Highly Filled Formaldehyde-Free Natural Fiber Polypropylene Composites[1]

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ABSTRACT

Considerable interest has been generated in the use of lignocellulosic fibers and wastes (both agricultural and wood based) as fillers and reinforcements in thermoplastics. In general, present technologies limit fiber loading in thermoplastics to about 50% by weight of fiber. To produce high fiber content composites for commercial use while maintaining adequate mechanical properties requires innovative processing techniques. A new technique has been developed that allows very high fiber loading. We have processed composites up to about 95 % by weight of fiber in polypropylene (PP). The process involves some additional processing steps, in addition to conventional compounding techniques, to achieve such high fiber content in PP.

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Studies on about 85 % kenaf-PP composites indicates that properties such as flexural modulus and strength are superior to most types of wood particle, low and medium density hardboards. The fiber Orientation is predominantly two dimensionally random for the kenaf-PP composite. The stiffness of the new materials (85 % by weight of kenaf) is very high, and comparable to high-density fiberboards. The range for the flexural strength (MOR) of medium density fiber-boards (MDF) using phenol formaldehyde as the binding system is typically from 13 MPa to 42 MPa. The flexural stiffness (MOE) range for MDF boards is from 2.24 GPa to about 4.9 GPa The high range for flexural strength of high-density fiberboards is typically about 70 MPa and the flexural stiffness about 7.58 GPa. The high density kenaf fiber polypropylene composite, with an MOR of 73 MPa and an MOE of 7.43 GPa has comparable properties to conventional high density fiberboards. Thermal analysis of the kenaf composites indicates that the crystallinity of the PP in the composites is not significantly affected.

INTRODUCTION

Considerable interest has been generated in the use of lignocellulosic, both agricultural (1,2) and wood based, and wastes as fillers and reinforcements in thermoplastics. In general, present technologies limit fiber loading in thermoplastics to about 50% by weight of fiber. To produce high fiber content composites for commercial use while maintaining adequate mechanical properties requires innovative processing techniques. A new technique has been developed that allows very high fiber loading. We have processed composites up to about 90 % to 95 % by weight of fiber in polypropylene.

Use of the higher strength bast fibers such as kenaf, jute, hemp, flax, etc. will result in high mechanical properties as long as there is good interfacial bonding to obtain adequate stress transfer. Kenaf was chosen for the study because it is now a fiber crop grown commercially in the United States. Several other fibers isolated from annual growth crops (jute, hemp, and flax) have potential as reinforcing fillers in plastics. The choice of the fiber for plastics applications depend on the availability of the fiber in the region and also on the ultimate composite properties needed for the specific application. Kenaf filaments are extracted from the bast of the plant *Hibiscus cannabinus.* These filaments consist of discrete individual fibers, generally 2 mm to 6 mm long, which are themselves, composites of predominantly cellulose, lignin and hemicelluloses. Filament and individual fiber properties can vary depending on the source, age, separating techniques, and history of the fiber. Furthermore, the properties of the individual fibers are difficult to measure and we have not done so.

EXPERIMENTAL METHODS

Kenaf fibers were cut to about 2 cm in length. The fibers and polymers were specially treated in order to attain such high fillings in composites- this will be discussed when presenting the paper. A polypropylene homopolymer (PP- Solvay 1602) and a maleated polypropylene was used as a coupling agent. The short fibers, MAPP and PP (the latter two in pellet form) were compounded in a one-liter high intensity kinetic mixer (Synergistics Industries Ltd., Canada) where the only source of heat is generated through the kinetic energy of rotating blades. The fibers and polymers were inserted into the

blender and compounded at 5000 rpm that resulted in a blade tip speed of about 30 m/s. The compounded mass was then automatically discharged at 200 °C. The precise time to discharge depended on the amount of fiber and polymer, and their ratios. On an average the time of blending varied from 2 to 3 min with higher fiber content blends taking longer to reach 200 °C. The compounded mass was then immediately pressed in a hot press.

Four flexural specimens and four impact specimen were cut from each of the three boards. Specimen dimensions were according to the respective ASTM standards. Samples were stored in controlled conditions prior to testing. Tests were conducted according to standard ASTM tests: Izod impact strength tests according to ASTM D 256-90, and flexural testing using the ASTM 790-90 standard.

