

Application of Cryogenic Grinding for Filler Preparation in the Form of Coconut Nanocomposites into the Thermoplastic Matrix with the Evaluation of Properties while Using Different Types of MAgPP Coupling agents

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ABSTRACT

The application of natural plant materials as fillers in polymeric materials is currently a very interesting area of research in order to achieve specific properties of polymer composites with a potential of the particular application in various industrial fields. One of these areas is the research concerning cryogenic grinding application for the preparation of nanoparticles from natural materials and the use of such prepared fillers in polymer matrices of a synthetic or natural origin. This paper focuses on the implementation of nanoparticles produced by cryogenic grinding of natural coconut fibers into a polypropylene matrix, evaluating the effects of different types of MAgPP coupling agents providing sufficient wettability and therefore compatibility at the interface between the hydrophobic polymer matrix and natural fillers, on final properties of polymeric nanocomposites.

Keywords: *Polymeric nanomaterials, Composites, Cryogenic grinding, Coupling agent, Injection moulding.*

Introduction

Currently, polymers and their composites are the most progressive materials, since they represent the most significant segment of production as well as consumption according to the volume among all other technical materials. There is no doubt that they constitute an essential key for a modern technical society. Current development of polymer materials and their processing technologies is going to continue to grow in a permanently greater volume and the success of individual materials is going to be crucially influenced by the ratio between the price and the utility value of the material. For these reasons, research and development have increasingly been focused on the application of natural fillers, where products based on the use of natural fibers are, undoubtedly, becoming more and more significant.

The use of natural fibers, for example, in technical applications, offers a wide scope for technical innovations as well as a sustainable development. In this respect, plant natural fibers are an optimized structure, which had been tested by the evolution. The field of natural fibers utilization includes applications using raw natural fibers in technical textiles up to applications in composites. Compared to the processing of glass or carbon fibers, natural fibers have naturally a better environmental as well as safety impact when using natural fiber products. The disadvantage is flammability, variable product quality, and in some cases poor or problematic compatibility of natural fibers with matrix composites. These areas are currently being solved intensively because elimination of these problems could lead to more technically improved products and hence an increase in demand concerning natural fibers.

An increasing interest in natural fibers is mainly given by their good mechanical properties, low density, and biodegradability at the end of their life cycle as well as their low production costs. These costs mainly result from the high rate of profit regarding fiber plants and relatively low work. From the already mentioned factors can be seen that price about getting natural fibers is three-times lower than for glass fibers, four-times lower than for aramid fibers and five-times lower than price for carbon fiber. With a low price and easy accessibility of natural fibers, they can serve as a cheap and ecological addition to the classically used reinforcing fibers [1].

In addition to natural fibers, another important area, where natural fillers are shifted, is the natural nanofillers area. This field of application has been growing dramatically. Nanofillers are currently been used in polymers mainly in the form of nanoclay (montmorillonite). Natural nanofillers are used at low volume content; therefore, represent an important material change. The preparation and modification of polymers via natural nanofillers and the

injection moulding of nanocomposites is an area with a huge potential as well as a prerequisite for an extensive growth. Pressure on the application of such materials has been constantly increasing as a result regarding the possibility of influencing final and utility properties of products.

At present, in nanocomposites with a thermoplastic matrix, montmorillonite is used as a filler, which is a crystallizing mineral in the monoclinic system, chemically hydrated alkaline silicate of sodium, calcium, magnesium and aluminum, which belongs to the group of clay minerals. The aim of this experiment was not only to replace clay minerals with natural fillers with very small dimensions on the basis of a coconut but also to apply the process of preparation regarding natural fillers (grinding) and processing of synthetic polymers with natural fillers (injection moulding) with the evaluation on selected finite properties with different percentage of nanofillers [2]. In the plant structure, there is a fiber the smallest identifiable unit of cell-wall [3]. Fibers are created by cellulose, hemicellulose, lignin, aromatics, waxes and other lipids, ashes and by water-soluble compounds. Cellulose, hemicellulose and lignin have the greatest volume [4-5].

The coconut fiber comes from coconut fruit, i.e. its palm tree bark and fibers are obtained from immature walnuts coming from the mesocarp layer. The fruit bark is wetted in seawater for several months so that the fiber bundles are released from the pectin casing and then spread to the individual fibers for further use. The length of the fibers as feedstock is 15-35 cm. Microscopic images of the fibers are shown in Figure 1, the properties of the coconut fibers are in Table 1 and the chemical composition is in Table 2.

