

# Injection Molding of Long Sisal Fiber–Reinforced Polypropylene: Effects of Compatibilizer Concentration and Viscosity on Fiber Adhesion and Thermal Degradation

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A two-step process was used to obtain long sisal fiber–polypropylene (SF/PP)–reinforced thermoplastic composites, using maleic anhydride grafted polypropylene (MA-g-PP) as a compatibilizer. At a first stage, modified polypropylenes (mPP) were used for an extrusion impregnation process, for the preparation of composite pellets containing about 70 wt% of SF. SF/mPP pellets with a large aspect ratio were prepared by continuous extrusion impregnation of a continuous SF yarn, using a single screw extruder and an adequate impregnation die. The mPP used were MA-g-PP and regular polypropylene (PP), modified by reaction with different amounts of an organic peroxide. The composite pellets were thus dry blended with regular PP pellets in an injection machine hopper, and injection molded to obtain composite tensile specimens with a minimum quantity of modified polypropylene, minimum fiber breakage and thermal degradation, and excellent mechanical properties. It is shown that the fiber breakage is reduced to a minimum, even for recycled composites, due to the presence of the low-viscosity polymer layer wetting the SF fibers. The bulk composite effective viscosity and the fiber breakage extent and thermal degradation during the injection-

molding step are found to be closely related. Blending with much less expensive mPP at the impregnation stage optimizes the amount of expensive MA-g-PP. POLYM. ENG. SCI., 45:613–621, 2005. © 2005 Society of Plastics Engineers

## INTRODUCTION

The incorporation of natural fibers into thermoplastic polymer matrices reduces cost and weight, as these fibers are cheaper than synthetic polymers and have lower density. The incorporation of cellulosic natural fibers in thermoplastic composites has increased in the past years. This trend is driven mainly by government regulations that promote the use of renewable and recyclable materials, aimed at reducing the environmental impact of much agricultural fiber waste.

Natural cellulosic fibers can be used to improve some mechanical properties of unfilled plastics [1]. Synthetic fibers usually display higher modulus and strength values, but for massive applications of medium mechanical properties requirements, natural fibers may be a cost-efficient alternative. Another desirable feature is recyclability; thermoplastic composites are expected to be recyclable without much loss in mechanical properties and appearance.

The preparation of composites made out of thermoplastics reinforced with natural fibers is usually a two-stage process. The first stage consists of compounding the com-

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posite by blending the fibers and the polymer together, and a twin-screw extruder is used to achieve good fiber impregnation and distribution. The second stage is the molding of the parts, usually by an injection molding process.

Polyolefins—particularly polypropylenes (PP)—are often used as matrices for natural fiber-reinforced composites. They have low prices, low density, processing temperatures that can be kept low to avoid or reduce cellulose and can be recycled.

Sisal fiber (SF) is one of the natural fibers used most in the automotive industry. It is renewable, nonabrasive, and biodegradable. SF shows a quite high specific strength and stiffness, and can be obtained at a low price (0.36 US\$/Kg.) [2]. SF has already been used as an effective reinforcing material in polymeric resin matrices to make useful structural composite materials [2].

While being a very interesting pair with many potential applications, SF and PP share important problems derived from two facts: the weak interfacial bonding between the polar fiber surface and the hydrophobic matrix, and the high viscosity of molten PP [3]. The polymer adhesion to the fiber surface controls the stress transfer between the matrix and the reinforcing fibers. Fiber impregnation depends mainly on processing variables, and the polymer-fiber adhesion depends on chemical identities [4]. For these cases of polar fibers and hydrophobic matrices, poor mechanical properties can be linked to weak interfacial bonding. Also, the PP high viscosity is assumed to be responsible for poor penetration of the molten PP into the fiber bundles, thus diminishing the SF/PP contact area. The viscosity of regular injection-grade polypropylenes at the temperature range at which the natural cellulosic fibers can be processed is high enough to reduce fiber bundle impregnation. For the injection molding process, high shear rates at the mold filling stage—combined with a high PP viscosity—cause bulk temperature rises that can easily degrade the cellulosic fibers by thermal depolymerization of hemicellulose and the glycoside linkages of cellulose [5].

These problems of interfacial bonding and high melt viscosity need to be solved, for a cost-efficient use of SF reinforcing. For improved SF/PP interface bonding, coupling agents can be used. Maleic anhydride grafted polypropylene (MA-g-PP) is an excellent choice, because the anhydride functionality of MA-g-PP reacts with cellulosic fiber hydroxyl groups and esterification gives stronger links between the fiber surface and the PP matrix [6]. Reducing the PP molecular weight lowers the viscosity of the molten polymer, reduces the shear stress between individual fibers and between fibers and PP melt [7], and reduces the viscous heat generation; the composite may then be processed by injection molding at lower temperatures.

Other aspects of the problem must also be considered. Commercial grades of MA-g-PP with high level of functionality (1.0 wt% MA) are very expensive (about 5 US\$/Kg), and therefore these must be used in small quantities to keep the SF/PP composite economically competitive.

