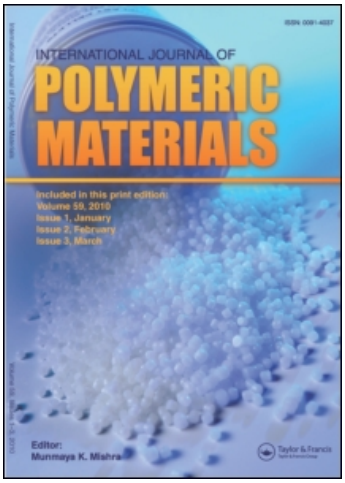

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Dried green coconut fibers (GCF) consist of fibers of various length mixed with a fine powder. Both components can be separated by simple screening techniques, and the present paper summarizes an experimental study on the mechanical and molecular dynamic behaviors and the morphological aspect of green coconut fiber-reinforced polypropylene composites, with respect to the effects of content and granularity of the filler in the powder (0,841–0,500 mm) and fiber (10 mm) forms. All compounds were prepared in an internal mixer at 170°C, 60 rpm for 8 min. It was observed that the flexural modulus increases with increasing fiber content, either in powder or fiber forms. Impact tests show that fiber-filled composites have greater impact strength than powder-filled composites. The results obtained by low-field NMR show that the stiffness of composites decreases with higher fiber loading, due to the poor compatibility between fibers and matrix. The morphology of the system was studied by SEM analysis. In general, composites with fiber showed better properties than those with powder.

Keywords: fiber granularity, green coconut fiber, mechanical properties, molecular dynamic behavior, polypropylene

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INTRODUCTION

Fiber-filled thermoplastic composites were first introduced into the market with the intention of producing a range of new materials for lightly stressed engineering applications. Over the past two decades, renewable resources such as plant fibers have received considerable attention as a potential substitute for synthetic fiber reinforcements, not only because of environmental concerns but also with respect to lower cost, density and abrasivity of the composites and acceptable specific strength [1].

In natural lignocellulosic fibers, cellulose is the main component. The elementary unit of a cellulose macromolecule is anhydro-d-glucose, which contains three hydroxyl groups (−OH). These hydroxyls form hydrogen intramolecular bonds as well as intermolecular bonds with hydroxyl groups from atmospheric moisture. So, all natural fibers are hydrophilic in nature and their moisture content can reach 3–13% [2].

Coconut fiber is an important lignocellulosic fiber obtained from coconut trees which grow extensively in tropical countries. Because of its hard-wearing quality, durability and other advantages, research and development efforts are underway to find new areas of application for green coconut fibers (GCF) as reinforcement in polymer composites [3,4].

The mechanical properties of composites depend on various factors such as strength, modulus, processing conditions and fiber-matrix interfacial bonding. Significant improvement in composite properties can be achieved by using coupling agents that are expected to enhance interfacial compatibility or adhesion through covalent bonding between the fiber and the matrix [5,6]. Graft copolymers, such as maleic anhydride polypropylene (MAPP), have proved to be suitable additives for cellulosic fiber-reinforced polypropylene [7–9].

In addition to mechanical characteristics, the knowledge of dynamic molecular behavior is also very important to evaluate the final properties of the materials, as well as their applications. This type of information can be supplied by solid-state nuclear magnetic resonance spectroscopy, which involves many techniques, one of them being the low-field NMR that can be used to determine proton spin-lattice relaxation time (T_1H) values, by applying the traditional inversion recovery pulse sequence ($180°$–τ–$90°$). Such data can help understanding the structural differences due to domain formation, as well as providing detailed information on chain mobility at the molecular level [10,11].

Thus the aim of this work is to characterize the molecular dynamic behavior of polypropylene (PP), green coconut filler and

their composites, obtained by mixing process with different filler contents through solid-state nuclear magnetic resonance (NMR), by measuring the proton spin-lattice relaxation time (T_1H). This investigation was performed on a low-field NMR Resonance MARAN ultra 23, and the mechanical analysis as flexural and impact tests were carried out to investigate a potential use of this waste material in polymeric composites.

EXPERIMENTAL

Materials

- Polypropylene (PP1074): Specific gravity of 0.9 g/cm^3 and MFI (230°C) of 20 g/10 min. Supplied by ExxonMobil Chemical, USA.
- Maleated polypropylene (PO1020) was used as the coupling agent: Specific gravity is 0.9 g/cm^3 and maleic anhydride content is 0.75%. Supplied by ExxonMobil Chemical, USA.
- Green coconut fibers in two shapes, powder, P, (0.841–0.500 mm) and fiber, F, (10 mm). Supplied by Embrapa Agroindustria Tropical, Fortaleza, Brazil.

