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Effect of silicon dots into coconut fibers on the nucleating capacity of β-crystals of polypropylene

Efecto de puntos de silicio de las fibras de coco en la capacidad nucleante de los cristales β del polipropileno

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Abstract

The nucleating capacity of polypropylene due to the presence of silicon dots in coconut fiber was evaluated. The influence of alkaline treatment on the fiber structure and its impact on the composite's thermal and mechanical characteristics was tested by different NaOH concentrations (3, 5, and 7% w/w) and reaction times (1 and 4 h). The TGA and SEM analysis showed that the untreated fiber contains spherical structures rich in silicon, which were eliminated with the treatment. Composites were prepared with untreated and treated fibers, and their crystallization was evaluated by DSC, finding that treated fiber incremented the melting temperature. This was attributable to the increment of α-crystals; however, the introduction of untreated fiber interrupted the crystallinity sequence for α-crystallinity and favored β-crystals. These results were confirmed by XRD showing that untreated fiber maintained the crystallinity of PP and the number of β-crystals, indicating that the β-nucleating capability of the fiber is related to the presence of silicon dots on its surface. Regarding, mechanical behavior, untreated fiber composites presented the best storage modulus values, thanks to formation of β-crystals in PP due to these silicon dots. Therefore, these results open the perspective that coconut fiber can be an effective β-nucleating agent.
Keywords: Coconut fiber; silicon dots; β-crystals; crystallization; polypropylene.

Resumen

Se evaluó la capacidad nucleante del polipropileno debido a la presencia de puntos de silicio en la fibra de coco. La influencia de tratamiento alcalino en la estructura de la fibra y su impacto en las características térmicas y mecánicas del composito fue probada a diferentes concentraciones de NaOH (3, 5 y 7% p/p) y tiempos de reacción (1 y 4 h). Los análisis TGA y SEM mostraron que la fibra pura contiene estructuras esféricas ricas en silicio, las cuales fueron eliminadas con el tratamiento. Se prepararon compositos con fibras tratadas y sin tratar, y su cristalización se evaluó mediante DSC, encontrando que la fibra tratada incrementó la temperatura de fusión. Esto debido al incremento de cristales-α; mientras que la fibra sin tratar interrumpió la secuencia de cristalinidad-α y favoreció los cristales-β, esto fue confirmado por análisis de XRD, indicando que su capacidad de nucleación-β está relacionada con la presencia de puntos de silicio. Respecto al comportamiento mecánico, los compositos de fibra pura presentaron los mejores valores de módulo de almacenamiento, gracias a la formación de cristales-β debido a estos puntos de silicio. Por lo tanto, se abre la perspectiva de que la fibra de coco puede ser un agente de nucleación-β eficaz.
Palabras clave: Fibra de coco; puntos de silicio; cristales-β; cristalización; polipropileno.

1   Introduction

The commercial interest in polypropylene (PP) lies mainly in its ease of being processed in conventional equipment, like extruders. PP is the most used polymer (35.6%) in the automotive industry due to its thermal and chemical stability; and usually, it is widely used as a matrix in natural composites. PP is a common thermoplastic polyolefin that has three isomers: a) Isotactic Polypropylene (iPP), in which all the methyl groups are at one side of the main chain and is the most commercialized form. The properties of PP are mainly determined by the level of crystallinity, morphology, and orientation. These aspects are determined both by the composition of the material and by the processing applied (method and conditions).

Commercially, iPP is available as homopolymer polypropylene and present high crystallinity, which confers good mechanical properties. iPP has three crystalline structures: a monolithic form α-PP, a hexagonal form β-PP, and a triclinic form γ-PP. The α-PP form is present in the highest proportion under normal processability conditions and it can be accompanied by a low amount of β-crystals. Due to the morphology of β-type spherulites, sheaves like structure, ramifications, fanning, and lamella torments, β-PP exhibits greater impact resistance; but lower yield strength and elastic modulus, when compared with α-PP form (Gou *et al.*, 2020; Huang *et al.*, 2020; Luo *et al.*, 2019).

The formation of β-crystals in iPP can be promoted by the addition of β-nucleating agents. Nevertheless, this promotion presents difficulties due to the crystalline species of polypropylene (α and β) have different nucleation and growth rates, and that the relative amount of each species is determined by the crystallization temperature or cooling rate. Besides, it has been previously reported that only α-phase is obtained when crystallization occurs isothermally at temperatures above 130 °C; while in the range of 105-130 °C, the crystallization essentially allows the formation of β-phase (Anastacio-López *et al.*, 2019; Gonzalez-Calderon *et al.*, 2015; Gonzalez-Calderon *et al.* 2015).

The use of lignocellulose fibers, as bio fillers or reinforcements in composite polymers, has increased due to its availability, biodegradability, low density, high rigidity, and low cost (Sanjuan-Raygoza *et al.*, 2009). The components of lignocellulosic fibers include cellulose, hemicellulose, lignin, pectin, waxes, and water-soluble substances. These fibers are formed by cellulose microfibrils linked together by hydrogen bonds, embedded in a matrix of lignin (amorphous), and inserted into a network formed by crystalline hemicellulose and pectin. Coconut fibers have an average length of 0.15 to 0.28 m and their diameter varies from 0.1 to 0.5 mm. Their cells can be either cylindrical or found around a channel named lacuna (Satyanarayana *et al.*, 1981). The individual cells have concentric layers identified as the primary wall, external secondary wall S1, middle secondary wall S2, and inner secondary wall S3. The last three layers are fibrillar in nature and their thickness, composition, and orientation of cellulosic microfibers are varied (Fahlén *et al.*, 2003).

