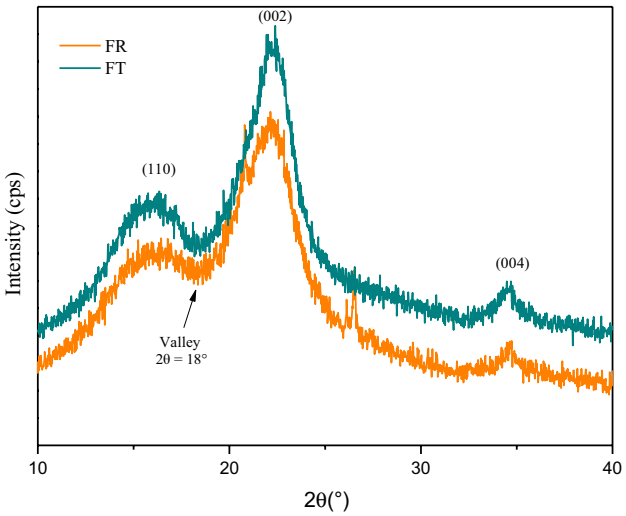


Fig. 4 XRD of the raw (FR) and treated (FT) macadamia nutshell fibers

to the digestion of cellulose structures by hydrolysis. Similar behavior was noted in the macadamia nutshell after pretreatment, which presented an increase in peak intensity at 22° and consequently showed an increase in the crystalline index. The diffractograms of both fibers are similar. However, the crystallinity index of fibers presented a slight difference. The raw and treated fibers showed a crystallinity index of 51.5% and 54.8, respectively. So, a difference of 6.4% was

noticed. This fact can be explained due to partial removal of amorphous components, such as lignin hemicelluloses, and extractives, causing an increase of crystallinity degree [16, 43, 44]. Tavares et al. [45] reported similar behavior for thermally treated açaí fiber with an increase of 4% in the crystallinity index and assimilated with the extraction of the amorphous fiber fractions. Besides, Cipriano et al. [7] reported analogous behavior for macadamia nutshell after alkaline treatment and noted an increase of 6.8% in the crystallinity index.

Thermal Characterization of the Composites

The composites reinforced with raw and treated fibers were evaluated by thermogravimetric analysis (TGA), as well as the use of the coupling agent to verify the thermal stability and degradation of the fibers, pure PP, and composites. Fibers were submitted to intense heat during composite manufacture. So, a thermal analysis study was necessary to determine the influence of fibers addition to polymer on the thermal stability of the composite.

The thermogravimetric curves of raw and treated fibers showed processes of weight loss which occurred at different temperatures (Fig. 5). The raw and treated macadamia fibers exhibited a mass loss of ~ 8% at 25–100 °C, which is related to the loss of water due to moisture of the fibers and hydrophilic character. An increase in thermal stability after the alkaline treatment was noted, which presented an increase of 5 °C in T_{onset} for treated fiber. Simão et al. [46] noted an increase in the thermal stability for sugarcane bagasse after the alkaline treatment, which presented a gain of 2 °C in T_{onset} values. Akhtar et al. [20] obtained similar thermal behavior with the kenaf fibers when they studied the influence of alkaline treatment and fiber loading

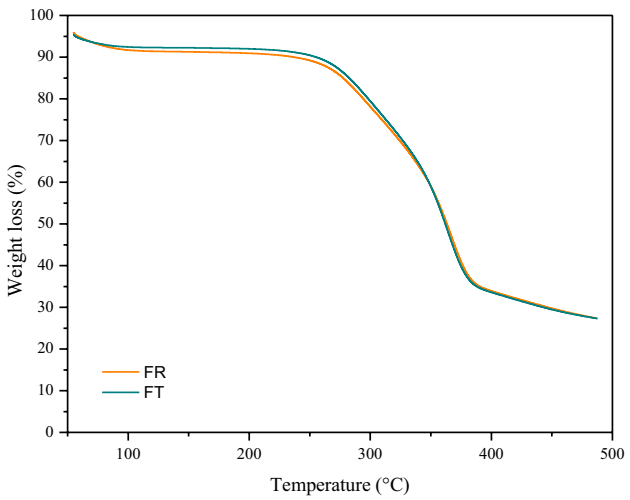


Fig. 5 Thermogravimetric curves of raw and treated fibers

on the physical and mechanical properties of kenaf/ polypropylene composites. Besides, hemicellulose and lignin decomposition were observed within a temperature range of 150–400 °C. Cholake et al. [37], cited that empty macadamia shells degrade in three stages, common for lignocellulosic residues, associated with hemicellulose, cellulose, and lignin degradation.

The thermogravimetric results obtained for the composites were compared to pure PP as can be observed in Fig. 6b, c. For neat PP the temperature range of decomposition occurred in one stage, within 400–500 °C, while for composites, two stages were noted. This fact is related to the presence of the fibers in the matrix, where the first stage corresponds to the decomposition of the fibers and the second one to the PP. The composites presented intermediary thermal stability between fiber-matrix. Besides, the addition of fibers (raw and treated) presented a slight increase in the T_{ons} of decomposition.

Table 2 shows the weight loss and degradation temperature peak of fibers, neat PP, and composites. Composites with a higher content of raw fiber presented lower thermal stability in the first stage. The opposite behavior was noted for composites with treated fiber and MAPP as a compatibilizer, which increased the thermal stability for the first stage and confirmed a better adhesion between fiber-matrix [19]. Besides, the composite with MAPP showed a higher char percentage compared to the treated fiber composite followed by raw fiber composite. Composites with a higher content of fiber presented higher ash content, where the highest content was observed for PP/FR30%/MAPP. According to Zainal et al. [47], when a good interaction between fiber-matrix occurs, it can result in the formation of an ash layer, which acts as a protection and increases the thermal stability.

Analyzing Table 2, it was observed that neat PP practically did not lose weight at 400 °C; however from 450 °C on the weight loss was accentuated, resulting in the minimum residue. PP started decomposition at about 429 °C, which was higher compared to the fiber. The composites presented different behaviors according to their formulations. The composites compatibilized with MAPP and with treated fibers are less stable, while the composites reinforced with raw fibers are more stable. Opposite behavior was reported by Zainal et al. [47] in PP/NBRr, based composites with raw and treated sugarcane bagasse, and an improvement in thermal stability of composites after the alkaline and silane treatment was observed, which was attributed to the covalent and hydrogen bonds that occur between fiber-matrix after treatment.

