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Statistical Experimental Design for Obtaining Nanocellulose from Curaua Fiber

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Summary: This study focuses on the methodology to obtain nanocellulose from vegetal fibers. An experimental planning was carried out for the treatment of curaua fibers and parameters were estimated, having the concentration of H_2SO_4, hydrolysis time, reaction temperature and time of applied sonication as independent variables for further statistical analysis. According to the estimated parameters, the statistically significant effects were determined for the process of obtaining nanocellulose. With the results obtained from the thermogravimetric analysis (TGA) it was observed that certain conditions led to cellulose with degradation temperatures near or even above that of the untreated cellulose fibers. The crystallinity index (I_C) obtained after fiber treatment (by X-ray diffraction technique) was higher than that of the pure fiber. Treatments with high acid concentrations led to higher IC. After the statistical experimental design, mixtures of polypropylene with fibers prepared after different treatments were performed in a mini-extruder. It was possible to observe a sharp increase in the mechanical properties through the dynamic mechanical thermal analysis (DMTA).

Keywords: composites; experimental planning; nanocellulose; polypropylene; vegetal fiber

Introduction

The use of natural fiber reinforced plastics represents an attractive and suitable method for replacing of glass fiber reinforced plastics.[1,2] Natural fibers are light and renewable; they are low cost and high specific-strength resources.[3,4] Research in the field of polymer science and technology has been focused on developing plastics, papers, adhesives, textile fibers, composites, blends and many other industrial products from renewable resources, mostly the abundantly available agro-waste and lignocellulosic materials.[5]

In polymer composites, the cellulose fibers have excellent potential as reinforcement, significantly reducing the cost of composite production and greatly increasing its mechanical properties under suitable processing.[6,7] However, the main disadvantage is the poor compatibility with the PP matrix, and increase the affinity between the components of this composite becomes a challenge.[8,9] Improvement of fiber-polymer adhesion can be performed through modification of either the fiber surface or the polymeric matrix. Another drawback is the low temperature of thermal degradation of these fibers, precluding mixture with polymers requiring processing temperatures above 220 °C.[10,11]

Cellulose fibers contain high amounts of hydroxyl groups and readily interact with water molecules by hydrogen bonding. Swelling of water leads to micro-cracking of composites and degradation of mechanical properties.[12] It is difficult to entirely eliminate the absorption of moisture in composites without using expensive surface barriers.[13] Good wetting of the fiber by the matrix and adequate fiber–matrix bonding can decrease the rate and amount of water absorption in the interface region of the

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composite.[14] Optimization of interfacial adhesion between cellulose-based fibers and thermoplastics has been the focus of a large number of researches conducted during the last two decades.[15]

Chemical methods cover the pretreatment of fiber surfaces by coupling agents, such as silanes and isocyanates, and modification of the matrix by grafting different chemical moieties on polymer chains. Nonpolar PP is usually grafted with polar acrylic acid, acrylic esters, maleic anhydride etc. Among these methods, maleic anhydride-grafted PP (MAPP) has been found to be the most efficient in improving interfacial adhesion of fibers and a PP matrix.[16]

The alkaline treatment, also known as mercerization, is one of the most commonly used chemical methods for the treatment of natural fibers where they are employed to reinforce thermoplastic and thermosetting polymers. A major change provided by the alkali treatment is the breaking of hydrogen bonds on the surface structure, thereby increasing its roughness. This treatment can remove some hemicellulose, lignin, waxes and oils that cover the outer surface of cell wall fibers. Depending on the concentration of alkali, the treatment is also able to depolymerize cellulose and expose some crystalline segments.[17] The addition of aqueous sodium hydroxide also promotes the ionization of the natural fibers by modifying the hydroxyl groups to alkoxide.[18] Thus, this process has a direct influence on the cellulose fibrils and may reduce their degree of polymerization, although it is used especially to extract components like hemicellulose and lignin.[19]

Acid hydrolysis is a well known technique for obtaining nanocellulose, and it is also used to remove amorphous components of natural fibers.[20] Thus, it becomes possible to isolate these cellulose fibers, which is desirable for using them as reinforcing components in polymer composites, as this fraction of natural fibers is responsible for the high intrinsic mechanical properties.[21]

In this work, a statistical design of experiments was performed to obtain more comprehensive information about the variables for the acid hydrolysis of curaua fibers, in a systematic way and with a minimum number of experiments. Planning was performed using as independent variables H_2SO_4 concentration, hydrolysis time, reaction temperature and time of sonication. Mixtures were also performed by extrusion of polypropylene with pure curaua fibers, as well as with fibers after chemical treatments. These mixtures were performed with and without compatibilizer agent (maleated polypropylene) to evaluate their mechanical properties through the dynamic mechanical thermal analysis (DMTA).

