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Development of new Thermoplastic Composites based on Polypropylene and Renewable Materials such as Hemp Fibres for Extrusion Flat Thick Sheet Manufacture.

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ABSTRACT

The main objective of the work is to develop an extrusionable thermoplastic composite based on polypropylene and different percentages of natural fibre, specifically natural hemp cultivated in the North of Europe. In past years natural fibres have become a true competitor for fibreglass. The improvement in mechanical properties is lower than with fibreglass, but it presents other obvious advantages, such as environmental, aesthetic, low density, and low machine abrasion characteristics, maintaining a good performance – weight ratio.

The main technical target has been to avoid the "classic" limitations related with this kind of complex systems. Basically, it is possible to summarize these problems in four important aspects:

- Low degradation temperatures of natural fibres.
- Low Impact strength behaviour.
- Feeding of short fibres in the extruder machine (limiting fibre break).
- Opposite polarity between polymer and fibre. It is necessary to develop a compatibilization system, based on the use of commercial coupling agents and other additives.
- Fibres increase significantly the viscosity of the composite.

Polypropylene has a moderated processing temperature, but it is enough to cause degradation processes in natural fibres. The work has been focused on the elimination of the discussed problems to increase the final properties of the thermoplastic composite, in a superior level than the current industrial products, controlling the different aspects of compounding, flat sheet extrusion and thermoforming processes. By using an extrusion-thermoforming process, you can manufacture 3D parts using high melt viscosity compounds.

KEYWORDS: Thermoplastic composite, natural fibre, compounding, compatibilization, thermoforming.

INTRODUCTION

The use of plastics in the automobile sector has increased in recent years. One of the advantages is the reduction in weight and hence CO_2 emissions. According to the plastics used, it is estimated that some 47% is used for interior components such as door trims and seat back covers.

Polypropylene is by far the most popular plastic. The Europe demand of polypropylene in 2004 was 8000 ktonnes [1]. Automotive sector consumes around 11% of this polypropylene and represents approximately the 50% of the total plastics in a car. It is an inexpensive polymer and easy of processing. However, polypropylene is rarely used as an unfilled material as it lacks the mechanical properties and it is inevitably filled with mainly inorganic fillers such as fibreglass, calcium carbonate, mica, talc, mica and so on.

In recent years the use of organic natural fillers such as wood fibre, wood powder and natural fibres such as flax, hemp, sisal and jute [2] have become popular. The reason is that natural fibres have a high strength to weight ratio and are more eco-friendly than the inorganic fillers.

In 2000, an estimated 28.300 Tonnes of natural fibres were used in the automotive industries 71% flax, 12% hemp, 7% kenaf, 6% jute, and 4% others [3]. This is predicted to grow to >100.000 Tonnes by 2010 (an annual growth rate). Nevertheless, a number of technical limitations may limit this growth, such as:

- The thermal degradation of the natural fibres during processing,
- The inconsistency of the fibre materials, i.e. the quality of the fibres depends on the place and time of harvest.
- The reduction of aspect ratio of the fibre by action of the machinery shear.
- The difficulty in processing on traditional processing machinery due its low apparent density.
- The low adhesion to non polar polymers (polyolefins) due to its hydrophilic character, they need coupling agents.

The purpose of this study is to develop a cost-effective, innovative non chemical theated hemp filled solid propylene sheet suitable for thermoforming.

The melt flow index is an important processing parameter that controls the suitability of the material for one specific conforming process. In the case of sheet extrusion, it is advisable to employ random copolymer polypropylene [4] materials with melt flow index (MFI) between 0,6-1 g/10 min. Usually, natural fibre reduces the fluidity of the melt, for this reason it is possible to use a virgin polymer with higher melt flow index.

It is well known that natural fibres are polar substances, whereas polypropylene is completely non-polar. This means compatibility problems in the compound natural fibre/polypropylene. To improve the mechanical properties it is necessary to use several additives or compatibiliser agents. A previous bibliographic [5,6] study has shown that the MAPP (polypropylene modified with maleic anhydride) is the best compatibiliser system in natural fibres. Grafted polypropylene may interact with the hidroxiles of the natural fibre and subsequently a decrease in the interfacial energy is observed and the compatibilisation is improved.