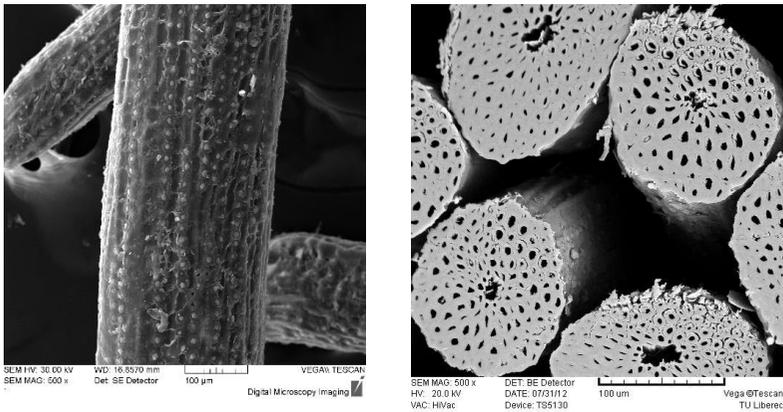


Figure 1: SEM image of coconut fibers (left) and its cross section (right)

The quality of adhesion among natural fibers and synthetic matrix has a great influence on the final properties of composites with natural fillers. That is mainly true about mechanical properties but adhesion can influence also

better dispersion of fibers and fillers [6]. Due to the strong intermolecular hydrogen bonds it is quite difficult to properly disperse natural fibers in polyolefin matrix which results in non-homogeneous distribution and creation of clusters. Chemical method represents one of the most used ways to ensure compatibility and connection on the interphase among fibers and matrix. Effectiveness of fibers surface modification by means of chemical compatibility coupling agents is influenced by chemical composition of polymer and type of fibers. High portion of hydroxyl group in cellulose results in hydrophilic behavior of these natural fibers. If natural fibers are used to reinforce hydrophobic polymer matrix, as a result there is very bad interphase and low resistance against moisture absorption. Chemical modification of fibers can activate hydroxyl groups through creation of new functional groups which can effectively react with polymer.

Table 1: Properties of coconut fibres [4]

Density [g.cm ⁻³]	Tensile strength [MPa]	Crystallinity [%]	MFA [°]
1.15 to 1.50	90 to 270	40 to 45	30 to 49

Table 2: Chemical properties of coconut fibres [4]

Cellulose [%]	Hemicellulose [%]	Lignin [%]	Pectin [%]
32 to 43	0.15 to 0.25	40 to 45	3 to 4

Therefore, one of the main factors influencing resulting properties of the composites is compatibility of filler with the matrix, not only from a physical point of view, but especially from a chemical point of view, where covalent bonding between the matrix and the filler is required. This is particularly true in the case of natural fibrous fillers which have a strong polar character. Thus, it is very difficult to incorporate them into a non-polar thermoplastic matrix. At the same time, due to strong intramolecular hydrogen bonds, it is difficult to disperse properly the natural fiber fillers in the polyolefin matrix, resulting in inhomogeneous distribution and formation of filler clusters [7].

Experimental

Paper aims to the application of cryogenic grinding for the preparation of nanoparticles from coconut fibers as well as the application of these particles to the synthetic polymeric matrix. It also includes the evaluation concerning the influence of different types of maleic anhydride grafted polypropylene

(MAGPP) coupling agents within the preparation and processing of polymer composites on selected final properties.

Materials

As a composite matrix was used semi-crystalline thermoplastic, polypropylene Thermofil PP E020M from Sumika Polymer Compounds Ltd. (UK). It has excellent flow properties and low melting point. These properties are particularly suitable for used natural fibers, which reduce flowability of the melted polymer and degrade at higher temperatures.

As a coupling agent coupling agents for preparation of composites were used two compounds based on MAGPP in pellete form. As a first coupling agent was used Fusabond from DuPont Company (USA), the second coupling agents was Priex 20097 from Addcomp Company (Netherlands). Both coupling agents were into composite added under the same percentage volume. The principle of MAGPP coupling agent function is based on presence of polar organic compounds, hydrolytic opening of the anhydride at elevated temperature occur to form a covalent bond with the polar organic substance.

Coconut fibres were purchased from Top Nature Textiles (Thailand).

Processing

Coconut fibres were milled in a shear mill RETSCH SM 300 (Germany) ($n = 3000 \text{ min}^{-1}$) with trapezoidal holes of 0.75 mm to shorten their length before cryogenic grinding. Subsequently, the fibers were washed with deionized water to remove organic impurities and lubricants. The milled fibers were then dried overnight at stationary laboratory oven (60°C).



