Cedar fiber / polypropylene (PP) matrix composites: influence of the PP-g-MA compatibilizer

Material compuesto de matriz polipropileno (PP) y fibra de cedro: influencia del compatibilizante PP-g-MA

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Abstract

Because the strength of the wood plastic composite (WPC) is based on the fiber-matrix interaction, we have studied the influence of a coupling agent to modify the plastic matrix with different proportions of maleic anhydride-grafted polypropylene (PP-g-MA). Therefore, the physical-mechanical properties of a novel series of WPC with 20% fiber by injection technique were evaluated. It is worth mentioning that in the previous step to the injection process, these materials were mixed in a co-rotating twin screw extruder under mild conditions, because it was possible to reduce by 50% the residence time of the fiber with regard to polymer. The thermogravimetric analysis (TGA) results for the WPC extrudates showed the onset temperatures of degradation with intermediate values T_{10} of ~295 °C compared to the starting components (fiber, PP). The final product had a loss of ~3.4% associated with the second thermal process suffered material. The mechanical analysis showed an increase in tensile strength of 20.3% in the new WPC, while the flexural strength reached 46.2%. In the micro-structural analysis of the final products incorporating the fiber into the matrix was made using Scanning Electron Microscope (SEM). Finally, the optimal mixing ratio necessary to achieve a significant increase in mechanical properties is determined.

Keywords: Wood-plastic composite (WPC); injection; mechanical properties; polypropylene; thermal analysis.

Introduction

There is a tendency throughout time where the conventional materials have been replaced by the development of polymeric matrix composed materials and functional polymers. (AL-Oqla *et al*., 2015; Kang, *et al*., 2015; Brenner, 2000). Nowadays the use of fibers and particulate matter has positioned itself as an efficient

reinforcement method with high elasticity and mechanical resistance modules. (Pouzet *et al*., 2015; Bledzki *et al*., 2015; Van Vuure *et al*., 2015; Kuo, 2009). The use of natural fibers has awakened increasing interest in researchers for two reasons, the first due to the increase of the mechanical properties that the cellulose provides and the second, is due to the ecological benefits and added value when using surpluses as in the case of the sawdust (Yang, 2015). Some additional advantages in the development of associated wood and plastic composites (WPC), is the decrease in the density and excellent cost/benefit relation that allows to compete with the market. The WPC are used in a wide variety of applications in which are found automotion and architecture. (Moritomi *et al*., 2010; Kissel *et al*., 2003). In the last one, the WPC, in comparison to wood, they show major durability, they require less maintenance, they absorb less humidity making them more resistant to superior fungi (Xu *et al*., 2013). However, the collection of these materials suggest a challenge in the control of associated parameters with the composites like size, fiber content and coupling agent that improves the sticking to the surface fiber-matrix (Thakura & Thakurb, 2014). The function of the fiber-matrix interface is a determining factor because through this, the applied charge from the matrix to the fibers this constitutes a direct relation between dissipation level and the impact resistance as a result from the effort (Moritomi *et al*., 2010; Wielage *et al*., 2013). Although, the homogenization process in the composites plays a high role due to the fail points that occur with the stress concentrators, thus, in regions of agglomerated fiber. Likewise, the technique for the gathering of lignocellulosic materials with thermoplastics suggest a high grade of process control (Shao-Yuan, 2012; Carlborn & Matuana, 2006; Zhang, 2009). Therefore, the most homogeny mixes have been achieved by the extrusion of gear with double spindle; the variables of the process in consideration are: the configuration of the different screwing zones, material feeding point, spindle spinning speed, material feeding speed and the extruder's temperature profile. In the current study five new mixes of thermoplastic matrix composites (PP) with the particulated material of the cidar fiber at 20% and different proportions of the PP-g-MA compatibilazing agent. The material was initially mixed in a double co-rotating spindles extruder using two feeding hoppers in different points of the cylinder with the goal to reduce the residence time of the fiber during the process. The thermic properties of the extruded and injected material were determined. Finally, the mechanical and micro-structural properties of the WPC were .