Methods

Sample Preparation

Green coconut fibers were air-dried for 48 h at 80°C and for at least 1 h at 100°C prior to composite preparation. Drying of fibers is a fundamental step since the presence of water reduces the adhesion between this filler and the matrix.

Blending of materials was carried out by melt mixing for 8 min in a Haake Torque Rheocord 9000 using roller blades. In our previous study [3] it was showed that best performance of PP based composites was obtained when prepared at 170°C, 60 rpm rotor speed and 1% of maleated polypropylene (MAPP) in relation to PP, as the coupling agent. So, in this work these processing conditions were fixed, and attempts were made to introduce higher fiber contents. The influence of two different fiber shapes, such as powder P (0.841–0.500 mm) and fiber F (10 mm), on the mechanical properties and on the molecular dynamic behavior of these composites was also evaluated.

After mixing, plaques of 3 mm thick were compression-molded under 7 MPa at 185°C for 2 min, and then cooled for 5 min under the same pressure. The resultant plaques were properly cut and polished for each test method.

Testing Methods

Flexural Test

Three point bending tests were performed on an Instron universal testing machine, according to ASTM D790, with crosshead speed of 1 mm/min, span between bars of 50 mm and cell load of 1 kN. At least 5 samples for each composite, of dimensions $12{,}7 \times 130 \times 3$ mm, were tested.

Impact Test

Izod impact tests were performed using a Resil Impactor tester (Ceast), in accordance with ASTM D256, with notch angle of 45° and "V" notch depth of 2.54 mm. Ten samples were tested for each composite. The width and thickness of the notched specimen were measured and recorded, and impact resistances were calculated.

Characterization of Molecular Dynamic Behavior

The samples were placed in the appropriate probe, and the measurements were carried out on a MARAN ultra 23 (Resonance, Oxford, UK), operating at 23 MHz (for protons) and equipped with a 18 mm variable temperature probe. The proton spin-lattice relaxation times (T_1H) were determined directly by the traditional inversion-recovery pulse sequence (180^o–τ–90^o) at 27°C. The amplitude of the FID was sampled for twenty τ data points, ranging from 0.1 to 5000 ms, with 4 scans for each point and 5 s of recycle delay. The distributed exponential fittings as a plot of relaxation amplitude versus relaxation time were performed by using the software WINDXP®, which comes with the equipment. The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of the WINFIT® software.

Scanning Electron Microscopy (SEM)

The fractured surfaces of composites containing 50% of filler, either in the powder P or fiber F forms, were coated with a thin layer of gold and analyzed on a JEOL JSM 5300 scanning electron microscope using an acceleration voltage of 15 kV. The morphology and the distribution of filler in the matrix were investigated.

RESULTS AND DISCUSSION

Flexural Modulus

The flexural modulii of green coconut fiber composites with respect to different fiber loads and shapes are given in Figure 1. It is essential to

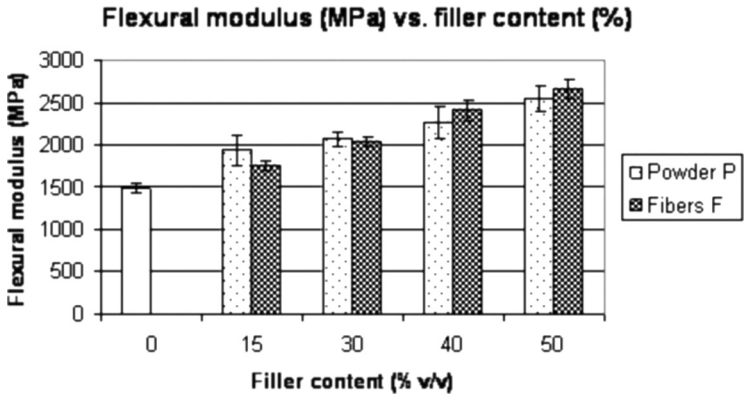

FIGURE 1 Influence of fiber load and granulometry on the flexural modulus of green coconut fiber-PP composites.

find out the optimum fiber loading to achieve maximum property [12]. It can be seen that the flexural modulus of all the composites is higher than that of neat PP and that it increases with larger fiber loading. Generally, it also increases with fiber length, as shown by composites with higher filler contents (40 and 50%). However, in lower filler contents such as 15 and 30%, powder, P, (0,841–0,500 mm) composites showed higher flexural modulus than fiber, F, (10 mm) composites, probably due to a better dispersion of the powder in the matrix. As filler content increased, fiber, F, composites showed higher flexural modulus.

