Processing and Mechanical Properties of Organic Filler–Polypropylene Composites

F. P. La Mantia,[1] M. Morreale,[1] Z. A. Mohd Ishak[2]

[1]*Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy*
[2]*School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Seberang Perai Selatan, Penang, Malaysia*

ABSTRACT: The addition of organic fillers into thermoplastic polymers is an interesting issue, which has had growing consideration and experimentation during the last years. It can give rise to several advantages. First, the cost of these fillers is usually very low. Also, the organic fillers are biodegradable (thus contributing to an improved environmental impact), and finally, some mechanical and thermomechanical properties can be enhanced. In this study, the effect of the addition of different organic fillers on the mechanical properties and processability of an extrusion-grade polypropylene were investigated. The organic fillers came from natural sources (wood, kenaf, and sago) and were compared to short glass fibers, a widely used inorganic filler. The organic fillers caused enhancements in the rigidity and thermomechanical resistance of the matrix in a way that was rather similar to the one observed for the inorganic filler. A reduction in impact strength was observed for both types of fillers. The use of an adhesion promoter could improve their behavior. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1906–1913, 2005

Key words: composites; fillers; mechanical properties; poly-(propylene) (PP); processing

INTRODUCTION

The first fillers studied and used for polymer-based composites were basically inorganic. The main reason that led to their use was the need for cheaper materials or for the significant improvement in some properties (rigidity, resistance to temperature, etc.) of the polymer matrix.[1] A new type of fillers has been recently investigated: organic ones.

There is a number of reasons suggesting the use of these fillers for composites: low cost, environmental issues (in fact, organic fillers are biodegradable and come from renewable sources, which gives rise to less concern about their disposal), fewer hazards to the health of the operators, and low specific weight in comparison to mineral fillers. Furthermore, organic fillers other than wood are preferable because of the decreasing availability of natural resources (especially wood) and the increase in the cost of raw materials and energy.[1–6]

According to literature data, several kinds of polymer–organic filler composites have been studied in recent years, especially those based on commodity polyolefin matrices.

Polyethylene has been studied in combination with wood fibers (WFs) and wood flakes,[7,8] corn starch,[9,10] potato starch,[9] sago starch,[11,12] sisal fibers,[3] and kenaf fibers (KFs).[13] On the whole, an elastic modulus (E) increase has been observed, whereas the ultimate properties have usually decreased.

Research on the utilization of natural organic fillers with polypropylene (PP) started only a few years ago. However, there is already great interest for possible application in industrial purposes. Among natural organic fillers that have been studied in combination with PP are WFs and sawdust,[14–17] flax,[18,19] sisal,[20,21] kenaf, jute, eucalyptus,[18] starch,[22] and also oil palm empty fruit bunches[2] and rice husk ashes.[23]

For instance, cellulosic fiber–PP composites have been reported to be used in the automotive industry for dashboards, rear window shelves, and roof and door upholstery;[21] kenaf has also been mentioned because of its good potential in producing light and rather noise-insulating panels.[24]

Organic fillers have been studied not only in conjunction with commodity polyolefins but also with

other polymer matrices, for instance, sisal fibers and polystyrene,[6] sisal fibers and Mater-Bi (which, however, is a rather different issue because the matrix is biodegradable as well and the aim is to obtain a biodegradable composite),[25] polycaprolactone and wood flour,[26] and starch and poly(ε-caprolactone).[27]

The aim of this study was to investigate the processability and the mechanical properties of a PP sample filled with different organic fillers and to investigate and compare them with those of short glass fiber (GF)-filled PP. These organic fillers gave rise to an enhancement in the rigidity and thermomechanical resistance of the PP matrix, like that observed for the inorganic-filler-filled material, although a reduction in the impact strength was observed.

EXPERIMENTAL

Materials

The PP used in this work was a material supplied by Basell (Milan, Italy), commercially known as Moplen C30S. The main characteristics were density = 0.9 g/cm^3, melt flow index = 6 g/10 min (at 230°C and 21.6 N), and melting temperature $\approx$ 170°C.

