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Synthesis of Polypropylene and Curauá Fiber Composites: Towards High Performance and Low Price Materials

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Abstract: The surface of Curauá (*Ananas Erectifolius*) fibers was successfully modified, characterized and applied as reinforcement on polypropylene composites through two different techniques: *in situ* polymerization and melt mixture. The best results in terms of mechanical performance were obtained for composites prepared through melt mixture technique with fibers submitted to moderate hydrolysis conditions (H_2SO_4 10 %, 1 h, 40 ºC, Ultrasound 30 min) and further acetylation with the incorporation of compatibilizing agent PPMA as well as for the fiber with further silanization without PPMA. Those fibers caused more than 100 % of elastic module improvement with respect to pristine polymer. Glass transition temperature also was increased with the incorporation of *A. Erectifolius* fibers as well as degradation temperature. Scanning electron microscopy permitted to verify that most of the mechanical properties is lost because of high ratio of empty spaces (mainly in the case of *in situ* composites).

Keywords: Curauá, Cellulose modification, Silanization, Acetylation

Introduction

Price and performance remain as the biggest challenges to overcome for polymer composites. After the boom of green chemistry and the necessity of taking advantage of natural resources, several researches have been conducted in order to attain high-performance composites at low prices, preferably giving a useful end to industrial waste or to abundant vegetal material. *Ananas Erectifolius*, known in Brazil as curauá, is a plant belonging to *bromeliaceae* family, which naturally grows in the amazon region and has been used by natives to fabricate different kind of elements [1]. It is closely related to *Ananas Comosus* (pineapple), nevertheless, it had not significant commercial value due to its small fruit, which changed with the discovery of the outstanding mechanical resistance of its fibers [2]. Due to the aforementioned fact, *A. Erectifolius* fibers (70.7 % cellulose and 11.1 % lignin) [3], are a suitable candidate for high resistance composites. Several authors have developed polyurethane composites reinforced with curauá fibers [3-5] and generally found good dispersion of fibers inside polymer matrix, which could be due to the compatibilization that comes from chemical bonds between urethane terminals of synthetic polymer with cellulose hydroxyls. Motheand co-workers [3] found that under 20 wt.% of fiber reinforcing, elastic modulus of composites were lower than that of unmodified polymer, Moreira and co-workers developed polyester composites using *A. Erectifolius* as reinforcement and found that void space between fibers is fundamental for a better interaction with polymer matrix, reason by which, fiber treatment becomes essential to attain proper dispersion inside matrix [4,5]. Automotive applications of curauá composites have been explored by Grafova and co-workers, who explored the atomic layer deposition of aluminum and tantalum oxides in curauá microfibers, which led to an increase in refractory properties of fibers [6]. The major issue for developing extruded polypropylene composites with curauá fibers is the low compatibility between cellulose fibers and polymer chains, which can be overcome by meanings of chemical modification, either of polymer or cellulose [1-5]. Polypropylene is one of the most common polyolefin in the market, with a global production of around 74 million ton; among its main advantages, it could be accounted the price, versatility, thermal and chemical resistance, which make them capable of being useful for several applications. Polypropylene, due to its pendant group, needs to be properly enchained to achieve high regiorregularity, which normally is reflected in high crystallinity and consequently, good mechanical properties. High regiorregularity of polypropylene chains can be achieved through catalytic polymerization, which can be also performed by the use of nanoparticles or nanofibers that contain the catalytic species and, from which, polymer chain can grow [7,8].

Along this work, we show the effects of incorporating modified curauá fibers into polypropylene composites. In order to overcome the already mentioned issue of compatibility between phases, this work explores the modification of curauá fibers with silane and acetyl groups, which substitute hydroxyl free groups on fiber surface and turn the material more hydrophobic (Figure 1 presents the schematic representation of chemical modifications over *A. Erectifolius* fibers). Through *in situ* polymerization and melt mixture, polypropylene-curauá composites were prepared and characterized, looking forward new applications of curauá fibers. This modification of Curauá aims to achieve substantial improvement in mechanical performance, which

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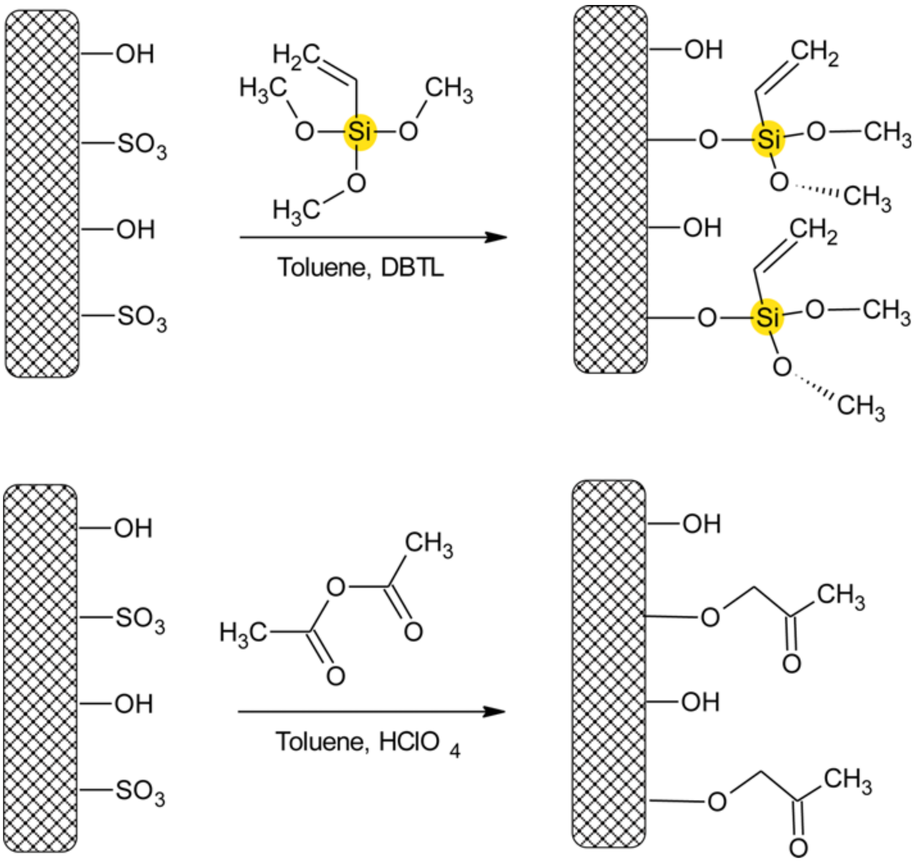

Figure 1. Schematic representation of chemical treatment of hydrolyzed *A. Erectifolius* fibers.

is expected to occur due to the reduction of void space inside composite matrix, caused by the good interaction of phases, promoted by the compatibilizing agents and chemical surface modifications.

Experimental

Materials

Curauá fiber was provided by Permatec Triangel do Brasil and homogenized with morter and pestle. Chemical treatment of curauá fibers has been already reported somewhere else by our research group [4].

Propylene gas was kindly donated by Polibrasil Resinas, glacial acetic acid, hydrochloric acid, acetone, sulfuric acid and Sodium hydroxide were supplied by Vetec, Brazil and used as received. Anhydrous magnesium chloride was supplied by Toho Catalyst Co., Ltd., Japan, and used as received. Dibutyl phthalate was provided by Elekeiroz S.A and used as received. Dichlorodimethylsilane, dimethoxydiphenylsilaneand hexane were purchased at Sigma Aldrich Brazil and used as received. Toluene was kindly provided by Ipiranga Petroquímica and distilled over sodium-benzophenone. Triethylaluminium was provided by Akzo Nobel, EUA in hexane solution (1 M). It was used as received.

Polypropylene was provided by: Quattor, code: HP550K, [MFI (230 °C/2.16 kg)=3.5 g/10 min, density (23 °C)= 0.905 g/cm^3, mechanical properties: tensile strength (50) mm/min)=36 MPa; flow elongation (50 mm/min)=9 %; flexural modulus (1.3 mm/min)=1550 MPa]. It was used as received, grade for the automotive industry;

Maleated polypropylene was purchased from Chemtura Ind. Brazil Ltd., grade Polybond 3200.

Glassware was dried at 120 ºC and cooled under nitrogen atmosphere before use in Schlenk line. Figure 2 shows the overall flux diagram followed in the present workfor composites preparation.

Several diverse treatments done over fibers are showed in Table 1. Those treatments are correspondingly associated with codes that will be used to identify composites along this work.