Some details of the preparation of composites made out

of thermoplastics reinforced with natural fibers must also be analyzed. The first stage usually consists of compounding the composite by blending the fibers, the polymer matrix, and a coupling agent together in a twin-screw extruder. With this practice, the maleic anhydride bonding efficiency is reduced by this dilution of the MA-g-PP into the PP matrix, because many anhydride functional groups may not reach the hydroxyl groups at the SF surface. The second stage is the molding of the parts, by an injection molding process. For good mechanical properties, a high molecular weight PP is used for the continuous thermoplastic matrix. Therefore, the injection molding process can generate bulk temperature and shear stress higher than allowed for low fiber thermal degradation and SF attrition. This is a very important feature of this process, since most of the fiber breakage found for these processes occurs inside the twin-screw extruder [8]. The combined operations of compounding and injection molding thermoplastics/natural fiber composites generally reduce the initial fiber length because of the severe temperature condition and shear stress imposed. The efficiency of the composite depends on the amount of stress transferred from the matrix to the fibers. This can be maximized by improving the interaction and adhesion between the two phases and also by maximizing the length of the fibers retained in the final composite [9].

This work is focused on long SF/PP composite processing by a less expensive method [10]. The usual two-stage process is modified to obtain parts with good mechanical properties at a reasonable cost, by using lower coupling agent contents. Also the feasibility of recycling these parts is improved: the twin-screw compounding stage is eliminated, reducing total fiber attrition, and the thermal degradation and breakage of the fibers at the injection molding stage is also diminished.

The method used can be summarized as follows:

As a first stage, an SF yarn is impregnated in a continuous process with small quantities of a low-viscosity MA-g-PP, and subsequently palletized. The fiber content of the pellets was measured, and averaged 70 wt%. This way the MA-g-PP overall concentration in the composite is minimized, while keeping a high bonding efficiency between MA-g-PP and the fibers. The blending of the PP pellets with the MA-g-PP/SF and the injection molding process are reduced to a single operation. The pellets made at stage 1 and PP pellets are dry-blended at the injection machine hopper, and the desired parts are injected. Injection bulk temperature rises are much reduced at low injection temperatures, most probably due to low shear stress at the SF-PP interface. Also, the length of the SF at the injected part is kept about the same as the pellet length, thus improving the final measured mechanical properties. The effect of the MA-g-PP concentration at the SF-PP interface is explored, by diluting the MA-g-PP used at stage 1 with a low-viscosity PP [11, 12]. The effects of the MA-g-PP concentration on the mechanical properties of the injected parts are quantified, and an economically convenient threshold is found. The effect of the viscosity of the PP used to

TABLE 1. Physical and chemical properties of PP, MA-g-PP, and SF.

Properties	PP	MA-g-PP	Sisal fiber
Melt flow index (180/2.16) (g/10 min)	1.76 <sup>a</sup>	110 <sup>a</sup>	—
Density (g/cm <sup>3</sup> )	0.930 <sup>b</sup>	0.910 <sup>b</sup>	1.450 <sup>b</sup>
Tensile strength (MPa)	24.3 <sup>c</sup>	—	561–684 <sup>d</sup>
Tensile modulus (GPa)	1.38 <sup>c</sup>	—	13.6–17.4 <sup>d</sup>
Cellulose content (%)	—	—	84–88 <sup>b</sup>
Lignin content (%)	—	—	4–6 <sup>b</sup>
Diameter (μm)	—	—	180–300 <sup>d</sup>

<sup>a</sup> Measured as established by ASTM D 1238.

<sup>b</sup> Reported by the producer.

<sup>c</sup> Five specimens measured as established by ASTM D 638.

<sup>d</sup> Twenty-five specimens measured as established by ASTM D3379-75.

dilute the MA-g-PP at stage 1 is explored, by using PPs with different melt flow index (MFI) values. The effects of the MFI of the low-viscosity PP on the mechanical properties of the injected parts and on SF thermal degradation are studied, and convenient limits are established. As a fringe benefit, a single recycling experiment was performed. Parts injected with 17 wt% SF were chopped, and used again to inject into the same mold used for the first injection molding. The same processing conditions were used for both consecutive injections, without any additives added for the second injection stage. No fiber breakage or thermal degradation was observed.

## EXPERIMENTAL

Sisal fiber (*Agave sisalana*) yarn with a fiber diameter of about 100–200 μm was obtained from Brascorda Co. (Brazil). The fibers were used for this work as received, without any surface modification or chemical treatment. MA-g-PP (1.0 wt% MA) (Polybond 3200, produced by Crompton Europe) was used as a coupling agent. Commercial unmodified PP (Stamylan CX02, produced by DSM) was used as received. An organic peroxide, 2,5-di(tert-butylperoxy)-hexane, with  $T_{1/2} = 4$  min at 170°C was supplied by Akzo Nobel Quimica S.A., and used as received. Table 1 shows some physical and chemical properties of PP, MA-g-PP, and SF.

The 2,5-di(tert-butylperoxy)-hexane was dissolved in n-

hexane. Batches of unmodified PP were impregnated with solutions with different peroxide concentrations. The solvent was removed by evaporation. The PP batches impregnated with different amounts of dispersed peroxide were melted at 180°C, mixed, cooled, and pelletized using a single screw extruder with a resident time of 1.5 min [11, 12]. These modified PPs were named after the peroxide concentration used in the modification process in parts per million (ppm). Therefore, PP1000, PP1500, PP3000, and PP9500 are PP modified with 1000, 1500, 3000, and 9500 ppm of peroxide.

