



Thermal Degradation of Polypropylene Pine Sawdust Composite Filaments through Successive Heating and Reprocessing

Sônia M.A. Veroneze¹, Thais H.S. Flores-Sahagun², Irineu Mazzaro³ and Kestur Gundappa Satyanarayana^{4,*}

¹Post Graduation Program in Engineering and Materials Science/PIPE, Federal University of Parana (UFPR), Caixa Postal 19049, CEP: 81531-980, Curitiba, Paraná, Brazil

²Department of Mechanical Engineering, Federal University of Paraná (UFPR), Caixa Postal 19049, CEP: 81531-980, Curitiba, Paraná, Brazil

³Department of Physics, Federal University of Paraná (UFPR), Caixa Postal 19049, CEP: 81531-980, Curitiba, Paraná, Brazil

⁴Honorary Professor, Poornaprajna Institute of Scientific Research (PPISR), Sy. No. 167, Poornaprajnapura, Bidalur Post, Devanahalli, Bengaluru- 562110, Karnataka, India

Abstract: Considering the use of the new molding thermoplastic technique, where viscous filaments can be artistically or technically manipulated to create three-dimensional pieces using an extruder, this paper discusses the optimal PP/wood fiber filament preparation conditions especially the thermal degradation. Not only is it essential to know the best processing conditions of the composites but also gain durability and/or advantageous color change when the final products made with viscous filaments are subjected to thermal treatments. Very few papers have been published on polypropylene-pine wood filament composites and the thermal degradation of such filaments. This paper presents the preparation and characterization of filament composites using 5, 10, and 20wt.% pine sawdust with a compatibilizer obtained by hot molding through the use of an extruder, and discusses the effect of both drying time and temperature on the prepared filament composites to understand thermal degradation when subjected to 60°C and/or 120°C. Prepared filament composites are characterized for physical (density, water absorption, and crystallinity), thermal and tensile properties besides their morphology along with fractography. X-ray diffraction results confirmed the data obtained in thermal studies indicating that increased fiber content decreased both the crystallinity and the thermal resistance while decreasing the melting temperature of the filament composites. Fractographic studies revealed low adhesion between the sawdust and the matrix, evidenced by the presence of loose and some unattached sawdust particles in some composites, thus, supporting the observed low strength in these composites, besides the influence of drying time and temperature on the mechanical properties of the composites.

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1. INTRODUCTION

Incorporating lignocellulosic/wood fibers in polymer matrices has attracted researchers' attention for various uses, including construction, transport, etc. The reason for this is their low cost, good specific strength properties, the possibility of processing by methods similar to the ones of composites containing synthetic fibers, besides safety of the tools used in their secondary processing, among other benefits [1-5].

However, caution is needed during the manufacturing process of polymer-based composites with wood/lignocellulosic fibers to protect fibers against humidity or in the selection of the processing temperature to remove any residual water in the composite, especially if the composites are in the filament form, more vulnerable to thermal degradation. Also, heating and reprocessing may lead to decreased mechanical properties. For this reason, thermal studies have been carried out because one of the major limitations found in natural fiber-reinforced composites being the degradation they undergo even at relatively low temperatures [6].

The determination of the number of fibers to be used in these polymer-based composites is related to the sensitivity of

*Honorary Professor, Poornaprajna Institute of Scientific Research (PPISR), Sy. No. 167, Poornaprajnapura, Bidalur Post, Devanahalli, Bengaluru- 562110, Karnataka, India; E-mail: gundsat42@hotmail.com

wood/lignocellulosic fibers to water and their final application. Therefore, this becomes an important criterion for plastic-wood composite products. Also, it is known that the wood particles are hydrophilic due to the presence of lumens, fine pores, and hydrogen bond sites. Thus, the water in the plastic-wood composites is absorbed by the wood fibers in the composites [3, 7]. The higher the amount of fiber incorporated, the greater the water absorption, especially when both the matrix and reinforcing materials are not sufficiently compatible [8-23]. Exposure to water swells wood particles inside the composite to swell, consequently causing micro-cracks in the matrix and degradation of the polymer-wood interface, which reduces the density of the material. This action leads to voids at the wood-matrix interface. The particles become loose in the composite, resulting in a porous product, causing deterioration of mechanical properties and dimensional stability [9-17, 24-30].

Selection of processing temperature of composites is necessary to drive out moisture (water) from composites with wood/lignocellulosic fibers. Thus, the use of low temperature avoids degradation of cellulose, which occurs in the range of 200 – 220°C [6]. Accordingly, processing temperatures below 190°C have been strongly recommended for a better quality of polymer composites containing lignocellulosic materials [31, 32]. Fiber degradation causes unsatisfactory organoleptic properties, such as odor and color change, as well as the production of gaseous products during processing. All these would lead to high porosity, low density, and reduction of the mechanical properties of the processed material [32].

This limitation concerning the use of wood/lignocellulosic fibers defines the types of thermoplastics that can be used as polymer matrices in wood-plastic composites, such as polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP), and polystyrene (PS) [33-34]. Polypropylene (PP) is preferred because when reinforced by lignocellulosic/ wood fibers, the composites have a similar appearance to the wood, besides having low cost and good mechanical properties. For this reason, PP has been chosen as the matrix in this study.

As a way to prepare PP based filament composites and to study the thermal degradation of such composites, wood residues were selected in this study due to the fact that large amounts of wood residues (about 30 million tonnes) are available in Brazil, most of which is being used basically only for power generation or the manufacture of by-products as glued panel and toys [35].

Some studies have indicated that adding 3 to 5wt.% of compatibilizer to a mixture of wood-plastic is sufficient to improve the fiber-matrix adhesion due to the esterification reaction with the hydroxyl group the wood [8-15]. In the present study, 10wt.% of maleated polypropylene (MAPP) has been used, and in the third step, fibers were previously coated with the compatibilizer before the preparation of

composites to ensure good fiber-matrix adhesion as well as better wettability [36-38].

A literature survey made by the authors indicated that there had not been many reports on PP-pine sawdust composites in the filament form. These filaments may be used not only to prepare pellets but also, to be manipulated by hands protected by gloves, so that plastic pieces are formed [39]. Accordingly, the objectives of this study are: (i) Developing PP-based filament composites containing 5, 10, and 20wt.% sawdust by hot molding technique; (ii) Subjecting thus prepared filament composites to different times and temperature (40°C, 60°C or 120°C); and (iii) Characterizing all these for their physical, thermal and tensile properties to understand the performance of these filament composites along with morphology and fractography studies of a set of samples, which would help in understanding the thermal degradation properties. Also, an attempt is made to prepare PP-based composites by hot molding through the use of a selected compatibilizer and evaluation of the most suitable characteristics of the filaments for hot molding of plastic pieces. It is interesting to know one of the practical applications of artistic or technical PP/wood fiber samples made through the use of the new molding thermoplastic technique that uses viscous filaments coming from an extruder is reported [39]. In view of this, present study is aimed not to give more details about some prepared articles but to find the optimal conditions for the molding technique, especially the thermal degradation of the composites subjected to different thermal treatments.

2. EXPERIMENTAL

2.1. Materials

The material sawdust of *Pinus Elliotti* (PSD), used in this study, was obtained from the timber company Centre (Paraná, Brazil) with sizes of 0.420 and 0.250mm (passing through 40 and 60 mesh screens) [31].

The polypropylene (PP) used in this study were purchased from Braskem (H 503 brand). This material had a density value of 905 kg.m⁻³, a flexural strength of 1300 MPa, a tensile strength of 35 MPa, and elongation of 11% [40].

The compatibilizer used in this study consisted of PP, maleated anhydride (MAH), and dicumyl peroxide (DP), called maleated polypropylene (MAPP), which was prepared by reactive extrusion in the authors' laboratory, details of which can be seen elsewhere [31, 36, 37]. The composition of this MAPP was 98.5% PP + 1% MAH + and 0.5% DP, which could help to obtain better dispersion of PSD in this polymer besides exhibiting better mechanical properties and lower water absorption as reported in earlier studies [31, 36, 37]. The melt flow indices of the maleated polypropylene (MAPP) and PP samples were reported to be 27.8g/10 min and 3.2g/10 min, respectively, measured according to ASTM D1238 [38, 41]. All the composites were produced in a single

thread extruder (Teck Trail Make/model EMT 25) with an L/D ratio of 30.