The compounding process also plays an important role in the composite properties, the right design of compounding equipment configuration is essential to maximize the contact fibre-matrix. Nowadays, the compounding of natural fibres composites in industrial scale is mainly carried out in co-rotational twin-screw extruders (TSE) [7] that were originally designed to process petro-based polymers and inorganic fibres. Due to the inherent flexibility of the machine design of TSE, where barrel segments, screw elements and dosing points can be varied, it was possible to adapt this machine to the manufacturing of composites containing natural fibres. During this work different screw configuration with different ratio distributive/dispersive mixing was evaluated for the preparation of polypropylene-hemp composite.

In order to achieve the objective of this work, the type of fibre, the type of compatibilizer and its percentage, the melt flow index of the matrix and the process parameters, like temperature profile, screw configuration and the correct feeding of the different materials were studied and the best parameters selected.

EXPERIMENTAL

Materials selection

Three polypropylene copolymers grades with different melt flow index (from 0.8 to 7 g/10 min) and one isomeric polypropylene (MFI=2.1 g/10 min) were selected. The materials were supplied by the company BOREALIS (Austria) and REPSOL QUIMICA (Spain).

Regarding to compatibilizer block copolymer and natural fibre, two maleic anhydride modified homopolymer polypropylene were used. To know the influence of coupling agent viscosity both coupling agents have a very different melt flow index. Integrate NP-594-008 has a MFI around 8.0 g/10 min measured at 230ºC and 2,16 Kg. This additive was purchased to the company Equistar (USA), and Polybond 3200 with MFI around 115 g/10 min measured at 190ºC/2,16 Kg was supplied by Crompton (USA). Both coupling agents have a 1% w/w of grafted maleic anhydride.

HEMPCORE (UK) provided powder and fibre hemp. Hemp fibres was decorticated, breaker and finisher carded fibre. Figure 1 shows the HEMPCORE's hemp fibre after they have been cut to 50 mm approximately. The natural fibres used are treated with none environmentally unfriendly chemicals.

FIGURE 1. HEMP FIBRES.

Table 1 shows the summary of the materials used during the compound optimization process.

TABLE 1. MATERIALS EMPLOYED TO PERFORM THE COMPOSITES.

Material	Supplier	Kind of material	MFI (g/10 min) (230ºC/ 2,16 Kg)
BA 204E	Borealis	Polymer	0.8
WB 130 HMS	Borealis	Polymer	2.1
ISPLEN PB 150 AMS	Repsol Química	Polymer	7.0
Hemp	Hempcore Ltd.	Natural Fibre	--------
Integrate NP594-008	Equistar	Compatibilizer	8.0
Polybond 3200	Crompton	Compatibilizer	115.0[a]

[a]190ºC/2,16 Kg

Sample Preparation

The natural fibres have been previously pelletized, due to their low apparent density, to ease the feeding during the compounding process. The natural fibres were been dried into an air-forced oven during 6 hours before feeding to compounding machine. Gravimetric Brabender) and volumetric (K-Tron) feeders were used.

Compounding was carried out using a Coperion Werner & Pfleiderer co-rotating twin screw extruder (diameter=25 mm, L/D=40). The screw speed was fixed at 200 rpm and two temperature profiles were used, one of these from 170ºC to 180ºC, and the other from 140ºC to 175ºC. Three screws were designed, the first with five dispersive elements and five distributive elements, the second with only the dispersive elements and the last without dispersive and distributive elements.

Extruded strands were cooled immediately by passing through a water cooling bath. The cooled strands were cut in cylinder shape pellets using a pelletizer and drier in an air forced oven at 70ºC during six hours prior injection moulding.

The specimens for mechanical characterization were injected in a standard ISO test bars mould using an Arburg injection moulding machine (Germany), model Allrounder 420C 1000/350. This machine has a barrel screw diameter: 35 mm, full hydraulic and clamp force 100Tn. The barrel temperature employed in all the test was 180ºC in the hopper until 205ºC in the die, the mold temperature was 60ºC in its both faces, the mould was heated using hot water. The injection speed was fixed in 80 mm/s, the holding pressure was 35 bars and the time 10 s.

Sample Characterization

The impact strength and flexural properties are two of the most important mechanical properties for the automotive application. It has been measured both properties according to next standards: EN-ISO 179 (Charpy impact strength) and EN-ISO 178 (flexure modulus). For the un-notched Charpy Impact Test, a CEAST equipment (Italy) model 6545/000 was used. The flexural properties were determined using a Universal Test Dynamometer of ZWICK (Germany) model 1465.