The preparation of *A. Erectifolius* melt mixture composites was carried on by adding fiber and polymer matrix into a twin screw mini-extruder of Haake MiniLab using the counter rotating technique at 180 ºC and 60 rpm for 10 min. Table 2 presents the fiber conditions of all composites prepared using 2, 5 and 10 % of fibers, which have

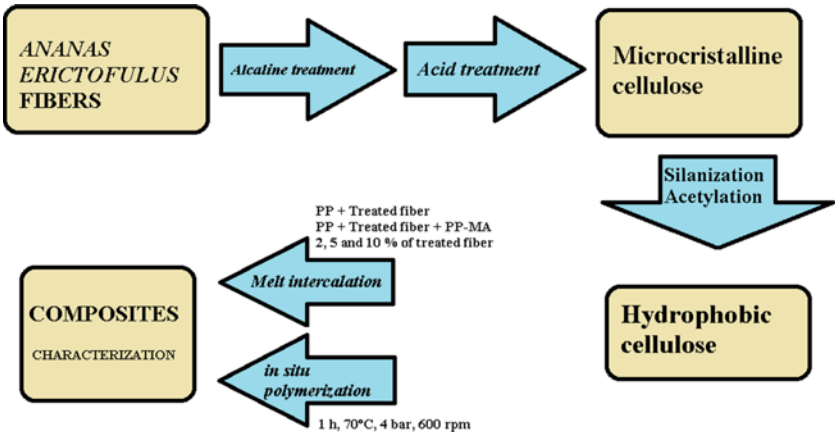

Figure 2. General procedure for preparation of PP-Curauá composites.

Table 1. Hydrolysis conditions and further treatment for each Curauá fiber used for PP composites

Hydrolysis conditions	Further treatment	Fiber code
H_2SO_4 10 %, 1 h, 40 ºC, Ultrasound 30 min	No further treatment	110 H
	Silanization	110 Si
	Acetylation	110 Ac
H_2SO_4 50 %, 4 h, 40 ºC, Ultrasound 30 min	No further treatment	450 H
	Silanization	450 Si
	Acetylation	450 Ac
H_2SO_4 10 %, 4 h, 40 ºC, Ultrasound 120 min	No further treatment	410 H
	Silanization	410 Si
	Acetylation	410 Ac

previously observed to show good mechanical properties for similar composites [9]. *A. Erectifolius* composites by *in situ* method were prepared as described in supporting information document, using the fibers already described in Table 1; their actual fiber proportions can be found in Table 3.

Figure 3 shows the modification process induced by PPMA presence on melt mixture composites; the figure has arbitrary scale for easer illustration. Maleate groups gets attached to free OH groups on fiber surface, generating a coupling zone in which PPMA is chemically attached to fiber surface and polypropylene chains and then an interdiffusion zone in which there are PP and PPMA chains [10,11]. The effect of this compatibilization is analyzed

Table 2. Composites prepared through melt mixture

Composites	Hydrolysis conditions of *A. Erectifolius* fiber	Further treatment	Polymer matrix
PP110H	H_2SO_4=10 % t=60 min T=40 °C Ultrasound=30 min	-	PP550
PP110Si		Silanization	PP550
PP110Ac		Acetylation	PP550
PPMA110H	H_2SO_4=10 % t=60 min T=40 °C Ultrasound=30 min	-	PP550+PPMA
PPMA110Si		Silanization	PP550+PPMA
PPMA110Ac		Acetylation	PP550+PPMA
PP450H	H_2SO_4=50 % t=240 min T=40 °C Ultrasound=30 min	-	PP550
PP450Si		Silanization	PP550
PP450Ac		Acetylation	PP550
PPMA450H	H_2SO_4=50 % t=240 min T=40 °C Ultrasound=30 min	-	PP550+PPMA
PPMA450Si		Silanization	PP550+PPMA
PPMA450Ac		Acetylation	PP550+PPMA
PP410H	H_2SO_4=10 % t=240 min T=40 °C Ultrasound=120 min	-	PP550
PP410Si		Silanization	PP550
PP410Ac		Acetylation	PP550
PPMA410H	H_2SO_4=50 % t=240 min T=40 °C Ultrasound=120 min	-	PP550+PPMA
PPMA410Si		Silanization	PP550+PPMA
PPMA410Ac		Acetylation	PP550+PPMA

Table 3. Consolidated cellulose content of all PP composites prepared through *in situ* polymerization. 5 % of cellulose were incorporated at the beginning of process

Synthesized composite	Yield (g)	Cellulose content (%)
PP-Si	2.5	x
PP-R110H	1.9	6.6
PP-R410H	2.1	5.9
PP-R450H	1.9	6.6
PP-R110Si	1.7	7.4
PP-R410Si	1.7	7.4
PP-R450Si	2.3	5.4
PP-R110Ac	1.6	7.8
PP-R410Ac	1.6	7.8
PP-R450Ac	1.8	6.9

through the present work.

Characterizations

Thermogravimetric Analysis

A Q500 TGA apparatus was used for TGA measurements. It was used nitrogen as carrier gas at 10 ºC/min between 30 and 700 C using platinum pans.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was conducted in order to estimate crystallinity degree (X_c) as well as melting and crystallization temperatures (T_m and T_c) of composites. For DSC analyses it was used a Q1000 apparatus from TA Instruments (USA). It was performed over samples with different masses between 4 and 5 mg and they were submitted to a first heating cycle at 180 ºC (10 ºC/min), then they were cooled down to -40 ºC at the same rate and a new heating cycle up to 180 ºC. Those cycles were used for determination of melting temperatures of the different composites. The crystallinity degree was estimated by relation of fusion enthalpy obtained and the theoretical 100 % crystalline polypropylene, which is 165 J/g according to Nam and co-workers [9].

Equation (1) was employed for estimation of crystallinity degree improvement, where X_{ci} stands for crystallinity degree improvement, X_{cc} is the crystallinity degree of composite with compatibilizing agent and X_{cu} is the crystallinity degree of uncompatibilized composite, prepared using the same proportions of pristine polymer and fiber. Through that equation it is possible to quantify the effect of incorporation of compatibilizing agent on crystallinity degree.

$$X_{ci} = \frac{X_{cc} - X_{cu}}{X_u} \times 100 \tag{1}$$

Dynamic Mechanical Analysis (DMA)

It was used a Q800 instrument from TA Instruments (United States). Several proof bodies were prepared by high pressure pressing into rectangular molds of 5×0.7×0.1 cm and submitted to 1 Hz dynamic deformation of 0.5 % between -40 and 200 ºC at a heating rate of 5 ºC/min.

The improvement in elastic modulus was estimated through equation (2), where E_{ci} stands for elastic modulus improvement, E_{cc} is the elastic modulus of composite with compatibilizing agent and E_{cu} is the elastic modulus of uncompatibilized composite. Through that equation it is possible to quantify the effect of incorporation of com-

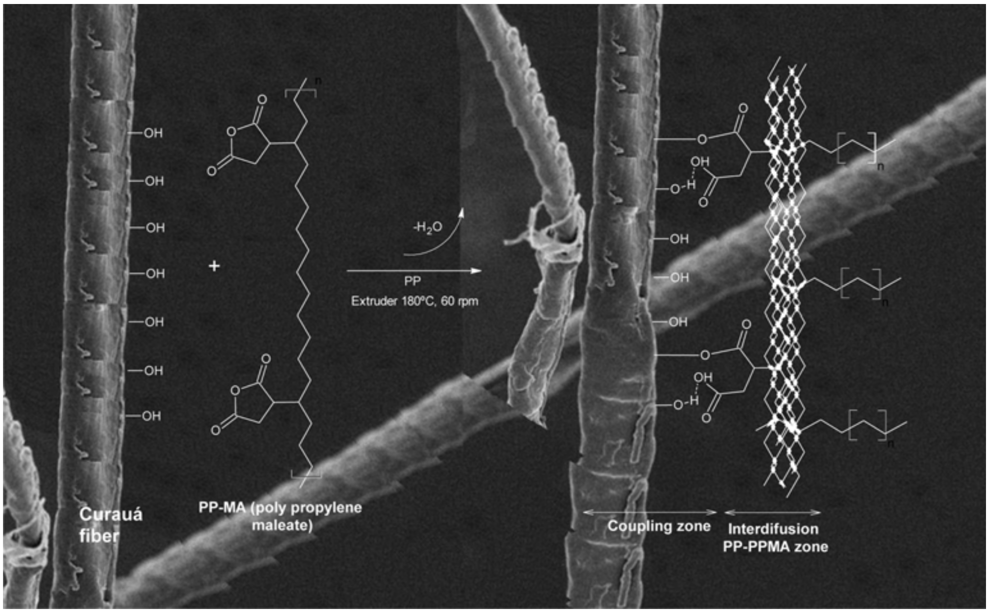

Figure 3. Schematic representation of compatibilization action of PPMA in fibers over original micrograph of curauá fiber. Scale is arbitrary for purposes of illustration.

patibilizing agent on crystallinity degree.

$$E_i = \frac{E_c - E_u}{E_u} \times 100 \tag{2}$$

X-ray Diffraction (XRD)

A Rigaku Miniflex was used for X-ray diffraction measurements at 0.05 º per s between 2 and 35 º using 1.54 Å wavelength.