Fiber length is an important parameter that determines the fiber loading limit, so that the higher the fiber length, the lower the loading limit. Brahmakumar [1] in his study on coconut fiber-polyethylene composites, observed that while a loading limit of about 25% was observed for fiber length of 20 mm, the strength of composites containing fiber length of 10 mm showed an increasing trend even beyond 30% loading. In our study with GCF-PP composites, it was observed that this increasing trend is even higher, 50%. Above this filler content, it was impossible to introduce more fiber into the mixing chamber of the equipment used.

This significant increase in the flexural modulus of the composites, comparing to neat PP, is primarily attributed to the reinforcing effect imparted by the presence of the fillers in the polymeric matrix [13]. These results show that even dealing with an apolar polymer, such as PP, and a polar filler, such as cellulose, which are expected to be incompatible, one can still enhance (low deflection) flexural performance by properly combining these components.

Impact Test

Impact resistance is the ability of a material and its structure to withstand impact-induced damages. The results from the notched Izod impact testing at 23°C are summarized in Figure 2 as a function of GCF concentration and granularity. It can be seen that the impact strength of the powder-filled composites decreases linearly with filler concentration. This may indicate that more stress concentration points are created as the powder content increases. Fiber-filled composites, however, exhibit improved impact strength that is dependent on the fiber length, with long fibers (fiber F) leading to higher values, relative to powder composites. The long fibers in the thermoplastic matrix seem to better absorb the impact energy by dissipating the associated energy through extended contacts with polymer chains.

The impact strengths of fiber-filled composites are in fact higher than that of neat PP, but the values decrease as fiber concentration increases. This indicates that, in terms of the impact resistance, MAPP is not really efficient as compatibilizing agent, at least in the concentration used in this study (1% in relation to PP content).

Characterization of the Molecular Dynamic Behavior

The distribution curves obtained by low-field NMR are illustrated in Figures 3 and 4 and the values found for T_1H are given in Tables 1 and 2.

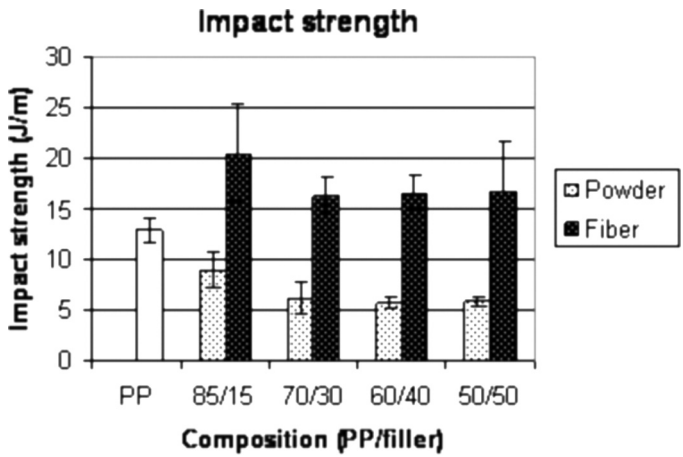

FIGURE 2 Effect of fiber loading and granulometry on the impact strength of composites.

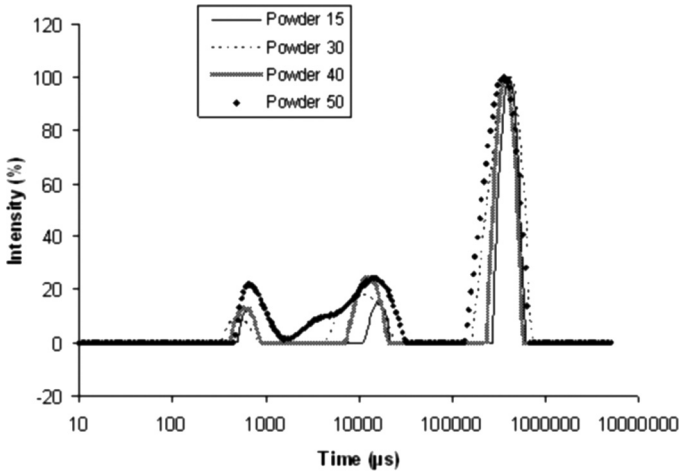

FIGURE 3 Distribution curves obtained by low-field NMR for the powder-PP composites.

