Thermoplastic Polyolefins as Formaldehyde Free Binders in Highly Filled Lignocellulosic Panel Boards: Using Glycerine as a Processing Aid in Kenaf Fiber Polypropylene Boards

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A new technique was developed to make highly loaded (up to 95%) formaldehyde free natural fiber boards. The purpose of the paper is to report a broad study on 85% kenaf boards using linear thermoplastic polymers as the binder in preparing the boards to determine if these materials have potential in commercial applications by comparing them to other commercial materials. In these materials, linear thermoplastic polymer chains act as an adhesive and the product resembles a typical wood based panel (e.g., phenol formaldehyde fiber board). The process involved the use of small amount of glycerine in the fiber to enhance processibility in a thermo-kinetic mixer followed by hot pressing. In this paper, we report the properties of 85% by weight kenaf fiber boards using polypropylene as the adhesive. A maleated polypropylene was used to improve the adhesion and stress transfer between the adhesive and kenaf fiber. The addition of 2% by weight of glycerine based on the dry weight of kenaf fiber resulted in the best properties of the boards. Differential scanning calorimetric studies suggested that the glycerine had a little effect on the percent crystallinity of the matrix. Dynamic mechanical tests of the 85% boards showed some differences compared to conventional 60% by weight kenaf-PP composites. The 85% kenaf boards had a flexural strength of 75 MPa and a flexural modulus of 6.8 GPa with a specific gravity of 1.24. These properties are comparable to standard formaldehyde free high density hardboards with flexural strengths of 48.3 MPa and flexural modulus of 5.5 GPa, and a specific gravity of 1.28. This paper gives a broad overview of an initial study of these new materials.

Keywords: wood panel boards, hard boards, wood composites, binderless hardboards, kenaf boards, lignin plasticization

1. Introduction

Wood based fiberboards are used extensively throughout the world in both the building and furniture industries. There are concerns regarding the use of toxic chemicals such as formaldehyde, phenols and isocyanates, and there is interest in developing new fiberboards without the use these chemicals. Research is ongoing in the development of fiberboards from various sources of fiber and also in studying the plasticization of lignin to obtain a deeper understating of board properties. There has also been research into the use of powder kenaf core in binderless boards.

The use of natural fibers and wood fibers as fillers and reinforcements in thermoplastics has increased recently, with considerable growth in the automotive and building materials sector. In the United States the building and construction industry is the predominant consumer of these materials, and this market is growing in Europe. In Brazil, fibers such as sisal have great potential and are used in the automotive sector and have great potential in the building and construction industry. There have also been studies of using non-wood natural fibers as reinforcements in polyester and other thermoset polymers.

A new technique was developed that allowed very high fiber loading, up to 95% by weight of kenaf fibers in polyolefins. This technique involved the use of glycerine during the compounding of the composite which permits high fiber loading in the polyolefins, without thermal degradation of the fiber. Initially we modeled the system as a typical natural fiber composites in which the matrix is the continuous phase and reinforced with kenaf fibers. However, additional experiments and a recent review of the work along with additional scanning electron microscopy have given us new insights into this material. It appears that linear polyolefin chains act more as a binder and adhesive between the kenaf fibers, similar to traditional wood composites, such as particle and fiber boards with urea or phenol formaldehyde adhesives. In these materials, typical thermoplastic polymers have been used as binding agents in natural fiber boards.

At present, in commercial applications, the amount of fibers or fillers being used is generally limited to about 60% and below by weight of fibers in the thermoplastics. In these systems, these materials are true fiber reinforced polymers since the polymer is in a continuous phase with fibers or fillers dispersed in the material. There are applications where higher lignocellulosic content thermoplastics are used commercially. For example, products from Strandex Corporation (Madison, WI, USA) are directly extruded using 70% wood fillers in plastics. However, their process is exclusive to extrusion, where higher viscosities are permissible. Also, to achieve higher performance, the process must also include thermosts (unsaturated binding agents e.g. isocyanates, polyurethanes) to help in binding the system together. We are not aware of any study or report on highly filled natural fiber composites with fairly high aspect ratios, at loadings greater than 75%. The aspect ratio of the kenaf fibers we have used can be higher than 100.