Scanning Electron Microscopy (SEM)

The scanning electron microscopy images were obtained in a Quanta 200 microscope coupled with EDS analyzer located at CETEM/UFRJ Rio de Janeiro, Brazil. The samples were previously submitted to metallization with gold and thus, the composites were ready for analysis of backscattered and secondary electrons.

Results and Discussion

After modification process carried out over the fiber as mentioned in experimental section, XRD, TGA, DMA and DSC analyses were performed and they are showed in Supporting information document; those analyses demonstrate that fibers were successfully modified. Figure 4 shows SEM micrographs of the *A. Erectifolius* fibers after hydrolysis (110H), silanization (110Si) and acetylation (110Ac). As the acid hydrolysis is the same for the three fibers, there are no significant differences on fiber diameter (around 6.7 μm of fiber diameter). At 1 μm scale one can observe how surface roughness seemshigher in silanized and acetylated fibers, which is expected to have an influence on chemical interaction between fiber and polymer chains.

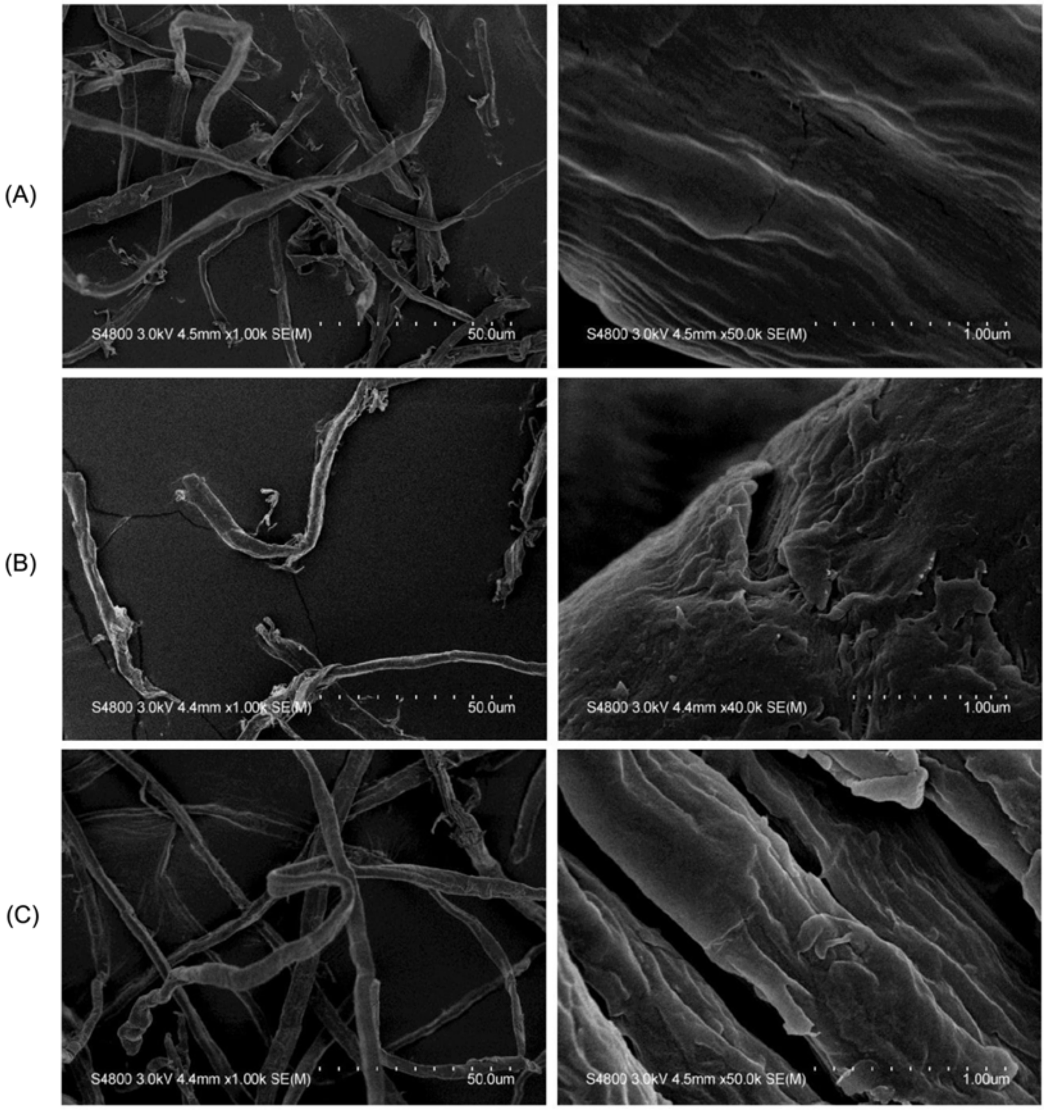

Figure 4. SEM micrographs of hydrolyzed, silanized and acetylated fibers with the same hydrolysis conditions; (A) fiber 410H, (B) fiber 410Si, and (C) fiber 410Ac.

Table 2 shows the yield and obtained cellulose content of the different composites prepared by means of *in situ* polymerization through the use of propylene and catalyst bisupported on modified fibers. The cellulose content tells about the degree of monomer conversion, taking into consideration it was initially added 5 wt.% of fiber with respect to the yield of PP-Si (polymer prepared without fiber). The best yield of *in situ* polymerization was obtained for composites using R450Si and R410H fibers.

Thermal Degradation of *A. Erectifolius* Composites

Thermal resistance of polymer composites along a temperature gradient is fundamental to find applications for materials that are obtained with cheap raw materials. The results are showed in Table 3. This table evidences the big difference that makes the introduction of curauá into PP matrix on thermal degradation of composites: an increase of at least 24 % on degradation onset temperature. Between curauá composites, the higher T_{onset} temperatures correspond to PP-R450Si, which is the composite made with curauá fiber treated with the most rigorous hydrolysis conditions and further silanization. This treatment led to a lower catalyst activity, which implies that a higher amount of fiber was present on composite, explaining thus the highest T_{onset} and also the lowest $T_{max}–T_{onset}$ values. Lowest T_{onset} corresponds to the composite with the fiber submitted to less rigorous hydrolysis conditions and no further treatment.

Figure 5 relates the T_{onset} behavior of melt intercalated composites as a function of fiber content. 5A corresponds to composites made with hydrolyzed fiber, 5B to composites made with silanized fiber and 5C to composites made with acetylated fibers. In 5A one can observe that increasing fiber percentage leads to materials with slightly higher T_{onset}, with the only exception of composite PPMA450H. This clear exception to general trend could mean that exist an antagonist effect resulting from those particular fiber hydrolysis conditions and the presence of compatibilizing agent. Rosa and co-workers did not find clear trends in the thermal behavior of melt mixture composites of PP and natural fiber with PPMA as compatibilizing agent [10], which agrees with the present study, since, depending on chemical treatment of fiber, the thermal behavior is different along load increase.

Regardless the slight variations in the thermal behavior as a function of load incorporation between different chemical treatments of load, the most important tendency is the lower average degradation temperature presented by the acetylated fibers compared to pristine PP and the other composites, result that is against observations by Luz and co-workers, who reported that acetylation of cellulose, renders an increase in degradation temperature, compared to pure PP [11].