2.2. Methods

2.2.1. Preparation of Composite Filaments

In order to prepare the composite filaments, above mentioned mono screw extruder was used with the rotation speed of 85rpm and the extruder temperature profile at 175°C (except the head, which was at 168°C). Composite filaments prepared in the second and third steps were analyzed with regard to their thermal degradation. The sawdust samples (PSD) used in all stages were dried at 60°C for 22h.

After the preliminary study (hereafter referred to as the first step), in which composites were containing 10 and 20wt.% of PSD and 10wt.% MAPP mixtures were prepared to find out the effect of the amount of PSD on the filaments produced, PP composite filaments containing only 5 and 10wt.% PSD, with 10wt.% MAPP, were prepared in the second step and cooled underwater, and dried at 60°C for 48h (samples named as A and B), aiming to remove the remaining water in the composite to dry the material as required for this study.

These steps aimed to find the optimal amount of fiber in the composites so that the filaments were flexible enough to be handled and could be used to prepare products—the 20 wt.% composite, of preliminary study (first step), was found to be both too hard and rough, and more brittle than the 10wt.% sample, which had enough flexibility. It was also tested the 5wt.% composite to verify if it would be better to handle and still had the wood appearance of the other compositions. Based on this study, just 5wt.% composite was then prepared in the third step.

Figure 1 shows a schematic diagram of the whole process of obtaining the composite in the second stage. In short, initially, composites filaments were prepared in the extruder containing 5 and 10wt.% PSD were cooled under water and dried at 60°C for 48h (samples named A and B), aiming to remove the remaining water in the composite to dry the material as required for this study.

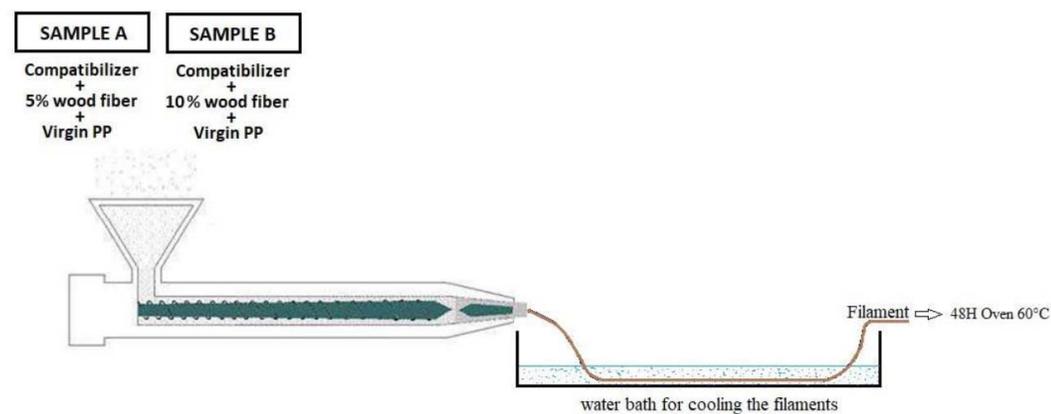


Figure 1: Schematic diagram of the second step where composite filaments were prepared with (a) 5wt.% (b) or 10wt.% sawdust.

Figure 2 shows schematically the third step of this study using reprocessing and different thermal treatment temperatures for the filaments produced. In this case, no immersion in water was used for cooling the filaments. But, in order to prepare composites having high resistance to water absorption and study the effects of this on the degradation of the composites, the fibers were coated with the compatibilizer (unlike the second step) at the beginning of the processing of composites, instead of using the compatibilizer, PP and sawdust together.

Fibers with compatibilizer were treated at 40°C for 24h followed by treatment at 60°C for 24h or treating at 120°C for 24h and mixed with PP to obtain composite filaments containing 5wt.% fibers. These filaments were then treated at 60°C for 24h (hereafter called sample C) or at 120°C for 24h (hereafter called sample D). These filaments were finally reprocessed and treated for 8h at 120°C (hereafter called samples E and F, derived from samples C and D, respectively).

To summarize the extrusion process carried out in this study, samples A and B were subjected to two extrusion processes (the second one is called reprocessing). Samples C, D, E, and F were prepared with PMMA coated fiber (coating made using one extrusion cycle), and so, samples C and D had each two extrusion cycles, while samples E and F had three extrusion cycles (these samples were reprocessed once as in the case of samples A and B).

The prepared composite filament samples, in both second and third steps, are listed in Table 1, presenting PSD content and drying temperatures.

2.2.2. Characterization of Composite Filaments or Pellets

Degradation of composites prepared in both second and third steps was followed through their characterization in density, water absorption, X-ray diffraction, thermo-gravimetric (TGA/DTG), mechanical properties, morphology, and Fractography studies.

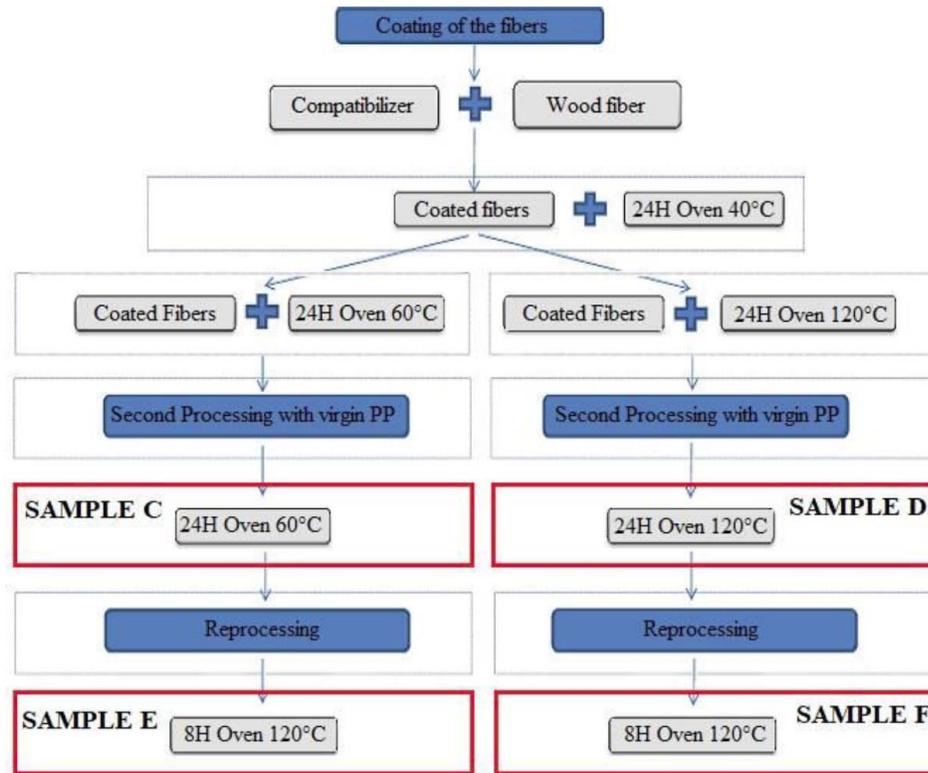


Figure 2: Schematic diagram of the third step.

Table 1: Constituents of Composites Prepared with their Designation

Step	Composite Produced	Pinewood fiber content (wt. %)	Drying temperature (°C)
Second	A	5	60
	B	10	60
Third	C	5	60
	D	5	120
	E	5	120
	F	5	120

2.2.2.1. Composite Density and Number of Voids (Pores)

Considering that the results of the measured density of composites may be used to understand both the thermal degradation and the effects of the water removal through the reprocessing cycles and the successive heating of composites, densities of the prepared composites were determined in the Polymer Laboratory of the Mechanical Engineering Program at Federal University of Paraná (UFPR), in Curitiba, following the ASTM D2395 [39, 42]. The method consists of immersion of the previously weighed composite filament in water kept in a graduated flask. Then, after the volume of water was spilled, due to filament immersion in water, it was measured, which reveals the volume of the sample, considering the density of water as 1g/mL at room temperature. Thus, the division of the weight of the composite by its volume results in the experimental density of the composite filament.