RESULTS AND DISCUSSION

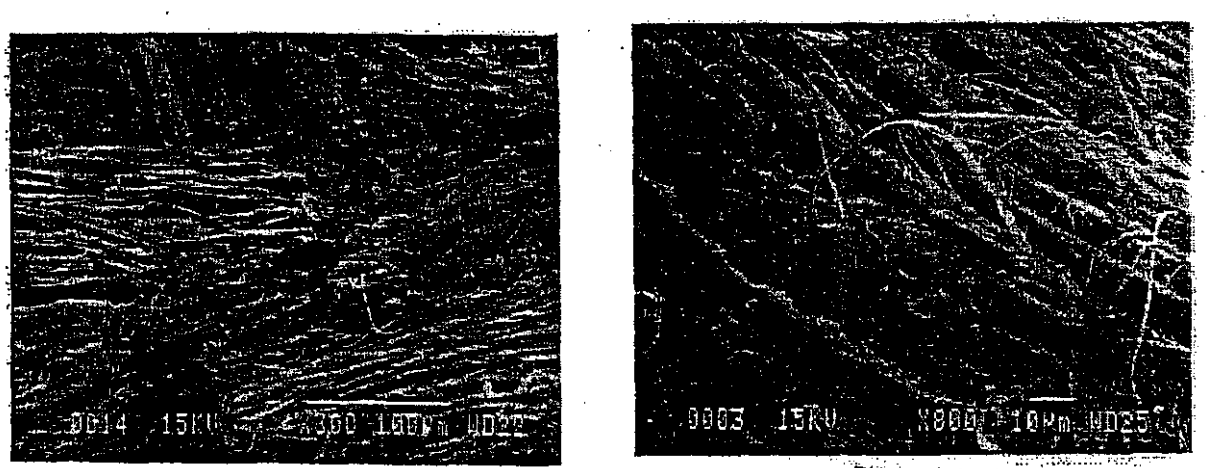
Studies on 85 % kenaf-thermoplastic composite indicates that properties such as flexural modulus and strength are superior to most types of wood particle, low and medium density hardboards. These results indicate the stiffness of the new materials (85 %by weight of kenaf) is very high, and could even compete with oriented strand board in some applications, (Table 1). The data for the 85 % composites were obtained from three different boards, with four specimens from each of the boards. *Note that the 85 % composites were compression molded and therefore the fibers were randomly oriented.*

Scanning electron microscopy of above 85 % boards showed that the matrix appears in a continuous phase and the bonding between the fiber and matrix is good, figure 1 a and b. There are some voids present in the composite and this is seen in figure 1 a. Fig. 1 b shows a

close-up of a fiber in an unnotched Izod test specimen. Considerable energy has been absorbed causing the fiber to split, resulting in fine fibrils being exposed.

TABLE 1: Comparison of Flexural Properties of Commercial Available Formaldehyde Based Wood Composites with Data on ~85 % filled Kenaf-PP composites. Standard deviation in brackets for the kenaf composites.

	Strength Range (MPa)		Modulus Range (GPa)	
	low	high	low	high
High Density Fiberboards (commercial)	38	69	4.48	7.58
Medium Density Fiberboards (commercial)	13.1	41.4	2.24	4.83
85 % kenaf–PP(compression molded- random alignment)	75 (± 9)		7.43 (± 0.5)	
60 % kenaf-PP injection molded (significant fibers alignment)	110		10.1	



(a) (b)

Figure 1. Fracture surface of 85 % kenaf composite (a) Izod notched (x300) and (b) Izod unnotched (x800).

The incorporating of a high fiber volume fraction in the composite poses practical difficulties in terms of formation or uniformity of mass distribution. The maximum volume fraction of perfectly aligned cylindrical and rigid fibers that can be packed into a composite is theoretically 90%. This is lower for randomly distributed fibers. However, it is possible that parts of the amorphous part of kenaf fibers, lignin and hemicellulose, can blend in with the PP/MAPP thermoplastic polymer and be part of the overall matrix.