Four different fillers were used to prepare the filled polymers: WFs, KFs, sago starch (SS), and for comparison purposes, GFs were also used.

WFs, kindly supplied by Isoroy (Paris Orly, France), were produced by thermomechanical pulp from softwood. Both length (L) and diameter (D) were highly variable, ranging between about 20 and 80 μm for the D, and the L/D ratio ranged from about 20 to 150.

The generic name *kenaf fibers* is used for the fibers drawn out of the base of the homonym plant, *Hibiscus cannabinus l.* (Malvaceae), a very productive annual crop, strictly related to cotton, with aspect and properties similar to jute and hemp.[24,28] The material used in this work was kindly offered by KEFI, SPA (Reggio Emilia, Italy), in the form of ground and then palletized fibers; this technique allows one to store a large amount of ground fibers in a relatively small space. The pellets were then crushed so the ground fibers could be used for this study; the D of the fiber was 40–110 μm, and the L/D ratio ranged from 10 to 100. The main component of kenaf is cellulose, which accounts for about 73% of its total weight. Previous studies have reported a Young's modulus of about 60 GPa and a tensile strength (TS) of 11.9 GPa.[13] This kind of fiber has been suggested to be used as a filler only for polymers with processing temperatures below 200°C because higher temperatures would lead to thermal decomposition.

Sago starch is extracted from the trunk of a number of palms, first of all the *Metroxylon sagus*, coming as white-like granules. The product has an average particle size of 20 μm and a decomposition temperature of about 230°C.[12]

TABLE I
Composition, Processing, and Sample Codes of All of the Investigated Materials

Material	Sample code
PP (mixer)	PP-m
PP (extruder)	PP-e
PP + 30% GF (mixer)	GF30-m
PP + 30% GF (extruder)	GF30-e
PP + 60% GF (mixer)	GF60-m
PP + 60% GF (extruder)	GF60-e
PP + 30% WF (mixer)	WF30-m
PP + 30% WF (extruder)	WF30-e
PP + 60% WF (mixer)	WF60-m
PP + 60% WF (extruder)	WF60-e
PP + 30% KF (mixer)	KF30-m
PP + 30% KF (extruder)	KF30-e
PP + 60% KF (mixer)	KF60-m
PP + 60% KF (extruder)	KF60-e
PP + 30% sago starch (mixer)	SS30-m
PP + 30% sago starch (extruder)	SS30-e
PP + 60% sago starch (mixer)	SS60-m
PP + 60% sago starch (extruder)	SS60-e
PP + 30% sago starch + MnSt (mixer)	(SS30 + MnSt)-m
PP + 30% sago starch + MnSt (extruder)	(SS30 + MnSt)-e
PP + 60% sago starch + MnSt (mixer)	(SS60 + MnSt)-m
PP + 60% sago starch + MnSt (extruder)	(SS60 + MnSt)-e

E-type short GFs, produced by Vetrotex (Milan, Italy), had a density about 2.6 g/cm^3, a D of 10 μm, and an L/D ratio of about 450.

The composites were prepared with two different compositions, namely, 30 and 60 wt % filler. Sago-starch-filled samples were also prepared with the addition of manganese stearate (MnSt) as 10% of the filler content (and, therefore, 3 and 6% of the total sample weight). MnSt was also added to improve the processability and the dispersion of sago particles in the sago-starch-filled samples.

Processing

For the compounding operation, two different apparatuses were used, a Brabender batch mixer (Duisburg, Germany) and a Brabender twin-screw compounder (Duisburg, Germany). In the mixer, the mixing temperature was fixed at 180°C, and the rotational speed was 60 rpm. Mixing was performed for about 4 min, which was sufficient to achieve a constant torque and to minimize the PP degradation. The twin-screw Brabender compounder (model DSK 42/7; D = 45 mm, L/D = 7) was an intermeshing counter-rotating twin screw, which allowed intensive high shearing and crossflow. The thermal profile of the twin-screw compounder was 120, 160, and 180°C; the screw speed was set to 60 rpm.