Methodology

Materials

Polypropylene copolymer random was used (PP-R) 02R01CA-1 produced by Propilco with a fluently rate 1.6 g/10 min. the coupling agent used was modified polypropylene with licocene PP-g-MA 7452 from Clariant, presenting an addition of 7% maleic anhydride, 156 °C melting point, 0.91 g/cm^3 density and high crystallinity. The wood cedar used is Mokufun Co. Ltd., Japan, with a particle size between e 70 – 120 µm according to the ASTM C136- standard 05. It is worth to mention that before the extrusion, the fibers were conditioned to 60 °C for 4 h and stabilized to room temperature with a desiccator.

Preparation of composites:

A new series of five composites was obtained with 20% w/w cedar wood fiber included in the polypropylene matrix. The used maleic anhydride concentrations were: 6.6%, 5.0%, 3.3%, 1.6% w/w and a white (0%, without coupling agent). The samples were referenced as next: MC [fiber]-[PP-g-MA]. E.g., MC20-6.6 is a material composed by 20% w/w of fiber and 6.6% w/w of PP-g-MA.

Extrusion cycle

The materials were mixed in an double spindle extruder branded *Thermo Scientific* Haake Rheomex OS ptw 16 model with 16 mm diameter and 40D of total length, in parallel co-rotating configuration, under the next operation conditions: temperature profile with gradual increase from 5 °C to 155 °C in the first feeding zone up to 200 °C being this the first feeding zone up to 200 °C in the end of the screws, divided in 10 cylinder zones, each zone covering a length of 4D. The nozzle was maintained in a temperature of 200 °C being this the process's maximum (it must be taken in account that the temperature measures are done with sensors without direct contact with the polymer, sensors in direct contact present in average 5 °C above the indirect values). The feeding systems were located above the cylinder of the 4D position for the polymer and position 24D for the fiber. Up next an image is shown (Figure 1) reliable of the extrusion process:

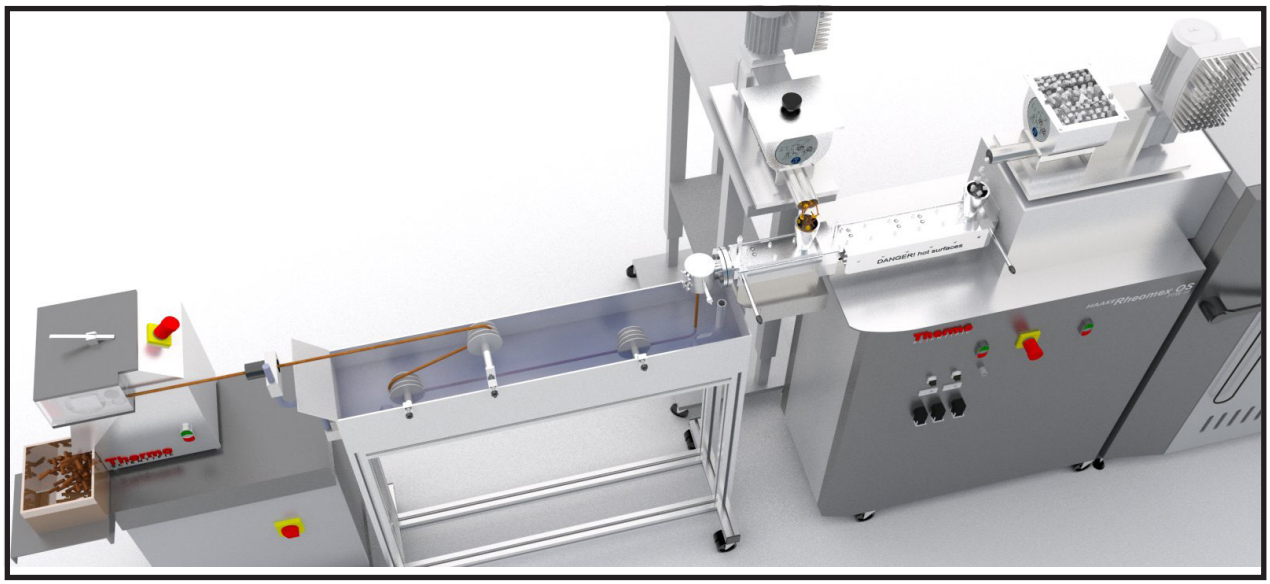

Figure 1. Image of the extrusion process
Source: The authors

Cycle injection

The WPC was molded by injection in a 150 ton DEMAG injector machine, model 1991, hydraulic and plug-in valves (maximum lamination capacity, 230 g; distance between columns, 460 mm; closing distances, minimum 200 mm, maximum 450 mm; maximum opening race, 450 mm). The temperature profile was 190 °C – 195 °C and 200 °C the muzzle. The injection pressure was constant in 80 bars; the mold was set in 45 °C and applied a constant injection speed of 45 $cm^3.s^{-1}$. The injection parameters were the same for all the mixes. The test tube obtained were type 1b "bone" according to ISO 527-2 standard.

Characterization

Thermogravimetry (TGA) and differential scanning calorimetry (DSC)

The thermal properties were determined in a thermogravimetric TGA/DSC 2 STAR System, *Mettler Toledo*. The samples (10±0.5 mg) were put in alumina crucibles in a temperature range between 25 °C to ~300 °C under nitrogen atmosphere (50 cm^3/min). It was worker according to the ASTM E1131-98 and ASTM D3418-12 standards, respectively.

Tensile and Flexural Properties

The mechanical property measures were done in a universal *Goodbrand* machine according with the ASTM D638 standard, with a test speed 500 mm/min and a load cell of 500 kgf. The enlargement values were determined (by extension of the jaws) to the tear resistance and tensile strength. The environmental chamber Dies, a Baker caliper gauge and an *Oakton* thermohygrometer. The flexure tests method were done in an *Instron 5500R* universal machine according to the ASTM D790-10 standard with a 5 mm/min test speed and a 50 kgf cell. Modules, resistances and elongation percentages were obtained. Five samples were analyzed for every WPC mix and the medium values are presented.

Micro-structural analysis

The WPC samples developed were characterized by the Scanning Electron Microscope (SEM). Micrographs were obtained in a *JEOL* de *Mesa JCM 50000*, were a high vacuum and a 5 kV voltage was used. The samples were submitted to a gold coverage using PVD before its analysis by SEM. It is worth to mention that for every analysis the samples were conditioned to 25 °C in an environment of relative humidity of 50±5% during 48 h.

Results

Thermic analysis

The thermic properties of starting materials, intermediate products and WPC ends were determined by the TGA and DSC as it is shown in the Figures 2, 3 and 4 respectively. The T_{10} values were analyzed that belong to the degradation temperature to the 10% weight loss and the melting temperatures.

In the figure 2A, PP-R and PP-g-MA exhibit a T_{10} ~405 °C and Tm ~150 °C. While the fibers presents a T_{10} = 274.5 °C, a humidity loss is observed at around 100 °C and a slight fall of the same curve at 150 °C due to slow thermal stability that present the lignin; in the DSC curve shows a widened endothermic peak is observed at 225°C corresponding to the Tm of cellulose contained in the fiber.