The lignin content in kenaf fiber is reported to be between 15 to 19 % and the hemicellulose content around 22 and 23 %. The crystalline cellulose content of kenaf fibers can vary between 44 and 57 % in the natural fiber. Thus for an 85 % kenaf filled PP/MAPP, the amount of lignin and hemicellulose content in the composite works out to be approximately 34 %. If one uses 55 % for the amount of cellulose content in kenaf fiber, then the 85 % by composite will have about 47% crystalline cellulose (the reinforcing element), 15 % PP/MAPP, and about 34 % lignin and hemicellulose in the blend. The lignin and hemicellulose is plasticized to allow molecular chain mobility. Thus, if one looks at this point of view, it is not inconceivable to have highly filled kenaf composites, since the reinforcing element is far below the limits imposed by packing of fibers in a composite.

Differential thermal analysis and dynamic mechanical analysis of the 85 % composites were compared to 60 % kenaf-PP composites that were also compatibilized using MAPP. The 60 % composites were not plasticized and samples were prepared by injection molding. DSC results indicate there is little difference in the onset and peak crystallization and the melting temperatures between the kenaf composites (table 2). This could indicate that the plasticizer used does not affect this factor. The percent crystallinity of the 85 % was marginally lower than the 60 % composite. These data were from an

average taken from two samples. It must be noted that we used about 10 mg of the composite for DSC data collection. The estimation of the exact percent of the plastic matrix in the 10 mg samples is needed to get accurate % crystallinity data. So the difference in the % crystallinity between the 85 % and other composites may result from a fluctuation of composite composition rather than representing the true value. All we can conclude is that the percent crystallinity of the 85 % composites is not much different from the other composites.

TABLE 2: Crystallinity data of the plastic matrix for kenaf composites. (MAPP was used as the compatibilizer/ coupling agent; Pure PP crystals- crystallization enthalpy = 209.3

Composite Type	Tc (°C) – peak	Onset Tc (°C)	Tm (°C) peak	% crystallinity
PP- 100%	110.63	116.33	161.70	44.5
60–PP/MAPP (injection molded)	122.96	127.12	163.67	44.1
85 % -PP/MAPP (compression molded)	122.96	127.51	163.70	42.6

The DMA spectra of the 85 % filled composites show some interesting features when compared to a 60 % filled kenaf composite that was injection molded. It should be noted the 60 % composites were injection molded, which results in significant amount of fiber alignment. This is as opposed to the compression molded 85 % composites where the fibers were randomly distributed. At low temperatures, the 60 % composites have a higher storage modulus (E'), which suggests a brittle material at these temperatures. However, after about 10 °C, the 85 % composites have a higher modulus. The difference in storage moduli become even more pronounced as the temperature increases. The

softening temperature of the 85 % is also higher than the 60 % composite. The lower modulus at low temperature and the higher modulus at higher temperature is an advantage of the 85 % composite, since the composite is not as brittle as the 60 % at lower temperatures but maintains its integrity better at higher temperatures.