Table I summarizes the composition and the processing devices used for all of the investigated materials and their sample codes.
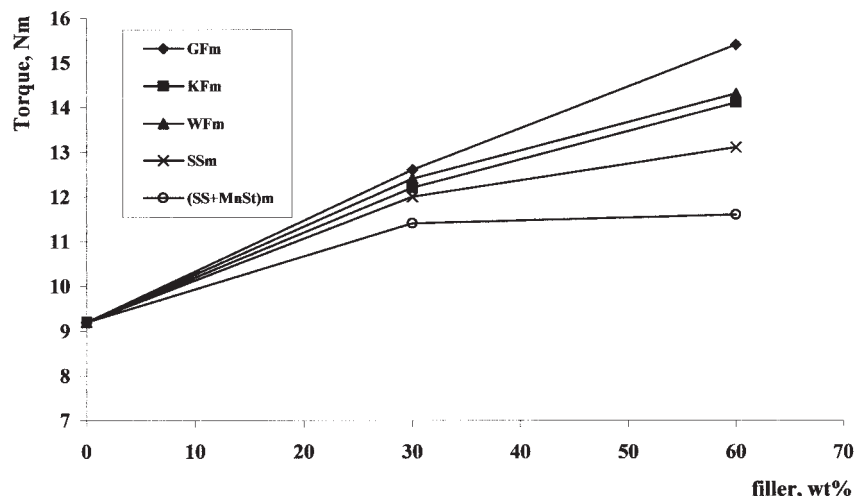
Figure 1 Torque as a function of the filler content.

The specimens for all of these tests were prepared by compression molding with a Carver laboratory press (Wabash, IN) at 180°C, with a molding time of approximately 3 min.

Mechanical and thermomechanical properties

The tensile properties were measured with an Instron universal testing machine (model 4443) (Canton, MA) on specimens (thickness $\approx$ 0.50 mm, width = 10 mm) cut out from compression-molded sheets, according to ASTM D 882. The crosshead speed was 5 mm/min, and the initial L was 30 mm.

The impact strength was evaluated on notched samples in Izod mode with a CEAST (Turin, Italy) apparatus (model 6545), according to ASTM D 256. Heat deflection temperature (HDT) values were determined following ASTM D 2990-77 (flexural load = 1.8 MPa, rate of increase in the temperature = 120°C/h) with an automatic CEAST apparatus.

For all of the tests, at least seven specimens were tested. The experimental data were quite reproducible ($\pm$10%); as for the composites with 60% filler, the reproducibility was not as good (up to $\pm$20%), perhaps because of poorer filler dispersion within the matrix.

RESULTS AND DISCUSSION

Processing

The torque during processing can be a useful parameter for evaluating the processability of the molten polymer systems. Indeed, the torque is a function of the viscosity of the melt in the processing conditions, and an increase in the torque is a direct measurement of the torque under these conditions. The torque values recorded at the end of the mixing for PP and for the PP–filler composites are plotted in Figure 1. Torque increased (and, therefore, processability decreased) in the presence of the fillers and with increasing filler content. The largest rise in the torque, and then of the viscosity, was shown in particular by the GF-filled materials. Sago starch caused the lowest increase in torque, and the presence of the stearate reduced the value of the torque.

We interpreted the larger rise in the torque for the GF-filled materials considering the fact that on average, GFs presented a larger value of the aspect ratio than WFs and KFs. This characteristic of the filler was the most important factor determining the rise of the viscosity in the filled polymers. Sago starch particles were in the form of powder and were almost spherical ($L/D \approx 1$) and, therefore, caused a lower rise in the

TABLE II
Fibers L and D Values Before and After Processing (Minimum to Maximum Values)

Filler	L (μm, virgin)	D (μm, virgin)	L/D (virgin)	L (after)/L (before), 30% filled samples (%)	L (after)/L (before), 60% filled samples (%)
Glass	~4,500	10	~450	2.5–22	—
Wood	1,600–12,000	20–80	20–150	2.5–23	1.3–20
Kenaf	430–4,000	40–110	10–100	7.5–75	6.3–58

TABLE III
DSC Test Results for Virgin PP, PP-m, and PP-e

Material	ΔH (J/g)
Virgin PP	71.2
PP-m	80.8
PP-e	72.3

ΔH: absorbed heat flow during the melting of the polymer sample.

viscosity. The presence of the stearate acted as a lubricant and decreased the viscosity of the melt.