In order to determine the percentage of fibres in the compound a Thermo-gravimetry analyzer was used. Equipment from TA Instruments (USA) and it is model SDT-2960. The test consists in increasing the temperature of the sample from room temperature until 600ºC with nitrogen atmosphere, and to 900ºC with oxygen/nitrogen atmosphere, at 20ºC/min. The results show the lost of weight due to the decomposition of the different components of the compound.

The dynamic-mechanical tests are the most sensitive techniques available to characterize and to interpret the mechanical behaviour of a material. A sinusoidal strength is employed over a sample of material. The rigidity of the material is determined from the amplitude of the answer and the properties of absorption are measured with the angle of the difference in the signal of answer. By modifying the temperature and/or the frequency of the strength applied, we can obtain a big group of data allowing full characterization of the composite. The properties of a material deformed under diary efforts of flexion are expressed by a module of storage, the module of loss and the factor of absorption defined attending to the theory of the viscoelasticity.

For the tests a DYNAMIC MECHANICAL ANALYZER model 2980 of TA Instruments (USA) was used. The method used has been the application of a ramp stress of 0.5 N/min to 15N at 160ºC and 180ºC. The strain of the material was measured before its break. The samples have been prepared in a hot press, obtaining one compressed sheet of 1 mm thickness. This method can not be absolute because the temperature and the orientation of molten material are not extrapolate parameters in a real transformation process. Nevertheless, it is very useful to know the relative stretching capabilities and to select the most adequate material for different thermoplastics processes.

RESULTS AND DISCUSSION

Selection of the type of fibre

In order to determine the best type of fibre, the first compounds were obtained using the same polypropylene and extrusion parameters as table 2 shows. Long hemp fibre was previously pelletized in order to solve the feeding problems.

The hemp fibres were fed by the central hopper with the polymeric matrix in the gravimetric feeder. Nevertheless, powder was fed separately by the hopper also due to the difference of density in comparison with the polymer.

TABLE 2. TEST TO FIBRE SELECTION..

Sample	Polypropylene	Compatibilizer	Type Hemp	% Fibre	Screw Conf.	Tª Profile
1	PP BA204E	-	Powder	30	1	170-180 ºC
2	PP BA204E	-	Fibre	30	1	170-180 ºC

The compound was injected to obtain the standardized test bars. A lower injection temperature profile than the typical polypropylene condition was chosen. During the injection process the residence time of the material is higher than the rest of processes. The injection parameters were controlled to avoid the degradation of natural fibres.

Table 3 shows the properties of compound containing both types of hemp. The fibre shows better mechanical properties than the powder. For this reason the rest of compounds will be done with the fibre. The aspect ratio of the fibre has an important role in the mechanical properties of the composites. The higher the fibre aspect ratio is, the better the mechanical properties.

TABLE 3. MECHANICAL RESULTS OF THE COMPOUNDS WITH DIFFERENT TYPE OF HEMP.

Sample	Flexural Modulus (MPa)	Frexural Strength (MPa)	Deformation at Break (mm)	Un-notched Charpy impact (KJ/m2)
1	1.750	36,1	8,9	18,0
2	2.650	46,1	8,7	19,4

Determination of amount of fibre

To ensure the correct feeding of natural fibres in the polymeric matrix some termo-gravimetric tests were done. Figure 2 shows the thermo-gravimetric analysis of the sample 2 in order to determinate the amount of fibre in the compound.