Experimental Part

Materials and Methods

The cellulose fibers used as fillers (obtained from Pematec Triangel, Brazil) were those of curaua leaves (*Ananas Erectifolius*), a native Brazilian plant related to the pineapple, and they were used after being grounded in a knife mill and size separated through a sieve with 200–270 mesh (50–73 μm). All the other materials were used as received: sulfuric acid and sodium hydroxide were supplied by Vetec, Brazil. Polypropylene - HP550 homopolymer (named PP) with a melt flow index of 3.5 g/10 min (230 °C, 2.16 Kg) and a density of 0.905 g/cm^3 in the form of pellets was supplied by Braskem, Brazil, and maleated polypropylene (MAPP) - Grade Polybond 3200 was obtained from Chemtura Ind. Quim., Brazil.

Sample Preparation

The experimental design of acid hydrolysis performed in cellulose fibers was carried out for samples obtained after the third treatment of the fibers with 5% aqueous NaOH solution at 80 °C during 1 h, each time. The treated fibers were washed with distilled water up to pH 7. These materials were dried, under vacuum until constant weight.[22] To perform the acid hydrolysis, deionized water was added to the pulp from the grinding. The suspension water/cellulose was then treated at 10 °C under stirring, and then sulfuric acid was added drop by drop until the desired acid concentration is reached. While stirring, the solution was heated for a certain time. Then, the samples were sonicated in ice bath. The suspension was then filtered and washed with deionized water. The wash cycle was repeated until the pH of the water was constant. Finally, the samples were dried at 60 °C and vacuum pump to constant weight.[20] The acid concentration, temperature of hydrolysis, hydrolysis time and time of sonication process of each experiment was defined according to the levels of the experimental design proposed in this paper.

The independent variables chosen were H_2SO_4 concentration, hydrolysis time, temperature of hydrolysis and time of sonication (after acid hydrolysis). The levels and concentrations chosen for each factor of the experimental design are presented in Table 1.

The levels of variables were chosen taking into account the most significant factors for hydrolysis described in the literature,[20] although with lower acid concentrations in order to decrease the effect of acid hydrolysis in the thermostability of the fiber.

The statistical design of experiments was randomly distributed over the experimental region and the factorial plan was used with all possible combinations. The results of the response variables were placed in the array generated by the software Statistica 7.0. The central points were used and average values of all variables were assumed, in order to determine the confidence interval by means of repetition of experiments. To determine the number of experiments Equation 1 was used and in this case, all variables having the same number of levels.

Table 1.
Levels of the factors of the employed experimental design.

Independent Variables	Levels		
	−1	0	1
Acid Conc. (%)	10	30	50
Hydrolysis time (min)	60	150	240
Temperature (°C)	40	60	80
Sonication (min)	30	75	120

$$\mathrm{NE} = \mathrm{L}^{\mathrm{NV}} + \mathrm{R} \qquad (1)$$

where: L = number of levels (2), NV = number of variables, R = number of replicates at the central point.

For the preparation of composites containing PP and curaua fibers, commercial polypropylene was processed with the original cellulose fibers, with fibers obtained after the third alkali treatment and with a specific fiber sample prepared after alkali and acid treatment from the design of experiments (sample that resulted in the highest onset degradation temperature). The composites were processed with 5% of maleated polypropylene (MAPP) as compatibilizer agent or without it. The mixtures were performed in a twin-screw mini-extruder at 60 rpm, 180 °C, for 10 min.

Commercial polypropylene and the fibers were previously grinded and mixed before being added to the mini-extruder.

Characterization

The characteristics of the cellulose fiber were evaluated through X-ray diffractometry (XRD). The analyses were performed in a Rigaku Miniflex diffractometer working with a potential difference in the tube of 30 kV and electrical current of 15 mA. The scan was carried out in the range of 2θ from 2 to 30°, with goniometer speed of 0.05°/min. The incident X-ray radiation used was that of Cukα whose wavelength is 1.5418 Å.