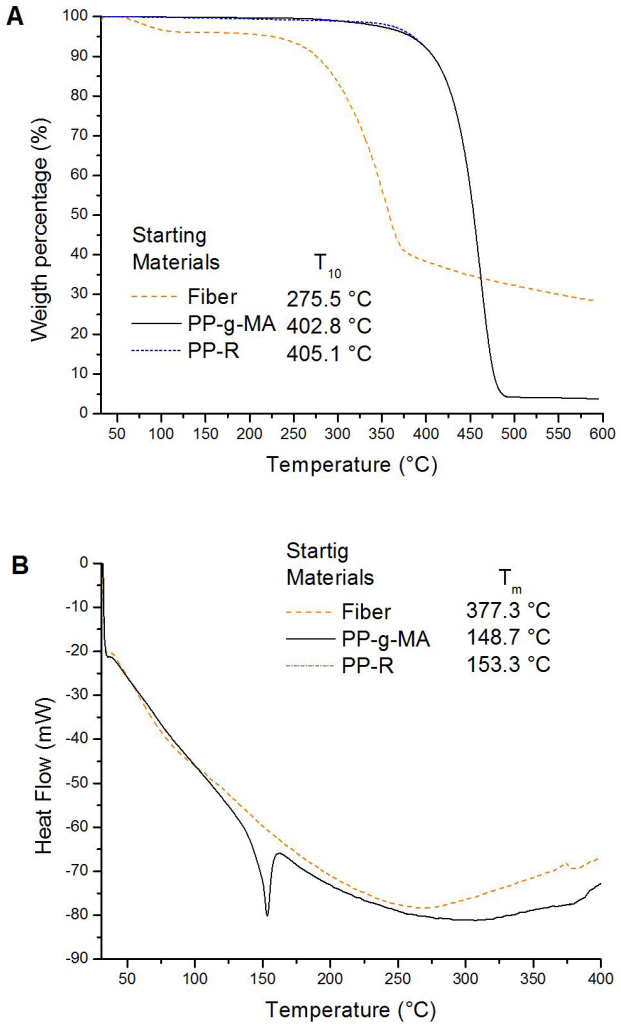

Figure 2. Thermic analysis of starting materials
A) TGA and B) DSC
Source: The authors

Forwardly, it was determined that T_2 that correspond to the degradation temperature values to the 2% loss weigh and the Tm of the intermediate products of extruded WPC (see Figure 3), the MC20-5.0, MC20-6.6 mixes with major percentages of maleic anhydride in the polymeric matrix (PP-R) presented low thermic stability, as a result for the high affinity with the water as the curves in the TGA with weight losses starting at 100 °C. The other samples, including the blank, showed a T2 ~297 °C, what suggests intermediate characteristics of the starting materials with respect to WPC. The Tm values presented a slight increase (~8 °C) assuring the change in the properties of the new material.