Moreover, it was noted that the MAPP composites with lower fiber content presented higher thermal stability compared to the treated fiber composites, due to the reaction between acid groups of maleic anhydride groups and hydrophilic groups on the surface of the fiber [28]. On the

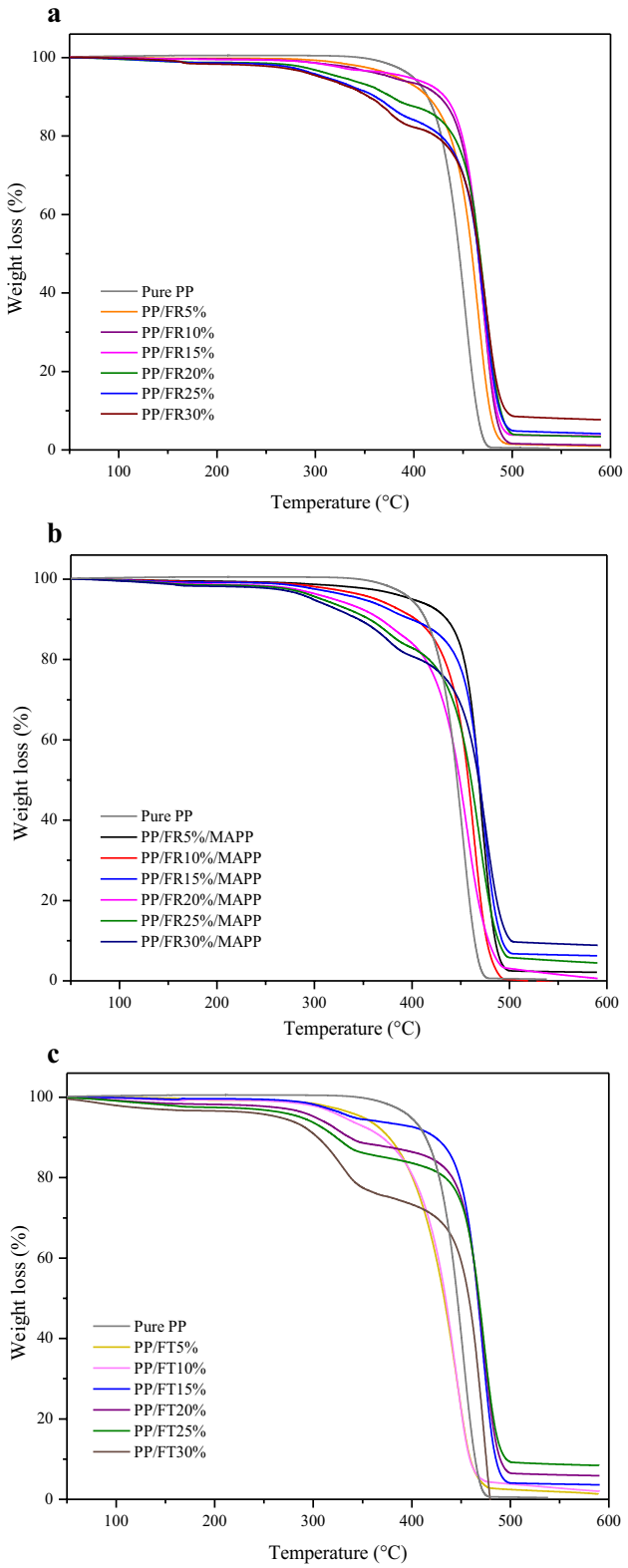


Fig. 6 Thermogravimetric curves of the composites: **a** PP with raw fiber; **b** PP with raw fiber and MAPP and **c** PP with treated fiber

other hand, the composites with high fiber loading (20% to 30% wt/wt) presented better thermal stability compared to the NaOH treated samples, which can be attributed to the stronger hydrogen bonds. Despite the loss in the thermal stability compared to raw fiber composite, the modification with NaOH and MAPP had a good influence on the mechanical properties due to the interfacial interactions.

Mechanical Characterization of the Composites

The mechanical properties of the composites varied considerably with the macadamia fiber content reinforced to the PP, as well as the type of fibers (raw and treated) and the use of a coupling agent (MAPP). Figure 7 highlights the results of tensile and impact tests for pure PP and composites.

Figure 7a shows the values of tensile modulus as a function of the fibers (raw and treated) content and the use of MAPP. The tensile modulus gradually increases from 1537.2 for pure PP to 2499.1 for PP/30%FR/MAPP. The content and type of fibers reinforced to the PP interfered in the mechanical properties were observed. However, it was also noted that the use coupling agent directly influenced in stiffness, which presented an increase of 62.6% (PP/30%FR/MAPP) when compared to the pure PP. However, PP/30%FR/MAPP composite also showed a considerable elongation values reduction, common to rigid reinforcement addition into the polymeric matrix, which limits the sliding of the polymer chains. This stiffness increase can also be explained because the compatibilizer in contact with the reinforcement surface interacted strongly with the fibers through covalent or hydrogen bonds causing a better interaction between fiber-matrix. Figure 8 shows a schematic of the interaction between the fiber surface and the MAPP.

Ghabeer et al. [48] verified an increase in the tensile modulus from 504 for neat PP to 736 for 40 wt%ES composites when studied new bio-composite materials of PP/chicken eggshell (ES) composites prepared via melt extrusion containing 10–40 wt% of untreated and stearic acid-treated eggshell. The results showed improvements in the tensile modulus of composites while the values of tensile strength, strain at break, and impact strength decreased compared to the neat PP. Abdelwahab et al. [28] also noted similar behavior when studied the effect of two compatibilizers (maleated polypropylene (MAPP) and ethylene butyl acrylate glycidyl methacrylate (EBGMA) on PP/lignin composites. Thomason and Férnandez [34] presented similar results from measurements of the interfacial adhesion of coir fiber-reinforced to various polypropylene matrices.

In opposition to the modulus, tensile strength is very sensitive to the interfacial adhesion between fiber-matrix, which plays a crucial role in transferring the stress from the matrix to the fiber. All composites showed low tensile strength values compared to the pure PP, as can be shown in Fig. 7b.