Molten PP9500 and MA-g-PP were mixed and pelletized to obtain other two modified polypropylenes. Identified as M1, M2, and M3, they contain 15%, 30%, and 70% of MA-g-PP.

Table 2 shows the melt flow index values for all polymers used, which were measured with a normalized melt index tester (CEAST T.Q., Type 6841) (ASTM D1238).

Standard MFI test conditions for polypropylenes are 230°C and 2.16 Kg. Due the scission of the polymer chains treated with the peroxide it is expected that the MFI values will be too high for the standard test condition. For this reason a temperature of 180°C and a load of 2.16 Kg. (180/2.16) were used for comparison purposes.

SF yarns were impregnated with six different modified polypropylenes: two peroxide-treated polypropylenes (PP3000 and PP9500), a commercial MA-g-PP, and three blends of MA-g-PP and PP9500 (M1, M2, and M3).

Continuous, dry SF yarns were pulled through a melt impregnation die especially designed, attached to a single-screw extruder (21 mm diameter, length/diameter = 22), to impregnate the SF yarn with molten polymer at low pressure (about 0.2–0.4 MPa) [10]. The low melt pressure operation significantly reduces fiber breakage, and allows a fast yarn impregnation rate. The thermoplastic pultrusion line was operated with an extruder mass flow of 0.75 Kg/h; the line speed of the sisal yarn was between 10 and 15 m/min. A continuous polymer/SF rod of about 1.5 mm in diameter was obtained. This continuous rod was then chopped into uniform pellets, typically 13 mm long. The fiber content of the pellets was measured, and averaged 70 wt%.

The pellets were then dry-blended at an injection ma-

TABLE 2. Polymers used.

Name	Composition	Melt index (g/10 min) (180/2.16)
PP	Unmodified commercial polypropylene	1.3
MA-g-PP	Commercial maleic anhydride grafted polypropylene	110
PP1000	PP, modified with 1000 ppm of 2,5-di(tert-butylperoxy)-hexane	23
PP1500	PP, modified with 1500 ppm of 2,5-di(tert-butylperoxy)-hexane	30
PP3000	PP, modified with 3000 ppm of 2,5-di(tert-butylperoxy)-hexane	64
PP9500	PP, modified with 9500 ppm of 2,5-di(tert-butylperoxy)-hexane	118
M1	Blend of MA-g-PP with PP9500 (15/85 w/w)	116
M2	Blend of MA-g-PP 3200 with PP9500 (30/70 w/w)	116
M3	Blend of MA-g-PP with PP9500 (70/30 w/w)	114

chine hopper with the required amounts of unfilled PP pellets. These blends were injection molded to make tensile specimens. The injection machine used has a barrel diameter of 45 mm. A regular injection nozzle was used, with a nozzle diameter of 3 mm. Tensile specimens were molded with specified mPP/SF, and PP concentrations. The SF concentrations used ranged from 0 up to 17.5 wt%. The injection process was carried out with the barrel temperature set at 180°C and a mass flow of 20.4 g/s.

Some of the SF/MA-g-PP/PP tensile specimens, containing 17.5 wt% of SF were chopped into smaller pieces and injection molded again under the same process conditions. SF from samples taken at each one of these stages were extracted. The polymer matrix was dissolved in a high-temperature Soxhlet extraction system, with boiling hot xylene acting for several hours. The fibers were then recovered by filtration, washed, dried, weighed, and measured. The number length distributions were studied, to verify the source of any fiber breakage during the two-stage process, and its effect on mechanical properties.

Melt viscosity for unfilled PP and four compounded blends were studied at 180°C. The compounds were prepared using SF/PP9500 pellets and SF/PP3000 pellets, melt blended with the required amounts of unfilled PP, and pelletized.

The equipment used to measure viscosity of the thermo-plastic compounds consists of a single screw extruder, a pressure sensor, and two capillary dies with different length and the same diameter. Measurements and corrections were performed as specified by ASTM D 5422-93.

Mechanical properties and optical observation of injection-molded specimens were used to analyze the adhesion between fibers and the polymer matrix.

Stress-strain curves were calculated from force-displacement graphs measured in an Instron 4467 Universal Mechanical Testing Machine. Tests were conducted under ASTM D 638 specifications.

Scanning electron microscopy (SEM) was used to study the break surfaces after mechanical test.

## VISCOUS HEAT GENERATION CALCULATIONS

The injection molding filling stage can be considered as an adiabatic process, depending on the value of a dimensionless number defined and used before [13, 14]

$$Ca = \frac{\alpha \times L}{V \times R^2} \quad (1)$$

Here  $\alpha$  and  $V$  are the thermal diffusivity and the average velocity of the polymer flow. If the  $Ca$  number is lower than  $10^{-2}$ , then the process is assumed to be in adiabatic regime. The polymer temperature increase can be calculated as:

$$\Delta T = \frac{\Delta P}{\rho \times Cp} \quad (2)$$

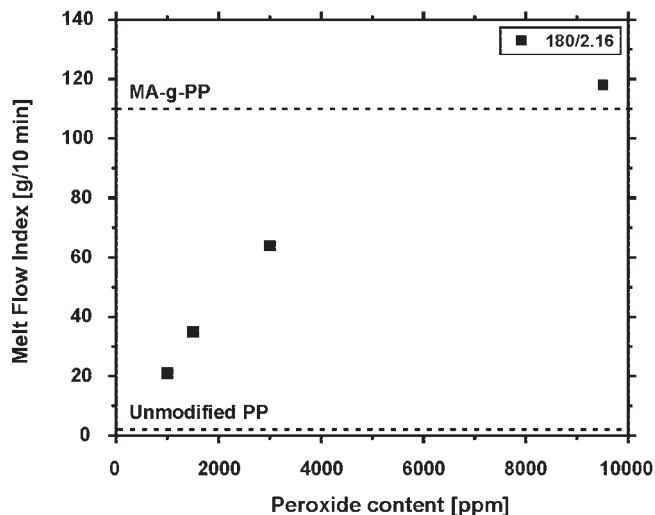


FIG. 1. Melt flow index values for all the used polypropylenes and for MA-g-PP.

where  $\Delta P$  is the pressure drop along the length of the tube,  $\rho$  the molten polymer density, and  $Cp$  the molten polymer heat capacity. For unmodified PP,  $\alpha_{180^\circ\text{C}} = 7.59 \times 10^{-8} \text{ m}^2/\text{s}$ . Considering a circular cross-sectional runner ( $L = 0.1 \text{ m}$  and  $R = 3.5 \times 10^{-3} \text{ m}$ ) with  $V = 0.885 \text{ m/s}$  and  $Ca = 2.45 \times 10^{-6}$ , the flow in the injection mold runner is adiabatic. Temperature rises for all the injections were calculated with this approach.

## RESULTS AND DISCUSSION

Figure 1 shows the MFI values for all the used polypropylenes, measured at 180°C and 2.16 Kg. Under these conditions, the unmodified PP shows a very low MFI of 1.3 g/10 min. Melt processing the unmodified PP with the addition of 2,5-di(tert-butylperoxy)-hexane causes the MFI to increase considerably. PP treated with 9500 ppm of organic peroxide shows a MFI = 118 g/10 min, very similar to the MFI of MA-g-PP.

The peroxide modification process allows us to obtain a PP with flow characteristics similar to MA-g-PP. The incorporation of SF increases the apparent viscosity of the molten polymer. Therefore, it is necessary to reduce the effective viscosity at the SF-matrix interphase by wetting the SF with small quantities of PP with very high MFI. Lowering this effective viscosity allows us to process the compound material by injection molding, avoiding the thermal degradation and diminishing the fiber breakage [15].

The peroxide modification process also reduces the PP toughness. The PP9500 is fragile and brittle. Similar mechanical characteristics are observed for the MA-g-PP.

Figure 2 shows the number length distribution of the individual SF for the final injection molded mPP/SF/PP composites. Before the injection molding, all the SF show a composite-pellet length of about 13 mm.

The SF/PP9500 and SF/MA-g-PP pellets were cut in

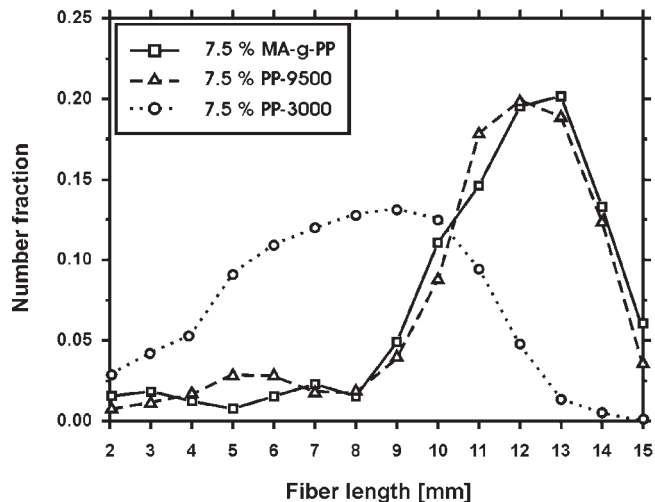


FIG. 2. Number length distribution for the individual sisal fibers.

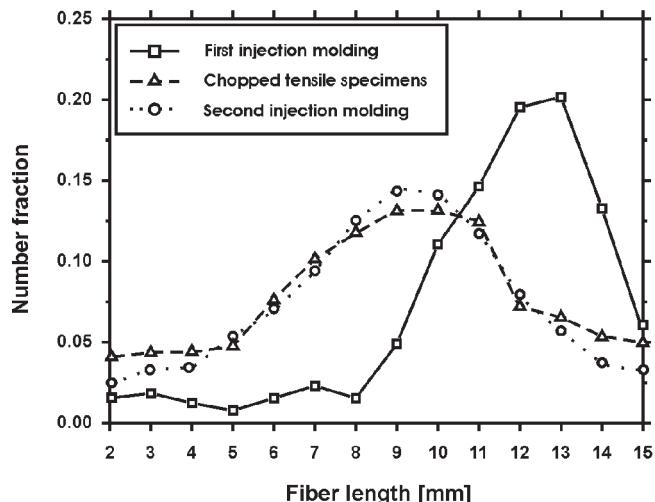


FIG. 3. Number length distribution of the individual sisal fibers, before and after reprocessing.

lengths varying in a narrow range, between 12 and 15 mm, and we understand that the fibers lengths in the pellets can be considered equal to the pellet lengths. SF extracted from parts that were injection molded from SF/PP9500 and SF/MA-g-PP show very similar length distributions. There is a large fraction of the population (over 90%) with lengths in the exact range of the original composite pellet length, and the rest (less than 10%) shows varied smaller lengths. Less than 5% of the total number of fibers in the pellets loaded at the injection machine break into pieces.