Figure 2: Retsch Cryomill

Final grinding was conducted at an oscillating CryoMill (Retsch, Germany) (see Figure 2). Coconut fibers with a length of 0.5 mm - 2 mm entered the process of cryogenic grinding. A 50 ml milling bowl with a 15 mm

diameter ball was used to prepare the nanoparticles. The grinding vessel was continuously chilled with liquid nitrogen from the integrated cooling system, both before and during milling itself. Liquid nitrogen circulated in the system and was continuously supplied with a self-service system in the exact amount required to keep the temperature at -196°C . The output product is shown in Figure 3.

Composites were produced by twin-screw extrusion followed by injection moulding. For fabrication of compound pellets was used twin-screw extruder (ZAMAK EHP-2x130di, Poland) followed by water bath and pelletizer. Temperature parameters of compounding process are shown in Table 3.



Figure 3: Coconut particles after cryogenic grinding (left) and SEM image of coconut particles after cryogenic grinding (right)

Coupling agents and coconut nanoparticles were dosed directly into the melting chamber (see Figure 4) of extruder in the recommended position by external device. The reason for dosing nanoparticles in the front parts of the extruder (near granulation head) is to prevent excessive shear stress of nanoparticles during compounding melt composite and thus their damage or thermal degradation.

Table 3 Compounding process temperature parameters (mixing zones)

Zone 5 [°C]	Zone 4 [°C]	Zone 3 [°C]	Zone 2 [°C]	Zone 1 [°C]
185	180	180	175	170

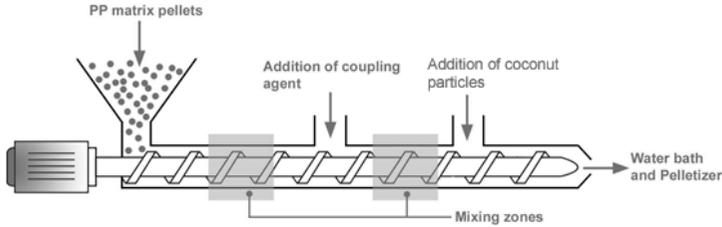


Figure 4: Schematic of compounding procedure

Due to the fact that in the previous operation extruded string passed through a water bath, it was necessary to dry compounds. For drying was used the Maguire Low Pressure Dryer (LPD 100) (USA) with following conditions: Temperature: 80°C, Time: 180 min., Vacuum: 0.8 bar. Device uses vacuum to accelerate the resin drying process. The moisture would adversely affect workability and properties (dimensional changes) of the final molded part, for this reason it was necessary to reduce the moisture content to the lowest possible level.

Further than were injection molded testing specimens according to ISO 527. Based on the experimental tests on injection molding machine (ARBURG 270S 400-100) (Figure 5) was chosen increasing temperature profile (see Table 4) of the melting chamber.

Results and Discussions

As it has previously been mentioned, the aim of this article was the application of cryogenic grinding for the preparation and obtaining nanoparticles from coconut fibers as well as the study of the influence of a different type of MAGPP coupling agents on selected properties concerning polymer composites (melt volume rate, tensile modulus, flexural modulus, melting temperature and enthalpy, etc.) which were prepared under the same technological conditions (see Table 3 and Table 4) and using an identical equipment.

Table 4: Injection moulding temperature parameters

Nozzle [°C]	Zone 4 [°C]	Zone 3 [°C]	Zone 2 [°C]	Zone 1 [°C]
190	185	180	175	170

Before conducting the tests, materials had been evaluated microscopically both in terms of uniform distribution and dispersion of

coconut nanoparticles as well as in terms of a control regarding sufficient wettability of nanoparticles by polymer matrix (see Figure 6).



Figure 5: Injection moulding machine ARBURG 270S 400-100

The resulting properties of the composites are not only affected by technological conditions of their preparation and production but also by adhesion of coconut nanoparticles to polypropylene matrix. As it is shown in Figure 6, filler clusters were not realized and at the same time, there was achieved an interconnection at the interfacial interface.