Table 2 Weight loss at different temperatures and degradation temperature peak of composites, neat PP, and fibers (raw and treated)

Samples	Weight loss (%)						Degradation temperature peak (°C)		Residue (%)
	100 °C	200 °C	300 °C	400 °C	450 °C	500 °C			
FR	8.32	9.07	21.9	66.07	70.2	72.6	267		27.4
FT	7.55	8.01	20.6	66.41	70.5	72.7	272		27.3
PP	0.00	0.00	0.00	5.42	58.78	99.45	429		0.55
PP/FR5%	0.01	0.21	0.69	7.12	33.6	98.5	–	434	1.5
PP/FR10%	0.05	0.37	1.34	6.47	22.9	98.4	–	444	1.6
PP/FR15%	0.10	0.47	1.41	5.42	21.0	96.2	328	443	3.8
PP/FR20%	0.39	1.23	3.18	12.45	25.7	95.9	318	450	4.1
PP/FR25%	0.32	1.36	4.20	15.89	29.8	95.1	302	450	4.9
PP/FR30%	0.17	1.67	4.55	17.74	29.9	91.3	300	452	8.7
PP/FR5%	0.13	0.50	1.29	4.97	16.94	97.46	–	448	2.54
PP/FR10%	0.14	0.71	1.86	9.35	36.21	99.64	–	439	0.36
PP/FR15%	0.20	0.79	2.45	10.07	22.23	92.93	333	452	7.07
PP/FR20%	0.31	1.29	3.61	15.95	51.73	96.92	321	423	3.08
PP/FR25%	0.32	1.47	4.33	17.11	36.95	94.21	323	437	5.79
PP/FR30%	0.43	1.78	5.19	19.17	66.07	89.58	319	446	10.42
PP/FT5%	0.00	0.66	1.56	19.63	77.55	97.57	–	402	2.43
PP/FT10%	0.23	0.64	2.11	19.13	77.76	96.19	335	406	3.81
PP/FT15%	0.12	0.37	1.76	7.32	21.62	95.96	300	444	4.04
PP/FT20%	0.78	1.78	4.77	13.59	24,98	93.48	285	446	6.52
PP/FT25%	0.90	2.56	6.31	16.38	26.25	90.70	290	449	9.30
PP/FT30%	2.04	3.41	9.04	26.67	40.79	100	293	447	0.00

The highest tensile strength values were for PP/25%FT composites (25 wt%) and the lowest ones were for PP/30%FR composites (30 wt%). During the analysis of composites, it was also perceived that the use coupling agent directly influenced the tensile strength, as well as the use of treated fiber.

Figure 7c evidences the effect of fiber type (raw and treated) and the use of MAPP on the elongation at break for composites. The addition of the raw fiber to the PP results in an abrupt drop in elongation at break compared to the pure PP. The addition of a higher fiber content caused a reduction in the elongation at break, indicating the incapability of the fiber to support the stress transfer from the polymer matrix. The addition of treated fiber to the PP resulted in more fragile composites compared to the raw fiber. By increasing the fiber content in the matrix, there was a decrease in the deformation of composites, causing a decrease in the toughness; consequently, a decrease in their impact strength, as shown in Fig. 7d.

Analyzing results obtained in impact strength, it was observed a gradual decrease from 29.1 kJ/m^2 for PP/5%FR/MAPP to 12.2 kJ/m^2 for PP/30%FR, compared to 34.2 kJ/m^2 for pure PP. It was noted that the composites that presented the greatest impact strength obtained the greatest elongation at break, as they absorbed more energy. The energy dissipation mechanisms that operate during impact fracture are matrix and fiber fracture, fiber-matrix debonding and fiber pull out. The main failure mechanism in these composites was fiber fracture (as there is not significant interfacial adhesion), resulting in less energy dissipation, and therefore, decreased impact strength [49]. Thus, the most rigid composites showed less impact strength. Thomason and Férnandez [34] also elucidated the decrease of impact strength with higher coir fiber loading in various polypropylene matrices. Ghabeer et al. [48] also reported a decrease in the impact strength by incorporating 10 to 40 wt% of untreated and stearic acid-treated eggshell in polypropylene composites. Nunes et al. [19] obtained similar behavior in the use of piassava fibers as reinforcement in polypropylene composites. The addition of piassava fibers (10, 20, and 30 wt%) to the PP decreased impact strength, with and without the use of maleic anhydride functionalized polypropylene (MAPP) (10 wt%) as compatibilizer. Ramos et al. [50] observed similar behavior in corncob fiber-PP composites. Ibrahim et al. [51] analyzed the addition of nano clay in PP composite with alkali-treated sisal fiber and MAPP as a coupling agent and concluded that the nano clay inclusion enhanced the

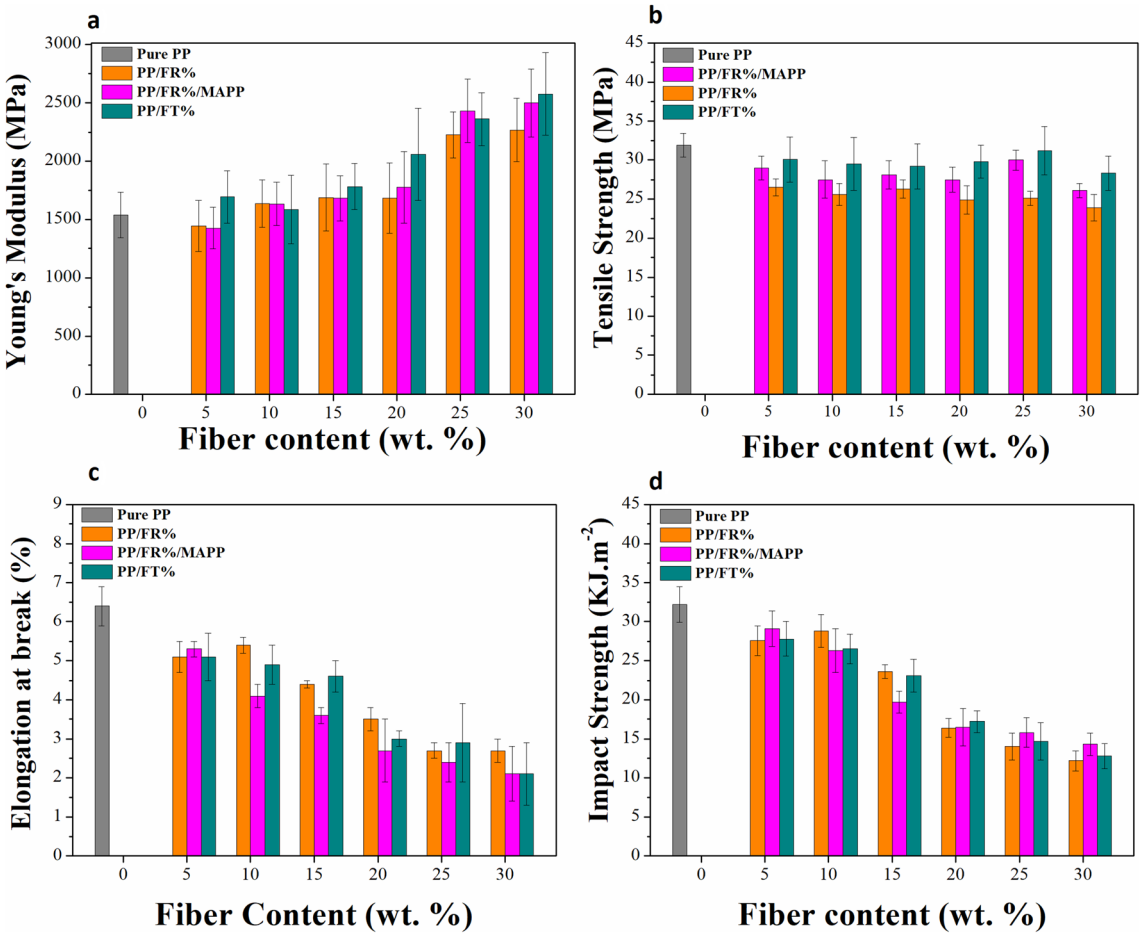


Fig. 7 Mechanical properties of pure PP and composites: **a** young's modulus; **b** tensile strength; **c** elongation at break and **d** impact strength

interfacial adhesion and consequently the tensile strength, young's modulus, and impact strength of the composites.