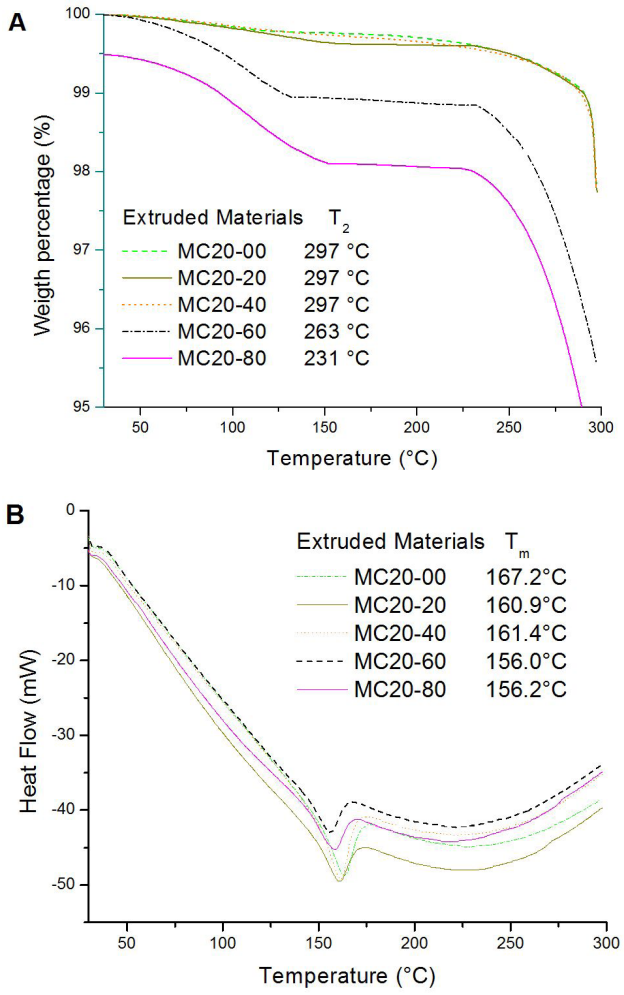

Figure 3. Thermal analysis of the extruded composite:
A) TGA and B) DSC
Source: The authors

In the final stage of the process, the WPC series obtained through the injection technique, showed an excellent thermic stability with the T_2 values around 287 °C, without presenting meaningful changes in degradation temperature respecting the extruded (Figure

4); these results support the importance of maintaining the minimum temperature conditions and short residence times to avoid the material wear. On the other side, the DSC for the MC20-00 sample evidence the lack of a coupling agent, due to that the curve represents two phase changes of first order at 159.8 °C and 245 °C that correspond to PP-R and fiber, respectively. The materials are found in a mix but not chemically linked as it is observed in the thermograms for the WPC´s that contain the PP-g-MA.

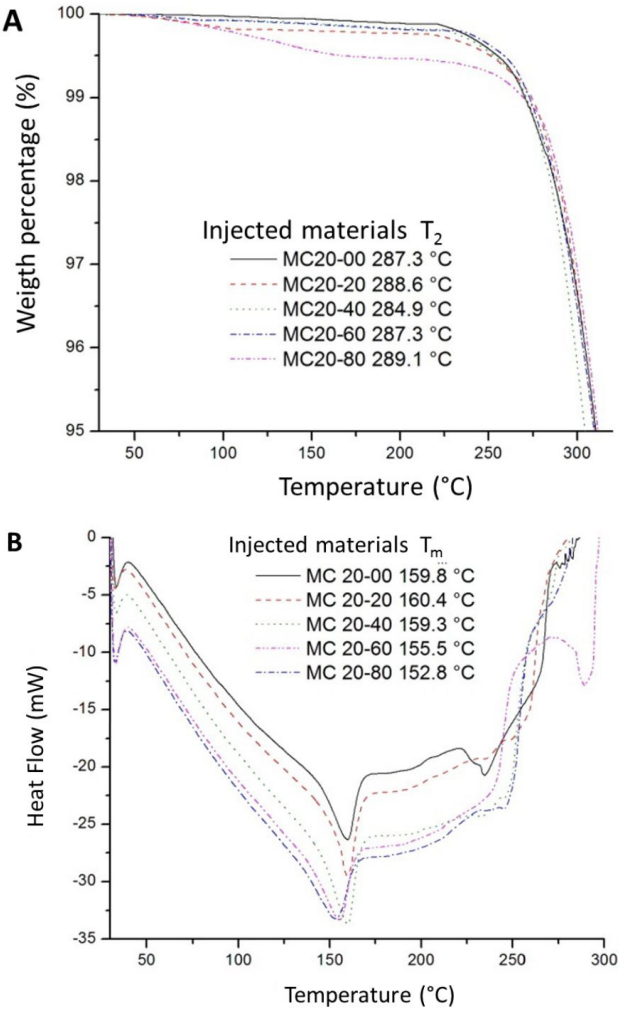

Figure 4. Thermal analysis of the injected composites: A) TGA and B) DSC
Source: The authors

Mechanical Analysis

Mechanical properties of the new WPC series were evaluated through tensile and flexure tests; the results are shown up next in the Figure 5.