The SF length distributions after injection molding change when PP3000 is used in the composite pellets. The length distribution is much wider, and the average value is about half the average value before injection molding. Pellets made by SF impregnation with modified PP with lower MFI result in larger fiber breakage after injection molding.

This feature suggests that most of the fiber breakage occurs during the injection molding process, and not during the impregnation process.

Figure 3 shows three sets of data for number length distribution of the individual SF fibers obtained from: 1) original tensile specimens SF/MA-g-PP/PP composite made in the first injection molding process (squares); 2) tensile specimens that were made out in the first injection molding, after chopping to reduce to small pieces that can be directly loaded into the injection machine hopper for a second, consecutive injection process (triangles); and 3) SF/MA-g-PP/PP composites from tensile specimens made in the above mentioned second, consecutive injection molding process (circles). There is no appreciable difference between the size distributions corresponding to samples 2 and 3. Therefore, these data show conclusively that the decrease in the average longitude of fibers can be safely attributed to the pelletizing (chopping) process.

Figure 4 shows the measured melt viscosity for the SF/PP compounds, as functions of shear rate, at 180°C. Unfilled, unmodified PP viscosity is plotted in the same graph. The additions of 5% and 15% of SF/PP/PP9500

increase the melt viscosity of the unmodified PP by about 30% and 80%, respectively. On the other hand, the additions of 5% and 15% of SF/PP/PP3000 increase the melt viscosity of the unmodified PP by about 200% and 800%. The PP3000, with lower MFI, is less effective than PP9500 in reducing the final compound melt viscosity. Even the addition of 5% SF/PP3000 pellets increases the PP viscosity above the viscosity for the blend with 15% SF/PP9500 pellets.

Table 3 shows the adiabatic-heat-generation calculation in Poiseuille flow, as described above, for the five materials under analysis. This method does not include the small viscosity changes due to the melt temperature rise.

The incorporation of low molecular weight PP in the SF/PP compounds reduces the viscosity increase due to the fibers, and therefore allows keeping a conveniently lower viscosity under the injection molding process conditions.

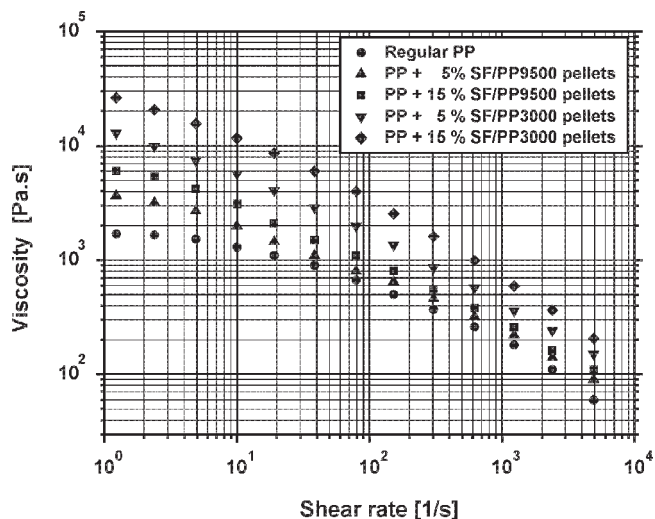


FIG. 4. Measured melt viscosity for the SF/PP compounds.

TABLE 3. Adiabatic-heat-generation calculation for poiseuille flow.

	$\gamma$ (1/s)	$\eta$ (Pa. s)	$\rho.C_p$ (J/m <sup>3</sup> .°C) $\times 10^{-6}$	$\Delta T_{ad}$ (°C)
Unmodified PP	1036.9	186.8	2.233	8.93
PP + 5% SF/PP9500	1137.1	208.2	2.225	10.95
PP + 15% SF/PP9500	1230.6	253.7	2.340	13.73
PP + 5% SF/PP3000	1270.1	355.5	2.225	20.87
PP + 15% SF/PP3000	1481.0	506.9	2.340	33.02

For this reason, the average bulk temperature rise over the runner lengths is moderate for the compounds with PP9500. Fung et al. [15] have also injection molded SF/PP compounds, adding MA-g-PP as a SF-PP coupling agent; their results also show a diminished SF thermal degradation during injection molding, and the effect is assigned to a lubrication effect of the MA-g-PP on the SF surface. It is also stated in that work that the SF/PP injection molding without the addition of MA-g-PP is not possible below 210°C while using a regular injection-molding machine (50 tons clamping force).

Figure 5 compares the after-molding coloring of two tensile specimens injected with the same process conditions. Specimen 1 (S1) contains 4.5 wt% of PP9500 and specimen 2 (S2) contains 4.5 wt% of PP3000. Viscous-adiabatic heating calculations suggest that—for an injection nozzle melt temperature of 180°C—the bulk temperature for S2 was higher than 213°C while the bulk temperature for S1 was lower than 195°C.