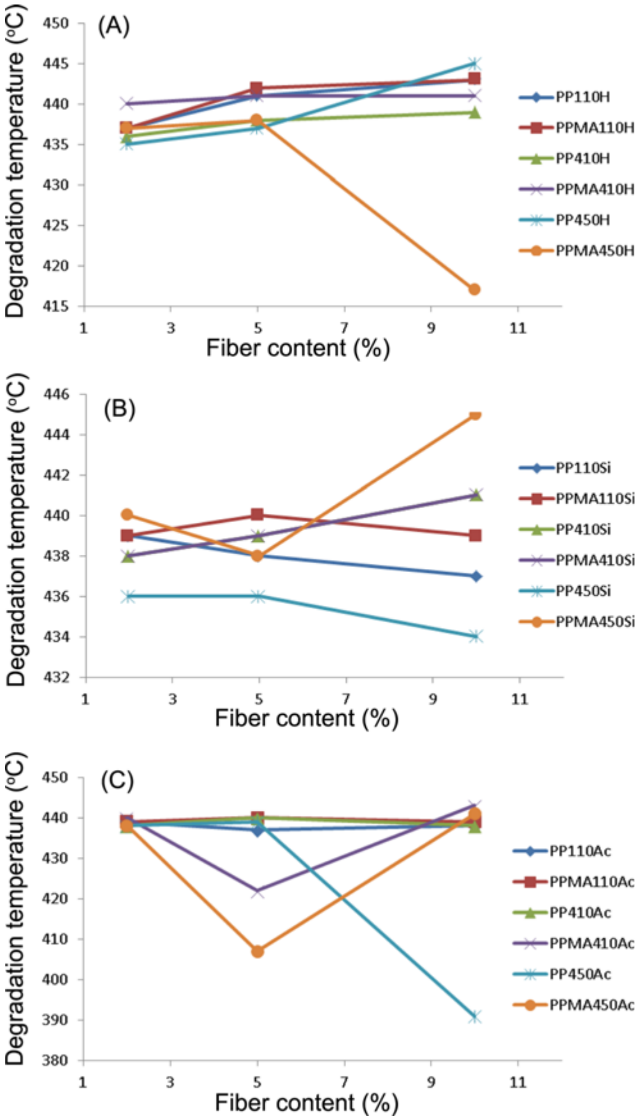

Figure 5. Thermal degradation onset temperatures of composites made through melt intercalation as a function of fiber content; (A) only hydrolyzed fiber, (B) hydrolyzed and silanized fiber, and (C) hydrolyzed and acetylated fiber.

Figure 6 shows a comparison of degradation temperatures between all composites prepared, classified according to composite preparation technique and type of fiber modification. One can observe how *in situ* polymerization led to composites with lower thermal resistance, with degradation temperatures around 5 % lower than melt mixture. The most significant difference was presented by fiber 450Ac, which when incorporated in 10 % on melt mixture, generates a composite with significantly lower thermal degradation, even lower than that of *in situ* composite. This result is in disagreement with Mahlberg and co-workers [12], who reported that incorporation of acetylated fiber in proportions up to 20 wt.%, led to increase in degradation temperature compared to pristine PP. In general, the incorporation of fibers in the present study, led to slight increase in

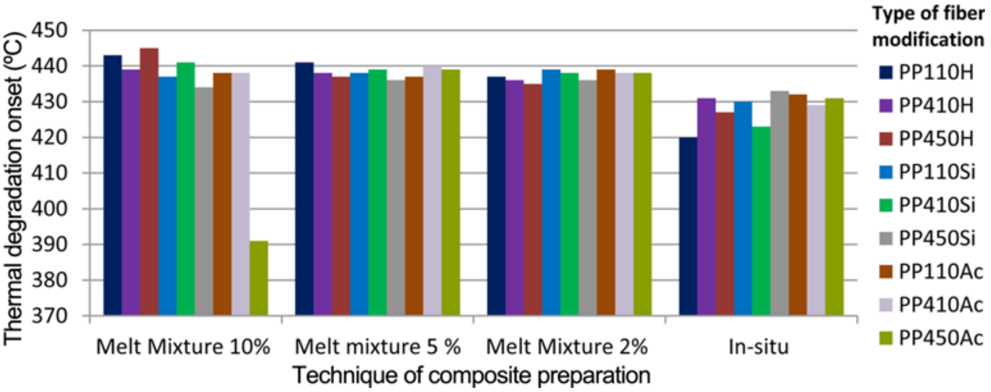

Figure 6. Comparison between thermal degradation values of all composites prepared, classified according to preparation technique and type of fiber modification.

degradation temperatures, which is in agreement with literature reports [10-12].

Differential Scanning Calorimetry (DSC)

Table 4 contains the collected data for *in situ* composites; the T_m and T_c values of pure PP made through coordination polymerization were 157 ºC and 123 ºC. Generally speaking, the T_m and T_c of composites did not present a significant difference, which means that crystalline nature was not affected by the incorporation of fibers (see in supporting information the XRD patterns) and implies that during processing (injection, blow injection, etc.) the composites will consume the same amount of energy that the pure polymer. Nevertheless, crystallinity degree did show significant differences between pure polymer and composites. Some fiber modifications seem to hinder crystal formation, resulting in lower X_c value compared to pristine PP (R410H, R110Si, R410Si and all the acetylated composites). The only composite with a significant increase of X_c was PP-R450H. It seems that neither acetylation nor silanization favor the formation of crystals. These results for the *in situ* composites could be explained by the low polymerization degree of composites, which is capable of hindering the crystal organization that is more likely to occur for greater polymer backbones [13].

Table 4. Thermal degradation temperatures for all the *in situ* composites prepared with *A. Erictofilus*

Composite	T_{onset} (ºC)	T_{max} (ºC)	T_{max}–T_{onset} (ºC)	Total mass loss (%)
PP-Si	338	381	43	99
PP-R110H	420	446	26	92
PP-R410H	431	450	19	72
PP-R450H	427	448	21	99
PP-R110Si	430	449	19	98
PP-R410Si	423	446	23	87
PP-R450Si	433	450	17	67
PP-R110Ac	432	452	20	98
PP-R410Ac	429	449	20	98
PP-R450Ac	431	450	19	96

DSC Analyses showed no significant differences between values of melting temperature (T_m) and crystallization temperature (T_c) for the different melt mixture composites, regardless the fiber nature (T_m=163±1 ºC; T_c=121±2 ºC), which indicates that the interaction between polymer matrix and fiber is not strong enough to significantly modify the way in which crystals are formed on PP matrix (T_m of pure PP=161 ºC) and consequently, the crystals possess the same nature. However, the incorporation of modified curauá fibers tends to increase the amount of crystals formed, as can be observed through comparison among 42 % X_c for pure PP and the different X_c values of the majority of curauá fiber composites.

Figure 7 shows the behavior of crystallinity degree as a function of fiber content and the different modifications of fiber for melt mixture composites. The most important fact that can be highlighted is that silanized fibers, when in melt mixture composites, rendered materials with similar X_c values of pristine polymer. This result is in agreement with reports made by Pan and co-workers, who studied the acetylation and other modifications of wheat fiber in polypropylene composites and observed a significant decrease of crystallinity index of their composites compared to pristine PP [14]. The composites with higher crystallinity degree obtained by melt mixture are those obtained when curauá fiber was hydrolyzed without further treatment. The most important result came from composite with the softest hydrolysis conditions through the use of compatibilization agent (PPMA110H), which presented a X_c value around 70 %, more than 49 % superior to that of pristine commercial polymer and, to the best of our knowledge, higher than reported by any other study on natural fiber composites [14,15]. PPMA410Ac, that with acetylated fiber and compatibilization agent, showed an important increase

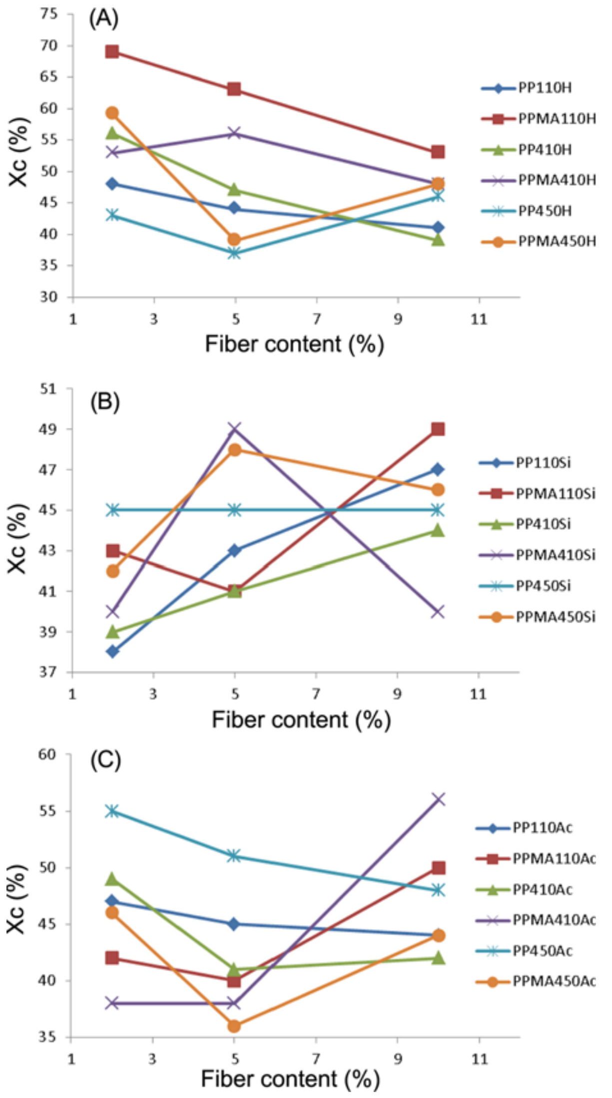

Figure 7. X_c as a function of fiber content for the different fiber composites; (A) only hydrolyzed fiber, (B) silanized fibers, and (C) acetylated fibers.

of X_c along increasing fiber content, which tells about the synergy effect of compatibilizing agent and modified fiber inside the melt mixture composite.