So, the mechanical properties results demonstrate that the macadamia nutshell fiber in different contents presents a high impact on composite stiffness, with a potential reinforcement material for composites.

Morphology

Figure 9 shows a visual aspect of the composites fracture surface obtained through an impact test by the optical microscope technique. It was noted that there was a significant content of fiber pull out and poor adhesion between fiber-matrix without the use of the coupling agent and treated fibers. Besides, it was observed that the fiber-matrix gap reduces bond properties. The visible gap between fiber-matrix suggests fiber dimensional changes after treatment and use the MAPP, as well as fiber content. The fiber-matrix gaps reduce the contact area between fiber-matrix diminishing the adhesion and affecting the frictional pull-out behavior causing a reduction in the bridging capacity of a single fiber [52]. Giri Dev and Dhanakodi [53] also observed similar behavior when studied thermoplastic composites prepared from flax fiber-polypropylene needle punched nonwovens.

Figure 10 shows the fractured surfaces of SEM micrographs of the composites with 15 wt% fibers (raw and treated), with and without a coupling agent. SEM micrographs evidenced that the incorporation of 15 wt% raw fibers to the PP matrix resulted in a phase separation due to the absence of any interaction between fiber-matrix (Fig. 10a). The micrograph of PP/15 wt% treated fibers composites showed a smoother surface, making it difficult to distinguish the fiber particles from the PP matrix, as shown in Fig. 10b.

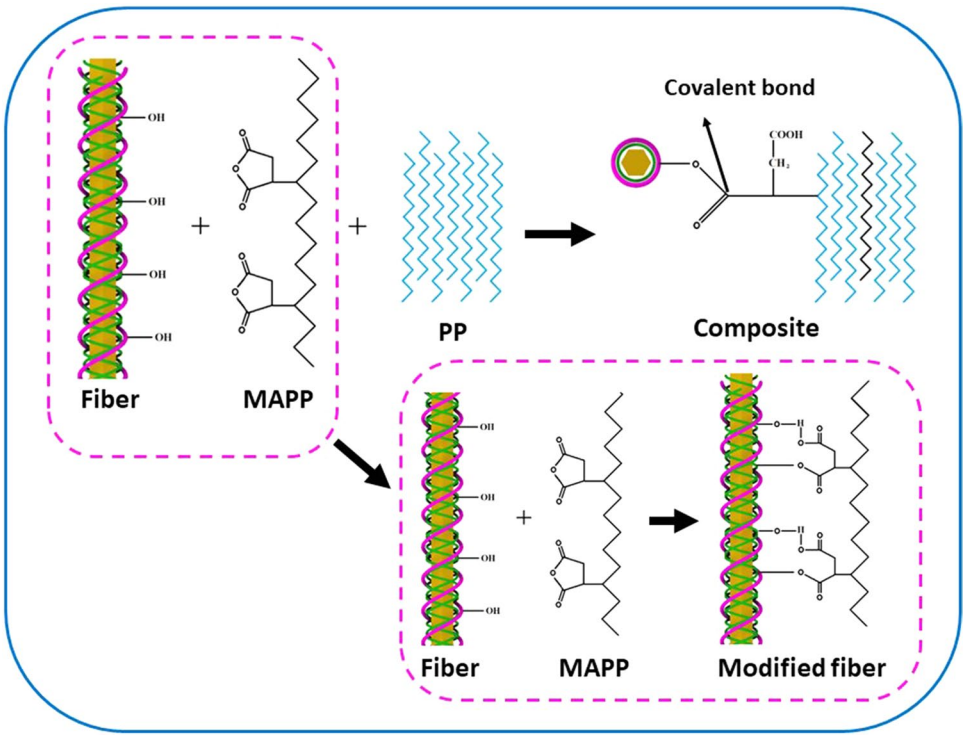


Fig. 8 Scheme representation of the interaction between fiber, polypropylene and MAPP

The same fracture surface was observed in the PP/15 wt% raw fibers composite with 2 wt% MAPP (Fig. 10c). However, the incorporation of the compatibilizer improved the interfacial adhesion between the fiber-PP matrix when compared to the composite without the use of the coupling agent. The fractured surface of the raw fibers reinforced to the PP exhibited dimpled fracture morphology, while the others appeared regular and smooth. The fiber pull out could be examined between the PP/15 wt% treated fibers composites, which improved adhesion and the impact strength of the composites. Figure 10a2–c2 presents a comparison of the composite's fractured surface under Image J with fiber's imprint in white color. Thus, it was possible to visualize a good fiber-matrix bond, sufficient for strain-hardening to occur, as well as some fiber-matrix gap and defibrillation.

Response Surface Methodology (RSM)

The interaction effects of factors such as fiber content, impact strength, and tensile modulus were demonstrated by the three-dimensional response surface statistical method and contour diagram, shown in Fig. 11.

The response surface methodology (RSM) provides for different combinations of parameters with less than 10% error. The 30 wt% fiber range demonstrated greater tensile modulus and smaller impact strength compared to the neat PP. On the other hand, the fiber type (raw and treated), as well as the use of the MAPP influenced the mechanical properties. Figure 11a shows that the higher fiber content presented higher tensile modulus, but a smaller impact strength (Fig. 11b). This behavior occurred in the raw macadamia fiber/PP/MAPP (Fig. 11c) and treated macadamia fiber/PP (Fig. 11d). The contour diagrams showed that the incorporation of 30 wt% treated fiber presented higher tensile modulus compared to the other composites. The combined effect of the fiber content and the tensile modulus could be seen more clearly by the three-dimensional response surface (Fig. 11b, d, and f).

Therefore, it is concluded that by combining a higher fiber content with PP and MAPP implies in a material with higher stiffness. Besides, the use of macadamia fiber (raw and treated) as reinforcement in PP was considered an interesting way of reducing solid waste incentivizing the utilization of agricultural waste, which can lead to expansion of environmental awareness.