The slope of the torque–filler content was high at low filler concentration and decreased with increasing filler content. This phenomenon could be interpreted by considering two different features. The first feature was correlated with the different non-Newtonian behavior of the materials with different filler contents. Indeed, with increasing viscosity (due to the higher filler content), the non-Newtonian behavior increased as well, and this led to a lower viscosity in the processing conditions as the filler content increased. In particular, rheological tests were performed for all of the samples by both a rotational and a capillary viscosometer. Unfortunately, the results showed a remarkable irreproducibility for all of the filled samples. These results may be interpreted with the important role of filler humidity considered. Humidity content caused the production during the tests at high temperature of vapor bubbles, which strongly disturbed the experimental tests. Surprisingly, this behavior occurred even though tests were performed on 24-h oven-dried samples, which was probably due to a difficult elimination of water molecules from the bulk. The second feature was correlated to the possible breaking of the fibers due to the mechanical stress acting on the melt during processing, which of course,

increased with increasing the viscosity and with the filler content. Then, the higher the viscosity (higher L/D ratio) was, the larger the stress and the breaking of the fibers that became shorter were. In particular, all of the fibers showed significant rupture after processing (see Table II). The highest attrition was shown by GFs and WFs, followed by KFs; these data confirmed all of the previous considerations.

As previously reported, a shorter L/D ratio of the fibers provoked a lower rise in the viscosity. Moreover, the higher mechanical stress could give rise to some degradation of the PP matrix, which could undergo rupture of the macromolecules. These considerations were also supported by the data from differential scanning calorimetry (DSC) tests performed for PP samples [both from the mixer (PP-m) and extruder (PP-e) and for the virgin PP; see Table III], which showed that the enthalpy of fusion increased in the processed materials. This occurred because with increasing thermomechanical stress in the processing operations, the molecular weight decreased, and consequently, the crystallinity degree rose. The degradation was larger in the mixer because of the longer processing time (more than twofold than in the extruder).

Mechanical properties

The values of the tensile properties [E, TS, and elongation at break (EB)] are plotted in Figures 2–4 for both the mixed and extruded samples.

On the whole, all of the filled systems showed a degree of stiffening, which increased with the filler content, and as a consequence, the material became more and more fragile; the presence of filler resulted in an increase in E. As expected, it also led to a reduction in TS and EB. This can be easily observed in the stress–strain curves shown in Figure 5 for some of the investigated samples.
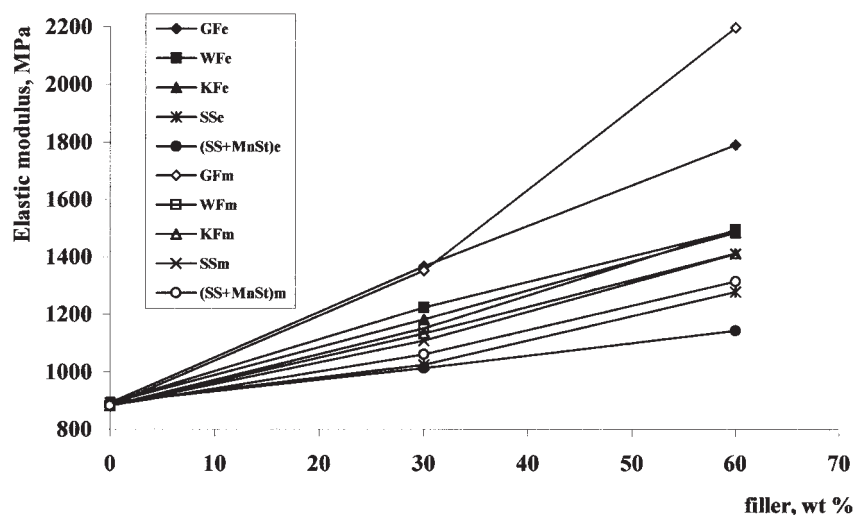
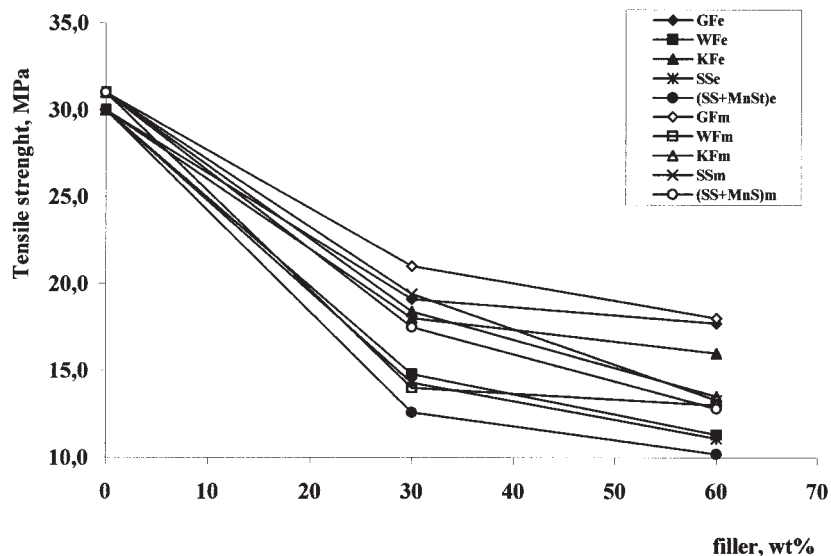**Figure 2** E as a function of the filler content.