The effect of compatibilizing agent is evaluated in Figure 8 through the calculation of the percentage of improvement of X_c when compatibilizing agent is incorporated. Elastic modulus improvement was calculated using the equation (1).

PP110H was the composite with higher X_{ci} value; this improvement was observed in fiber concentrations of 2 and 5 %, with a reduction in 10 % fiber which could mean that there is not enough compatibilizing agent to act over all incorporated fiber, which is an already observed phenomenon that has been observed in other systems [16].

However, a remarkable result comes from PP410Ac, which presented a bad interaction with compatibilizing agent that reduces its crystallinity at fiber concentrations of 2 and 5 %, but increases composite crystallinity when in fiber concentration of 10 %; this result implies that it is not possible to affirm that the amount of fibers make the difference as it did for PP110H. What probably occurred here is that depending on chemical nature of fiber surface, there is a higher tendency to form fiber aggregates that could make the composite more or less crystalline. PP410H for example, presented a similar behavior to that of PP110H, however, with a constant increase on crystallinity degree along all the fiber concentration range. Among the fibers that were just hydrolyzed with no further treatment, PP450H presented a significant increase of X_c when 2 % was incorporated, while for higher concentrations the effect of compatibilizing agent was not very significant. Between the composites made with acetylated and silanized fibers, significant improvements on crystallinity degree index were only observed for fiber content of 10 %.

Dynamical Mechanical Analysis (DMA)

Behavior of elastic and viscous modulus as a function of temperature, and the consequent glass transition temperature of composites were measured by DMA. Table 5 shows the

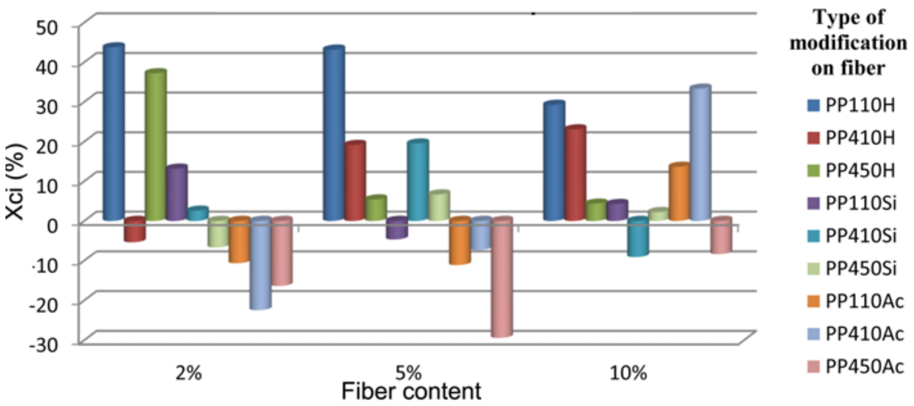

Figure 8. Percentage of elastic modulus improvement after incorporation of PPMA as compatibilizing agent in melt mixture composites.

Table 5. Differential scanning calorimetry results for *in situ* composites

Composite	T_m (°C)	T_c (°C)	$\Delta H_m{}^a$ (J/g)	X_c (%)
PP-Si	157	123	91	47
PP-R110H	159	124	88	48
PP-R410H	158	123	60	32
PP-R450H	157	120	106	58
PP-R110Si	157	121	64	35
PP-R410Si	158	123	67	37
PP-R450Si	159	123	77	42
PP-R110Ac	159	122	73	41
PP-R410Ac	157	121	73	41
PP-R450Ac	158	123	81	45

main features obtained through DMA, along with Tg obtained through DSC for *in situ* composites.

Elastic moduli at 25 °C of all *in situ* composites were higher than that of pristine polymer, which tells about the positive effect of incorporation of curauá fiber on polymer matrix, regardless its chemical treatment, which is positive for the incorporation of a low cost and biodegradable raw material. Not only elastic modulus is an important measure of mechanical resistance, but also the viscous modulus and tan δ; all of those features are improved trough incorporation of curauá fibers, which is an important factor to be considered at the moment of including this bio renewable material as second phase in commodity polymer composites. Transition temperatures as Tg and Tα are also improved by *A. Erectifolius* fibers, which implies a reduction in polymer chains mobility due to the restriction generated by cellulose fibers.

Figure 9 shows a comparison among the three different modifications of *A. Erectifolius* fiber and the effect of those in different composites prepared through melt mixture; the results are presented as a graphic of elastic modulus at 25 °C as a function of fiber incorporated on melt mixture. As it was observed for *in situ* composites, all the outperformed the mechanical performance of pristine PP, which is of big importance as melt mixture is a cheap processing technique. Fibers that were only hydrolyzed and those fibers that were silanized generated composites with a tendency of augmentation on elastic modulus along increasing fiber content, which is important in order to make materials with a higher content of low-cost renewable raw material. The results suggest that the final treatment of fiber makes great difference, because fibers with the same hydrolysis treatment (PP450Si and PP450Ac) presented a totally different trend: elastic modulus diminution and augmentation respectively; when PPMA was incorporated, it inverted the performance of composites along fiber content increase, which is against similar studies reported in literature [10-16]. In general, the values of elastic modulus at 25 °C were higher for melt mixture composites than for *in situ* composites. The highest values were obtained for composites containing 10 % of 110H and 410Si and 2 % 410Ac with PPMA. Those values outperformed pristine polymer elastic modulus in 139, 197 and 223 %, which represents a significant difference with respect to those improvements obtained through *in situ* polymerization is clearly higher than the reported improvements on mechanical performance for other composites involving modified natural fibers [12,17].

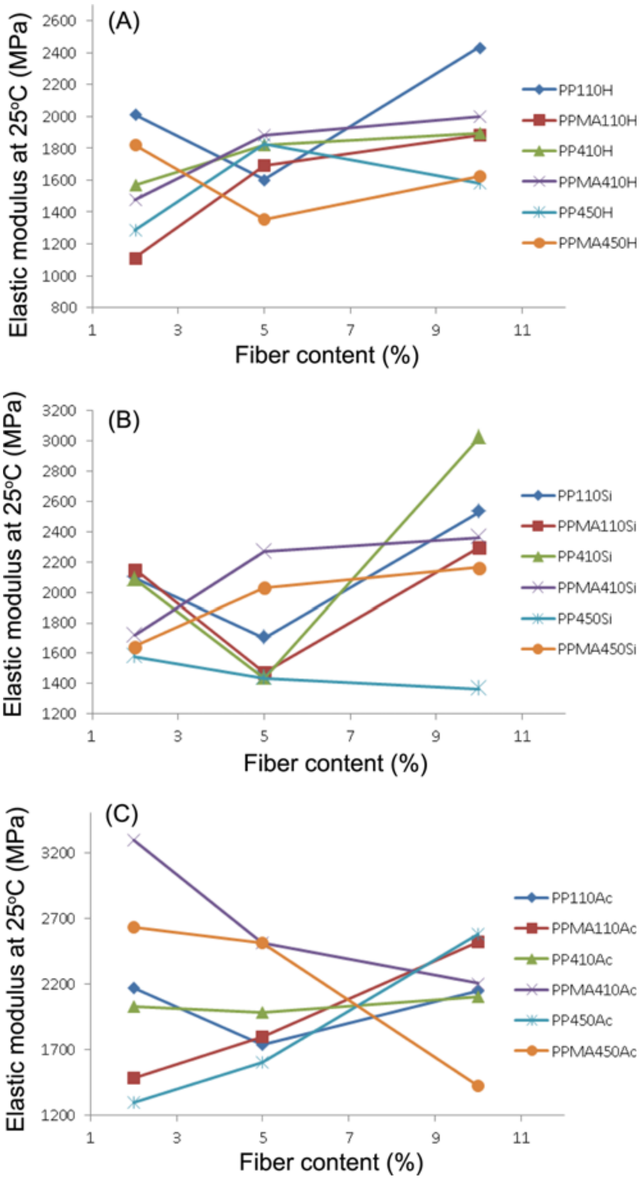

Figure 9. Elastic modulus as a function of fiber content for (A) composites of PP and *A. Erectifolius* hydrolyzed fiber without fiber treatment, (B) composites of PP and silanized *A. Erectifolius* fiber, and (C) composites of PP and acetylated *A. Erectifolius* fiber.