Figure 6 shows the tensile mechanical properties for SF/PP composites with and without the addition of MA-g-PP, for different SF contents. Increases in tensile strength and tensile modulus might be considered as evidence for an efficient adhesion between SF surface and bulk PP matrix.

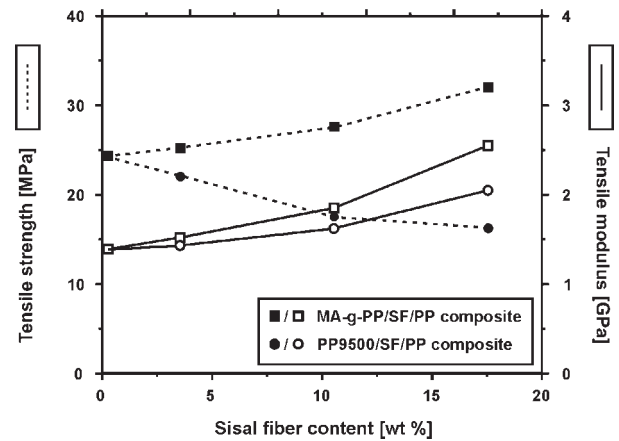


FIG. 6. Tensile mechanical properties for SF/PP composites with and without the incorporation of MA-g-PP.

Composites containing 17.5 wt% of SF and 7.5 wt% of MA-g-PP show a 28% increase in measured tensile strength, and an 85% increase in tensile modulus, when compared with unfilled PP.

We now compare composites with similar SF content, similar fiber length distribution, and injected with the same process conditions, without any MA-g-PP addition. Composites with 7.5 wt% of PP9500 reduce the unfilled PP tensile strength by 30% and only increase the unfilled PP tensile modulus by 57%. Other authors have also reported similar reductions for tensile strength for composites made out with polyolefins and cellulosic fibers [6], and the effect was assigned to poor fiber-matrix adhesion. The MA-g-PP addition seems to produce a good adhesion of the SF surface to the bulk PP matrix, resulting in an effective stress transfer between the fibers and the thermoplastic matrix.

The use of small quantities of MA-g-PP did not affect



FIG. 5. After-molding coloring of two tensile specimens with different compositions. S1 (lower side) and S2 (upper side).

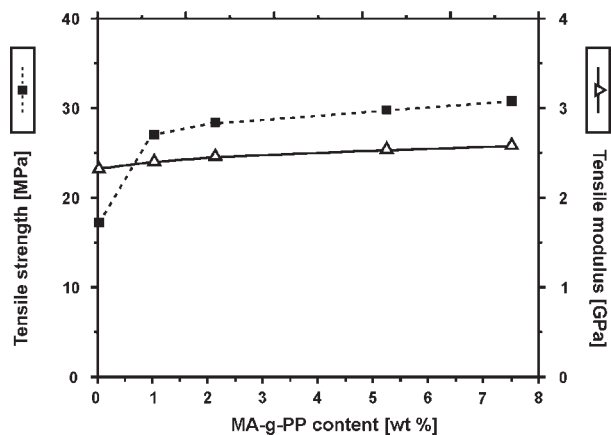


FIG. 7. Tensile mechanical properties for composites containing 17.5 wt% of SF.

substantially the tensile modulus for the samples in this study. The tensile modulus for PP reinforced with high-modulus fibers may increase due to at least two effects. For short fibers, the matrix-fiber adhesion is the main source for the modulus increase, while for long fibers at least part of the modulus increase is assigned by some authors to the formation of a transcrystalline zone around the fibers [3, 16]. For the samples used in this study—as the effect of the MA-g-PP on the composite modulus is very small—the most important contribution to the modulus increase is assigned to the presence of very long fibers. Also, the good fiber spatial distribution contributes to the high tensile modulus value, and to the increase in the tensile modulus value with the increase in fiber weigh content.

Use of MA-g-PP affects the composite tensile strength substantially. The anhydride functionality of MA-g-PP reacts with many cellulose fiber hydroxyl groups by esterification, giving strong chemical links between the fibers and the matrix [3]. During tensile tests, the PP matrix transfers stress to the fibers, and failure occurs mainly after the fibers break or when the fibers are pulled out, dragging out some of the MA-g-PP chains and consuming a large amount of energy.

Figure 7 shows measured tensile mechanical properties for composites containing 17.5 wt% of SF. The amount of MA-g-PP added to the composites is varied, always keeping a 30/70 wt% polymer/fiber relationship for making the pellets. The original composite pellets were obtained by the extrusion impregnation process and using PP9500, M1, M2, M3, and MA-g-PP to obtain growing proportions of MA-g-PP in the polymer in the composite pellets. A noticeable effect of the coupling agent is evident with the incorporation of only 1.125 wt% of MA-g-PP in the composite. Further increases in MA-g-PP content cause only a moderate rise of the tensile modulus and tensile strength for the composites. This fact indicates that the two-step procedure used for this work allows the use of small weight fractions of MA-g-PP, still obtaining an excellent SF/PP interfacial adhesion, and

the effect is due solely to the previous wetting of the SF surface with only the required amount of MA-g-PP.