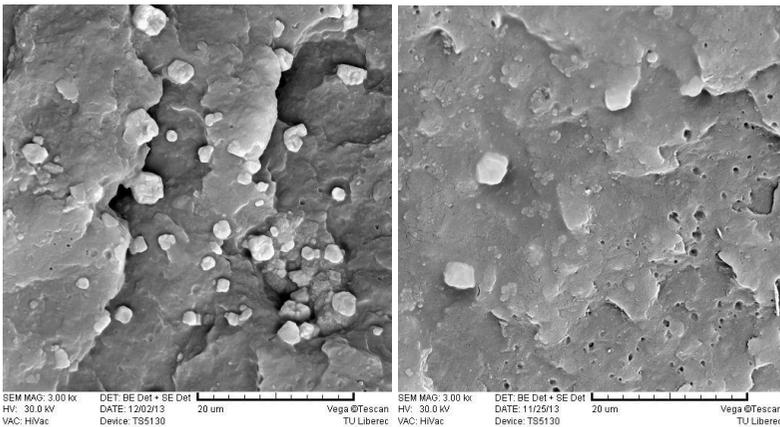


Figure 6: SEM image of a composite fractured surface with polypropylene matrix with 2% coconut nanoparticles and Fusabond coupling agent (left) and 6% coconut nanoparticles and Priex coupling agent (right)

The percentage of nanoparticles in the polymer matrix has also a major effect on final properties, so the properties selected have been evaluated for

the different percentage content of the filler in the synthetic polypropylene matrix. For the results mentioned below, percentage volumes of 2, 4 and 6% of nanoparticles were chosen. Only selected properties of coconut nanoparticle composites with different filling volume percentages and MAgPP coupling agents: melt volume rate according to ISO 1133; tensile modulus according to ISO 527 and flexural modulus according to ISO 178 are shown in the following figures (see Figures 7 to 9).

Testing specimens and samples subjected to selected tests show results that can be evaluated for both: the finite properties of the coconut nanoparticle composite and the type of coupling agent. As far as the MAgPP coupling agent is concerned, it can be stated that the different type of coupling agents does not have a significant effect on the final properties in relation to the type of the coupling agent used. When evaluating numerical values, it can be concluded that the melt volume rate is higher for the Priex coupling agent, the tensile modulus is comparable, and the flexural modulus is higher with the use of Priex coupling agent compatibilizer compared to Fusabond coupling agent (see Figure 9).

When comparing the observed values between virgin polypropylene and polypropylene with coconut nanoparticles, the increase in the tension modulus and the flexural modulus is evident. There is seen the decrease in the melt volume rate with the increasing percentage of coconut nanoparticles. The melt volume rate for polypropylene, with two percent of nanofillers, is about 4% lower than the virgin polypropylene, and with another two percent of filler added, it drops another percentage for the Fusabond coupling agent.

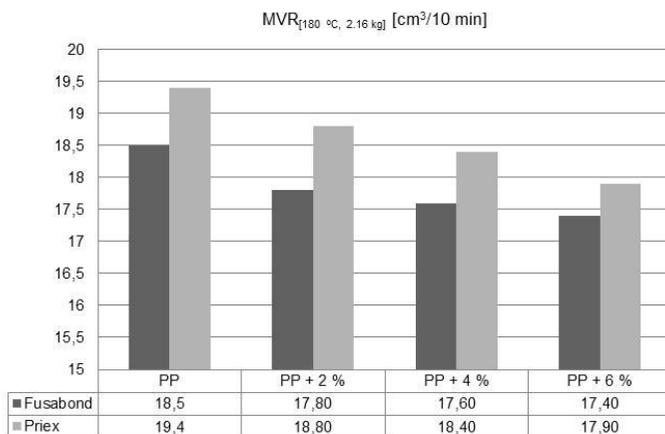


Figure 7: Melt volume rate for composites with a different percentage of filler from cryogenic grinding and different type of the coupling agent

For the Priex coupling agent, the melt volume rate for polypropylene with two percent of the nanoparticle is about 3% less than the non-filler polypropylene, and with another two percent of the filler added, it drops by about two percent (see Figure 7). In conclusion, however, it should be noted that even though the rheological properties of the composite had been reduced, we did not notice any problems while processing (injection moulding) of these materials.

In terms of tensile modulus and flexural modulus, the tension modulus is about 7% higher than polypropylene without filler and polypropylene with two percent nanofillers addition, and with an additional two percent of the filler added by about 3% to 14% final for six percent nanoparticles in a polypropylene matrix and Fusabond coupling agent. For the Priex coupling agent, the tension modulus for polypropylene with two percent nanofillers is higher by approximately 5% compared to the non-filler polypropylene, and with the addition of two more percent of the filler up to the final 12% (see Figure 8).