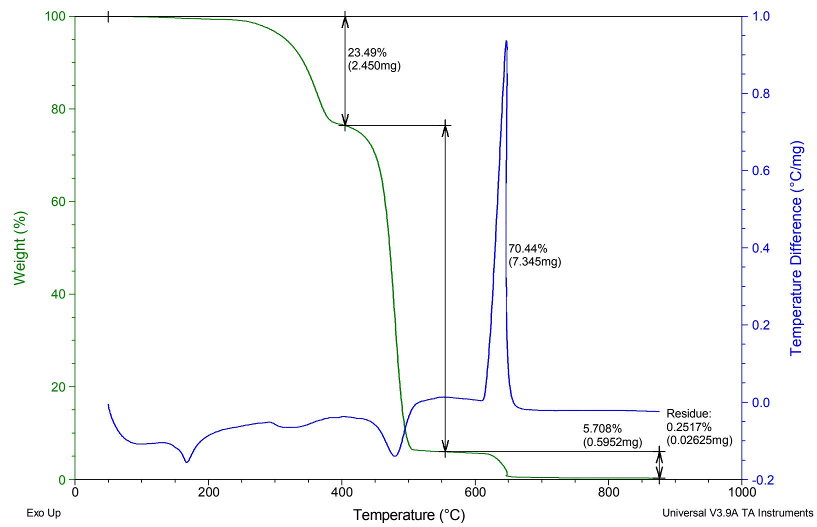

FIGURE 2. THERMOGRAVIMETRY CURVE OF SAMPLE NUMBER 2.

The figure 3 shows a first weight lost due to the moisture of the sample, around 100ºC. After, a second lost around 300ºC due to the natural fibre decomposition. The great lost at 400ºC is due to the decomposition of the polymeric matrix.

Finally, the oxidation lost beyond 600ºC also corresponds to the natural fibre. Considering the result obtained in the fibre and polymer thermogravimetry and comparing with the residue from the compound, the fibre content was calculated. The result was 30,1% the fibre in the compound, this confirms the correct feeding.

Selection of the type of compatibilizer

The following experiments were carried out to obtain the best compatibilizer. Table 4 shows the compound composition and compounding conditions.

TABLE 4. COMPOSITES FOR COUPLING AGENT SELECTION.

Sample	Polypropylene	Compatibilizer	% Compatibilizer	% Fibre	Screw Conf.	Tª Profile (ºC)
3	PP BA204E	Integrate NP594	4,5	30	1	170-180
4	PP BA204E	Polybond 3200	4,5	30	1	170-180

Table 5 shows mechanicals results of the samples prepared to select the coupling agent. The improvement due the compatibilizer agent in the impact strength is spectacular (until 100%), comparing the results of sample 3 and 4 with the sample 2. Integrate NP594 and Polybond 3200 do not show differences, but NP594 has better coupling agent to improve the impact properties of the polypropylene-hemp composites. For this reason, the rest of experiments will be done with Integrate as a compatibilizer.

TABLE 5. MECHANICAL PROPERTIES OF THE COMPOUNDS WITH DIFFERENT TYPE OF COMPATIBILIZER.

Sample	Flexural Modulus (MPa)	Frexural Strength (MPa)	Deformation at Break (mm)	Un-notched Charpy impact (KJ/m2)
2	2.650	46,1	8,7	19,4
3	2.400	55,0	11,3	39,7
4	2.500	57,0	11,3	37,5

Determination of the suitable percentage of compatibilizer

Once it is known the best compatibilizer, it is necessary to find out what percentage obtains the best mechanical properties. For this purpose, the mechanical results of sample 3 were compared with two compounds with different percentage of compatibilizer as we summarized in table 6.

TABLE 6. COMPOSITES FOR PERCENTAGE OF COUPLING AGENT DETERMINATION.

Sample	Polypropylene	Compatibilizer	%Compatib.	% Fibre	Screw Conf.	Tª Profile (ºC)
3	PP BA204E	Integrate NP594	4,5	30	1	170-180
4	PP BA204E	Integrate NP594	3,0	30	1	145-175
5	PP BA204E	Integrate NP594	7,5	30	1	170-180

Table 7 shows the mechanical results of the samples with different percentage of compatibilizer and figure 3 plot the variation of the impact resistance in function of the amount of compatibilizer. Impact Strength improves until 4.5%, from this value the properties do not improve, even get worse. This can be due to the appearance of another phase when compatibilizer saturation takes place. Several papers showed that low percentages of coupling agent is enough to improve the interphase matrix-fibre. In the other hand, an excess of coupling agent introduces a low viscosity material non 100% compatible with the base polymer and in consequence a point of break. The following experiments were done using 3% of compatibilizer.

TABLE 7. MECHANICAL PROPERTIES OF THE COMPOUNDS WITH DIFFERENT PERCENTAGE OF COMPATIBILIZER.