On the other hand, theoretical densities of composites were calculated using Equation 1:

$$\rho = \frac{M_s}{V_w} \tag{Eqn. 1}$$

Where: ρ = experimental density of composite, M_s = weight of the sample, and V_w = variation of water volume displaced.

The number of voids in the composites was calculated using Equation 2:

$$V_v = 1 - \rho_c \left[\left(\frac{W_s}{\rho_s} \right) + \left(\frac{W}{\rho} \right) + \left(\frac{W}{\rho} \right) \right] \tag{Eqn. 2},$$

Where: V_v = volume of voids in the composite, ρ_c = experimental density of the composite, W_s = weight fraction of sawdust, ρ_s = density of the wood fibers in the composite,

W = weight fraction of PP, ρ = density of polypropylene, W = weight fraction of MAPP, and ρ = density of MAPP.

2.2.2.2. Water Absorption

Water absorption of the pelletized composite filaments having 5 and 10wt.% of sawdust without MAPP coating (second step) and 5wt.% of sawdust with MAPP coating (third step) was determined according to NBR 14810-3 [43, 44]. For this purpose, the material was first kept in an oven at 50°C for 24h to remove the moisture obtained in contact with the environment. Then, the samples were weighed after taking out the filaments from the oven. The pellets of composite filaments were kept in distilled water at room temperature for 24h. After that, the samples were taken out, and the surface water was removed by wiping with absorbent paper before weighing them again. The moisture content was calculated using the following equation:

$$A = \frac{M1 - M2}{M0} \times 100 \quad (\text{Eqn. 3})$$

Where: A = water absorption of the specimens, M1 = mass of the specimen after the immersion for a given time, and M0 = mass of the specimen before immersion.

2.2.2.3. X-Ray Diffraction Studies

The X-ray diffraction technique was used in this study to identify the crystalline phases present in the prepared composite filaments of the second and third steps. For this purpose, a Bruker Avance D8 X-ray diffractometer was used with a 2θ scanning range of 5-60°. Smooth flat samples obtained with polishing paper were used for this study. The crystallinity index was obtained from the obtained XRD spectra using the ratio of areas using the Bruker EVA software at the X-Ray Optics Laboratory, Department of Physics at Federal University of Paraná (UFPR).

2.2.2.4. Thermal Characterization:

To understand the thermal degradation of the composites, thermo-gravimetric (TGA/DTG) studies of the prepared samples were carried out. For this purpose, a TA Instruments Q50 V6.7 Build 203 Analyzer was used, and the samples were heated up to 600°C in a nitrogen atmosphere (100ml/min) at a heating rate of 20°C/min.

2.2.2.5. Tensile Testing

Following the ASTM D638 [45, 46] tensile test was carried out on the composite filaments processed in the second and third steps, which had the shape of filaments of 5mm diameter. In both cases, operational conditions used were applied load of 5N and a test speed of 50mm/min.

In samples obtained in the second step, testing was carried out at LACTEC (Curitiba, PR, Brazil) using a universal testing machine (Make: Instron, Model: 33R4467) at room temperature relative humidity of 59%. On the other hand, the filaments processed in the third step were tested at Research Center in Applied Chemistry (CEPESQ), at Federal University

of Paraná (UFPR), using the universal machine (Make: Instron, Model: 5567) with the climatic conditions at 25 ± 2°C and relative humidity of 43 ± 2%.

2.2.2.6. Morphology and Fractography Studies

Prepared composite filaments processed and tensile tested in the second and third steps were first gold coated. These coated samples were then analyzed using a scanning electron microscope (SEM) (Make: Tescan Vega, Model: 3 LMU - operating voltage of 20 kV). Five samples were used for each analysis.

3. RESULTS AND DISCUSSION

3.1. Processing of Composite Samples

As mentioned earlier, it was intended, in the preliminary study or the first step, to produce composite filaments containing 10 and 20wt.% PSD, and, based on these results, only composites containing 5 and 10wt.% PSD were prepared and used for further studies, viz., in the second step of this study. This study aims to determine the optimum conditions for preparing the PP/wood fiber composite filaments considering the fiber content and various treatments (with and without the use of water bath in the extruder, duration, and temperature used in the thermal treatment). Finding the optimal filament preparation conditions is essential for preparing samples made of filaments following a reported new molding thermoplastic technique [39]. This is because they were more flexible and less brittle than those obtained in the preliminary study (wherein 20wt.% PSD were used).

Furthermore, because the color of composites containing 5wt.% PSD was still the same, and they exhibited similar strength values compared to 10wt.%, only composites containing 5wt.% wood fibers were prepared in the third step.

3.2. Density Measurement

Determination of density is of great importance for plastic-wood composites, as this property influences both the mechanical and physical behavior of these materials once that higher density may result in greater deformation at break or greater strength [47]. Both the experimental and calculated density values of composite samples prepared in the second and third steps are listed in Table 2. It may be observed that experimental density values of MAPP and virgin PP have been reported to be 0.88 ± 0.02 and 0.91 ± 0.03 (g/cm³), respectively, while the apparent density of pine sawdust is 374 kg.m⁻³ [48]. According to the ASTM D792 [49], compression of fibers takes place during the extrusion process [43], while the reported values of sawdust in the composites range between 1300 to 1500 kg.m⁻³ [50]. The density of sawdust in the present study was taken as 1300 kg.m⁻³.

A higher density value is expected for the composite having a larger quantity of wood particles [36, 50]. However, in the

Table 2: Test Results of Density and Water Absorption of Virgin PP (Matrix) and its Composites Containing Pine Sawdust

Specimens	Average density Experimental (kg.m ⁻³)	Average density Theoretical (kg.m ⁻³)	Average volume of pores (kg.m ⁻³)	Standard deviation (kg.m ⁻³)	Water absorption %
PP	–	905*	–	–	–
A	903	905	Very low	1.41	3.52
B	881	910	129	2.51	7.34
C	656	907	378.9	17.48	2.51
D	775	907	247.8	9.34	1.75
E	904	907	Very low	2.12	0.87
F	909	907	Very low	1.41	0.35

*Value given by Braskem S/A.

present study, as shown in Table 2, the experimental density values of the composites with the larger sawdust content are lower than those with a minor percentage of sawdust.

A comparison between theoretical and experimental densities of composites with 10wt.% sawdust revealed higher theoretical density values than those observed experimentally, suggesting that these composite samples contained more pores. In fact, calculated average density of pores in the specimen with 10wt.% sawdust was found to be 129kg.m⁻³. On the other hand, for composites with 5wt.% sawdust, the values of average volume of pores were very small (samples A, E, and F), probably because of the lower amount of sawdust incorporated into the composite.

Theoretical and experimental density values of composite samples produced in the second and third steps, as well as the average pore volume, shown in Table 2, suggest that increasing processing cycles leads to closer experimental and theoretical density values, while the average volume of pores decreased sharply. Consequently, according to the results shown in Table 2, the number of reprocessing cycles influenced the density of these materials and decreased the number of pores. Besides, the value of standard deviation decreased with the amount of reprocessing because the material became more homogeneous.

Further, it is relevant to highlight that heating of samples at 120°C helped increase the experimental density, as can be seen in the case of sample F, which showed the value of experimental density very close to that of theoretical density. This confirmed the reduction in the number of pores and moisture in the sample due to the heating process.

3.3. Water Absorption

It can be seen in Table 2 that the composites containing 10wt.% fiber filaments absorbed approximately twice the amount of water compared to those of 5wt.% fiber filaments in the second step.

After these results, allied to density results, in the third step, the samples were submitted to further heating, which led to the removal of water residues from the samples, allowing,

this way, the evaluation of both their degradation and resistance to thermal treatment.

As observed in Table 2, the water absorption by the filaments of the third step shows a significant difference between samples treated at 60°C and those treated at 120°C. Also, there is a gradual reduction in water absorption by these samples.