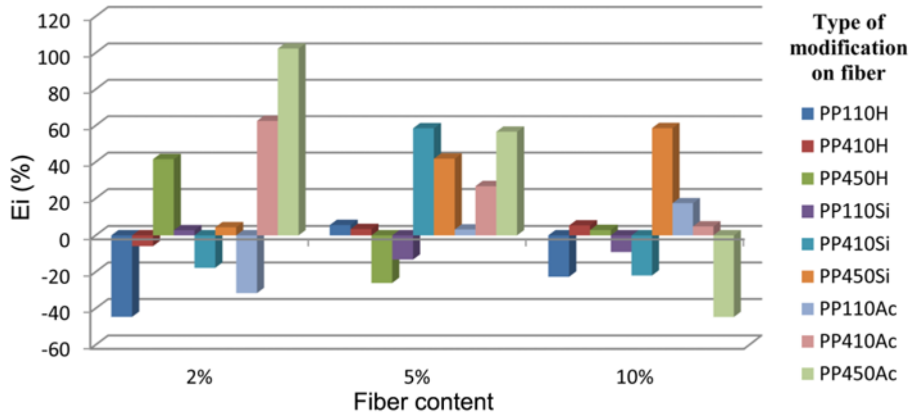

Figure 10. E_i as a function of fiber content for all *A. Erectifolius* composites prepared through melt mixture process.

Figure 10 shows the effect of the introduction of PPMA as a compatibilizing agent on melt mixture process. The elastic modulus improvement value was obtained through the use of equation (2). The most significant improvement obtained by the incorporation of PPMA on melt mixture is the 102 % in the composite made with 2 % of the fiber with acetylation treatment. It is important to highlight how the inclusion of compatibilizing agent leads to more significant improvements when 2 % of fibers are incorporated, which tells about the need of accompany the increase of fiber amount with addition of more PPMA as it was also observed for crystallinity index [12-15]. The acetylated fiber 410Ac also was benefited with an E_i of 60 % due to incorporation of PPMA. A fact that needs to be highlighted is that PPMA incorporation generated high improvement on crystallinity degree for hydrolyzed fibers but this behavior, contradictorily, was not reflected on elastic modulus improvement. That is to say, in the case of hydrolyzed and silanized fibers, the incorporation of PPMA is not so desirable in terms of the relation E_i/\$ for those fibers, being acceptable only in the case of 2 % of acetylated fiber composites. These results are in agreement with literature reports that related that the incorporation of PPMA renders overall increase of mechanical performances [16-18].

X-ray Diffraction

Figure 11 shows the XRD pattern of the melt mixture composites that showed significant changes with respect to pristine polymer (complete patterns of all composites are showed in S.I). The patterns of *in situ* composites did not present any significant changes with respect to that of pristine polymer.

None of the above mentioned composites presented a X_c value higher than 55 %, which permits to infer that the change in crystalline morphology of pristine PP, actually did not favor the generation of more crystalline materials. The alteration of peaks at around 14.5 ° and 22 °, original from PP, can be attributed to crystalline peak of cellulose β corresponding to plane 200, shoulder that becomes more evident when proportion of fiber increases. One can also observe that the nature of chemical treatment conducted on fiber surface, is able to cause a shift of crystalline peaks of polymer, result in agreement to reports found in literature [18,19]. The patterns show that the most evident shifts correspond to the composites with higher fiber content, which is expected according to El Oudiani *et al.* and

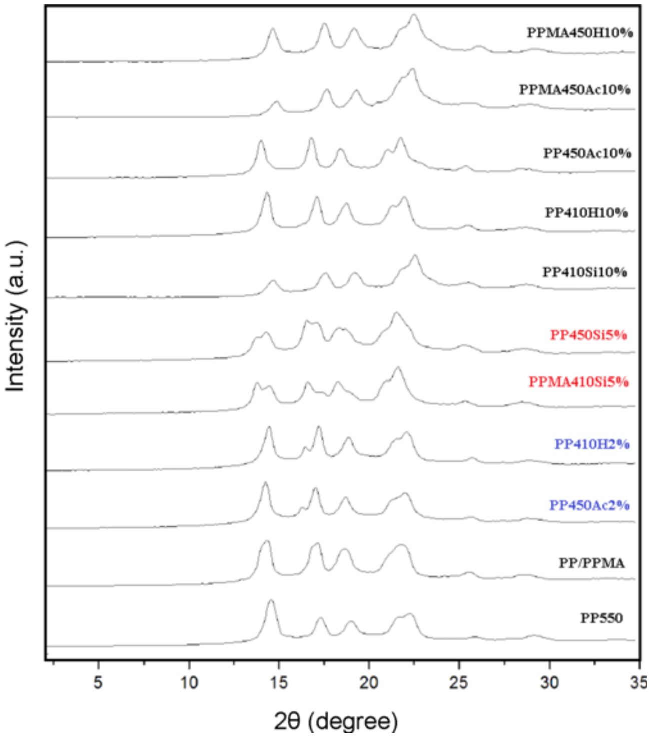

Figure 11. X-rays diffraction pattern of all melt mixture composites that presented any significant difference with respect to PP550.

Table 6. Elastic and viscous modulus and different features obtained through DMA analysis for *in situ* composites

Composites	*E'* (-40 °C) MPa	*E'* (25 °C) MPa	*E''* (-40 °C) MPa	*E''* (25 °C) MPa	*Tg* (°C) Tan δ	Tan δ_{max}	*Tg* (°C)	*Tα* (°C)
PP-Si	2852	1019	48	69	5.5	0.0992	2.8	80
PP-R110H	2782	1213	66	76	8.1	0.0824	4.8	91.6
PP-R410H	4851	2378	229	159	6.7	0.0862	3.9	87.8
PP-R450H	4216	1851	135	106	5.7	0.0819	2.2	85.6
PP-R110Si	3972	2047	118	118	9.9	0.0695	7.2	82.9
PP-R410Si	4314	2184	138	138	6.7	0.0759	3.5	78.2
PP-R450Si	4870	2394	106	128	8.5	0.0668	5.9	78.5
PP-R110Ac	4960	2512	157	143	9.4	0.0705	6.4	78.2
PP-R410Ac	4224	1990	251	154	5.7	0.1055	2.7	87.9
PP-R450Ac	3004	1256	109	99	6.7	0.0945	2.9	77.8

Dányádi *et al*. [20,21].

Scanning Electron Microscopy (SEM)

In order to obtain a visualization of composites morphologies, SEM micrographs were conducted in the prepared composites. Figure 12 shows a comparison between analogous compounds at the same scales. In 12A one can observe sections of fibers of miscellaneous sizes and empty spaces; the soft conditions of hydrolysis probably caused those sections of fibers to be easily observed through the material. In 5 µm scale one can observe how small nanofibers are peeled from fiber surface, probably due to shearing during melt mixing, as has been reported by other authors [12-14]. On the other hand, the *in situ* composite also shows big fiber sections with more phase separation that probably explain the difference on mechanical performance between those composites (melt mixing composite has 65 % higher elastic modulus than *in situ* composite).