Sample	Flexural Modulus (MPa)	Frexural Strength (MPa)	Deformation at Break (mm)	Un-notched Charpy impact (KJ/m2)
2	2.650	46,1	8,7	19,4
4	2420	53,7	11,1	39,0
3	2.400	55,0	11,3	39,7
5	2.390	52,0	11,1	35,2

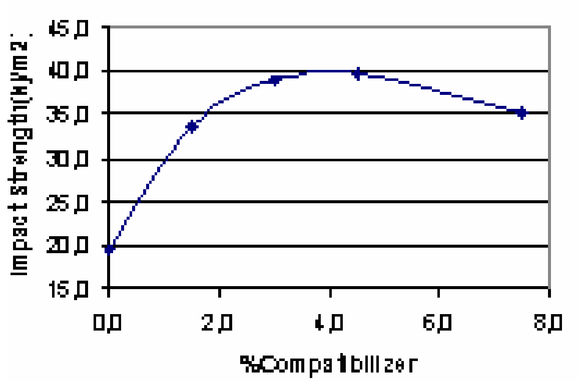

FIGURE 3. VARIATION OF IMPACT RESISTANCE IN FUNCTION OF THE PERCENTAGE OF COUPLIBG AGENT.

Determination of the optimal temperature compounding profile

The melt temperature of the compounding process is a very critical parameter for the natural fibres degradation. Co-rotating process implies a great heat generation by shear. Two different temperatures profiles of co-rotating extruder were studied: i) 170-180ºC and ii) 145-175 ºC. This first one causes around 210ºC of melt temperature and with the second profile a melt temperature of 185ºC was reached. Beyond 200ºC the natural fibres begin their degradation process, accompanied by a decrease in mechanical properties.

Table 8 shows different compounds prepared at two different profile temperature. Samples 8 and 7 were made with low temperature profile

TABLE 8. COMPOSITES PREPARED FOR COMPOUNDING TEMPERTURE DETERMINATION

Sample	Polypropylene	Compatibilizer	% Compatibilizer	% Fibre	Screw Conf.	Tª Profile (ºC)
2	PP BA204E	-	-	30	1	170-180
8	PP BA204E	-	-	30	1	145-175
5	PP BA204E	Integrate NP594	7,5	30	1	170-180
7	PP BA204E	Integrate NP594	7,5	30	1	145-175

In table 9 is observed that the best impact properties were obtained when melt temperature decreases.

TABLE 9. MECHANICAL PROPERTIES OF THE COMPOUNDS EXTRUDED AT DIFFERENT TEMPERTURE PROFILES.

Sample	Flexural Modulus (MPa)	Frexural Strength (MPa)	Deformation at Break (mm)	Un-notched Charpy impact (KJ/m2)
2	2.650	46,1	8,7	19,4
8	2.670	47,1	9,44	23,2
5	2.390	52,0	11,1	35,2
7	2.460	56,0	11,4	38,9

Selection of the polypropylene grad.

In order to determine the effect of the melt flow index of the polymeric matrix over the hemp composite properties, two polypropylenes were added to the experiments with different melt flow index. The new compounds proposed are described in table 10. In all the samples a 3% of Integrate NP 595 coupling agent were used.

TABLE 10. COMPOUNDS PREPARED FOR DELECTION OF BASE MATRIX..

Sample	Polypropylene	% Fibre	Screw Conf.	Tª Profile (ºC)
4	PP BA204E MFI 0,8 g/10 min	30	1	145-175
9	ISPLEN PB150A2M MFI 2,1 g/10 min	30	1	145-175
10	PP WB130HMS MFI 7,0 g/10 min	30	1	145-175

Table 11 summarized the mechanical properties of the compounds containing different grades of polypropylene. The impact resistance decreases when the MFI increases, but it does not observe any appreciable change in elastic modulus. Maybe, these differences are due to the differences in impact properties of the polypropylene. Normally, in all thermoplastics when the MFI increases the impact resistance is reduced. Whereas the flexural strength increases with the MFI increase this could be due to the higher capacity of the low viscosity polymer to cover the fibre. The flexural properties of natural fibres composites are controlled by the type and amount of fibre.

TABLE 11. MECHANICAL PROPERTIES OF THE COMPOUNDS WITH DIFFERENT GRADES OF POLYPROPYLENE.

Sample	Flexural Modulus (MPa)	Frexural Strength (MPa)	Deformation at Break (mm)	Un-notched Charpy impact (KJ/m2)
4	2.600	56,7	10,9	39,0
9	2.670	57,1	10,5	28,3
10	2.780	66,1	11,0	27,9

In addition, during the compounding process, the mix with higher melt flow index polymer, shows a poor melt strength. The melt strand is broken when is stretched. This aspect may be important for the sheet extrusion and thermoforming suitability of these high flow composites.