Further, the lowest water absorption values are observed in the samples treated at 120°C, with the absorption of only 0.35% after 24 hours of immersion. Therefore, it can be assumed that this result could have been caused by the better wettability of the fibers, the increase of the matrix melt index (i.e., its lower viscosity), the reduction in fiber size, or even by the combination of all these factors, as already discussed earlier [50-52].

Another factor related to the reprocessing of composites that may have contributed to a smaller amount of water absorption could be the thermal degradation of wood (fibers), which consists of mainly cellulose, hemicellulose, and lignin. According to Shahi *et al.* [47], among these components, hemicellulose is the main responsible for the water absorption in lignocellulosic materials because it is less thermally stable as its decomposition begins at 200°C. This way, it is possible that partial removal of these fewer stable components can occur even at lower temperatures, as their decomposition rate is accelerated by the combination of shear forces and the temperatures involved in such a process. Considering the standard deviation of each sample, water absorption, and the number of pores, which decreased in the order B > A > C > D > E > F and C > D > B > E ~ F ~ A, respectively, all values were compared according to their ranges that were calculated using the average value ± standard deviation. Although the discussion in the paper was made comparing average values because it shows a tendency, it can be seen that many properties are statistically the same.

3.4. X-Ray Diffraction (XRD) Studies

Figure 3 shows XRD patterns obtained for the matrix (PP) and different composites prepared in this study. Samples A

and B are those with 5 and 10wt.% PSD, respectively, processed in the second step, while samples E and F are those with 5wt.% sawdust containing composites processed in the third step and thermally treated at 60/120°C and 120°C, respectively.

As shown in Figure 3, two distinct phases are present, and one of them is amorphous due to the presence of lignin and hemicelluloses, while the other is crystalline due to cellulose.

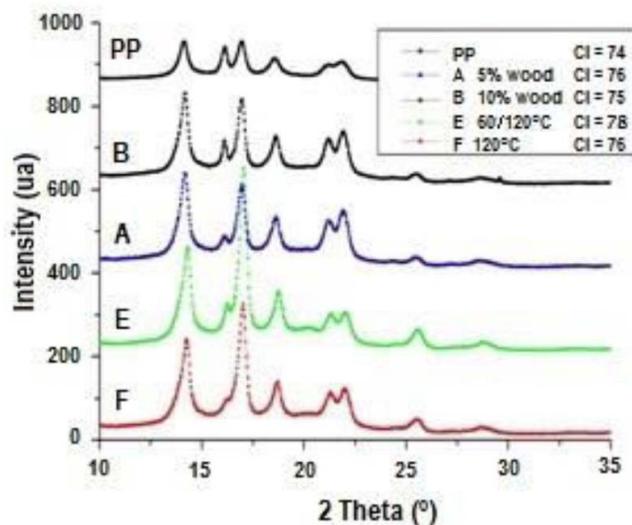


Figure 3: XRD patterns obtained for the matrix (PP) and different composites.

The XRD patterns of samples A and B, in the second step, reveals that the incorporation of sawdust had an effect on the XRD pattern of the virgin PP. Higher peaks can be seen in both the composites, compared to that one of PP, although no changes are observed in the peak positions. A very small increase in the crystallinity index (CI) is observed with 74% for virgin PP while 76% and 75% for composites A and B, respectively. This difference between the matrix and the composites can be attributed to the material processing, which occurs its heating, leading to higher molecular mobility and better packing of the polypropylene chains, even in the presence of sawdust [36, 38].

Sample A having lower PSD content, showed higher crystallinity in comparison to that of sample B. This is understandable as sample A contained 5wt.% fiber, while sample B contained 10wt.%. Accordingly, sample A contained a higher amount of PP, which has led to a higher crystallinity index due to the fact the amount of crystalline PP is higher. Also, as the melt index of composites prepared with PP tends to increase due to the scission of PP chains during the extrusion process, it is expected that samples containing PP of smaller molecular weight would crystallize more easily, besides showing a higher crystallinity index [36, 37].

However, the average matrix crystallinity increased in the composites processed in the third step, probably due to better dispersion of sawdust, which may have increased the

number of nucleation sites, resulting in a higher crystallization rate. Higher crystallinity indices for samples E and F (78 and 76%, respectively) than the one of virgin PP suggest that the thermal treatment increased the mobility of PP chains.

Besides, these samples (E and F) were not cooled in water, and therefore, their chains had more time to organize during annealing, which probably might have led to an increase in the crystallinity index. Furthermore, although both composites E and F contained the same amount of sawdust (5 wt.%), composite F showed a lower crystallinity index (76%) than composite E (78%), which may be due to some degradation in composite F caused by the thermal treatment at 120°C. The darker brownish color of filaments F (See Section 3.7.1), along with different smells in these samples, was also noticed, suggesting the possible occurrence of some degradation process in the material.

It could also be noted that despite the melt index of samples were not evaluated, and the reprocessing caused ease in the extrusion processing showing that scission of PP chains occurred and was higher in samples E and F. A higher melt index of the composite (i.e., the lowest viscosity) reflects (when comparing equal wood contents) the lower molecular weight of the matrix [36-38].

3.5. Thermogravimetric Studies

The effects of both reprocessing and successive heating can also be verified in the thermal stability of the prepared composites. Accordingly, thermo-gravimetric analysis (TGA) studies were performed on the samples of the second and third steps. Figure 4a-g shows the TGA curves of virgin PP (Matrix) and its composites with PSD containing 5 and 10 wt. % (A and B, respectively), without the coating of compatibilizer, and 5 wt. % (samples C to F), with the coating of compatibilizer and treated at 60°C and 120°C. These curves showed the percentage of mass loss as a function of temperature.

At the outset, curves indicate the temperature at which mass loss actually begins (i.e., the point that marks the end of the first level of the mass loss curve where mass remains at about 100%), which is called T_0 , and also the temperature where the mass loss curve stabilizes (T_{MAX}).

The first stage of the TGA curve indicates the elimination of moisture besides the decomposition of volatile components at low temperatures, with mass loss differing according to moisture content. The second stage indicates an abrupt mass loss related to the oxidative decomposition of the material. Finally, as the temperature rises, the last stage begins with a slower decomposition, which may correspond to the formation of ash.

As can be seen from Figure 4 and Table 3, the composites processed in the second step (sample B), which contained 10 wt.% of PSD, show initially thermal decomposition at lower temperatures (lower initial degradation temperature)