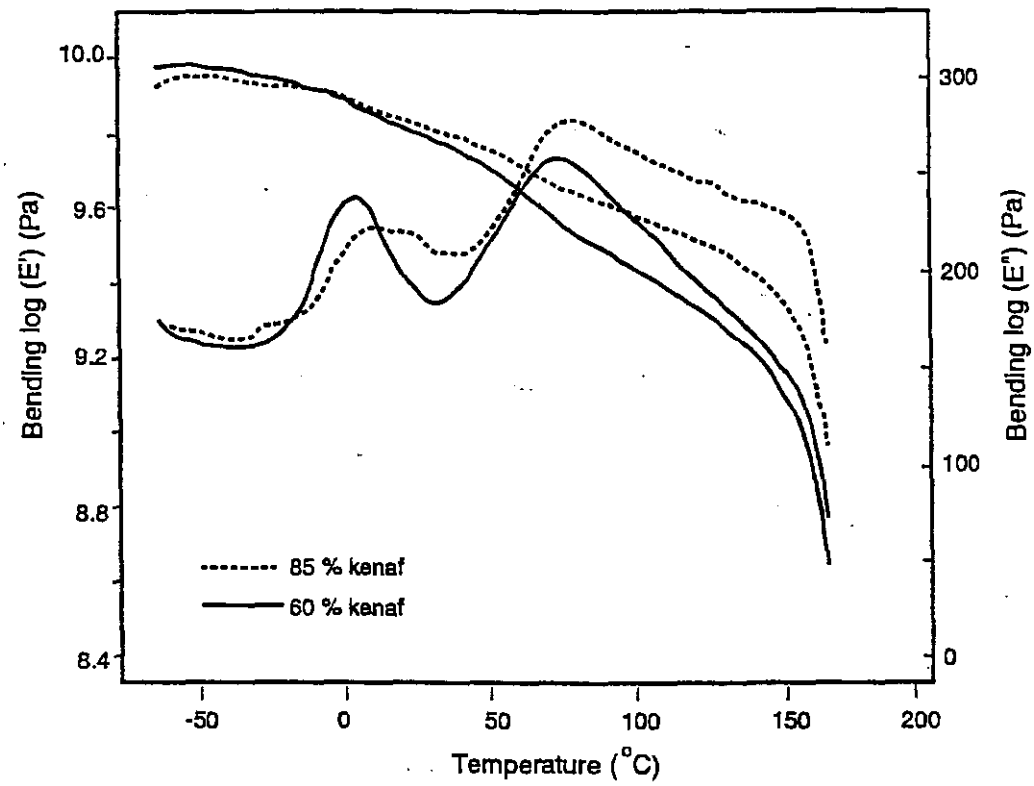


Figure 2. Storage and loss modulus of a 85 % fiber filled composite compared to injection molded 60 % fiber filled composite.

In terms of the loss modulus (E") spectra, two transitions can be clearly seen. The β transition, occurring at about 10 to 25 °C is associated with the glassy-rubbery transition of the amorphous chains of the polymer. The a transition is related to the crystallites, but the relaxation occurs due to the presence of "rigid" amorphous molecules present in the crystal (3, 4, 5). These regions disrupt the purity of the crystals and thus can be termed as defects. The β relaxation for the 85 % composite is much wider than the 60

% composite. The wider relaxation generally indicates that some of the amorphous molecules are more restricted than others. This is possible when amorphous molecules bridge two crystals and result in higher temperatures for their glass-rubbery transition. Secondly, any amorphous molecules near the fiber surface are restricted in mobility due to interactions with the solid fiber surface. Since the 85 % composite has a significantly higher fiber surface exposed to the matrix, the polymer molecules near the surface have restricted mobility and therefore result in highex β relaxation temperatures.

CONCLUSION

The plasticization technique allows the processing of highly filled composites using melt blending technology. Highly filled 85 % kenaf fiber PP composites show some interesting results. Their flexural properties exceed those of typical, commercially available formaldehyde based wood composites. DSC and DMA results were compared to 60 % injection molded kenaf-PP composites that were prepared without using the plasticization technique. The DSC results indicate that the crystallinity of the PP matrix phase is not significantly affected in the 85 % composite. The dynamic mechanical properties of the 85 % composites has a higher storage moduli above 10 °C and a higher softening temperature as compared to the 60 % kenaf-PP composite. The flexural modulus and strength (MOR and MOE) of the 85 % kenaf-PP composites are superior to most types of wood low, medium and high density fiberboards.

The possibility of using highly filled agro-based fiber thermoplastic composites for furniture, automotive and building applications makes this a particularly attractive

material for countries that have scarce wood resources or those countries that want to develop crops for new uses to save precious forest resources.

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Problem 3 Improved techniques are needed tor better understanding of the Interface and Interphase chemistry between wood-based resources and other resources to Improve surface interactions.

FY2000 Research Attainments

Publications

Extramural

Sanadi, Anand R.; Caulfield, Daniel F. 2000. Highly filled formaldehyde-free natural fiber polypropylene composites. In: Third international symposium of natural polymers and composites-ISNaPol/200 and the workshop on progress in production and processing of cellulosic fibres and natural polymers; 2000 May 14-17: Sao Pedro, SP. BR. 10 pgs.