Previous studies have shown that alkaline treatment can have effects on fiber, such as changing the surface roughness by improving mechanical anchoring, as well as increasing the amount of cellulose exposed on the fiber surface; which increases the number of possible reaction sites. For example, Jacob *et al.* (2004) examined the effect of the sodium hydroxide (NaOH) concentration to treat composite materials reinforced with sisal fibers concluding that maximum tensile strength was obtained at 4% NaOH. Mishra *et al.* (2003) reported that polyester reinforced with sisal fiber previously treated at lower NaOH concentration had better tensile strength values due to high concentrations caused de-lignification resulting in a weaker or damaged fiber. Etaati *et al.* (2014) studied mechanical and viscoelastic properties of PP compounds with short hemp fiber, founding notable changes in the transition temperature at high levels of fiber or using coupling agents, as maleic anhydride (MAPOE). In recent years, interest has increased in using natural fibers to reinforce polymeric compounds due to their potential in generating better and structured materials, for example, to improve mechanical, optical, and barrier properties (Diaz-Pedraza *et al.*, 2020). Coconut fibers are of special interest because, compared to other natural fibers, such as sisal, jute, and agave, they have high lignin content and low cellulose and hemicellulose content. Previously, it has been reported (Dorez *et al.*, 2014; de Rodriguez *et al.*, 2006; Jahan *et al.*, 2011; Morán *et al.*, 2008; Pereira *et al.*, 2015; Thomas *et al.*, 2015; Wang *et al.*, 2009) that coconut fiber has a lower cellulose content (51.3%) compared to flax fibers (80%), jute (59-71.5%) and sisal (61-74%), which affects the elongation at break (Pereira *et al.*, 2015). Finally, various studies have shown that a large portion (33-35%) of the coconut is a husk, which has

a high content of silica. Uses of silica in industrial applications are varied due to its high melting point of 1700 °C (Anuar *et al.*, 2018; Tan *et al.*, 2008), which could improve the crystallization process of polymers.

The present paper outlines the effect of coconut fiber, especially the presence of silicon dots located on its surface, within a polypropylene matrix to evaluate the nucleating capacity of this filler. First, the pristine fiber and the fibers treated at different concentrations and times with NaOH were analyzed by Thermogravimetric analysis (TGA) and with the aim to identify the influence of the alkaline treatment on the fiber surface. In addition, the crystallization of these iPP composites was performed by DSC and XPS, and the effect of the fiber their mechanical properties was investigated by DMA.

2 Materials and methods

The polymer used in this study was commercial polypropylene homopolymer Formolene® 4100N, which has a melt flow index of 12 g/10 min (at 230 °C, 2.16 kg) and a density of 0.9 g/cm^3. Coconut fibers were purchased from a company in southeastern Mexico. The size of the fibers was reduced to a length of 0.5 to 1 cm and washed with a 1% w/v solution of phosphate-free detergent and water; and then, they were dried at 80 °C for 24 h.

2.1 Alkaline treatment with NaOH

The alkaline coconut fiber treatment was carried out at three different concentrations of NaOH (3%, 5% and 7% w/w) and two reaction times (1 and 4 h). Afterward, the fibers were neutralized with acetic acid, and rinsed three times with distilled water, and dried at 80 °C for 24 h. Table 1 shows the mercerization conditions for coconut fibers and the labeling for each sample. All the mercerization treatments were carried out using 120 g of coconut fiber, at a constant stirring of 300 rpm and at room temperature.

Table 1. Conditions of mercerization treatment for coconut fiber.

Time (h)	NaOH concentration % w/w	Label
1	3, 5, 7	1N3, 1N5, 1N7
4	3, 5, 7	4N3, 4N5, 4N7

2.2 Preparation of composites by melt extrusion

The composites were obtained by extrusion, adding 10% w/w of fiber and 1% of Irganox® 1076 to polypropylene in a double screw extruder model TM 20 HT (Maris), with a temperature profile of 180 °C-195 °C at 100 rpm. The PP was previously mixed in a single screw extruder with an UV protection agent 33x at 3% w/w. The composites were labeled as follows: BF-E for untreated fibers, 1N3, 1N5, 1N7, and 4N3, 4N5, 4N7 for treated fibers according to the respective conditions specified in Table 1.

2.3 Thermogravimetric analysis (TGA)

The thermal stability of the fibers was studied by thermogravimetric analysis using TA Instruments Q500 equipment, in the temperature range of 30-600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.4 Scanning electron microscopy (SEM)

The morphology of fibers was analyzed in order to evaluate how the alkaline treatment affect their structure; therefore the fibers were measured before and after the treatment in a FEI Environmental Scanning Electron Microscope (ESEM) Quanta 200 equipped with Everhart Thornley (ETD) and backscatter electrons (BSD) detectors, at a low vacuum mode and a voltage of 15 kV. The fibers were analyzed in longitudinal and transverse directions.

2.5 Differential Scanning Calorimetry (DSC)

In order to evaluate the isothermal crystallization of iPP and its composites, they were analyzed in a TA Instrument Q2000 differential scanning calorimeter, in a temperature range of -90 to 250 ºC at a heating rate of 10 °C/min. To eliminate the thermal history of the materials, the samples were preheated up to 250 °C at 10 °C/min and then suddenly cooled to -90 °C. The degree of crystallization was determined from the melting enthalpy of the second heating cycle according to the following Equation (Nayak *et al.*, 2009):

$$X_C = \frac{\Delta H_m}{\Delta H^*} \times 100 \tag{1}$$

where ΔH_m and ΔH_H^* are the melting enthalpies of the compound and the 100% crystalline polypropylene,

which according to the literature has been estimated at 240.5 J/g.