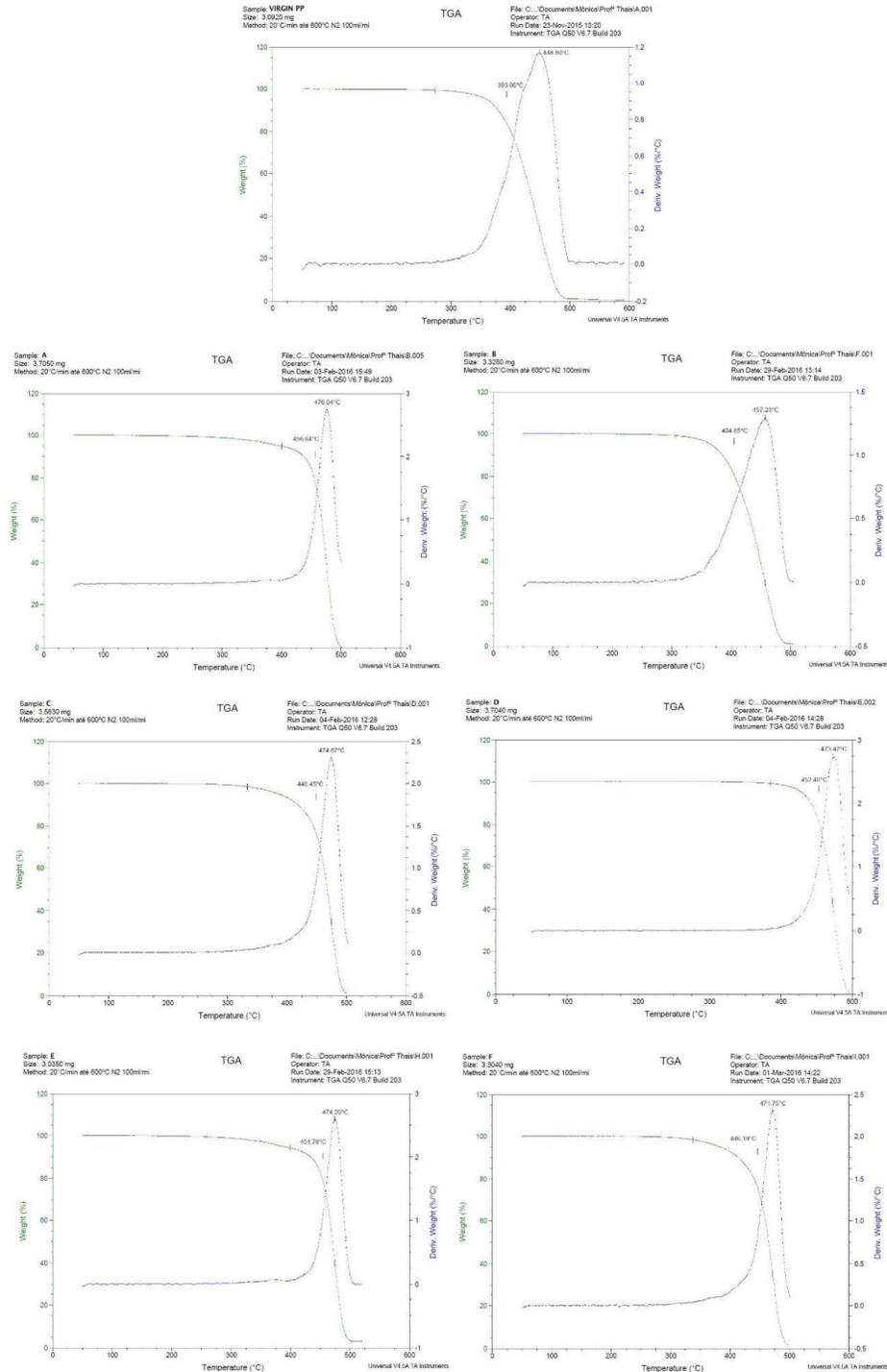


Figure 4: (a-g): TGA and DTA curves: (a)- Virgin PP; (b)- Sample A; (c)- Sample B; (d)-Sample C; (e)- Sample D; (f)- Sample E; (g)- Sample F.

compared to the 5% composites, which are represented by sample A (processed in the second step) and samples C, D, E and F (processed in the third step). This suggests that the higher thermal stability in the composites with 5 wt. % PSD is possibly caused by the higher crystallinity of the samples when compared to sample B (10 wt.%). Also, the loss of mass with the thermal treatment of samples in the third step tends to decrease, in comparison to sample A (second step), due to the higher crystallinity index of the samples C, D, and

E, which were subjected to both more reprocessing and thermal treatment. The maximum degradation temperature (DTG) of samples C, D, and E tends to increase also due to the higher crystallinity index. About sample F, which was more exposed to the thermal treatment at 120°C, because of the degradation of the wood fibers, observed through the characteristic smell and browner color of the sample, DTG decreased, as well as the initial degradation temperature.

Table 3: Thermal Data from TGA Analysis for PP and Composites

Specimens	Initial degradation temperature (°C)	Final degradation temperature (°C)	Mass loss (%)	DTG
PP	393.8	590	100	448.8
A	456.64	500	99.5	476.04
B	404.65	500	98.5	457.23
C	448.45	500	98.5	474.67
D	452.4	495	99.0	473.42
E	454.78	520	96.5	474.20
F	446.19	500	98.5	471.75

Ratanawilai *et al.* has reported [53] that higher interfacial adhesion between wood particles and polymer matrix results in a lower percentage of mass loss and higher thermal stability. In the present study, comparison of the processing steps among the composites containing the same amount of filler (PSD), the percentage of mass losses is very similar. This reinforces that the thermal stability of the materials changed little with reprocessing and successive heating.

Natural fibers decompose in two main stages when exposed to heat: first, thermal de-polymerization of hemicelluloses occurs, and breakdown of cellulose glycosidic bonds takes place; in the second, decomposition of α -cellulose occurs so that decomposition of lignin takes place at a temperature range of 200-500°C [45]. In the present study, although the fibers were dried before the tests, total elimination of the water was difficult due to the fibers' hydrophilic character [54].

It can be seen from Figures 4b and c that the composite samples A and B (obtained in the second step), with PSD fibers without coating with compatibilizer before being mixed with the virgin PP, showed a mass loss of 0.5 wt.% at around 180°C. This is attributed to the loss of water from the fiber. Then, a second mass loss can be observed between 210 and 300°C for both samples, corresponding to the loss of mass of the PSD fibers in the composite (approximately 5%) and due to the degradation of hemicellulose and cellulose. A third loss at the temperature range of 500°C can be attributed to the degradation of lignin. Probably the presence of functional groups more strongly linked to the lignin of the samples with better homogeneity explains their greater resistance to decomposition. Finally, above 500°C, the curves do not reach zero residue value, indicating about 1.5% ash for the composite samples. These values are attributed to inorganic compounds present in plants fibers, which do not undergo thermal decomposition.

Further, from Figure 4d-g, it is evident that the thermal degradation of samples C, D, E, and F (obtained in the third step), also prepared with 5wt.% PSD fibers, are similar to the ones of samples A, although these were differently treated both thermally and mechanically (via extrusion). Thus, probably the longest time or the higher temperature used in

the thermal treatment did not contribute to the higher thermal resistance of PSD fibers in comparison to sample A.

However, the thermal treatment induced higher homogeneity of the samples and higher crystallinity of PP due to the higher mobility of PP chains. As already discussed earlier, in the presence of smaller PP chains (lower molecular weight), which is formed due to reprocessing, it tends to increase the thermal resistance of samples due to a better packaging of PP chains [36-38].

On the other hand, it seems that the thermal treatment of sample F was too drastic because the initial degradation temperature and DTG become lower in comparison to sample E, which suggests that the sample F is weaker than the sample E by thermal treatment at 120°C. But, when samples C and D are compared to each other, the thermal treatment was beneficial to enhance the thermal resistance of sample D.

Also, samples with the addition of MAPP-coated PSD show an increase in the onset temperature, indicating increased thermal resistance compared to PP. Concerning sample B (10wt.% PSD fibers), it was observed that the heat resistance is lower because of its higher fiber content than all other samples besides the relatively high speed of heating.

It should be noted that samples processed in the third step were prepared with PSD coated with MAPP, which not only improves their homogeneous distribution in the PP matrix but also improves the matrix-fiber adhesion, besides protecting the sawdust from heat [36, 37]. Thus, sample E showed increased resistance after being heated for 8h at 120°C (initial degradation temperature varied from 448.45 – sample C – to 454.78°C – sample E), possibly due to the better adhesion between matrix and PSD fiber. However, when heated for an additional 8h at 120°C, sample F showed reduced resistance (initial degradation temperature varied from 452.40 – sample D – to 446.19°C – sample F). This composite exhibited a still darker brown color, which is a sign of a more pronounced degradation of the material.

In general, samples from the third step presented thermal degradation profiles slightly lower than sample A (with the

same amount of PSD), processed in the second step, indicating reduced thermal stability. This can be attributed to both the number of processing steps used and the duration of the heating process of the samples in the third step.

However, these extra heating cycles are probably responsible for reducing the number of voids observed in samples E and F and the reduction in water uptake. Thus, the additional heating is advantageous for the analysis of thermal degradation, which is important for this study.

3.6. Tensile Testing

Table 4 shows the plots of Young's modulus, maximum tensile strength, and deformation (% elongation at break) of the composites prepared in the second and third steps in this study. Besides that, all the tensile properties were obtained from PP based composites with 5 and 10 wt. % PSD, processed at different conditions and treated at different temperatures.