Computer software was used for the deconvolution of the diffractogram to evaluate the percent of crystallinity (I_C) of the samples by an area under the corresponding diffractions:[23]

$$I_c(\%) = \frac{\mathrm{A}_{\mathrm{Crystalline}}}{\mathrm{A}_{\mathrm{Total}}} \times 100 \qquad (2)$$

The crystalline region of the lignocellulosic material is associated with the peak[23] around 2θ = 23° (for cellulose II), while the amorphous region is related with the peak around $2\theta = 15^\circ$.

The degradation temperatures of the fiber were analyzed by thermogravimetric analysis (TGA). These analyses were carried out in a TA model Q500 apparatus. The samples were heated in the range from room temperature to 700 °C, under inert atmosphere, with a heating rate of 10 °C/min., for the determination of the onset degradation temperature.

The morphologies of the fiber was observed by scanning electron microscopy (SEM) using a JEOL-JSM-S610 LV microscope. The samples were sputtered with gold before SEM analysis. The content of sulfate groups of the fiber was determined by EDX, Shimadzu model 720, under vacuum for 320 seconds. Mass balance was made for the cellulose molecule and the contents of these elements have been identified in the oxide form.

The composites of PP with curaua fibers as well as neat PP were characterized by dynamic mechanical thermal analysis (DMTA, model DMA Q800, TA Instruments, USA) performed to determine the moduli (storage and loss moduli) of the materials and the glass transition temperature (Tg), which was determined from the tan δ x T curve. Samples with dimensions $17 \times 12 \times 2$ mm were prepared by compression and conditioned for 48 h at 80 °C. They were analyzed heating from −50 °C to 150 °C with a heating rate of 3 °C/min, using 1 Hz frequency, strain of 0.1% with a single cantilever clamp.

Results and Discussion

The results of the experimental planning performed for the acid treatment of the curaua fibers after previous alkaline extraction were obtained from the determination of onset degradation temperatures (T_{onset}) by TGA and the crystallinity index (I_c) from XRD. They were the response variables of the study having H_2SO_4 concentration, hydrolysis time, temperature of hydrolysis, and time of sonication after hydrolysis as independent variables.

Table 2 shows that the thermal stability of the fibers after acid hydrolysis decreased

Table 2.
Matrix standard with two-level factorial design and center points, with both degradation temperature (T_{onset}) and crystallinity index (I_c) as response variables.

	Factors				Results	
Exp	Concentration (%)	Time (min)	Temperature (°C)	Sonication time (min)	T_{onset} (°C)	I_c (%)
E01	−1	−1	−1	−1	333	72
E02	1	−1	−1	−1	282	75
E03	−1	1	−1	−1	324	71
E04	1	1	−1	−1	279	71
E05	−1	−1	1	−1	310	68
E06	1	−1	1	−1	277	76
E07	−1	1	1	−1	320	76
E08	1	1	1	−1	179	77
E09	−1	−1	−1	1	329	69
E10	1	−1	−1	1	282	72
E11	−1	1	−1	1	338	69
E12	1	1	−1	1	274	78
E13	−1	−1	1	1	332	72
E14	1	−1	1	1	267	74
E15	−1	1	1	1	319	75
E16	1	1	1	1	182	77
E17*	0	0	0	0	301	72
E18*	0	0	0	0	304	76
E19*	0	0	0	0	302	70

*Central point.

with increasing crystallinity index of samples. In general it was observed that samples with higher content of sulfate groups (determined by EDX analysis) after the treatments with higher acid concentrations have lower thermal stability, as shown in Figure 1.

According to the literature,[24,25] the sulfate groups are introduced through the esterification of the hydroxyl groups by introducing negative charges on the surface of the cellulose crystal, thus creating double layer electron repulsion between the microfibers. However, hydrolysis, and therefore, esterification occurs heterogeneously, reaching only the more accessible regions of the fiber after swelling with water, so that the crystalline regions remain with the same domain. Introduction of sulfate groups lead to decreased thermostability of the fiber,[26] as suggested by the results in this work.

However, it can be observed in Table 2 that the crystallinity index of the fibers treated with 50% H_2SO_4 have not sharply increased in comparison with that where the fibers were treated at 10% H_2SO_4. This indicates that after successive alkali treatment the fibers may be treated with a much lower acid concentration, incorporating less content of sulfate groups and maintaining higher degradation temperatures.

In Figure 2, through the surface graphics where T_{onset} was used as response factor, it was observed that all independent variables (time of hydrolysis, acid concentration and temperature), the lower level (−) should be used in order to obtain fibers with higher degradation temperatures.