2.6 X-ray diffraction

Pure iPP and its composite with untreated fibers were analyzed by wide-angle X-ray diffraction (WAXD) with the aim of investigating the crystalline structure. A Bruker Model D8 ADVANCE brand powder diffractometer with Lynx Eye detector and Copper tube (Wavelength 1.5406 A) was used. The scanning of the samples (2θ) was performed at 7-25° with a 0.02° increment and an exposure time of 21 min. The percentage of β crystals (K_β) in the iPP matrix of both samples was estimated using the Turner Jones Equation (Turner Jones *et al.*, 1964) as follows:

$$K_\beta = \frac{H_\beta}{H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3} + H_\beta} \quad (2)$$

where H_α are the intensities of the diffraction peaks 2θ for α crystals, corresponding to $\alpha 1$= 14.2 °, $\alpha 2$= 16.6 °, $\alpha 3$= 18.5 °; and H_β is related to the diffraction peak of β crystals at 16.0.

2.7 Dynamic mechanical analysis (DMA)

To determine the effect of the untreated and treated fiber within the iPP matrix on their mechanical properties, the storage modulus, and the loss factor or tangent delta (Tan δ) were measured. The composites were subjected to dynamic mechanical analysis in a DMA Q800 equipment from TA Instrument, using a single cantilever jaw in a frequency range of -60 to 120 °C, with a heating ramp of 3 °C/min at a frequency of 1 Hz and deformation (strain) of 0.03%. The samples for the mechanical dynamic analysis were made by pressing the material at 190 °C for 3 min, with a force of 5 Ton and a preheating time of 1 min. Rectangular samples of 12.3 × 34.6 × 1.64 cm were obtained.

3 Results and discussion

3.1 Thermogravimetric analysis (TGA)

The results of the thermal analysis of the fibers are summarized in Table 2. It was decided to follow the classification of lignocellulosic components proposed by Raveendran *et al.* (1996) to identify the decomposition pattern. The alkaline treated fibers exhibited a greater weight loss than the untreated fiber. This difference can be attributed to the evaporation of superficial water present in the sample (< 100 °C) and to the volatile and removable compounds (100-250 ºC) (Hidalgo-Salazar *et al.*, 2018). This phenomenon occurred perhaps due to alkaline digestion of long-chain structural compounds or complex structures. This leads to the formation of molecules with lower molecular weight and/or thermal stability.

Regarding hemicellulose, the weight loss in the range of 250-350 °C was significantly reduced when the fiber was treated with NaOH. This is due to the fact that the alkaline treatment could solubilize or degrade the natural fiber matrix, composed of lignin and hemicellulose. Meanwhile, the decomposition of cellulose and lignin could be observed in the range of 350-500 ºC (Hosokawa *et al.*, 2017), which did not present significant differences.

3.2 Scanning electron microscopy (SEM)

The structure of the coconut fibers is well-documented in several works, for example, Bledzki *et al.* (2010) and Mishra and Basu (2020) reported that coconut fiber contains impurities making its surface extremely heterogeneous and that this surface will change and offer different properties when a treatment is applied.

Table 2. Percentages of thermal degradation data of the untreated and treated fibers.

| Degradation or effect	Temperature / °C	Untreated fiber	Treatment for 1 h			Treatment for 4 h		
			3% (1N3)	5% (1N5)	7% (1N7)	3% (4N3)	5% (4N5)	7% (4N7)
Superficial water	<100	7%	8%	10%	9%	8%	10%	9%
Volatile and removable degradation	100 - 250	7%	4%	5%	5%	4%	5%	5%
Hemicellulose degradation	250 - 350	52%	39%	37%	36%	38%	35%	34%
Cellulose and lignin decomposition	350 - 500	13%	16%	11%	14%	15%	13%	13%
Lignin decomposition	>500	8%	6%	2%	2%	5%	4%	3%

Fibers   treated   with   NaOH
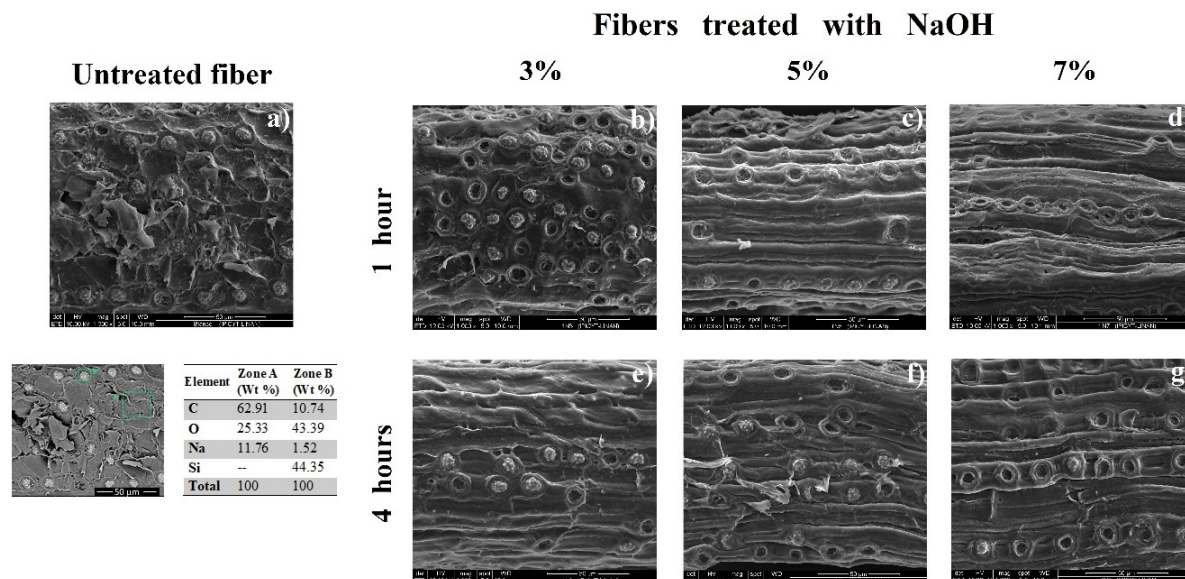
Fig. 1. Scanning Electron Microscopy images (SEM) at 1000x of the a) untreated coconut fiber and its Elementary analysis by EDX. Fibers after the alkaline treatment for one hour: b) NaOH 3% c) NaOH 5%, d) NaOH 7%; and after 4 hours: e) NaOH 3%, f) NaOH 5% and g) NaOH 7%.