Figure 13 Compares composites made with 110Ac fiber (soft hydrolysis conditions and further acetylation) through

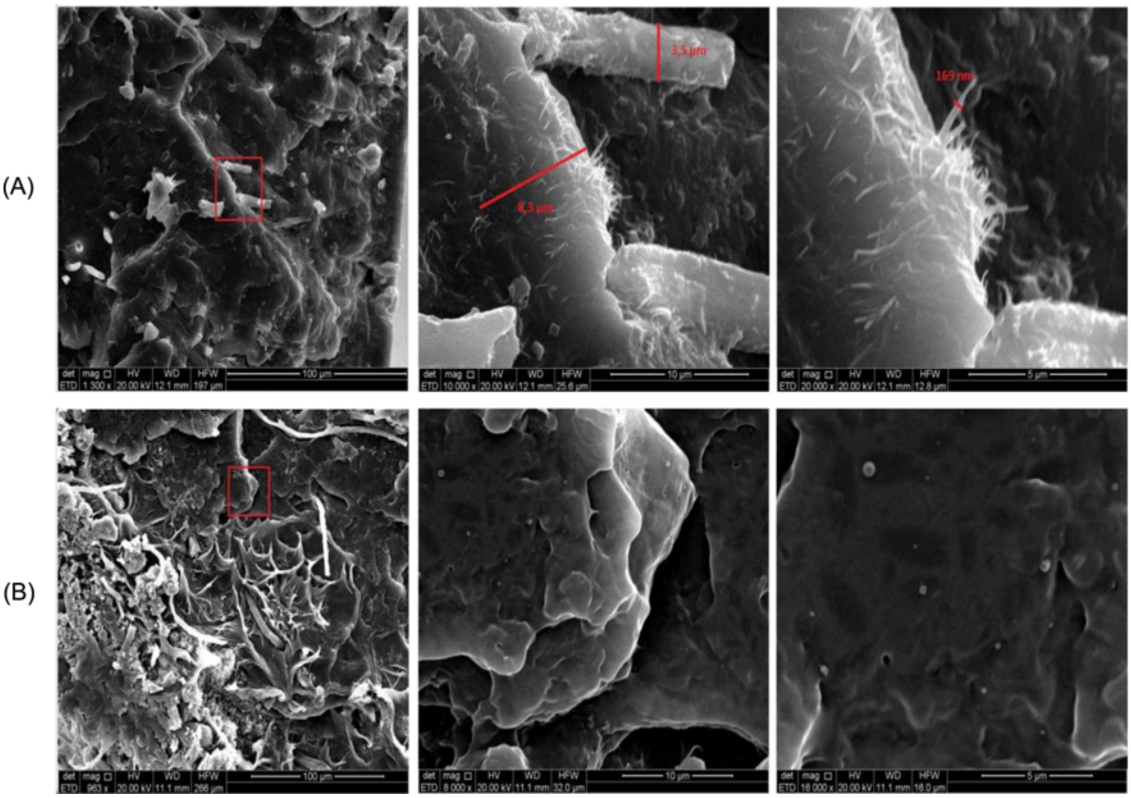

Figure 12. Comparison between SEM micrographs of *A. Erectifolius* composites, prepared with hydrolyzed fiber 110H (soft hydrolysis conditions) through melt mixture 10 % (A) and *in situ* polymerization (B).

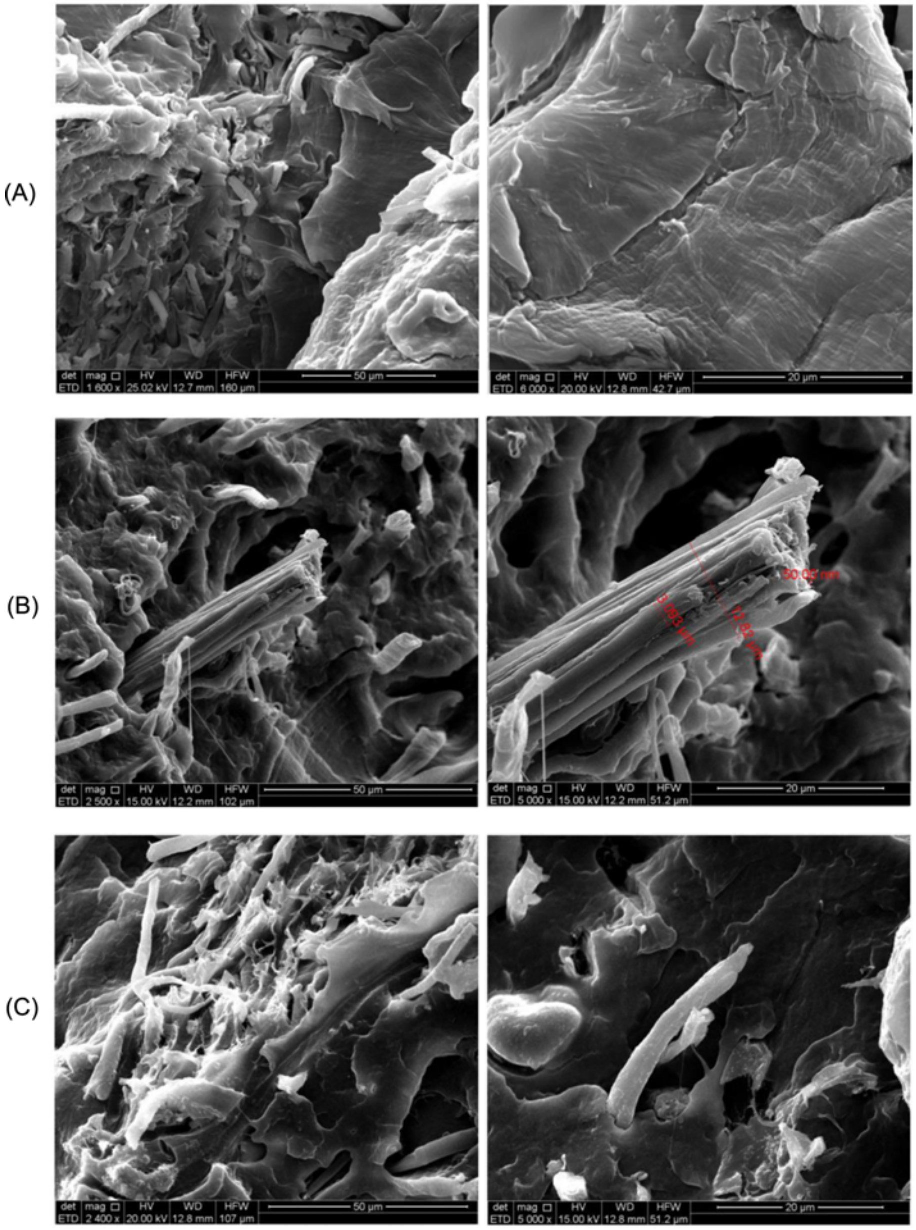

Figure 13. Micrographs of three different composites made with fiber 110Ac; (A) *in situ* composite, (B) melt mixture composite with 10 % of fiber, and (C) melt mixture composite with 10 % of fiber and compatibilizing agent.

in situ polymerization (A) and melt mixture with (B) and without PPMA (C). Cryofracture shows a higher size and amount of unaltered fiber in the case of melt mixture composites without PPMA; fibers of 15 μm were observed, which are composed of nanofibrils between 75 and 200 nm diameter; furthermore, a significant amount of empty spaces can be observed, which are responsible of fails on structural integrity of material. When compatibilizing agent is incorporated, the amount of empty spaces diminishes but still it is possible to see entire sections of fibers, which are responsible for load distribution on material. *In situ* composite shows also a low rate of empty spaces, reason by which this composite along with PPMA110Ac presented elastic modulus around 19 % higher than the melt mixture composite prepared with the same fiber but without compatibilization agent.

SEM micrographs of three composites made with fiber 450Ac (moderate acidic conditions) are showed in Figure 14. One can observe how the moderate acidic conditions and further acetylation, led to a material with a very different morphology in the case of *in situ* polymerization. Spherical sections of nanofibrils are exposed in cryofracture, which