Figure 3   TS as a function of the filler content.

The best performance among all of the fillers was achieved by GFs. In particular, with 60% of this filler, the modulus was twofold the initial value, whereas the reduction of the breaking characteristics was the lower one. However, KFs were rather interesting because the obtained results were near to those of the GFs. Sago starch gave the lowest enhancement of *E*, whereas the breaking values were similar to those of the other systems. In particular, the sago starch systems with added MnSt showed performed slightly worse than the ones without MnSt; therefore, the additive succeeded in producing better processability without any considerable worsening of the tensile properties. The improved interfacial adhesion, however, did not seem to have any significant improvement.

There were not significant differences between the mixer-processed samples and the extruder-processed ones, except for the 60% GF sample from the mixer and all of the sago-based samples from the extruder, for which the overall performance was lower.

With regard to 60% GF-based system, these effects were likely due to an early degradation in the mixer (as already mentioned), followed by a recrystallization of the macromolecules, which led to a higher rigidity. This was confirmed by the fact that virgin PP itself was subject to the early effects of a degradation, and it is well known that filled materials show a higher sensitivity to degradation than the virgin ones. This seems to be due to viscosity increases at low frequencies.[29]
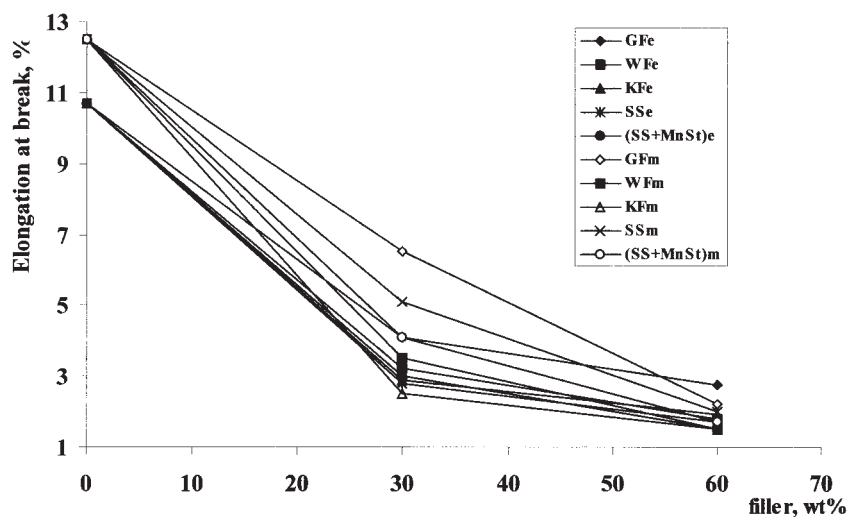