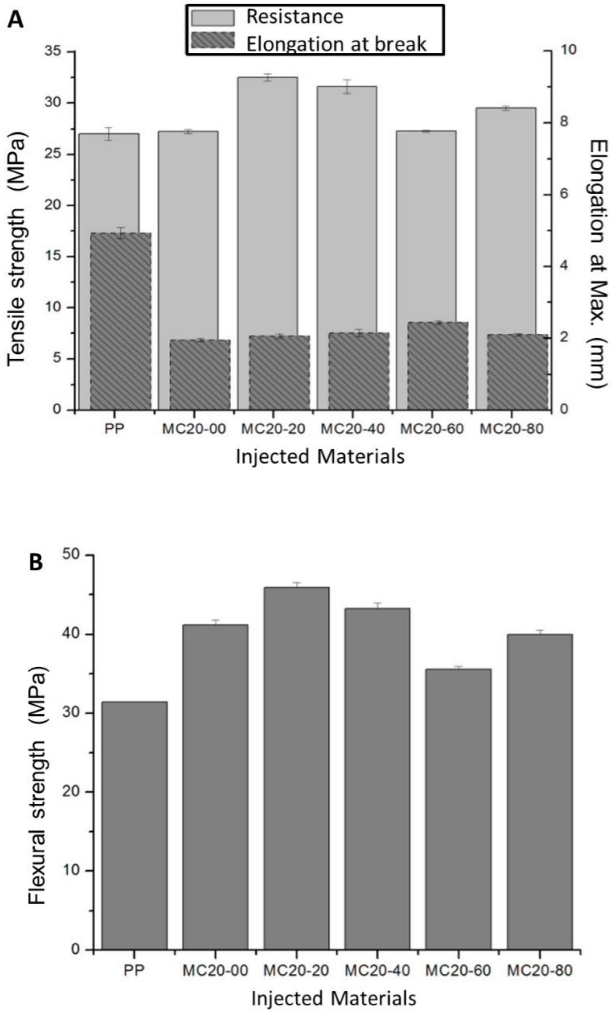

Figure 5. Effect of the composites in the: A) tensile strength and maximum elongation, B) Flexural Strength.
Source: The authors

The addition of the fiber and the coupling agent gave place to a reinforcement of the propylene matrix in terms of stiffness and strength. The results suggest a good fiber dispersion and good fiber-matrix coupling as expected. The highest mechanical performance was observed MC20-1.6 with the minimum quantity of PP-g-MA proposed in the mix design; the tendency is represented by a gaussian-like curve that allowed to identify the optimum mix (Figure 6). The MC20-00 doesn't represent a clear disadvantage against the PP-R which is considerated filling for the development of wood plastic. It is worth to mention the flexural strength for the MC20-1.6 reached a 46.2% value increase.

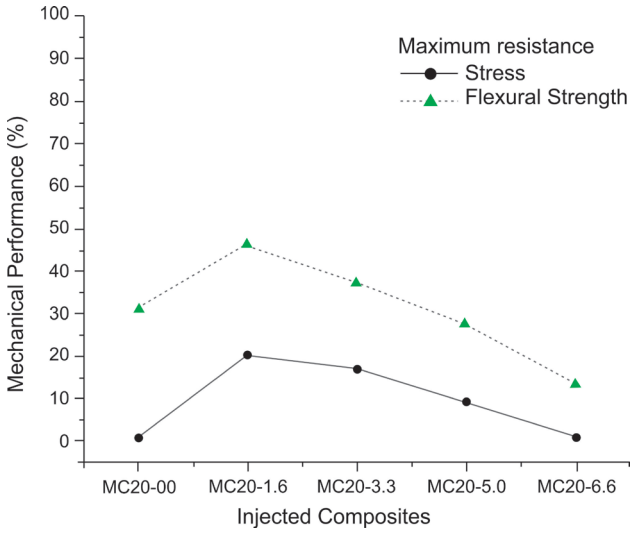

Figure 6. injected materials.
Source: The authors

Micro-structural analysis

The morphologic study was carried by the SEM; the profiles on the surfaces of the fractured specimens of the tensile test were analyzed: the blank MC20-00 and MC20-1.6. In Figure 7, it's observed the presence of particulated material exposed with a size that vary between 15 mm and 30 mm. The size decrease is principally due to the lignin migration and the wearing of extractives and hemicellulose by the different thermic treatments (Soccalingame *et al.*, 2015).