However, in Figure 3 (the surface graphic where crystallinity index was used as response factor) it was observed that at higher acid concentrations and higher hydrolysis time, there was an increase in the crystallinity index. On the other hand, at a minimum concentration and less hydrolysis time, the opposite was observed.

For the morphological study, the aqueous suspension of nanocelulose was dried and then observed by means of scanning electron microscopy (SEM) analysis (micrographies presented in Figure 4). It was possible to observe the formation of two types of morphologies: either fibrous or agglomerated particles, mainly depending on the acid concentration used. Moreover, at high acid concentration there was clearly over hydrolysis of the fibers, which was noticed by the darkness of the fiber samples.

It can be observed in Figure 4A that, in spite of the cellulose fibers appear to be still bonded with each other, they have between 25–40 nm of diameter.

Composites of curauá fibers (original, after alkaline treatment, and after hydrolysis – sample E11) were prepared with a commercial polypropylene in a mini-extruder at 60 rpm, 180 °C, for 10 min. Characterization of the obtained PP composites was performed by DMTA, which evaluates

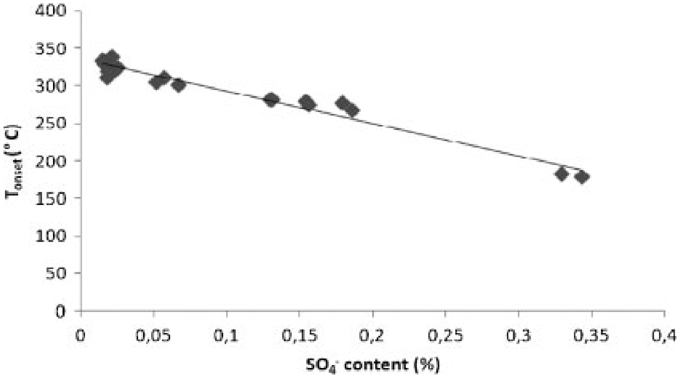

Figure 1.
Relationship between T_{onset} and the amount of sulfate groups incorporated after acid hydrolysis.

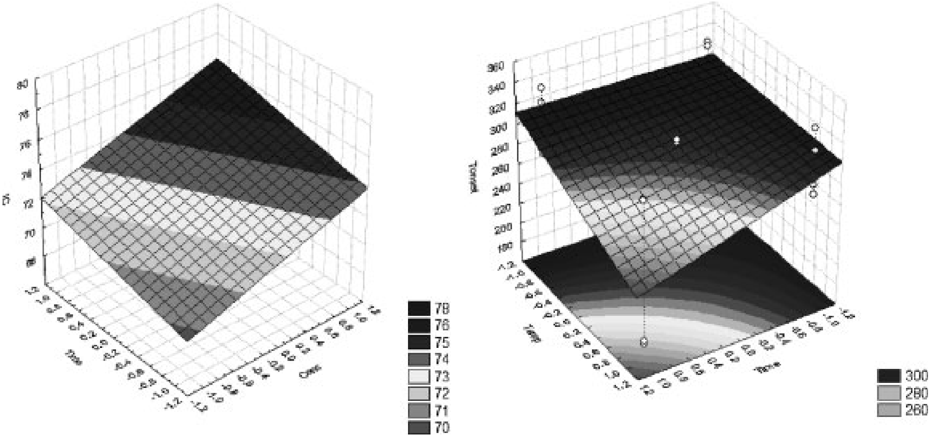

Figure 2.
Fitted surface, dependent variable: T_{onset} in relation to the independent variables: (a) (time *vs.* acid concentration) and (b) (temperature *vs.* time of hydrolysis).

the behavior of storage (E′) and loss (E″) moduli with temperature, and the thermal transitions through tan δ x T. According to the results presented in Table 3, it was observed that both storage and loss moduli of the sample containing untreated fiber as load slightly increased, although increased considerably in the composite with NaOH-treated fiber in comparison with the moduli of neat PP (Figure 5). This was due to the removal of amorphous components of the fiber with the alkaline treatment, increasing the reinforcing amount of cellulose. However, the moduli of the composites contain-