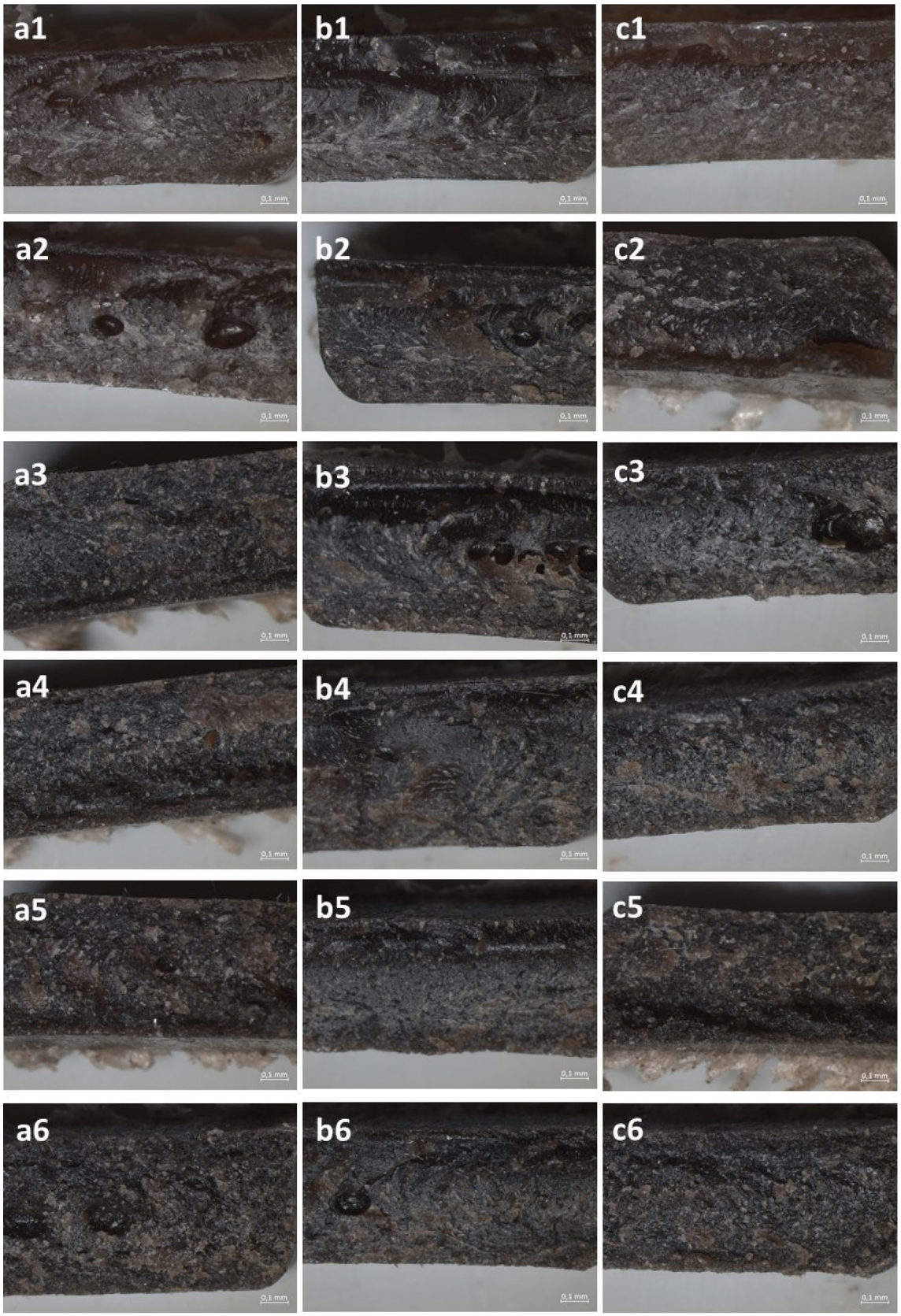


Fig. 9 Optical microscope of the compostites: PP/FR5 wt% to 30 wt% (**a1**–**a6**); PP/FR5/MAPP wt% to 30 wt% (**b1**–**b6**); PP/FT5 wt% to 30 wt% (**c1**–**c6**)