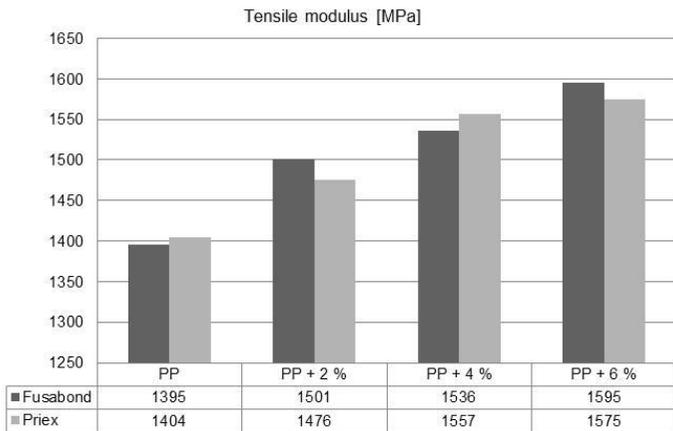


Figure 8: Tensile modulus for composites with a different percentage of filler from cryogenic grinding and different type of the coupling agent

In contrast, the flexural modulus is approximately 18% higher than polypropylene free of filler in polypropylene with two percent of fillers grows up to a final 24% for six percent nanoparticles in the polypropylene matrix and Fusabond coupling agent. For the Priex coupling agent, the flexural modulus for polypropylene with two percent of the nanoparticle is higher by approximately 15% compared to the non-filler polypropylene, and with the addition of two additional percent of the filler, grows up to the final 22% for six percent nanoparticles in the polypropylene matrix (Figure 9).

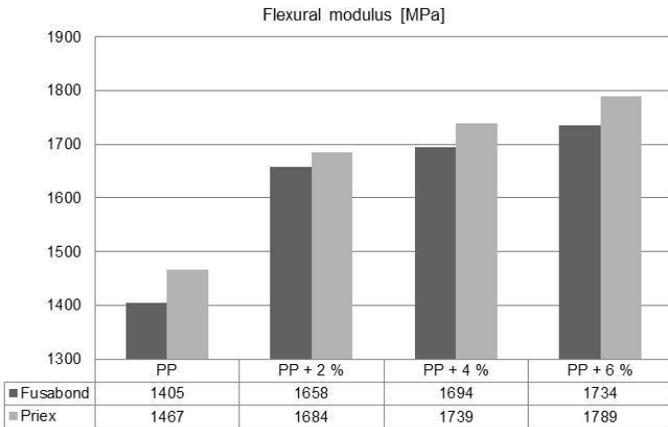


Figure 9: Flexural modulus for composites with a different percentage of

Filler from cryogenic grinding and different type of the coupling agent
 When comparing the modulus, it can be concluded that the flexural modulus is approximately 150 MPa higher than the tension modulus for the Fusabond coupling agent and approximately 200 MPa higher for the Priex coupling agent.

Table 5 Temperature and energetic characteristics of phase transformations

	T_m [°C]	ΔH_m [J/g]	T_c [°C]	ΔH_c [J/g]
PP without a filler	168	90	122	117
PP + 20% coconut fibers	167	74	121	92
PP + 4% coconut particles after cryogenic grinding	167	83	122	103

In addition to the above rheological and mechanical properties, the temperature characteristics of the composite material were also carried out by using the DSC method according to ISO 11357. However, this measurement was not carried out in terms of comparing the effect of the compatibilizing coupling agent type (Fusabond and Priex), but in terms of the influence concerning the size of the filler (fibers – the input material before cryogenic grinding, particles – the output material after the process of cryogenic grinding) and the effect of the percent aged content of fillers (20 % coconut fibers, 4 % particles of the coconut) in polypropylene matrix with the coupling

agent Fusabond on melting temperature and enthalpy (see Table 5 and Figure 10 to 12).