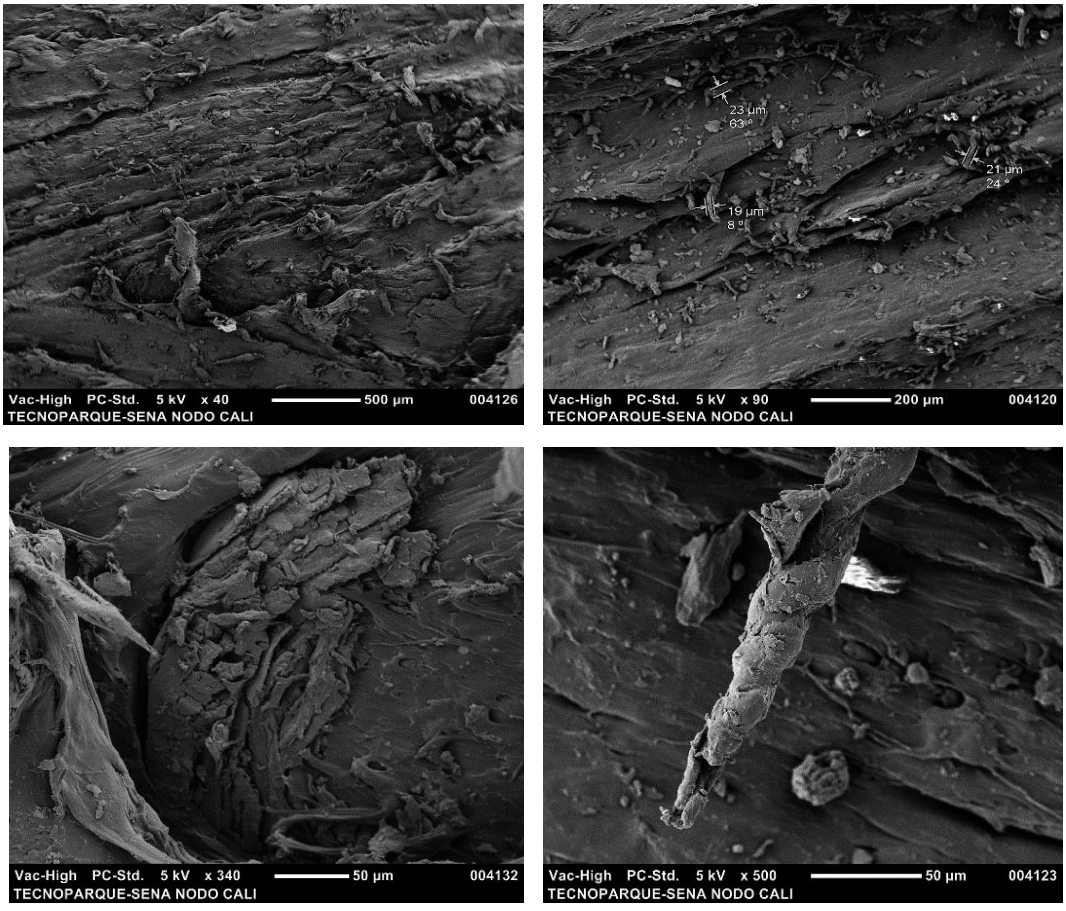

Figure 7. Micrography WPC without compatibilizing agent (MC20-00)
Source: The authors

The images of the MC20-1.6 with the MC20-00 were compared because the first one presented a better thermic and mechanic behavior. The Figure 7 shows that 40x, 90x, 350x and 500x lenses were used; this makes it comparable to the micrographies.