While Lomelí-Ramírez *et al*. (2014) stated that it is important to fully characterize the materials used to prepare new composites in order to clarify how will be the behavior of the used fibers. Therefore, a SEM analysis of the coconut fibers was performed and reported in Fig. 1.

First, it can be seen in Fig. 1a that the fibers present spherical structures with protuberances, which have been named by some authors as silica dots (Neethirajan *et al*., 2009). The elementary analysis on the fiber surface performed by EDXA (zone A) indicated a mostly organic composition with the presence of sodium, which could be due to salts present in the fiber or due to contamination during the washing process of the fibers. While the analysis carried out on the spherical structures of the fiber (zone B) indicated that they are mainly formed by silicon (Si), carbon (C) and oxygen (O). In addition, Figs. 1b-g show the results of the fibers treated with 3, 5, and 7% of sodium hydroxide and at an exposure time of 1 and 4 hours, respectively. Similarly, it is possible to observe the presence of silica dots but in a smaller amount. When comparing the treated fibers with the pristine fiber, it is clear that the alkaline medium caused the reduction of the vegetable cuticle, and also, the elimination of the silicon dots on the fiber surface. This phenomenon was accented when the amount of NaOH increased since fewer silicon dots were present at 7% NaOH concentration. In contrast, when the treatment time was increased to 4 hours, no significant impact was observed either on the fibers or on the presence of silicon dots, compared to 1 hour of alkaline exposure.

Fig. 2 shows the TGA and DTG curves of composites with untreated (discontinuous lines) and treated (solid lines) fibers as a function of temperature. It is clear that all composites showed similar degradation profiles and that the composite with untreated fiber has better thermal stability than those with treated fiber. In this Fig. (2), it can be seen that in the interval of greatest thermal decomposition (250-350 °C), the untreated fiber (solid line) has a peak at 282.7 °C that corresponds to the decomposition of hemicellulose, which is not exhibited in the alkaline-treated fibers. Whereas, the peak in the untreated fiber at 335.9 °C is attributable to the decomposition of cellulose and the reduction of the size of the lignin, since there was a shift towards lower temperatures as the NaOH concentration increased.

The DTG curve for untreated fiber shows a first endothermic peak at 280 °C corresponding to the temperature of maximum weight loss rate (Tmax) of hemicellulose, while the second peak at 335 °C is related to the Tmax of cellulose (Hidalgo-Salazar *et al*., 2018; Lomelí-Ramírez *et al*., 2014). In addition, it is well noted that in the case of the treated fiber, the peak corresponding to hemicellulose disappears, since the alkaline treatment solubilizes or degrades the matrix of the natural fiber, as previously discussed.
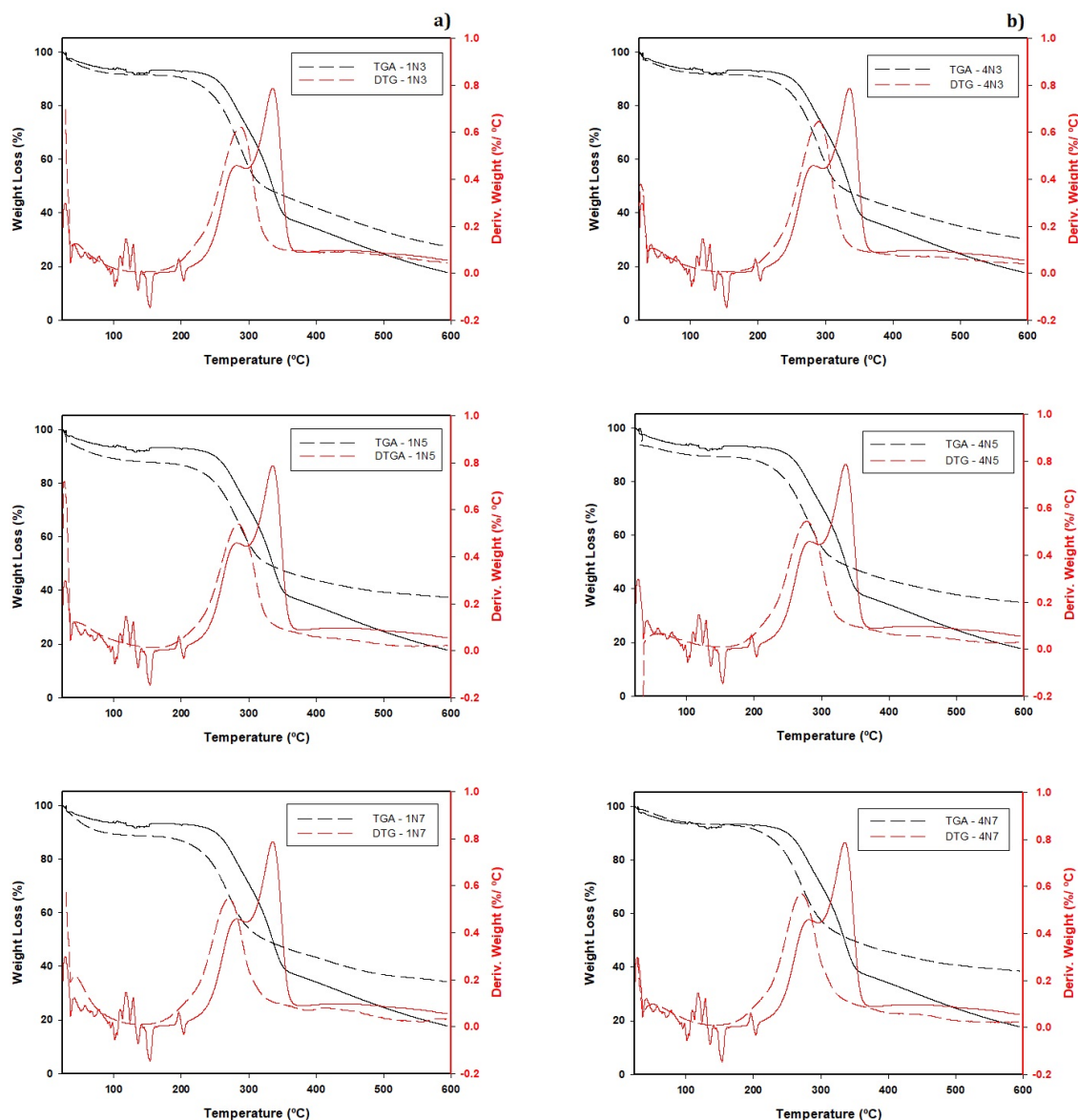
Fig. 2. TGA and DTG curves of untreated fibers (solid line) and fibers treated (dashed line) for a) 1h and b) 4h.