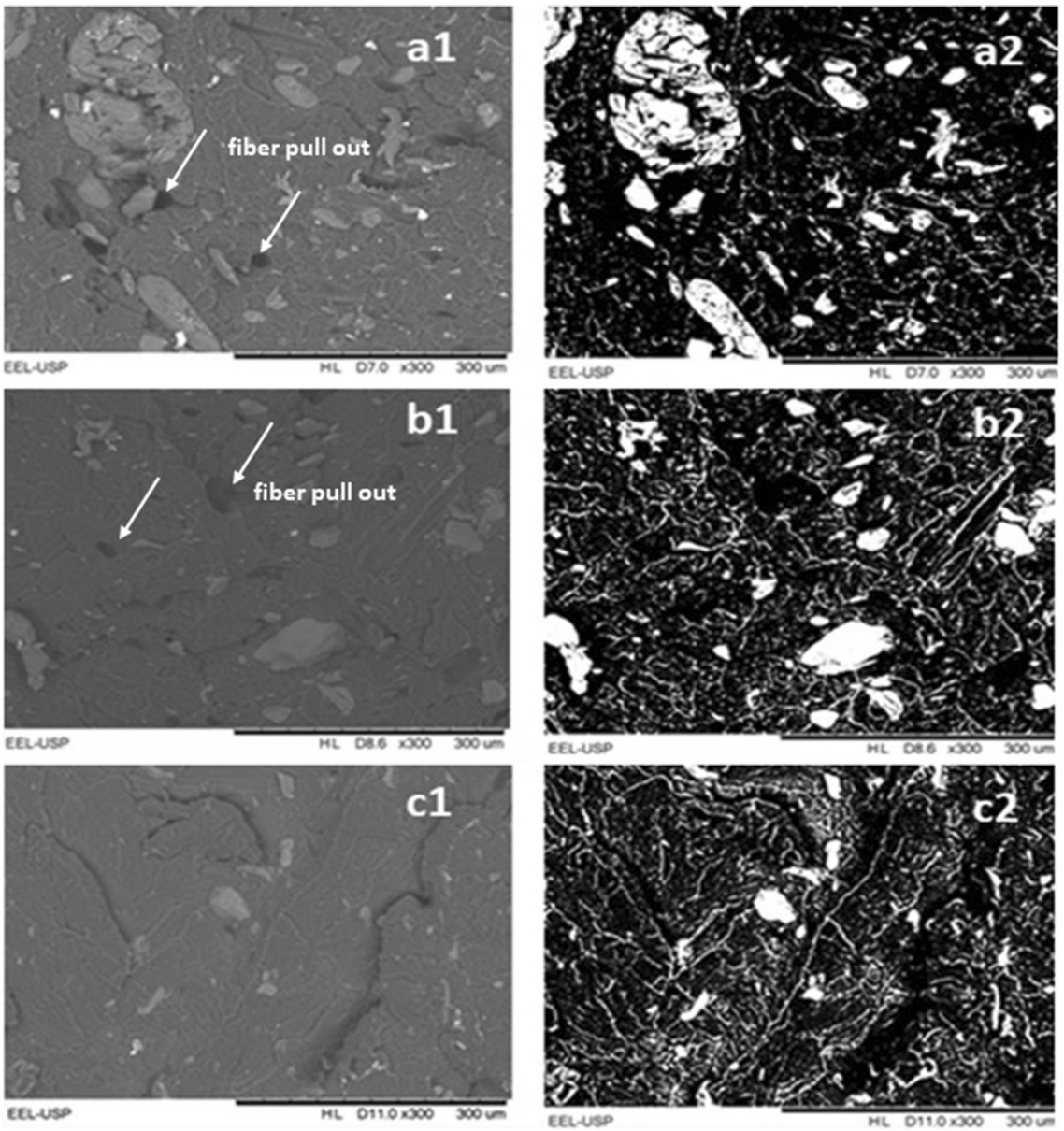


Fig. 10 SEM of the composite`s fracture surface: PP/FR15 wt% (**a1**, **a2**); PP/FR/MAPP 15 wt% (**b1**, **b2**); PP/FT15 wt% (**c1**, **c2**)

Conclusion

The effect of the alkaline treatment, compatibilizer, and fiber loading on the thermal and mechanical properties of the macadamia nutshell fiber/PP composites was studied. Results revealed that the addition of raw and treated fiber to the PP composites presented intermediary thermal stability between fiber-matrix. However, it was noted that the addition of treated fiber and MAPP as a compatibilizer to the PP composites, presented a slight decrease in the thermal stability compared to raw fiber composites. Also, the composites with higher fiber content and MAPP (PP/30%RF/MAPP) produced more residues, which are associated with good interactions that occur between fiber-matrix. The addition of raw and treated fibers to the PP increased the stiffness of the composites, as well as the use of a coupling agent when compared to the neat PP, due to interfacial interactions, which was stronger for PP/FT30% with an increase of 67.5%. Hence, a considerable

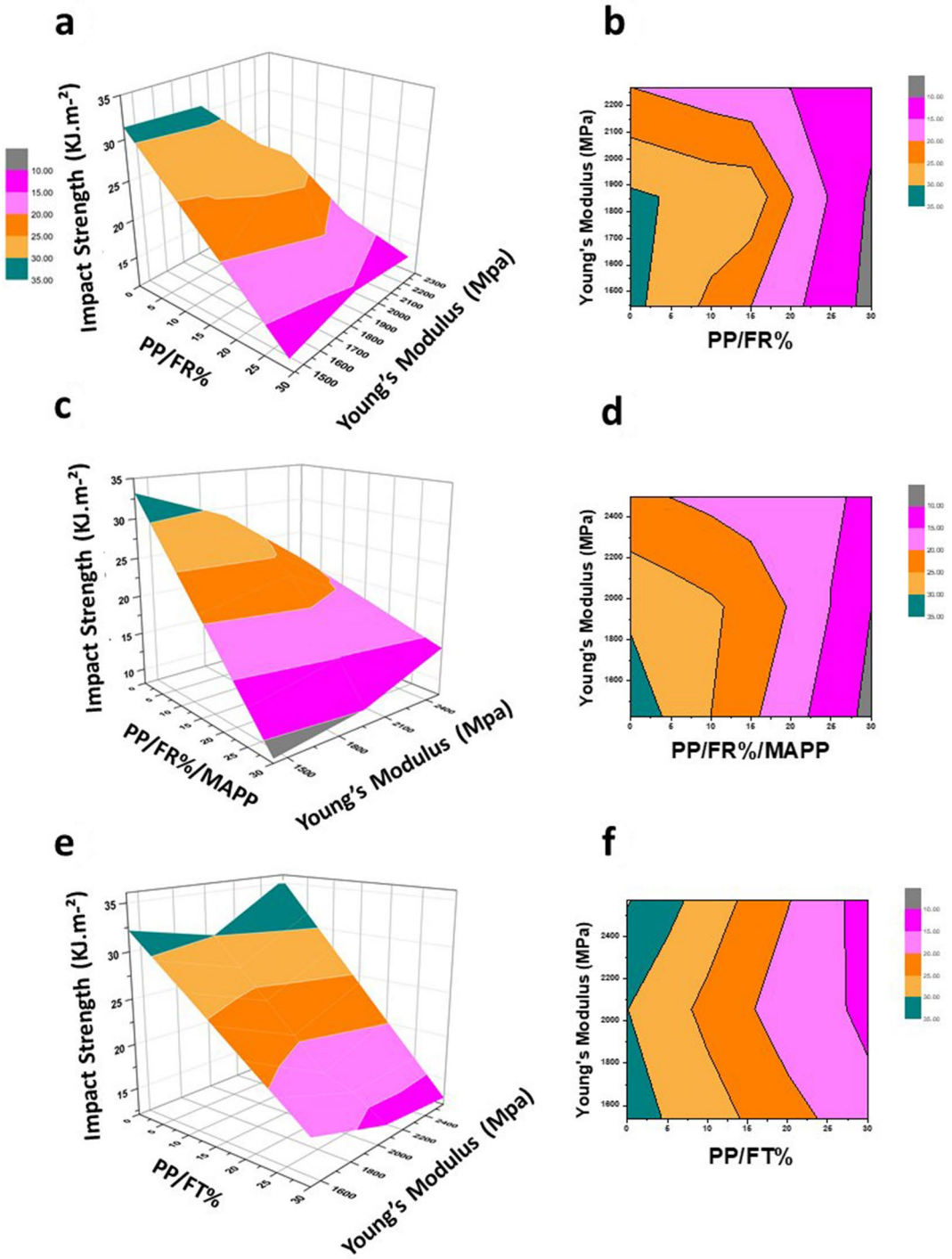


Fig. 11 Response surface methology (RSM) of mechanical properties for different content of fiber and different composites: **a** and **b** PP with raw fiber; **c** and **d** PP with raw fiber and MAPP as compatibilizer; **e** and **f** PP with treated fiber

elongation at break values reduction was observed, which decreased the toughness, and consequently, their impact strength. The morphological analysis facilitated to evaluate the efficiency of the coupling agent and treated fibers adhered to matrix. Regarding the results, the use of macadamia fiber as reinforcement to the PP was considered an insight to reduce solid waste, being that the raw fiber composites presented comparable performance to other composites formulations, making then more environmentally and economically friendly. The response surface

methodology (RSM) technique confirmed the influence of the content and type of fiber in the composites formulation on mechanical properties, showing that the fiber content increased the stiffness and consequently decreased the impact strength of the materials.