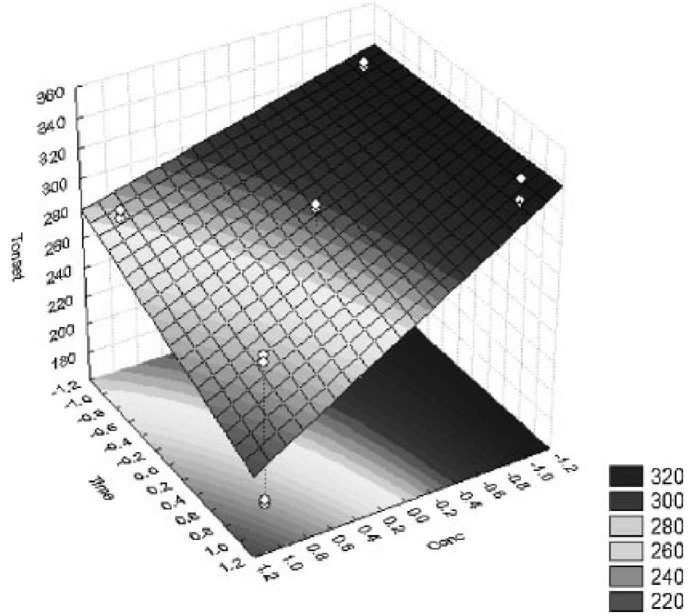

Figure 3.
Fitted surface, dependent variable: crystallinity index in relation to the independent variables (time *vs.* acid concentration).

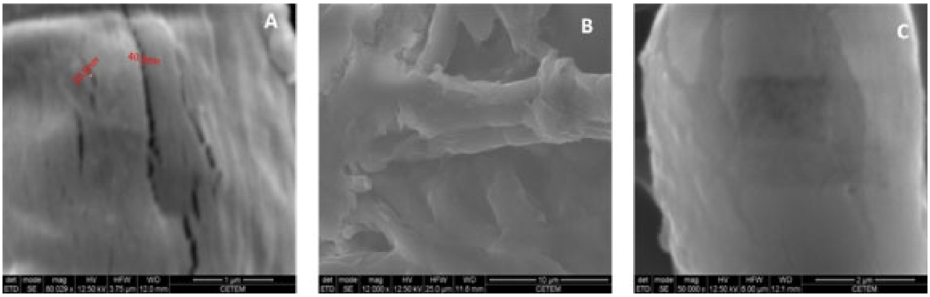

Figure 4.
Scanning electron microscopy of sample hydrolyzed under: acid concentration/hydrolysis time/temperature/sonication time. (A) 10% H_2SO_4/60 min/40 °C/30 min, (B) 50% H_2SO_4/240 min/40 °C/30 min, (C) 10% H_2SO_4/240 min/40 °C/120 min.

Table 3.
Results of Dynamic Mechanical Thermal Analysis of pure polypropylene and polypropylene processed with curaua fibers with and without treatments.

Sample	E′(MPa) (−40 °C)	E′(MPa) (25 °C)	E″ (MPa) (−40 °C)	E″ (MPa) (25 °C)	Tg (°C)	tan δ max
PP neat	1680	819	40	45	6.8	0.0727
PP 10% curaua (original)	2334	1083	53	50	7.1	0.0669
PP 10% curaua (treated with NaOH)	3022	1393	69	63	5.9	0.0645
PP/MAPP/10% curaua (treated with NaOH)	2235	1075	47	54	7.3	0.0631
PP 10% curaua (acid treatment)	5332	2431	231	159	13.1	0.0758
PP/MAPP/10% curaua (acid treatment)	3295	1880	717	315	12.3	0.1988

Pure PP = Polypropylene commercial (HP550K, Braskem); PPMA = maleated PP (Polybond 3200).Tg obtained from Tan δ curve.

ing acid-treated fibers were much higher, achieving 2431 MPa at 25 °C against 819 MPa in the neat PP.

The use of MAPP as compatibilizer did not lead to improved dynamic mechanical behavior compared with the composites processed without MAPP. It is suggested that the humidity present on the fibers difficult the wetability of the compatibilizer with the fibers. Since the fibers obtained are not totally crystalline, they are liable to absorb moisture. Chemical treatments performed on the fibers have increased the crystallinity index of cellulose to 78%, reducing the absorption of humidity by the sample. The crystalline regions of cellulose are inaccessible to water molecules, therefore there is a direct dependency between the accessibility of the water molecules and the amount of amorphous fraction of the fibers.[27,28]

Several factors should be considered for understanding the transitions occurring in the system consisting of polymer matrix/fibers in the absence or in the presence of a compatibilizing agent. In the results presented in Table 3, Tg have not varied in the samples with the original fibers, as well as those with NaOH-treated fibers, although a sharp increase of Tg in the composite of PP with the acid-treated fibers can be noticed. This behavior is a result of interactions between the nanofibers and the polymer matrix, restricting the mobility of the PP molecules and consequently increasing the Tg of the material.