Generally, the increase in the T_1H values means that the sample becomes more rigid, due to a good interaction between the components. From this parameter we can also obtain information on the sample homogeneity, since T_1H changes as a function of changes in the molecular mobility. The observation of only one value of T_1H

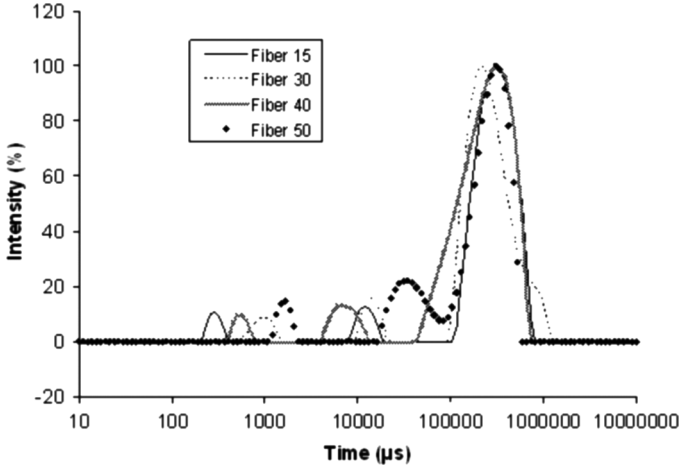

FIGURE 4 Distribution curves obtained by low-field NMR for the fiber-PP composites.

TABLE 1 T_1H Values Obtained from Low-Field NMR for Powder-Filled GCF-PP Composites

Samples	T_1H ($\times 10^3$ μs)	%	$T_1H_{(1FIT)}$ ($\times 10^3$ μs)
PP	9.4	12	319.9
	352.5	88	
Powder 15	0.4	8	294.3
	16.2	11	
	407.2	81	
Powder 30	0.5	8	222.2
	12.6	17	
	370.8	75	
Powder 40	0.4	9	193.8
	12.2	20	
	365.8	71	
Powder 50	0.7	13	127.5
	11.9	23	
	331.8	64	

indicates that the sample is homogeneous in the scale of the measurement. The same behavior can be expected for domains curves; one curve only may be derived from a homogeneous sample [14].

For all samples (composites with powder P and with fiber F), three relaxation domains in the distribution curves are observed since the materials are heterogeneous. The rigid domain (higher T_1H values) produces the dominating curve, and therefore controls the total

TABLE 2 T_1H Values Obtained from Low-Field NMR for Fiber-Filled GCF-PP Composites

Samples	T_1H ($\times 10^3$ μs)	%	$T_1H_{(1FIT)}$ ($\times 10^3$ μs)
PP	9.4	12	319.9
	352.5	88	
Fiber 15	0.3	4	262.7
	13.0	7	
	309.8	89	
Fiber 30	0.9	4	221.5
	15.0	9	
	276.9	87	
Fiber 40	0.5	2	196.2
	7.0	10	
	243.4	88	
Fiber 50	1.0	4	178.5
	18.0	11	
	222.0	85	

relaxation process. It can also be observed that the values in this domain and for $T_1H_{(1FIT)}$ decrease with increasing fiber loading, whatever their shape, thus indicating a reduction in the material stiffness at molecular level. This can be due to a more effective chain separation as increasing amounts of filler are introduced, thus resulting in lower polymer-polymer interaction.

These results show that, at a molecular level, there is not enough compatibility between filler and matrix to impart an increase in the