Acknowledgement This research was funded by FAPERJ (E-26/260.026/2018 and E-26/010.001800/2015).

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Väisänen T, Haapala A, Lappalainen R, Tomppo L (2016) Utilization of agricultural and forest industry waste and residues in natural fiber-polymer composites: a review. Waste Manage 54:62–73. https://doi.org/10.1016/j.wasman.2016.04.037
2. Wang B, Dong F, Chen M et al (2016) Advances in recycling and utilization of agricultural wastes in China: based on environmental risk, crucial pathways, influencing factors, policy mechanism. Procedia Environ Sci 31:12–17. https://doi.org/10.1016/j.proenv.2016.02.002
3. Nguyen H, Jamali Moghadam M, Moayedi H (2019) Agricultural wastes preparation, management, and applications in civil engineering: a review. J Mater Cycles Waste Manage 21:1039–1051. https://doi.org/10.1007/s10163-019-00872-y
4. Wei J, Liang G, Alex J et al (2020) Research progress of energy utilization of agricultural waste in China: bibliometric analysis by citespace. Sustainability. https://doi.org/10.3390/su12030812
5. Obi F, Ugwuishiwu B, Nwakaire J (2016) Agricultural waste concept, generation, utilization and management. Niger J Technol 35:957. https://doi.org/10.4314/njt.v35i4.34
6. de Souza AG, Barbosa RFS, Rosa DS (2020) Nanocellulose from industrial and agricultural waste for further use in PLA composites. J Polym Environ. https://doi.org/10.1007/s10924-020-01731-w
7. de Cipriano JP, Zanini NC, Dantas IR, Mulinari DR (2019) Mechanical properties of polypropylene composites reinforced with macadamia nutshell fibers. J Renew Mater 7:1047–1053. https://doi.org/10.32604/jrm.2019.00001
8. Dong C, Davies IJ (2012) Flexural properties of macadamia nutshell particle reinforced polyester composites. Compos Part B Eng 43:2751–2756. https://doi.org/10.1016/j.compositesb.2012.04.035
9. Bae JS, Su S (2013) Macadamia nut shell-derived carbon composites for post combustion CO2 capture. Int J Greenh Gas Control 19:174–182. https://doi.org/10.1016/j.ijggc.2013.08.013
10. Song X, He W, Qin H et al (2020) Fused deposition modeling of poly (lactic acid)/macadamia composites-thermal, mechanical properties and scaffolds. Materials (Basel). https://doi.org/10.3390/ma13020258
11. Sang L, Han S, Li Z et al (2019) Development of short basalt fiber reinforced polylactide composites and their feasible evaluation for 3D printing applications. Compos Part B Eng 164:629–639. https://doi.org/10.1016/j.compositesb.2019.01.085
12. Chandramohan D, Presin Kumar AJ (2017) Experimental data on the properties of natural fiber particle reinforced polymer composite material. Data Br 13:460–468. https://doi.org/10.1016/j.dib.2017.06.020
13. Chung TJ, Park JW, Lee HJ et al (2018) The improvement of mechanical properties, thermal stability, and water absorption resistance of an eco-friendly PLA/kenaf biocomposite using acetylation. Appl Sci. https://doi.org/10.3390/app8030376
14. Delzendehrooy F, Ayatollahi MR, Akhavan-Safar A, da Silva LFM (2020) Strength improvement of adhesively bonded single lap joints with date palm fibers: effect of type, size, treatment method and density of fibers. Compos Part B Eng 188:107874. https://doi.org/10.1016/j.compositesb.2020.107874
15. Meng X, Liu F, Xiao Y et al (2019) Alterations in physicochemical and functional properties of buckwheat straw insoluble dietary fiber by alkaline hydrogen peroxide treatment. Food Chem X 3:100029. https://doi.org/10.1016/j.fochx.2019.100029
16. Sánchez ML, Patiño W, Cárdenas J (2020) Physical-mechanical properties of bamboo fibers-reinforced biocomposites: influence of surface treatment of fibers. J Build Eng. https://doi.org/10.1016/j.jobe.2019.101058
17. Li M, Yin J, Hu L et al (2020) Effect of hydrogen peroxide bleaching on anionic groups and structures of sulfonated chemo-mechanical pulp fibers. Coll Surf A Physicochem Eng Asp 585:124068. https://doi.org/10.1016/j.colsurfa.2019.124068
18. Fonseca AS, Panthapulakkal S, Konar SK et al (2019) Improving cellulose nanofibrillation of non-wood fiber using alkaline and bleaching pre-treatments. Ind Crops Prod 131:203–212. https://doi.org/10.1016/j.indcrop.2019.01.046
19. Nunes SG, Da Silva LV, Amico SC et al (2017) Study of composites produced with recovered polypropylene and piassava fiber. Mater Res 20:144–150. https://doi.org/10.1590/1980-5373-MR-2016-0659
20. Akhtar MN, Sulong AB, Radzi MF, Ismail NF, Raza MR, Muhamad N, Khan MA (2016) Influence of alkaline treatment and fiber loading on the physical and mechanical properties of kenaf/polypropylene composites for variety of applications. Progress Nat Sci 26:657
21. Alharbi MAH, Hirai S, Tuan HA et al (2020) Effects of chemical composition, mild alkaline pretreatment and particle size on mechanical, thermal, and structural properties of binderless lignocellulosic biopolymers prepared by hot-pressing raw microfibrillated Phoenix dactylifera and Cocos nucifera. Polym Test 84:106384. https://doi.org/10.1016/j.polymertesting.2020.106384
22. Atruct J, Nagalakshmaiah M, Laroche G, Grandbois M, Elkoun SRM (2017) Isolation of cellulose-II nanospheres from flax strems and their physical and morphological properties. Carbohydr Polym. https://doi.org/10.1016/j.carbpol.2017.08.138
23. Nagarajan S, Skillen NC, Irvine JTS, Lawton LA, Robertson K (2017) Cellulose II as bioethanol feedstock and its advantages over native cellulose. Renew Sustain Energy Rev. https://doi.org/10.1016/j.rser.2017.03.118
24. Ko SW, Soriano JPE, Unnithan AR, Lee JY, Park CHKCS (2018) Development of bioactive cellulose nanocrystals derived from dominant cellulose polymorphs I and II from Capsosiphon Fulvescens for biomedical applications. Int J Biol Macromol. https://doi.org/10.1016/j.ijbiomac.2017.11.047
25. Opoku A (2008) The effect of fiber pretreatment and compatibilizer on mechanical and physical properties of flax fiber-polypropylene composites. J Polym Environ. https://doi.org/10.1007/s10924-008-0102-y
26. Nayak SK, Dixit G, Appukuttan KK (2012) Sisal fiber (SF) reinforced recycled polypropylene (RPP) composites. Int J Plast Technol 16:150–165. https://doi.org/10.1007/s12588-012-9042-4
27. Vidyashri V, Lewis H, Narayanasamy P et al (2019) Preparation of chemically treated sugarcane bagasse fiber reinforced epoxy composites and their characterization. Cogent Eng. https://doi.org/10.1080/23311916.2019.1708644