Another explanation is that silica could alter the thermal properties and pore structure in fibers (Raveendran *et al.*, 1996) since the alkaline treatment is commonly used to break the lignocellulosic cell walls by removing hemicellulose, lignin, and silica (Bledzki *et al.*, 1999; Gil-López *et al.*, 2019; Vieira *et al.*, 2018). Therefore, for the treated fibers, the volatilization rate increased, which promotes the initial decomposition temperature to be lowered in all cases. From the observed curves, the treatment time does not show a significant effect with respect to the rate of weight loss. However, there is a slight effect on initial weight loss as a function of NaOH concentration; since there is a decrease in weight of around 65% when the concentration is increased. This behavior could be explained by the saturation of the fiber since it tends to soak up the surface quickly in the presence of low molecular weight species. These low weight molecular species could prevent the intrusion of the alkaline solution into the internal parts of the fiber.

3.3 Differential Scanning Calorimetry (DSC)

Composites prepared with the untreated and treated fibers at different concentrations of NaOH during 1 and 4 hours were analyzed by DSC (Fig. 3). According to several research works (Anastacio-López *et al.*, 2019; Ding *et al.*, 2013; Papageorgiou *et al.*, 2015; Varga, 2002), the melting peak of iPP for α-crystals is around 160 °C and for β-crystals is 150 °C. Fig. 3a shows the thermograms of the melting curves for all samples. It is possible to observe that the melting curve for BF-E (untreated fiber) is different from those of treated fibers since the two characteristics peaks for α- and β-crystals are observed clearly; contrary to the treated fibers in which it is observed that the peak for β-crystals decreases as the NaOH concentration increases. Indeed, the peak for β-crystals disappeared when the NaOH concentration was 7%, and such behavior is also observed for the composites with treated fiber at 4 h (Fig. 3b), the peak for β-crystals disappears with the increasing of NaOH concentration; while no difference is observed regarding time of the alkaline treatment. According

to these results and to the SEM results in Fig. 1, it is possible to infer that the melting peak intensity of β-crystals is associated to silicon dots, which act as effective nucleating agents (Vieira *et al.*, 2018). Thus, as the silicon dots are eliminated by the NaOH treatment, the β-crystals are less frequently created and the α-crystals are the dominant crystal species, therefore, their melting peak is broader and deeper.

According to literature (Gradys *et al.*, 2005; Li *et al.*, 2018), it is well known that silica is widely used as a nucleating agent for isotactic polypropylene (iPP); since the compatibility between the iPP matrix and the fillers increases due to the action of the silicon points as nucleation centers (larger spherulites). These nucleation centers lead to heterogeneous crystallization. Furthermore, the formation of β crystals could be enriched during the melt extrusion process with the incorporation of untreated fibers. This is due to the redispersion of silicon dots from untreated fibers when fractured by shear action within a twin-screw extruder. Besides, the compatibility between the iPP matrix and the cellulosic filler could be increased due to the hydrophobic nature of the filler.

Table 3. Thermal parameters from DSC analysis of untreated and treated fibers.