Tensile testing of composite filaments (samples A and B from step 2), with 5 and 10wt.% PSD, reveals that these composites are highly sensitive to deformation, as shown in Table 4. Also, the maximum stress of these materials became lower with the increase in the sawdust content. This is evident from the maximum tensile strength for the composites with 5wt.% sawdust (39.59 MPa), which is higher when compared to that of the composite with 10wt.% sawdust (35.63 MPa). The latter value of tensile strength is comparable to Braskem reported value of 35 MPa for PP, according to ASTM D638 [46].

In fact, pure PP filament was not tested for tensile properties, but the tensile strength of PP available in literature was used for comparison here. A comparison of the tensile strength of matrix PP and that of composite B (PP+ 10wt.% sawdust) indicates that there was practically no reinforcement of the matrix after the addition of 10wt.% sawdust. In the case of composites A (PP+5wt.% sawdust) and B (PP+ 10wt.% sawdust), more reinforcement in composite B was expected than that of sample A because if a better matrix-fiber adhesion was observed (better reinforcement), with less visible pull-out, possibly tensile strength of composite B would have been higher than that of composite A. However, the slightly higher tensile strength of the composite B, in

relation to pure PP, indicates that, even without a very good fiber-matrix adhesion, some adhesion occurred.

The process of non-reinforcement of the matrix (in composite B) could be explained by an insufficient fiber-matrix adhesion, indicating that the mixture of PP with sawdust was not efficient in this case. One reason for this non-reinforcement could be that the sawdust used was uncoated; once better sawdust coating might lead to higher wettability, besides greater protection of wood particles during the initial reprocessing cycles, reducing their degradation. This non-reinforcement also suggests that the amount of compatibilizer (MAPP) was not enough to compatibilized the polar-non-polar PP/wood fiber when it was used a higher amount of fibers, in the case of 10% (composite B), instead of 5% (composite A). Another factor may be the remaining water, which was possibly the reason for an insufficient coating of fibers with MAPP.

Although better fiber-matrix adhesion is reported when MAPP-coated fibers are used [36, 37], the tensile strength values of samples C to F (all these samples containing coated sawdust) suggest that bonding of coated PSD with the matrix PP has not improved even with the coating of PSD using the MAPP compatibilizer. This inference is supported by the fractography studies presented in the next section and is further evident from the thermal studies described earlier, in Section 3.5, where the degradation of wood fibers in these composites was observed. Also, the degradation of fibers during the processing of composites can cause substantial changes in the mechanical properties of the materials due to the modification of the structure of reinforcements (here it is PSD), leading to lower resistance [55].

As can be seen in Table 4, composites processed in the third step (C to F), all the samples with 5wt.% PSD, and thermally treated at two different temperatures, show lower tensile strength values than that of composite A, which also contains 5wt.% PSD. But the result seen for composites C and D, compared to composite A, is also lower because those presented more pores. Samples E and F did not present visible pores, although they were also obtained in the third step.

Again, from Table 4, it can be seen that the tensile strength of composite D (34.74 MPa) is higher than that of the other

Table 4: Obtained Tensile Properties of Virgin PP (Matrix) and its Composites Containing Pine Sawdust

Specimen	Young (MPa)	Tensile strength (MPa)	Elongation at break (%)
A	559.6 ± 66.5	39.59±1.68	18.5±2.52
B	540.36±100.3	35.63±3.64	18.42±3.14
C	369.90±48.37	28.47±3.65	30.91±2.61
D	373.90±77.94	34.74±1.61	23.87±6.90
E	433.43±60.27	33.43±1.72	25.09±1.00
F	389.54±73.18	26.88±1.94	24.74±2.68

three composites, viz., C (28.47 MPa), E (33.43 MPa), and F (26.88 MPa), which were also obtained in the third step. These values can be attributed to the heating of composite D at 120°C, which also resulted in good resistance to thermal treatment, while another composite sample (C) showed lower tensile strength besides low resistance to thermal treatment when compared to that of sample D, due to their heating at 60°C.

Sample E, also subjected to heating at 60°C during almost the major amount of the process and heating at 120°C at the end, exhibited better tensile results than that of sample C. This suggests that more than one processor, and heated at 120°C, may have led to higher crystallinity and reinforcement, which was also demonstrated by density values showing very fewer pores, as well as by thermal degradation testing, which showed better thermal resistance.

Lower tensile strength of composites C to F (all of them processed in the third step), when compared to those of composites A and B (both processed in the second step) could be explained by both reprocessing and heating process of the composite that caused degradation of the fibers, and lower viscosity, as well as the intertwining ability of the molecules, ultimately reducing the strength of the materials [36-38]. Besides that, the number of extrusion cycles carried out to produce these samples resulted in lower dimensions (both fiber length and diameter) of sawdust particles [56]. Considering the standard deviation of each sample, it was observed that tensile strength decreased in the order $A > B \sim C \sim D \sim E > F$, which indicates that statistically tensile strength values of various samples were the same, although there is a behavior tendency, as discussed.

In Young's modulus (YM), as shown in Table 4, composite A shows the highest YM value of amongst all the composites studied in this study, followed by that of composite B. The lower value of YM in composite B, when compared to composite A, indicates there might not be good homogenization in the material structure (in terms of particle size and dispersion) inside this composite because the composite would have been stiffer if the wood had actually acted as reinforcement.

It is well known that material stiffness depends on reinforcement or filler (in the present study PSD) content and material homogeneity. Thus, the reduction in the modulus of the samples can be attributed to the degradation of PSD particles in the matrix, which also showed lower deformation at the break. Considering the standard deviation of each sample, Young Modulus shows decreasing tendency in the order $B > A \sim C \sim D \sim E \sim F$, suggesting that, statistically, sample B, with 10wt.% fiber, exhibits a higher Young Modulus value than all other 5wt.% fiber composites.

In the case of deformation (% elongation), according to Table 4, all the composites seem to show higher % elongation when compared to 11% at the breaking point of virgin matrix

PP. Amongst the composites processed in the second step, composites A and B showed a similar % elongation value, which, following Young's modulus, confirms that composite B did not present higher rigidity with higher sawdust content (10wt.%) when compared to sample A, which contained 5wt.% sawdust.

In relation to all the composites prepared in this study, composite C (processed in the third step and heated at 60°C) shows the highest % elongation value, followed by composites E and F (which are almost the same), while that of composite D being the lowest. A higher % elongation value observed in composite C can be attributed to the lower rigidity of the material. These results may also be attributed to the reduction in the molecular weight of the PP matrix and chain scission due to reprocessing cycles [48] and successive heating. Considering the standard deviation of each sample, elongation at break decreased in the order of $C > D \sim E \sim F > A \sim B$, suggesting that only sample C exhibited a higher elongation at break and all other samples showed statistically the same value of elongation at break.

Furthermore, it can be seen in Table 2 that theoretical density values of samples A, E, and F are approximately equal to the experimental densities, while those of samples B, C, and D are much smaller than the theoretical ones. The smaller density value may be due to the presence of pores or due to a smaller amount of fiber incorporated. In the case of this work, the reason was the presence of pores because the Young Modulus of sample B is higher than all other samples that contained 5wt.% fibers, considering the standard deviation of each sample. Since sample B is a composite containing 10wt.% fibers, it was expected that this sample would show a higher Young modulus. As mentioned earlier, the Young Modulus values of all samples containing 5wt.% fibers were statistically the same. The highest absorption of water was found for sample B, although samples C and D showed to contain more pores than that in sample B and also showed experimental densities much lower than the theoretical ones. This behavior is because samples C and D were prepared with PMMA coated fibers that expose less the fibers to water than the composites prepared with uncoated wood fibers used in samples B and A.

Figures 5 and 6 shows SEM micrographs of Pinus fibers and Pinus PMMA coated fibers, respectively. It can be seen the morphological characteristic of the uncoated fibers [31] and that the coated fibers show good wettability in the PMMA matrix without any uncoated fibers.