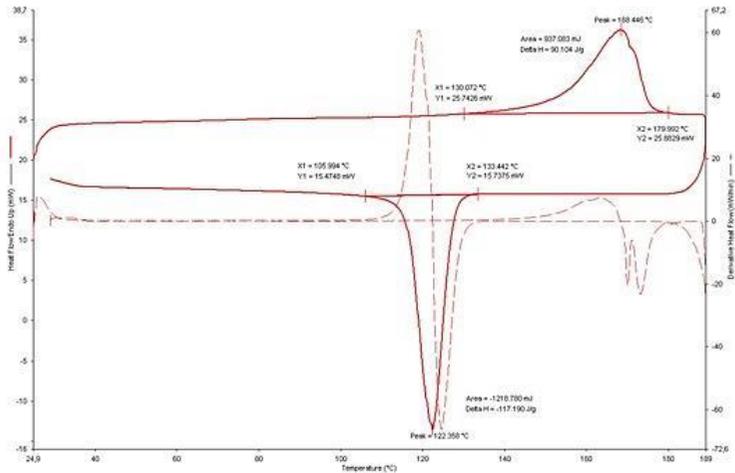


Figure 10 DSC graph curves polypropylene matrix

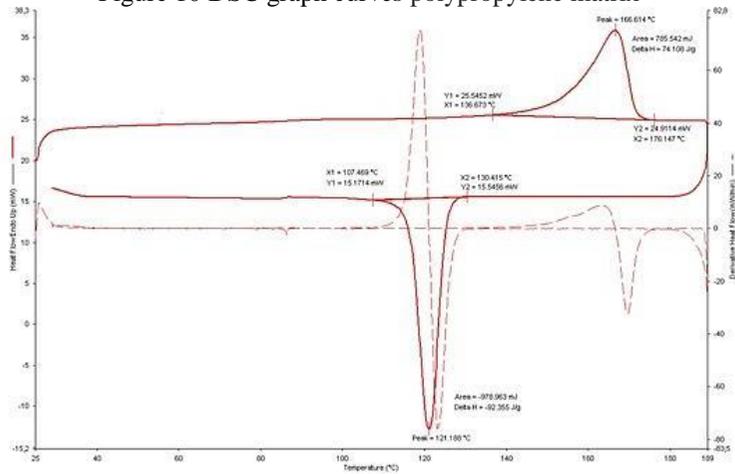


Figure 11 DSC graph curves polypropylene matrix with 20% coconut fibers

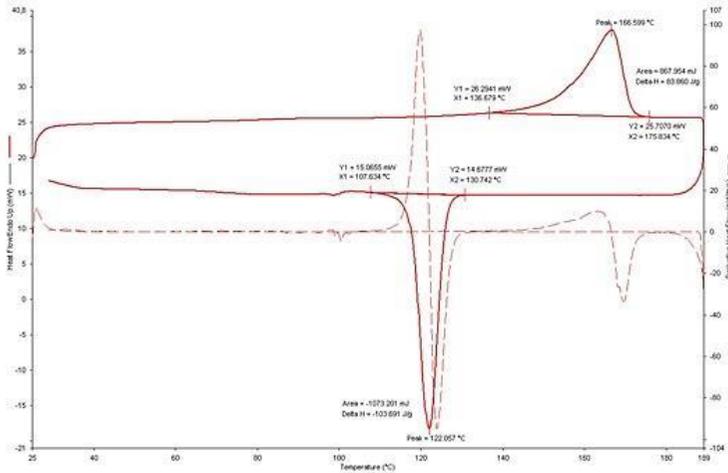


Figure 12 DSC graph curves polypropylene matrix with 4% of coconut nanoparticles from cryogenic grinding

Specimens of composites with Fusabond coupling agent but with a different filler type and a percentage of a filler content put to the test of thermic analyses via differential scanning calorimetry method do not show differences in measured melting temperatures but show differences in measured enthalpy melting values (see Table 5). By using natural fillers, the crystallization of polymer composites has been beneficial.

Conclusion

The development of composites with a thermoplastic matrix and natural fillers is a continuous as well as a constantly evolving process, which is going to lead to the development of composite materials in the near future. Their properties will not only be influenced by the type of natural filler, the filler percentage volume, filler shape or size but also by the type of compatibilizing coupling agent. Undoubtedly, the very key for development and application deployment of composites with natural fillers are going to lead to both methods concerning preparation of fillers and composites as well as coupling agents added to the polymer matrix during the compounding process, where this article was trying to contribute.

From the general point of view, the addition of coupling agents and natural coconut nanoparticle in to PP polymer matrix caused the following advantages and benefits:

- Improvement of mechanical properties of the final composite because due to the addition of nanofillers coming from the natural type the mechanical properties of the composite are ameliorated. Their increase is dependent on the amount of particular filler.
- Shortening of technological times, because the nanofillers act as a nucleating agent.
- Higher dimensional stability of products, as increasing the percentage of nanofillers, there also increases the dimensional stability of a particular part and shrinkage decreases.
- Reaching environmental aspects.

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