28. Abdelwahab MA, Misra MMAK (2019) Injection molded biocomposites from polypropylene and lignin: effect of compatibilizers on interfacial adhesion and performance. Ind Crop Prod 132:497–510
29. Techawinyutham L, Frick A, Siengchin S (2016) Polypropylene/maleic anhydride grafted polypropylene (MAgPP)/coconut fiber composites. Adv Mech Eng 8:1–9. https://doi.org/10.1177/1687814016645446
30. Chauhan SS, Aggarwal P, Venkatesh GS, Abhilash RM (2018) Mechanical characterization, modelling and application design of bamboo-polypropylene composites. Int J Plast Technol 22:85–103. https://doi.org/10.1007/s12588-018-9204-0
31. Arsad A, Suradi NL, Rahmat AR, Danlami JM (2013) The influence of kenaf fiber as reinforcement on recycled polypropylene/recycled polyamide-6 composites. Int J Plast Technol 17:149–162. https://doi.org/10.1007/s12588-013-9055-7
32. Balasundar P, Narayanasamy P, Senthil S et al (2019) Physicochemical study of pistachio (Pistacia vera) nutshell particles as a bio-filler for eco-friendly composites. Mater Res Express 6:18
33. Muñoz-Pascual S, Saiz-Arroyo C, Vuluga Z et al (2020) Foams with enhanced ductility and impact behavior based on polypropylene composites. Polymers (Basel) 12:1–19. https://doi.org/10.3390/POLYM12040943
34. Thomason JL, Rudeiros-Fernández JL (2019) Evaluation of injection moulded natural fiber-polyoleofin for potential in automotive applications. Mater Today. https://doi.org/10.1016/j.matpr.2019.11.059
35. Fan M, Dai D, Huang B (2012) Fourier transform infrared spectroscopy for natural fibres. Fourier Transform Mater Anal 3:46–68
36. Oh SY, Dong IY, Shin Y et al (2005) Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy. Carbohydr Res 340:2376–2391. https://doi.org/10.1016/j.carres.2005.08.007
37. Cholake ST, Rajarao R, Henderson P et al (2017) Composite panels obtained from automotive waste plastics and agricultural macadamia shell waste. J Clean Prod 151:163–171. https://doi.org/10.1016/j.jclepro.2017.03.074
38. Ratanasumarn N, Chitprasert P (2020) Cosmetic potential of lignin extracts from alkaline-treated sugarcane bagasse: optimization of extraction conditions using response surface methodology. Int J Biol Macromol 153:138–145. https://doi.org/10.1016/j.ijbiomac.2020.02.328
39. Bin BMK, Jayamani E, Hamdan S (2017) Processing and characterization of banana fiber/epoxy composites: effect of alkaline treatment. Mater Today Proc 4:2871–2878. https://doi.org/10.1016/j.matpr.2017.02.167
40. Zhou Y, Fan M, Chen L (2016) Interface and bonding mechanisms of plant fibre composites: an overview. Elsevier, Amsterdam
41. Prithivirajan R, Narayanasamy P, Al-Dhabi NA et al (2019) Characterization of Musa paradisiaca L. cellulosic natural fibers from agro-discarded blossom petal waste. J Nat Fibers. https://doi.org/10.1080/15440478.2019.1588826
42. Ganguly P, Sengupta S, Das P, Bhowal A (2020) Valorization of food waste: extraction of cellulose, lignin and their application in energy use and water treatment. Fuel 280:118581. https://doi.org/10.1016/j.fuel.2020.118581
43. Ramlee NA, Jawaid M, Zainudin ES, Yamani SAK (2019) Modification of oil palm empty fruit bunch and sugarcane bagasse biomass as potential reinforcement for composites panel and thermal insulation materials. J Bionic Eng 16:175–188. https://doi.org/10.1007/s42235-019-0016-5
44. Paixão WA, Martins LS, Zanini NC, Mulinari DR (2019) Modification and characterization of cellulose fibers from palm coated by ZrO2·nH2O particles for sorption of dichromate ions. J Inorg Organomet Polym Mater. https://doi.org/10.1007/s10904-019-01415-6
45. da Tavares FFC, de Almeida MDC, da Silva JAP et al (2020) Thermal treatment of açaí (Euterpe oleracea) fiber for composite reinforcement. Polímeros. https://doi.org/10.1590/0104-1428.09819
46. Simão JA, Carmona VB, Marconcini JM et al (2016) Effect of fiber treatment condition and coupling agent on the mechanical and thermal properties in highly filled composites of sugarcane bagasse Fiber/PP. Mater Res 19:746–751. https://doi.org/10.1590/1980-5373-MR-2015-0609
47. Zainal M, Santiagoo R, Ayob A et al (2019) Thermal and mechanical properties of chemical modification on sugarcane bagasse mixed with polypropylene and recycle acrylonitrile butadiene rubber composite. J Thermoplast Compos Mater. https://doi.org/10.1177/0892705719832072
48. Ghabeer T, Dweiri R, Al-Khateeb S (2013) Thermal and mechanical characterization of polypropylene/eggshell biocomposites. J Reinf Plast Compos 32:402–409. https://doi.org/10.1177/0731684412470015
49. Arencón D, Velasco JI (2009) Fracture toughness of polypropylene-based particulate composites. Materials (Basel) 2:2046–2094. https://doi.org/10.3390/ma2042046
50. Ramos RR, Siqueira DD, Wellen RM, Leite IF, Glenn GM, Medeiros ES (2019) Development of green composites based on polypropylene and corncob agricultural residue. J Polym Environ 27:1677–1685. https://doi.org/10.1007/s10924-019-01462-7
51. Ibrahim ID, Jamiru T, Sadiku RE et al (2016) Dependency of the mechanical properties of sisal fiber reinforced recycled polypropylene composites on fiber surface treatment, fiber content and nanoclay. J Polym Environ. https://doi.org/10.1007/s10924-016-0823-2
52. Zukowski B, dos Santos Mendonça YG, de Andrade SF, Toledo Filho RD (2020) Effect of moisture movement on the tensile stress–strain behavior of SHCC with alkali treated curauá fiber. Mater Struct Constr. https://doi.org/10.1617/s11527-020-01486-9
53. Dev VRG, Dhanakodi AKP (2018) Studies on mechanical properties of thermoplastic composites prepared from flax-polypropylene needle punched nonwovens. IEEE J Sel Top Quantum Electron 25:489–499. https://doi.org/10.1515/secm-2016-0147