The presence of compatibilizing agent in the composite PP/acid-treated fibers/MAPP decreased slightly Tg of the material. As reported in the literature,[29] MAPP can act as plasticizer leading to a slight decrease in Tg values, as found in the

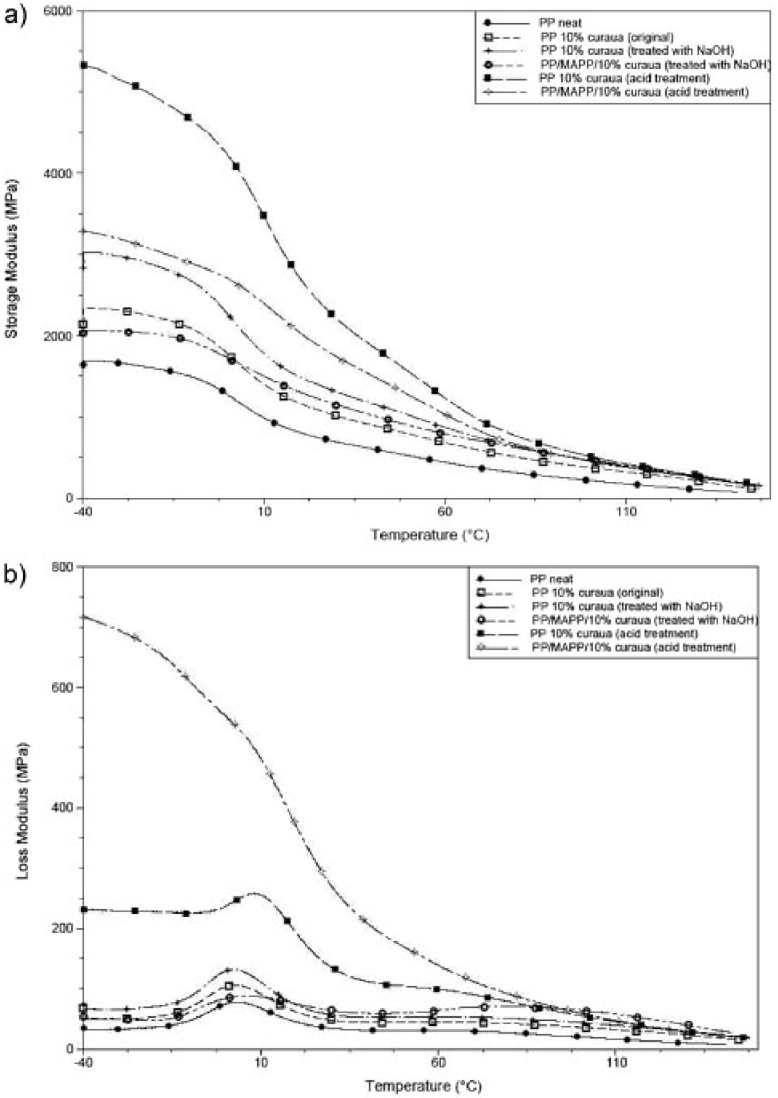

Figure 5.
DMTA results of pure polypropylene and polypropylene processed with curaua fibers: (a) Storage modulus x T, (b) Loss modulus x T.

present work. Moreover, the damping factor (tan δ) showed a significant increase in composites with the acid-treated fibers containing MAPP, which shows that this component actually act as plasticizer.

Conclusion

The fiber treated with 10 wt% solution of H_2SO_4, 240 min of hydrolysis at 40 °C, reached the highest degradation temperature ($T_{onset} = 338\,°C$), although it does not present the largest crystallinity index. Therefore, high crystallinity index leads to a decrease in degradation temperature of the fiber, which occurred when high acid concentration was used. It was concluded through the SEM analysis that at high acid concentration with more severe conditions of hydrolysis the formation of crystal clusters was observed, which means that the fiber was overhydrolysed and resulted in dark samples. According to DMA results, both storage and loss moduli sharply increased in the PP composites with the acid treated fibers without the addition of maleated polypropylene. This composite also presented the highest Tg. The addition of maleated PP as compatibilizer did not improve the mechanical properties of the composite with fibers.

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