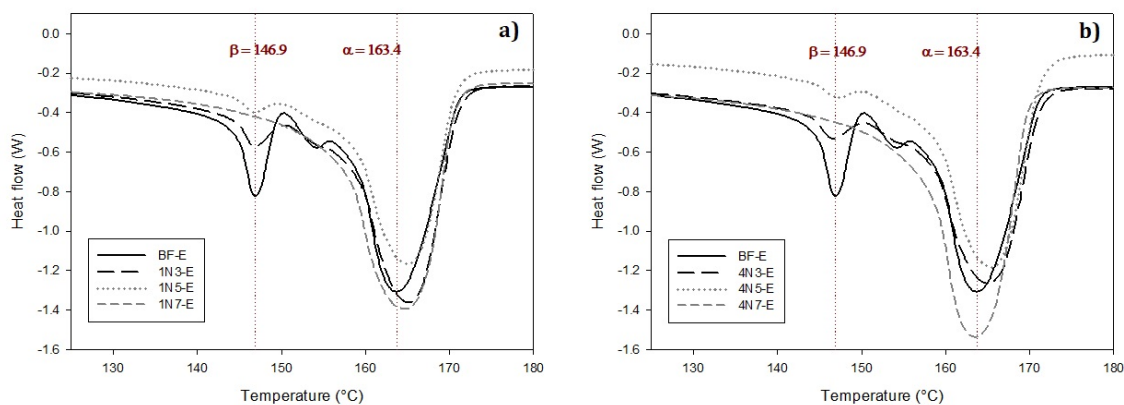| Sample | β -crystal | | α -crystal | | | | |
	T_m/°C	ΔH_m/Jg^{-1}	T_m/°C	ΔH_m/Jg^{-1}	T_c/°C	ΔH_c/Jg^{-1}	Total X_c
BF-E	146.89	12.55	164.03	54.66	122.97	89.54	43.8
1N3-E	144.31	1.457	165.55	56.47	123.24	92.47	37.8
1N5-E	146.87	0.924	164.61	91.15	120.14	96.05	59.4
1N7-E	0	0	165.56	52.35	122.79	79.95	34.7
4N3-E	146.41	3.058	165.57	53.83	122.44	85.78	37.1
4N5-E	144.19	1.47	165.84	57.47	121.3	89.24	38.4
4N7-E	0	0	163.66	88.96	121.73	97.12	58

Fig. 3. Melting behavior of composites by DSC: untreated fibers and fibers treated for a) 1 h and b) 4 h.

Thermal properties such as crystallization temperature (T_c), crystallization enthalpy (ΔH_m), melting temperature (T_m) and melting enthalpy (ΔH_m) obtained from DSC studies of polypropylene and its composites are summarized in Table 3. The crystallinity of PP and the composites were determined through equation 1.

According to the results, the inclusion of treated fiber in iPP does not have a significant influence on the melting temperature, which is attributable to the presence of α-crystals, despite the fact that the α-enthalpy with the lower NaOH concentration (3 and 5%) was reduced, due to the presence of β-crystals. Thus, the introduction of the untreated fiber interrupts the crystallinity sequence of this polymer and favors the formation of the β-crystals due to the silicon dots presence. With all these data, it is possible to confirm that the composites with treated fibers, with high NaOH concentration (7%), behave as pure iPP, for example when analyzing the composites with the fibers treated for four hours, the thermal transition associated with this β phase disappears as the NaOH concentration increases. Therefore, the composite with fibers treated at 7% NaOH (4N7-E) practically has the same ΔH_m value as the pure PP.

3.4 XRD analysis

The X-ray diffraction patterns were obtained for pure iPP and for the composite with untreated fiber (Fig. 4). Pure iPP shows two types of crystals, the signals at 2θ are related to $\alpha 1 = 14.2°$ (1,1,0), $\alpha 2 = 16.6°$ (0,4,0), $\alpha 3 = 18.5°$ (1,3,0), and all peaks correspond to the α-crystal structure; in addition, another peak is clearly observed, which is related to the diffraction peak of β-crystals at $2\theta = 16.0$ (3,1,1). On the other hand, it is observed a reduction in the crystallinity percentage of PP for the polymer blends, therefore, it can be stated that the addition of untreated coconut fibers affects some of the main pathways during the polymer crystallization (Torres-Huerta *et al*., 2018); this may due to the presence of the fibers can limit the formation of nuclei or alter the growth of the spherulite. The peak associated to the plane (1,1,0) changed with the presence of untreated fiber, which implies that the crystallinity was reduced. In addition, the planes (3,0,0) and (0,4,0) were slightly shifted toward lower 2θ values, and that means that the lattice parameters were changed, probably expanded, due to the presence of fibers. Furthermore, a decrease in the intensity of the $\alpha 1$ peak and an increase in the intensity of β crystals is observed.
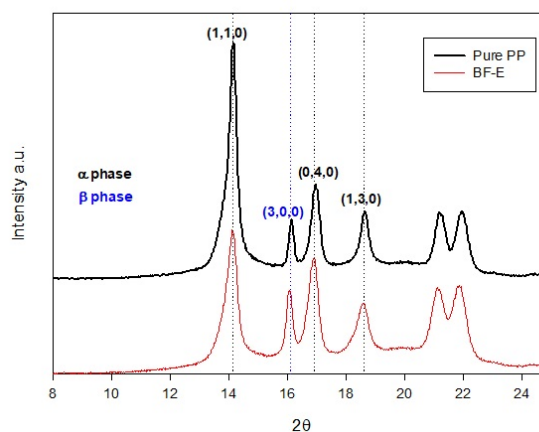

Fig. 4. X-ray diffraction patterns of the pure iPP and composite with untreated fiber.