Figure 8a and b shows the different adhesion effectiveness between SF and PP matrix, for tensile samples made out of composites with and without MA-g-PP. The adhesion between polar SF and nonpolar PP is very poor. For this reason, in tensile tests the SF are pulled out of the PP matrix with little stress transfer. Also, the nonbonded fibers act as PP matrix discontinuities or void nucleation points. In Fig. 8a, a large number of holes are shown, which come from fiber pullout from the PP matrix. On the other hand, in Fig. 8b, a considerably fewer number of pullout holes are shown, and many broken fiber ends—embedded in the PP matrix—are evident. From the observation of the tensile-fractured specimen micrographs it is clear that the adhesion between the SF and PP is much better for the composites with MA-g-PP.

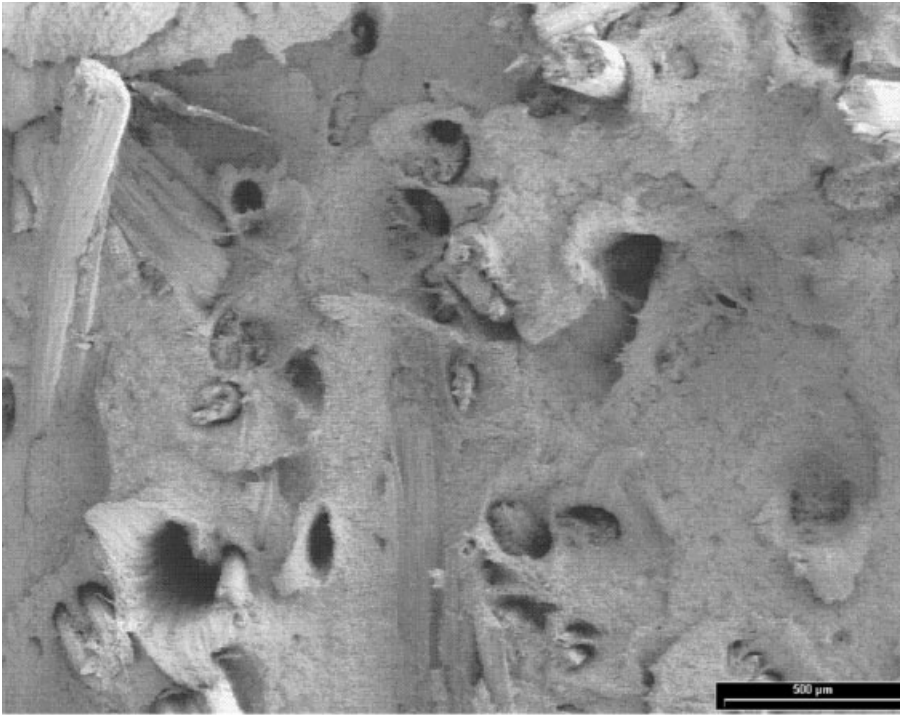
Figure 9 contains data for measured tensile modulus and tensile strength for three types of materials used for this study. All these composites contain 17 wt% SF, that correspond to 25 wt% of SF/MA-g-PP and 75 wt% of regular PP. The phrase “original composite” is used to design composites obtained in a first injection molding stage, while “reprocessed” is used for tensile specimens made from “original composite” pieces, chopped and injection molded again. The purpose of this figure is to show that the reprocessing of the composites made in this two-step process does not significantly affect the composite mechanical properties originally obtained in the first injection molding; the mechanical properties continue to be very good. These data show that the small changes in fiber length distribution caused by the reprocessing of these composites does not affect the composite mechanical properties much. This benefit is obtained because—for this fiber length range—these mechanical properties of SF/PP depend more strongly on the fiber/matrix adhesion than on the fiber length distribution.

## CONCLUSIONS

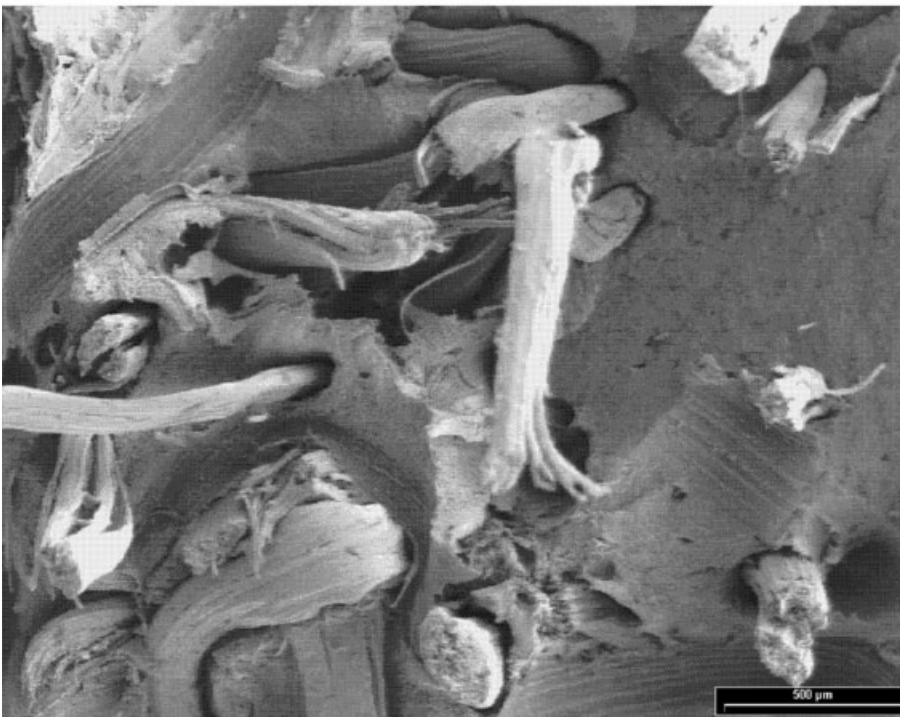
In this work we have shown that a new two-step process allows easier processing of SF/PP composites, controlling the final mechanical properties, sisal fiber thermal degradation, and cost.