The compound with PP Borealis WB130HMS (MFI = 2.1), and overcoat ISPLEN PB150A24 (MFI = 7), suffered many breaks during the stretching process into the cold batch. For this reason, it was difficult to achieve a continuous pattern. Probably the compound with lowest melt flow index polypropylene presents more cohesiveness than others two polymeric matrixes.

In order to know thermoforming behaviour we need to understand the relationship between the inherent nature of the rubbery plastic and the forces needed to stretch it into shape. This interaction is related directly to the stress-strain behaviour of the polymer at the forming temperature. For this, a specific study based on DMA (Dynamical Mechanical Analizer) techniques will be done. Figure 4 shows the stress-strain curves obtained at 160ºC of several compounding systems.

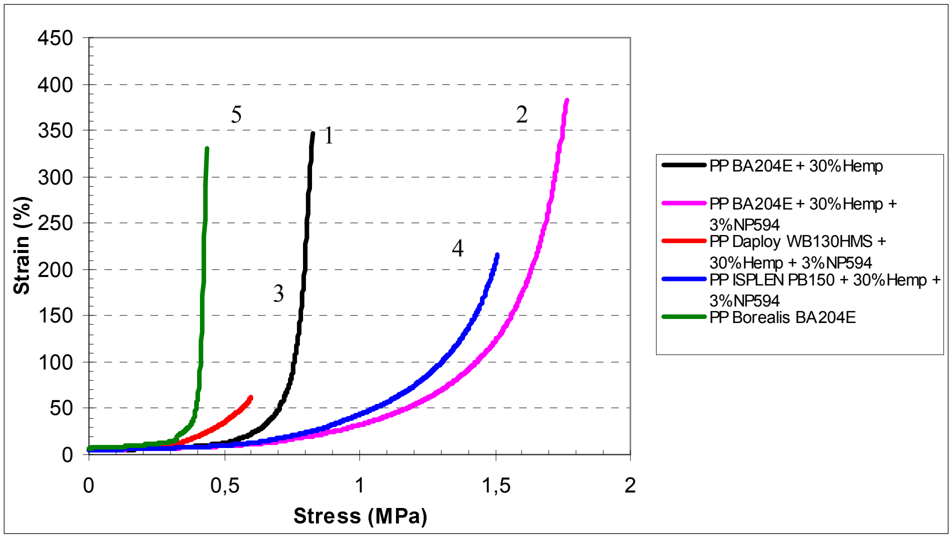

FIGURE 4. STRESS/STRAIN CURVES AT 160ºC OF SOME COMPOUNDS OF HEMP-POLYPROPYLENE.

The stretched samples with the higher melt flow index polypropylene shows an evident break in the melt. The lower melt flow index polymeric matrix shows the best stretching properties. This is very important for the sheet extrusion capabilities and, overcoat for the thermoforming process.

The copolymer polypropylene with MFI=0.8 overcomes the 350% in melt stretching (the maximum of the equipment), while the polypropylene with MFI=2.1 reaches 50% and with MFI= 7, 200%.Besides, the thickness of the stretched samples has reduced it to the half of its thickness.Generally, a significant increase is observed in melt strength when the compatibiliser is added. The yield point in the samples with compatibiliser agent is delayed and these allow more elasticity and less possibilities to the sheet breaks during the stretching process.

The polypropylene BOREALIS BA204E has proved to be in this work the best material considering the mechanical properties and in terms of processing suitability.

4. CONCLUSIONS

The most critical point is to prepare the fibre for the correct feeding into twin screw extruder. This was solved obtaining pellets from fibres.

The temperature profile and the screw configuration can cause the fibre degradation. If the screw configuration makes high shear it will be necessary to reduce the temperature profile. The mechanical results have showed that it is fundamental to break fibre agglomerates without degradation of the fibre or the matrix.

Mechanical tests show that the compatibilizer is only effective up to a specific percentage; In this project this was fixed in the 3% w/w.

The mechanical and reological characterization has shown the effectiveness of the polymeric matrix with less melt flow index to produce thermoformed sheet filled with natural fibres.

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