This behavior was validated with the results obtained from the Turner-Jones equation (Eq. 2). A value of $K_\beta = 0.18$ was obtained for pure iPP and $K_\beta = 0.20$ for the untreated coconut fiber compound. These results are consistent with those obtained in the DSC analysis. According to previous research works (Anastacio-López *et al*., 2019; Turner Jones *et al*., 1964), the behavior of the composite with untreated fiber is attributable to the nucleating effect of the silicon points. Which cause a heterogeneous nucleation mechanism in the polymeric matrix when its crystallization process takes place.

3.5 Dynamic mechanical analysis

According to some authors, it is known that natural materials used in polymeric blends can influence the final properties of the resulting composite, especially in mechanical properties (García-Cruz *et al*., 2020; Tapia-Picazo *et al*., 2014). The thermomechanical behavior of iPP and its compounds are visualized in Fig. 5; in this analysis, a decrease in the elastic capacity of the samples can be observed as a function of temperature. This decrease is reflected in turn in the decrease of the storage module. The reduction in stiffness and the increase in toughness is associated with the reinforcement of the polymeric matrix with cellulosic material. Moreover, a remarkably different behavior was observed in the storage modulus when the composite with untreated fiber was subjected to low temperatures. As the temperature is lowered, the incorporation of coconut fiber causes that the composite to absorb a greater amount of energy without dissipating it.
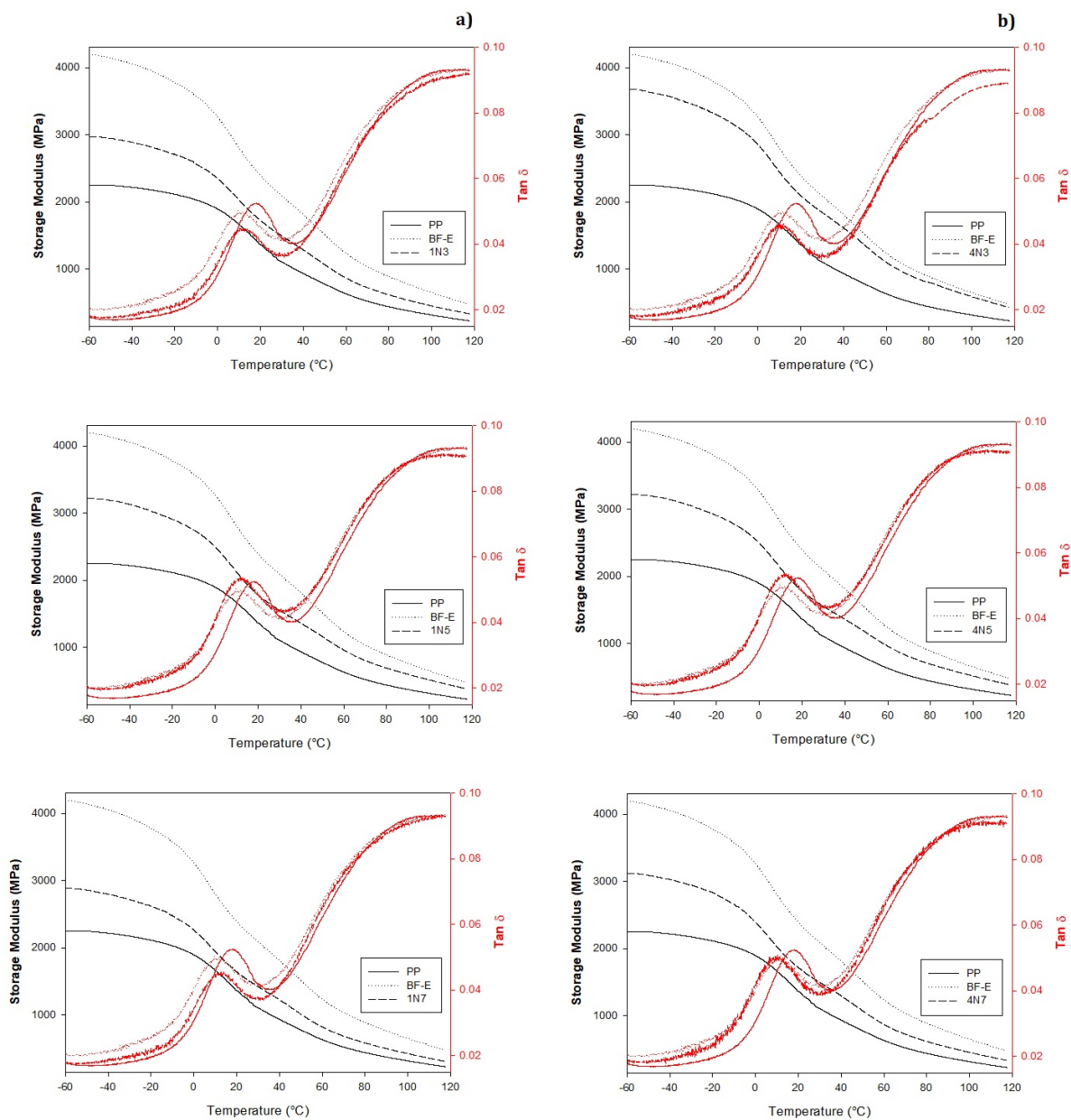
Fig. 5. DMA measurements of iPP and its composites with untreated fibers and fibers treated for a) 1 h and b) 4 h.