As a first step, a single screw extruder and a thermoplastic pultrusion line were used to obtain long pellets made out of SF impregnated with small quantities of modified polypropylenes. The use of modified, low viscosity polypropylenes helps to give a good compromise solution for the three main problems involved in this process—namely fiber breakage, thermal degradation, and interfacial bonding—by reducing the bulk effective viscosity of the composite mixture during the injection molding, and acting as a coupling agent between the fibers and the PP matrix.

Tensile specimens were injection-molded in a second step. The usual PP/mPP/SF blending and the injection molding process were reduced to a single operation.



(a)



(b)

FIG. 8. SEM micrographs for tensile fractured surfaces of 24.5 wt% SF in PP matrix. a: Without the incorporation of MA-g-PP. b: With the incorporation of MA-g-PP.

A convenient lower limit is established for the MFI of the PP used to dilute the MA-g-PP at the fiber impregnation step, and injection bulk temperature rises are much reduced at low injection molding temperatures. Also, the SF breakage at the injected part is almost completely avoided, thus improving the measured mechanical properties.

The effect of the MA-g-PP concentration at the SF-PP interface is explored, and an economically convenient threshold is found.

A single recycling experiment was performed. The same processing conditions were used for both consecutive injections, without any additives used for the second injection



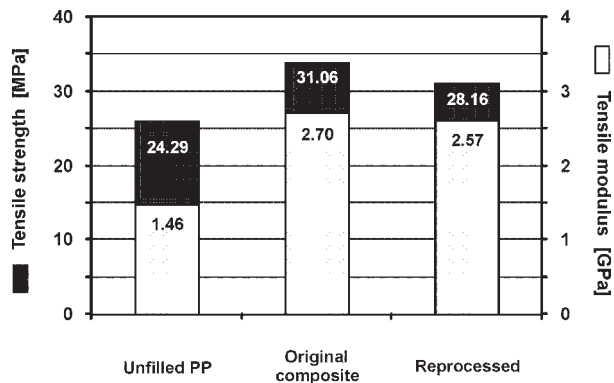


FIG. 9. Tensile mechanical properties for samples before and after re-processing.

stage. No thermal degradation was observed, and good mechanical properties were kept, showing that parts made by this two-stage process can be safely recycled, at least once.

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## REFERENCES

1. R. Karnani, M. Krishnana, and R. Narayan, *Polym. Eng. Sci.*, **37**, 477 (1997).

2. Y. Li, Y.-W. Mai, and L. Ye, *Comp. Sci. Technol.*, **60**, 2037 (2000).

3. R. Gauthier, C. Joly, A.C. Coupas, H. Gauthier, and M. Escoubes, *Polym. Commun.*, **3**, 287 (1998).

4. V.P. Cyras, S. Iannace, J.M. Kenny, and A. Vazquez, *Polym. Compos.*, **1**, 104 (2001).

5. C. Albano, J. Gonzalez, M. Ichazo, and D. Kaiser, *Polym. Degrad. Stab.*, **66**, 179 (1999).

6. J.M. Felix and P. Gatenholm, *J. Appl. Polym. Sci.*, **42**, 609 (1991).

7. A.C. Karmaker and J.A. Youngquist, *J. Appl. Polym. Sci.*, **62**, 1147 (1996).

8. K. Jayaraman, *Compos. Sci. Technol.*, **63**, 367 (2003).

9. D.M. Bigg, D.F. Hiscock, J.R. Preston, and E.J. Bradbury, *J. Therm. Compos. Mater.*, **1**, 146 (1988).

10. L.M. Arzondo, A. Vazquez, J.M. Carella, and J.M. Pastor, *Polym. Eng. Sci.*, **44**, 1766 (2004).

11. B. Vergnes and F. Berzin, *Macromol. Sympos.*, **158**, 77 (2000).

12. C. Tzoganakis, Y. Tang, J. Vlachopoulos, and A.E. Hamielec, *J. Appl. Polym. Sci.*, **37**, 681 (1989).

13. J. Agassant, P. Avenas, J. Sergent, and P.J. Carreau, "Energy and Heat Transfer Processes," in *Polymer Processing. Principles and Modeling*, Hanser Publisher, New York, 41–89 (1991).

14. A. Cameron, *Green Principles of Lubrication*, Lougmans, London (1966).

15. K.L. Fung, X.S. Xing, R.K.Y. Li, S.C. Tjong, and Y.W. Mai, *Compos. Sci. Technol.*, **63**, 1255 (2003).

16. A.K. Rana, A. Mandal, B.C. Mitra, R. Jacobson, R. Rowell, and A.N. Banerjee, *J. Appl. Polym. Sci.*, **69**, 329 (1998).