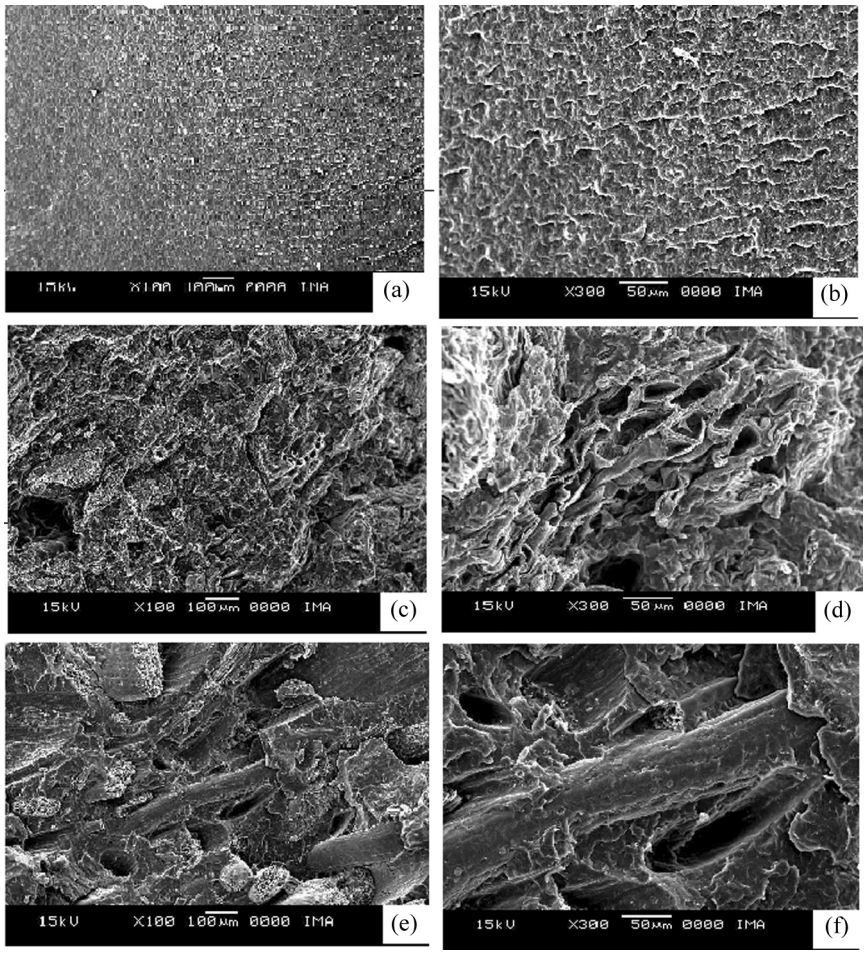

FIGURE 5 SEM of fractured surfaces of neat PP: (a) 100×, (b) 300×, and composites containing 50% of filler, powder P: (c) 100×, (d) 300× and fiber F: (e) 100×, (f) 300×.

materials stiffness, so the values found in both analyses decreased with the increase in fiber loading. This was also detected for the impact test, which is a test that evaluates macro regions, but obviously reflects the behavior in micro regions.

Scanning Electron Microscopy (SEM)

Scanning electron micrographs of the fractured surfaces of neat PP and composites containing 50% of filler (powder or fiber) are shown in Figure 5. The morphology of the composites shows the presence of the fillers in the matrix, which leads to higher flexural modulus, as discussed above. The micrographs clearly show the morphological differences between GCF powder and fiber fractions when used as reinforcing materials. Due to these morphological differences, the composites present different mechanical behavior, especially with respect to impact strength. This property was lower for the powder-filled composites than for neat PP, which can be considered as a consequence of the morphology shown in Figures 5c and 5d. Indeed it can be observed that the powder-filled composite may have acted as if there were micro defects in the matrix, thus preventing this composite from having good impact strength. On the other hand, fiber-filled composites showed impact strength higher than neat PP, due to the presence of long fibers, as seen in Figures 5e and 5f, which dissipate the impact energy throughout the polymer chains.

The micrographs clearly show that, some fibers are well-embedded in the polymer matrix, likely because of enhanced wetting due to the compatibilizing agent (MAPP), but it can also be observed that there are voids due to fiber pull-out. This suggests that the MAPP content (1% of PP) may not be sufficient, as already suggested by the NMR analysis.

CONCLUSIONS

In this study, the flexural modulus of green coconut fiber-PP composites was found to increase with fiber content, whatever the shape used. Based on these studies, it was concluded that GCF can effectively reinforce PP matrix when used in an optimal concentration, that is dependent on the shape of the fibers.

The results obtained by low-field NMR and impact tests show that the materials' stiffness decreases with increasing fiber loading, due to a poor compatibility between the components. The level of compatibilizing agent used in this work, i.e., 1% of MAPP in relation to PP, is not efficient in terms of impact resistance. This is confirmed by SEM analysis.

However, the whole system becomes rigid upon the addition of filler, as observed with flexural modulus. Therefore, the green coconut fiber can still be considered as an interesting reinforcement for polypropylene, even if it is not really compatible with the polymer matrix.

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