Figure 4   EB as a function of the filler content.
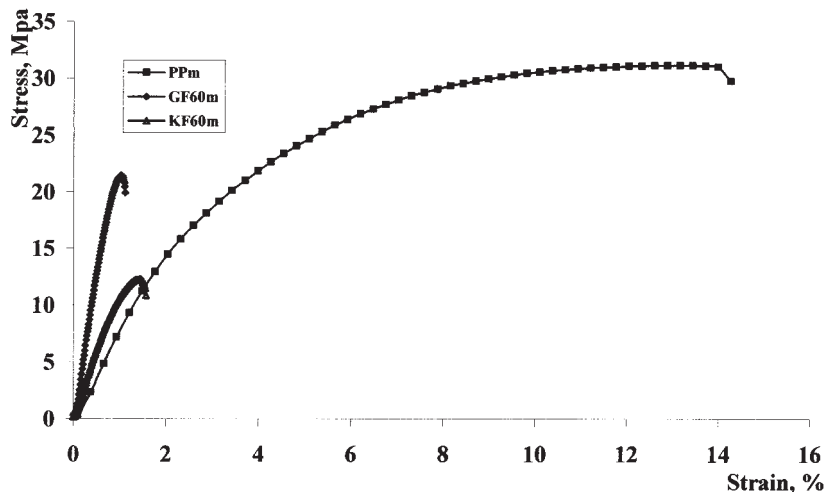
Figure 5 Stress–strain curves for some materials.

For the sago-based materials, poorer performance in the extruded material (in comparison with mixed material) could be interpreted by the fact that sago starch particle dispersion in the matrix was well inferior in the samples processed by the extruder: it was clear that the extruder-processed samples showed clusters of sago particles (and, consequently, a rough surface), whereas the mixer-processed ones were much more uniform, both in color and smoothness. The reason for this different behavior can be explained once more by the role of humidity: in fact, recent studies have highlighted that sago starch shows a deep tendency to water absorption and, thus, the formation of agglomerates of particles in a polymer matrix:[12] it is reasonable to consider that the mixer allowed a better elimination of humidity from the charging hole by evaporation, whereas this was impossible for the extruder (which

had no venting facility). Thus, the higher humidity level may have led to the agglomeration of the sago particles.

The impact strength values are shown in Figure 6. The impact strength was slightly enhanced only in the GF-filled systems, whereas all of the other fillers worsened it; this behavior increased with increasing filler content. KF and sago starch performances were similar to WF ones. The results were in line with literature data and predictions.[1,2,30]

The results for the HDT determination tests are plotted in Figure 7. It was easy to anticipate an increase in HDT with increasing filler content (even though the enhancement obtained passing from 30 to 60 wt % was less than we expected).

The best results were achieved with GFs, whereas a less significant effect was displayed by sago starch; KF behavior was rather similar to that of WFs.
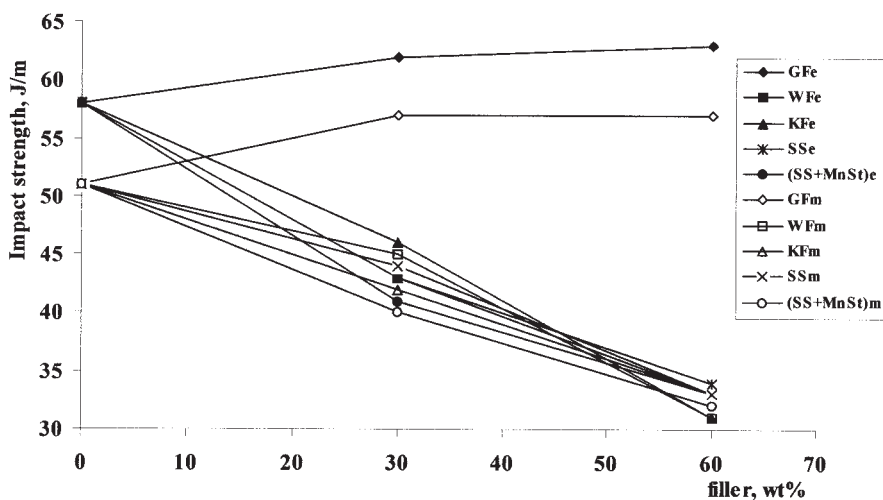