Nevertheless, for the composite with NaOH-treated fiber, the elastic modulus is higher than pure iPP but lower than the composite with untreated fiber, indicating that the NaOH treatment contributes to reduce the stiffness of the composite, especially at sub-ambient temperatures, probably due to the lower silicon dots concentration, and consequently lower β-crystals content. While at high temperatures such

composite has a higher storage modulus than the pure iPP, due to the reinforcement imparted by the fiber that transfers the stress from the matrix to the fiber. It is well-noted that the storage modulus increased when the composites contain fiber, especially the composite with untreated fiber, which had the highest value (4260 MPa), which is an improvement of 89.2% regarding pure iPP, this due to the mechanical

reinforcement provided by the fiber. Also, it is important to mention that when the composite had untreated fiber, the storage modulus exhibited the greatest value due to high percentage of β-crystals (Anastacio-López *et al*., 2019). These results agree with the trend observed by DSC, in which the β-crystal content into the composite was higher in comparison to pure iPP (Fig. 3).

Finally, it is well-noted in Fig. 5 that time of treatment had low effect on these mechanical properties since the values of the composites with fibers treated for 4 hours is greater than the composites with fibers treated for one hour. On the other hand, when analyzing tan δ, which is the ratio of viscous to elastic modulus of the elastic phase between the viscous phase of a polymeric material, it can be seen that the incorporation of the fibers in general increased the values, especially at temperatures below its T_g (tanδ_{max}); this is associated with an increase in its ability to dissipate stress, and a reduction of the temperature at which the peak of tan δ occurs. Also, it is observed that the values of tanδ increased with higher temperature, reaching a maximum value at 18.1 °C for iPP and 10.3 °C for composite with untreated fiber. This could be related to the temperature of the glass transition (β-transition). Then, tan δ value decreases and tends to present another maximum due to the α transition of polypropylene; this transition is related to the crystals and to the relaxation that occurs due to the presence of amorphous fiber molecules present between the crystals.

In this study, the effect of alkaline treatment is appreciated because the composite with the untreated fibers has greater values than the composites with the treated fibers; this would demonstrate that a composite with poor interfacial adhesion between the filler and the matrix will tend to dissipate more energy, showing a higher tanδ peak compared to materials with higher interfacial adhesion (Poletto, 2017).

Finally, it can be observed that the addition of fibers reduces the T_g for tanδ, which is attributable to a good incorporation of the cellulosic filler with the polymeric matrix; since the fibers allow the polymer chains to start moving with a lower energy amount. It is important to mention that according to the SEM, DSC and XRD results, the composite with untreated fibers has more β-crystals thanks to the silicon dots and therefore, these particles improve the internal load transfer on the fiber reinforcement, increasing the strength and stiffness of the composites (Vieira *et al*., 2016).

Conclusions

This work described that the use of coconut fibers as fillers had a direct effect on the β-crystals formation during the crystallization of the polypropylene. The results of DSC showed that the composite with untreated fiber (BF-E) exhibited an endothermic peak at 146.9 °C, and that the intensity of this peak decreased for the other composites with alkaline-treated fibers, as the concentration of NaOH increased. This phenomenon was also studied by XRD analysis and dynamic mechanical test (DMT); thus, the XRD analysis and the Turner-Jones equation confirm that the sample with untreated fiber presented a higher diffraction peak of β-crystals at $2\theta = 16.0$, while the α-crystal peak at $2\theta = 14.2$ decreased, in comparison to pure iPP. This result agrees with the DSC analysis, in which the melting peak of iPP for β-crystals at 150 °C is greater for the composite with untreated fiber. The DMT indicated that the composites with untreated fiber had the highest storage modulus value (4260 MPa), improving the value in 89.2% in comparison to pure iPP, thanks to the higher content of β-crystals in the iPP matrix.

Therefore, it was possible to confirm that pristine coconut (BF-E) fiber can be an efficient β-nucleating agent when it is used with no alkaline treatment, thanks to the presence of silicon dots. The NaOH-treated fibers gave no growing of β-crystals, since the treatment reduced the silicon dots in their fiber structure, which act as effective nucleating agent. The alkaline treatment gradually removes the amount of silicon dots as NaOH concentration and reaction time increased, obtaining a treated fiber that does intervene in the nucleation process of polypropylene; which was confirmed by the similar fusion enthalpy values of pure iPP and the composite with these fibers.

It should be noted that the presence of these silicon points can play an important role in b-nucleation in iPP polymeric matrices. Since as they are removed they considerably affect the β-type crystallization capacity of the polymer. In this work, pristine coconut fiber is positioned as a good nucleating agent thanks to the silicon points found on the surface. These silicon dots promote the formation of crystalline domains in the polymer. The good arrangement of these domains is reflected in a decrease in tanδ; so energy savings can be obtained when these materials are processed. Furthermore, the good integration of the fiber into the polymer makes the fiber an excellent candidate for the

migration of biodegradable fillers. The incorporation of untreated waste fibers is an excellent option to reduce the problem of agro-industrial waste disposal, with the reward of producing hybrid materials with good mechanical properties and thermal stability.

Acknowledgements

Nomenclature

BF-E	Untreated coconut fibers
1N3	Coconut fibers treated with 3% w/w NaOH for 1 hour
1N5	Coconut fibers treated with 5% w/w NaOH for 1 hour
1N7	Coconut fibers treated with 7% w/w NaOH for 1 hour
4N3	Coconut fibers treated with 3% w/w NaOH for 4 hours
4N5	Coconut fibers treated with 5% w/w NaOH for 4 hours
4N7	Coconut fibers treated with 7% w/w NaOH for 4 hour

Greek symbols

K_β	% crystallinity of β crystals
H_α	Intensities of the diffraction peaks 2θ for α crystals
H_β	Intensities of the diffraction peaks 2θ for β crystals

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