Another point that should be noted is the higher standard deviation observed in all the composites (Table 4), suggesting that these materials are less homogeneous. This is understandable since these values are lower after the reprocessing of composites. As already discussed, the extrusion cycles performed on the samples would lead to a microstructural homogenization of the material with better

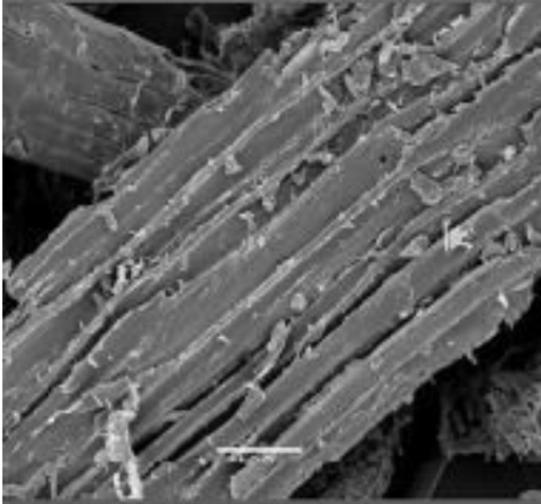


Figure 5: Uncoated fibers (x 200) [31].

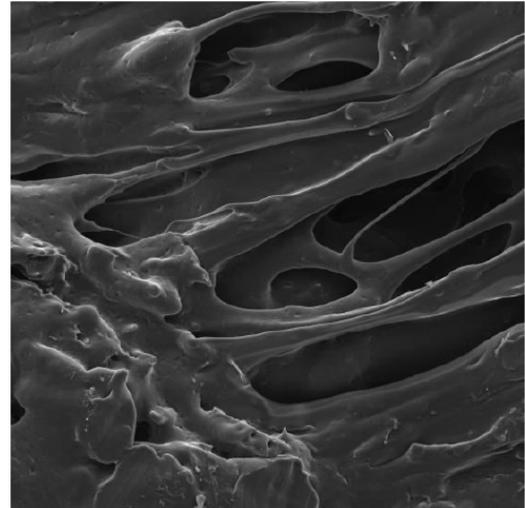


Figure 6: PMMA coated fibers (x 250).

dispersion of wood fibers in the polymeric matrix, despite their possible degradation, as will be seen in the next section.

3.7. Morphology and Fractography Studies

3.7.1. Morphology

The filaments obtained in the third step, after heating at 60°C and 120°C, showed brownish color with the composite treated at 120°C being darker than the one treated at 60°C, Figure 7. Similar observations have been made by Soccalingame *et al.* [56] in their study about reprocessing of wood-fiber-reinforced PP matrix composites. They have attributed the darkening not only to the degradation of hemicellulose but also to the migration of lignin, which, due to the high temperatures involved in the process, can fuse, coalesce and migrate from the wood particles to the matrix.

3.7.2. Fractography Studies

Figure 8 shows the fractured surface of sample B after the tensile test. It can be seen that the wood fibers are not adhering to the PP matrix, and although of all samples, sample B exhibited the lowest value of elongation at break, which is equal only to the elongation at break of sample A, the sample shows a ductile fracture mechanism [57-61]. Therefore, all samples seem to have undergone a ductile fracture under traction, the same behavior as of PP matrix.

No fragile fracture mechanism was seen to operate in any of the fractured samples, even with the addition of 10wt.% of wood fibers.

Figure 9a-f shows fracture surfaces of tensile tested composite filaments containing 5wt.% and 10wt.% PSD obtained by scanning electron microscope, all taken at x100. Figure 9a shows the fracture surface of sample A (containing 5wt.% PSD), and the presence of some loose fibers, while Figure 9b shows that of sample B (containing 10wt.% PSD) having a higher number of loose fibers. It is also evident from both these figures that the fibers were not well adhered to the matrix, resulting in some loose fibers.

On the other hand, Figure 9c shows the fracture surface of sample C (composite filament with 5wt.% PSD and heated at 60°C), wherein a large number of pores are revealed in comparison to Figure 9d, which is fracture surface of sample D (composite filament containing 5wt.% PSD and heated at 120°C) showing fewer and smaller pores. In fact, no loose pieces of fiber are seen on the surfaces of these composite filaments. This may possibly be due to the absence of any contact with water during their processing, besides the slow cooling of filaments, which resulted in thermal loss only to the environment. In addition to their reprocessing, these composite samples were heated at 60°C or 120°C to remove

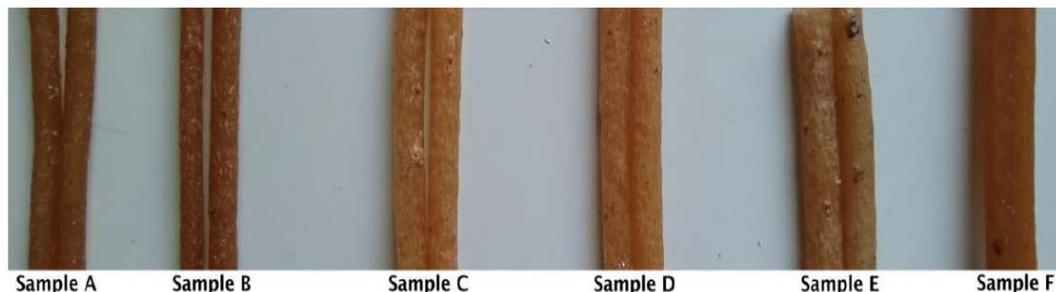


Figure 7: Color and aspect of filament samples.

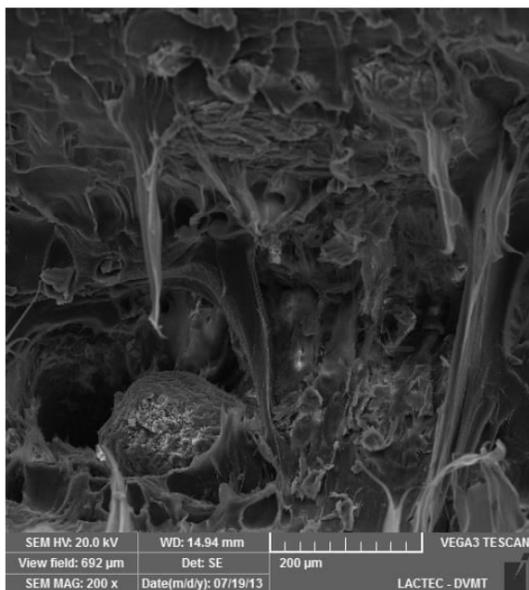


Figure 8: Sample B ductile fracture.

as much moisture as possible from the composites in addition to enhancing the homogeneity of the samples.

Finally, Figure 9e shows the fracture surface of sample E (composite filament with 5wt.% PSD, heated at 60°C, followed by heating at 120°C), revealing a homogeneous appearance without any loose fibers or visible pores, despite this sample exhibited a slightly lower experimental relative density value than that of a theoretical one. On the other hand, Figure 9f shows the fracture surface of sample F (composite filament with 5wt.% PSD, heated at 120°C) revealing the presence of loose fibers and less homogeneous appearance in comparison to that of sample E but exhibited more homogeneous fracture surface appearance, with fewer visible pores, compared to that of sample D.

Observation of greater homogeneity of fracture surfaces of composites E and F is understandable in view of the reduction of the number of larger wood particles with reprocessing. This is because these composites at the initial stage contain sawdust particles of different sizes, while the reprocessed composites tend to have an increasingly homogeneous fiber size and structure. This, in turn, is due to subjecting the reprocessed composite to a greater amount of mixing cycles and greater shear stresses, leading to a better distribution of wood particles in the matrix and thus making the material structure more homogeneous [47].

The other reason for this greater homogeneity may be the reduction in matrix viscosity (which was visually observed during material reprocessing and through the composites flow rate), allowing better dispersion and wettability of wood particles. This reduction in viscosity is caused by the sequence of reprocessing cycles, which also implies greater exposure of the material to heating cycles. Such exposure leads to the scission of the polypropylene chains [62-64].

Regarding the verification of reduction of viscosity in the presence of large particles, it can be said that during reprocessing, despite better dispersion of fibers in the matrix, repeated shear stresses also led to degradation of sawdust (wood particles) as observed in the thermal analysis study [6, 46].