In the Figure 8, it was observed an improvement compatibility between the fiber and the matrix that is seen reflected in the interface; this is attributed to the PP-g-MA effect (Du *et al*, 2013). This compatibility is evidence due to the wet fiber in the matrix that issues in the mechanical properties of the material due to that the interface allows the effort transference from the matrix to the fiber. The compatibility between the interfaces as a possible consecuence to the decreasing of the hydrophilicity, which also contributes with the improval of mechanical properties.

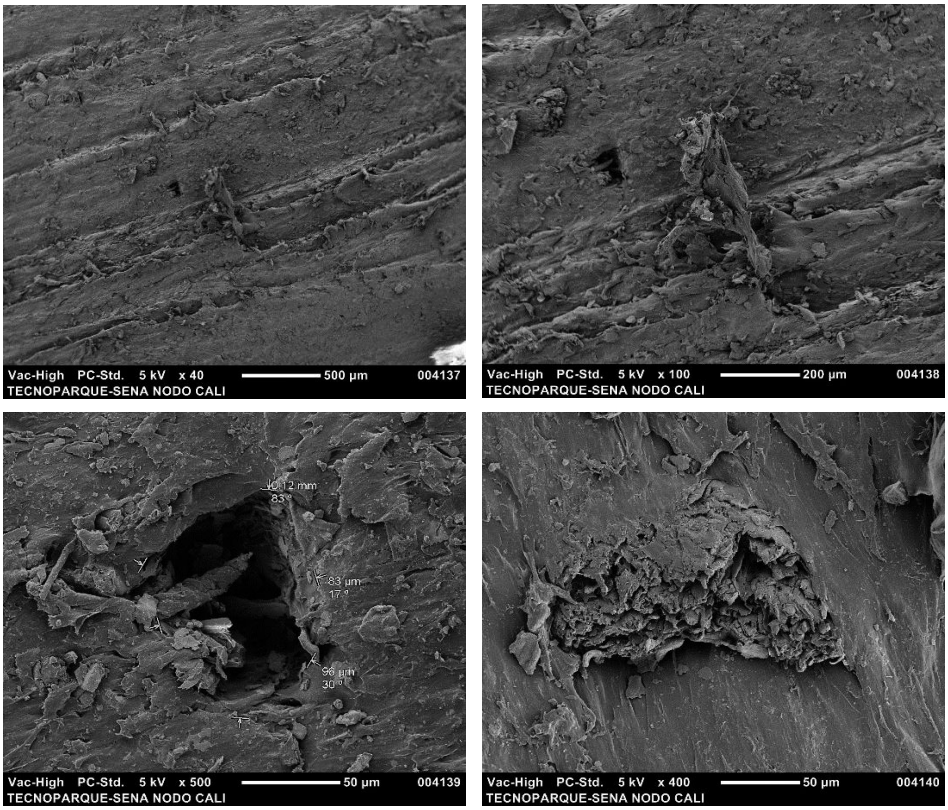

Figure 8. Micrography WPC with compatibilizing agent (MC20-1.6)
Source: The authors

Conclusions

This research work presents results about the thermic and mechanical development composites with thermoplastic matrix and natural fibers, includes as innovation the use of fibers from cedar word incorporated in a 20% w/w and different concentrations of compatibilizing PP-g-MA agents. Some authors previously mentioned like the PP-g-MA provider suggest using in a 3% w/w upon the final mix, but with the found results we consider important to optimize the use of additives with the goal to improve and maintain the mechanical properties of the new materials. On the other side, the MC20-00 doesn't show thermomechanic disadvantage against the PP-R. According with the previous, it can be considered as a filling the addition the particulated material of cedar fiber. The developed WPC with values higher to 5% w/w of PP-g-MA have a better affinity with water (hydrophilic) due to that the remaining of the PP-g-MA in the matrix can drown the wood's surface generating composites with inferior thermic and mechanical characteristics. Therefore, an excessive dosification or insufficient can reduce the compatibility effect. Finally, the new MC20-1.6 presented a new important mechanical performance reaching 20.3% increase of stress strength and 46.2% flexural strength.

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