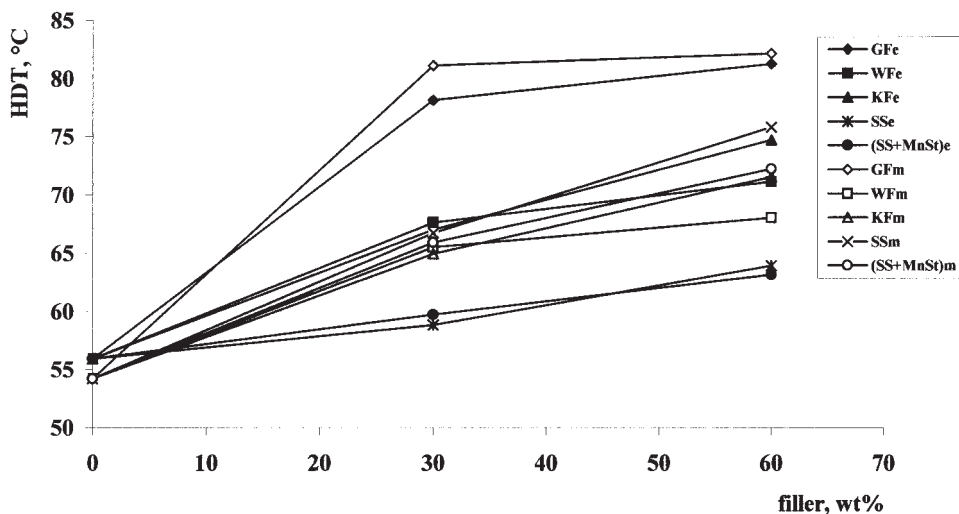**Figure 6** Impact strength as a function of the filler content.

Figure 7 HDT as a function of the filler content.

CONCLUSIONS

The addition of fillers to the PP matrix causes, according to several studies performed with inorganic fillers, an enhancement in E (and therefore of stiffness) and a reduction in TS and EB. These effects were more marked with increasing filler content. Furthermore, all of the fillers enhanced thermomechanical resistance but caused a reduction in impact strength (except for GF-reinforced systems).

The best overall mechanical performances were provided by GFs (the reference inorganic filler), albeit they gave some problems in term of cost and processing. The alternative natural fillers showed somewhat interesting mechanical properties. In particular, kenaf and sago may be regarded as valid substitutes for the more famous WFs.

The processing technology did not significantly affect those properties, except for in the sago-starch-filled systems. This was been attributed to the hydrophilic nature of sago starch, which led to agglomeration.

All of the filled systems showed a higher viscosity than the virgin matrix, thus they were more difficult to process. This effect increased with increasing filler content. However, kenaf and sago produced the lowest increase, whereas the inorganically filled samples exhibited the worst processability.

Processing by the mixer led to slightly lower viscosities than processing by the twin-screw extruder. The addition of MnSt did not lead to any improvement in mechanical properties, although it lowered the viscosity of the sago-starch-filled PP composite.

The processing technology did not greatly affect final results except for, once more, the sago-starch-filled samples.

Kenaf and sago are, therefore, interesting alternatives for wood within the family of natural organic fillers (e.g., kenaf-based composites have an appearance similar to the darkest wood species) to produce materials that are both low in cost and more environmentally friendly than conventional unfilled polymers. However, to achieve significant enhancements in terms of mechanical resistance (especially for impact strength), it would be necessary to develop specific compatibilizers to overcome the difficulties related to filler dispersion in the matrix and interface adhesion between the filler and matrix.

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