Finally, the results mentioned above of microscopy studies, together with those of thermal analysis, clearly explain the observed differences in the fracture surfaces of the composites processed in the third step in relation to those of the samples processed in the second step, which can also explain the observed results of tensile properties and water absorption studies. This also supports visible changes in the filaments resulted from heating the composite samples at 60°C and/or 120°C during the drying and reprocessing process of the material.

4. CONCLUSIONS

Considering the use of the new molding thermoplastic technique, where viscous filaments can be artistically or technically manipulated to create three-dimensional pieces using an extruder, polypropylene - Pine sawdust filament composites using 5, 10, and 20wt.% pine sawdust filaments and compatibilizer have been prepared, in three steps, by hot molding using an extruder. Thermal degradation of these composites is studied by subjecting these composites to different heating cycles and different times. Thermal degradation of these composites is studied by subjecting these composites to different heating cycles and different times. Following are the summary of the obtained results:

1. Results of both density and water absorption studies, as well as a more homogeneous material revealed by fractography studies, revealed no significant number of pores for the E and F filament composite samples. The successive heating reduced moisture in the samples besides providing a better adhesion between the fibers and the matrix.
2. X-ray diffraction studies showed a very small increase in crystallinity (75 to 78%) for filament composites when compared to that of PP matrix (74%). This difference can be attributed to the incorporation of sawdust and also to the thermal treatment given to the composite. However, a decrease in the crystallinity index of filament composites F (76%), with 5wt.% sawdust and thermally treated at 120°C, in comparison to that of composite E (78%), with 5wt.% sawdust and thermally treated at 60/120°C, was observed besides its darker brown color that occurred together with lateral reactions of this degradation process.
3. Observed XRD results were confirmed by the data obtained in the TGA analysis, supporting that the

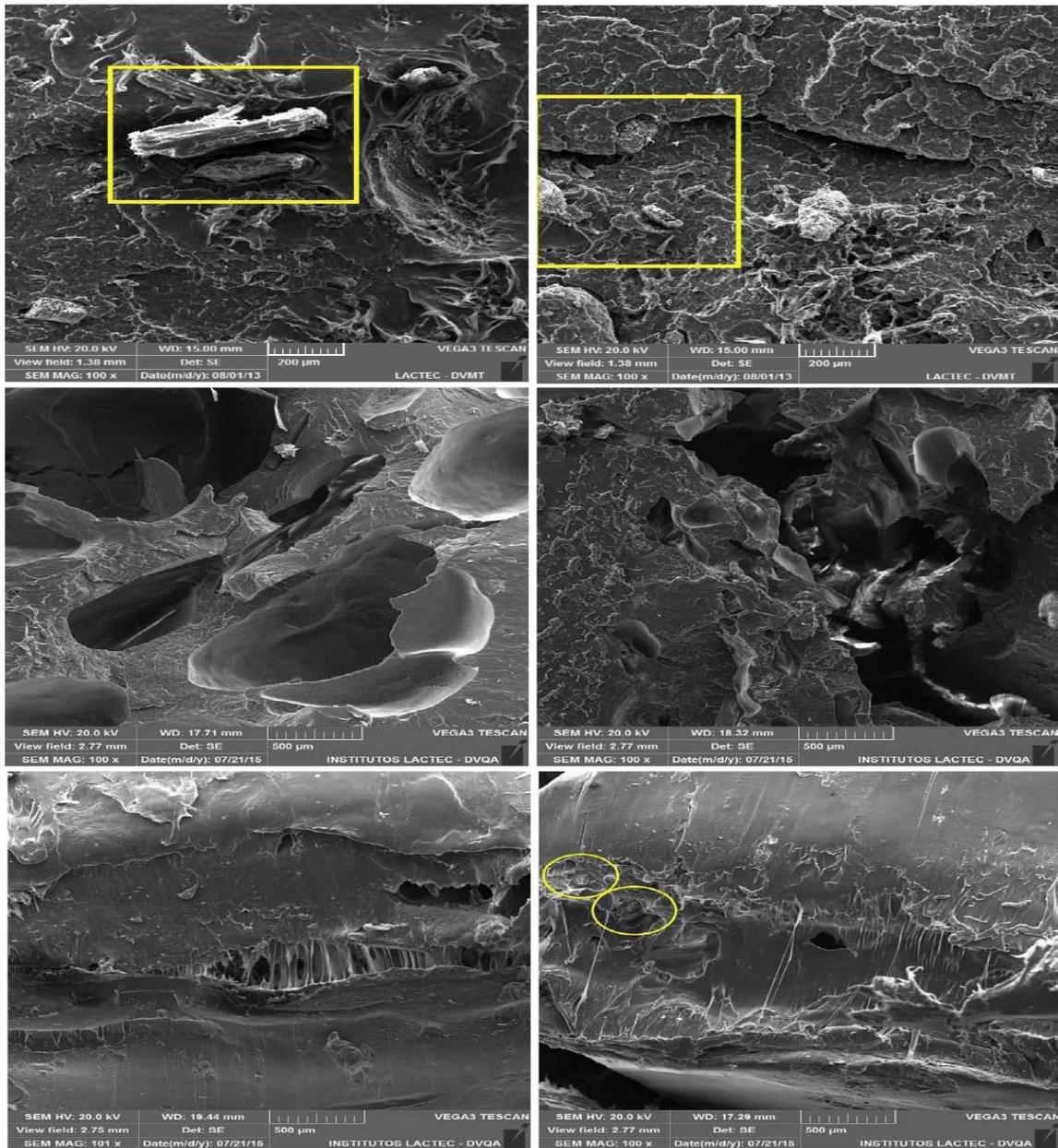


Figure 9: Scanning electron micrographs showing fracture surfaces of tensile tested A-F composite filaments (a)- Sample A showing the presence of low adhesion of the fibers with the PP matrix; (b)- Sample B showing loose fibers; (c)-Sample C showing larger pores; (d)- Sample D showing smaller pores, but less than that seen in Sample C; (e)- Sample E showing homogeneous appearance without any loose fibers or visible pores; (f)- Sample F showing presence of loose fibers and less homogeneous appearance compared to sample E.

increase in the fiber content decreased both the crystallinity and the thermal resistance.

4. Thermo-gravimetric analysis (TGA) studies indicated that degradation temperature of prepared filament composites increased with the incorporation of sawdust, with or without coating, as well as with or without thermal treatment of composites, when compared to the sample of virgin PP. But, samples processed in the third step showed slightly lower thermal degradation profile than those with the same amount of sawdust (5wt.%) processed in the second step, indicating reduced thermal stability. This can be

attributed to the number of processing steps involved and their duration.

5. The filament composites samples of the third step, subjected to heating at 60°C (sample C) and at 60/120°C (sample E), as well as samples subjected to heating at 120°C (samples D and F) showed reduced values of their Young's modulus and maximum tensile strength when reprocessed and heated in comparison to those of composite sample A (second step).
6. Fractographic studies of filament composites containing 5 wt. % PSD, without heat treatment, in the

second step, revealed low adhesion of sawdust to the PP matrix, as evidenced by the presence of some loose and unattached sawdust particles in the micrographs. Samples treated at 60°C and 120°C showed a more homogeneous appearance, less loose fiber (samples C to F), and less visible pores (samples E and F).

7. Finally, this study has revealed the following: the best composition and processing conditions of the PP/wood fiber composites are the use of 5 wt. % PP/wood fiber composites; use of at least three extrusion cycles when the extrusion is made with the equipment described in this paper and use of thermal treatment at 60 °C instead of 120 °C; although the thermal treatment did not result in an increase in the strength of the composite, it helped to reduce the pores and the consequential absorption of water by the composites; also verified that when the composites were subjected to double heating at 120 °C (sample F), it caused more degradation of fibers showing the darker color of the material; finally, despite the addition of 5 or 10 wt. % wood fibers, all samples showed a ductile fracture behavior, which would be beneficial during the molding step of the filaments to produce thermoplastic pieces, work that was not emphasized in this study.

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DECLARATIONS OF INTEREST/CONFLICTS OF INTEREST

The authors declare there are no financial and personal relationships with other people or organizations through the following: employment, consultancies, stock ownership, honoraria, paid expert testimony, patent applications/registrations, and grants or other funding, which would inappropriately influence this study.

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