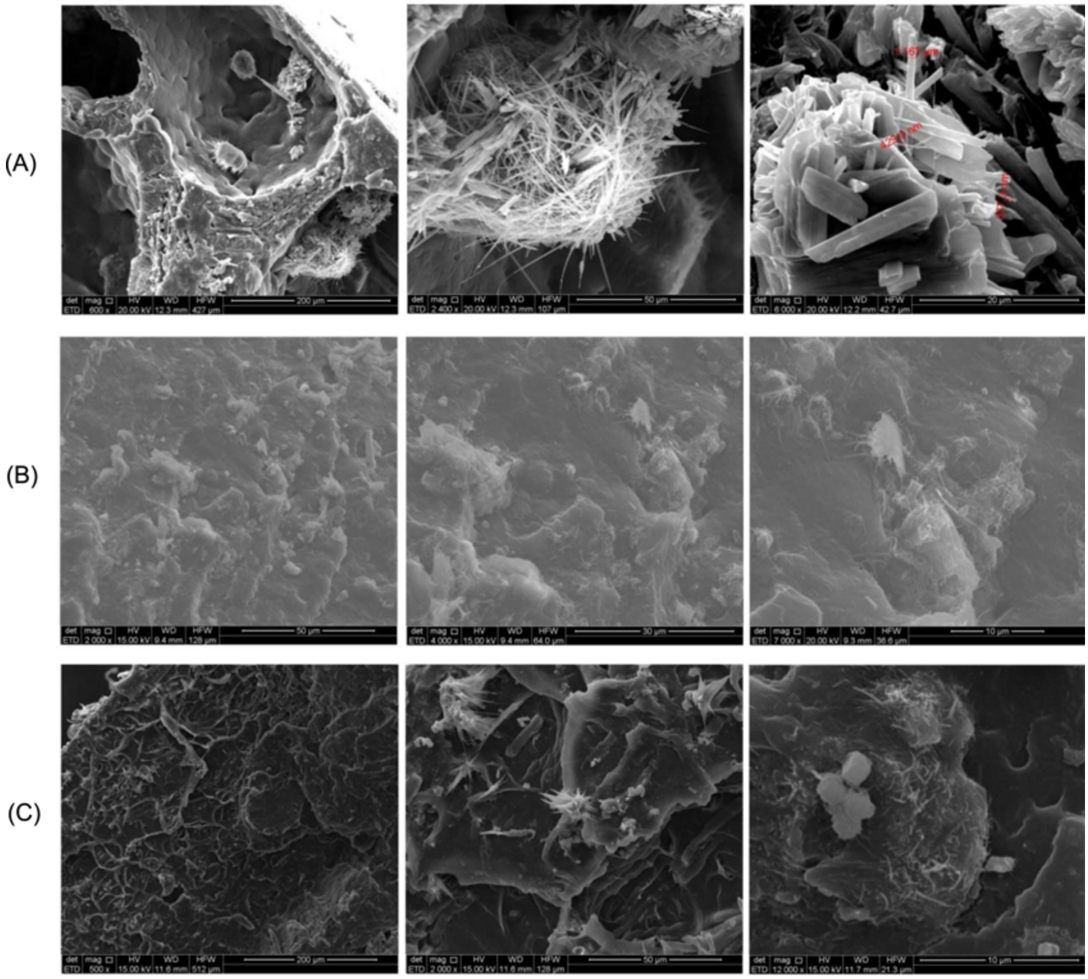

Figure 14. Composites made with fiber 450Ac; (A) *in situ* composite, (B) melt mixture composite with 10 % of fiber, and (C) melt mixture composite made with 10 % of fiber and compatibilizing agent PPMA.

could be responsible for the low elastic modulus of compound (near from PP550 elastic modulus) with respect to the other *in situ* composites and to the composites PP450Ac and PPMA450Ac prepared through melt mixture. Comparing 14B and 14C it is possible to attribute the negative effect of PPMA incorporation to the high fraction of empty spaces observed in micrograph 14C, higher than 14B.

In Figure 15 are presented the SEM micrographs of composites prepared with silanized fiber 110Si through *in situ* polymerization and melt mixture. Empty spaces fraction is not as high as in the case of 450Ac composites, which is reflected in the values of elastic modulus. There is no perceptible difference between melt mixture composites, which could be a consequence of the low amount of PPMA that is not always in all the regions of composites, and as a consequence of that, some regions of compatibilized and uncompatibilized composites can present very similar morphologies. Nevertheless, the *in situ* composite presents higher fraction of empty spaces and exposed fiber, which could be responsible for the 16 % lower elastic modulus presented by *in situ* composites of 110Si fibers when compared with melt mixture composites made with the same material. Complete SEM micrographs of all the composites are showed in supporting information document.

Conclusion

Several chemical treatments were done over *Ananas Erectifolius* fibers, which showed to be an excellent reinforcement to mechanical properties of pristine polypropylene, increasing its elastic modulus and restringing the mobility of chains, which gives to the new materials higher operation limits through the use of renewable resource that is not a source of food for population in Brazil and South America. *A. Erectifolius* fibers showed also to increase degradation temperature and with some exceptions, increased also the crystallinity of polypropylene pieces.

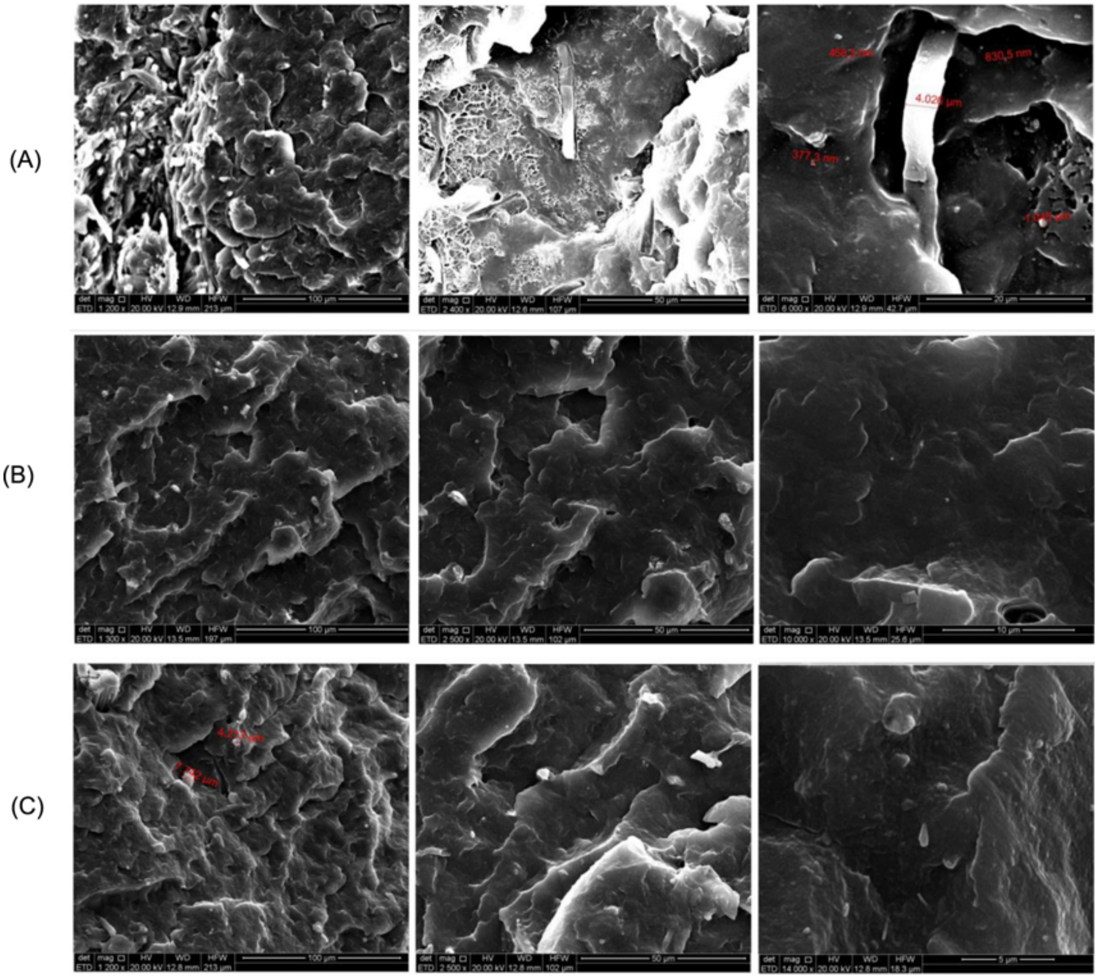

Figure 15. SEM micrographs of composites made with fiber 110Si; (A) *in situ* composite, (B) melt mixture composite with 10 % of fiber, and (C) melt mixture composite with 10 % of fiber and PPMA as compatibilizing agent.

Crystallinity degree improvements greater than 40 % were achieved through incorporation of silanized fibers into PP matrix; furthermore, elastic modulus improvements over 150 % were obtained for the same type of composite. It was observed that incorporation of natural curauá fibers into PP matrix, did not affect the thermal degradation temperature, regardless the nature of chemical modification on fiber surface. It was observed that the introduction of Curauá fibers has no effect on the crystalline nature of the sample, however, it did show an effect in the amount of formed crystals. It was determined that 49 % improvement of crystallinity degree can be obtained when compatibilizing agent was used in the hydrolyzed fiber; furthermore, it was also observed that the compatibilized system needs to follow the increase of incorporated load, in order to obtain improvements over all the range of load proportion.

The obtained results permit to think that Curauá is a promising natural reinforcement of PP for highly demanding applications.

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