The inherent polar and hydrophilic nature of the lignocellulosic fibers and the non-polar characteristics of the polyolefins create difficulties in compounding and result in composites with low stress transfer efficiency. Proper selection of coupling agents and other additives are necessary in improving the interaction, adhesion and stress transfer efficiency. The use of maleated polyolefins as compatibilizers/coupling agents in lignocellulosic-polyolefin systems is well established.

The purpose of the paper is to report a broad study on 85% kenaf boards using linear polymers (PP/MAPP) as the binder in...
preparing the boards to determine if these materials have potential in commercial applications by comparing them to other commercial materials. The amount of glycerine used to make these boards was optimized for the best properties. Differential scanning calorimeter (DSC) studies were conducted to determine if glycerine had any effect on the crystallinity of the PP based binder system. Dynamic mechanical analysis (DMA) was used to compare the low and high temperature properties to typical 60% by weight kenaf-PP injection molded composites. Flexural properties were compared with 60% kenaf-PP composites and also with typical traditional commercially available wood based panel boards.

2. Experimental Procedure

Kenaf fibers, a few inches long, harvested from mature plants were obtained from Ken-Gro Corporation, Mississippi, USA. The polypropylene was the homopolymer—Fortilene 1602 (Solvay Polymers, Houston, TX, USA) with a melt flow index of 12 g/10 min (manufacturers data) measured using ASTM D-1238. A maleated polypropylene, G-3002 (Eastman Chemical Products, TN, USA) was used as a coupling agent. This MAPP had about 6 wt.%(%) of maleic anhydride grafted on to the polymer chain and the MW, was 11,000 Daltons and MW, was 40,000 Daltons. Glycerine (glycerol and IUPAC name: propane-1,2,3-triol) was obtained from Aldrich Chemical and had a purity of 99%, and a boiling point of 290 °C.

Kenaf bast fibers were cut into about 1 cm in length. Glycerine was added to water at about a 1:50 ratio. The amount of glycerine used varied between 1.2 and 4% of the dry weight of kenaf fibers. The mixture was stirred and put into a typical garden spray bottle. The fibers were spread out and the mixture sprayed over the fibers, while constantly turning and moving the fibers to get uniform distribution of the glycerine. The samples were air dried for at least one week at ambient conditions prior to the next stage of preparing the boards.

The short bast fibers (85%), MAPP (5%) and PP (10%) were compounded in a one-liter high intensity kinetic mixer (hence forth known as k-mixer) from Synergistics Industries Ltd., Canada, where the only source of heat is generated through the kinetic energy of rotating blades. The required weight of dry fibers (dry fiber without both moisture and glycerine taken into account) and polymers were inserted into the blender and compounded at 3000 rpm resulting 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 and how hot the mixer was when the blending started. The average time of blending varied from 2 to 3 minutes with higher fiber content blends taking longer to reach 200 °C. However, in this paper, data for 85% boards are the only ones reported. The compounded mass was then immediately compression molded, between flat plates, in a hot press at 190 °C for 3 minutes.

Three boards were made for each set of experiments. The specimens were stored under controlled conditions (20% relative humidity and 32 °C) for 3 days before testing. Four flexural specimens were cut from each of the three boards. Six specimens (two from each board) were tested for each data point. Specimen dimensions were according to the respective ASTM standards. Flexural testing was done using the ASTM 790-90 standard. The fracture surfaces of some of the tested specimen were observed using a JEOL scanning electron microscope.

A Perkin Elmer DSC was used to evaluate the crystallization and melting behaviour of the boards. The samples were first heated to 220 °C at 20 °C/min and then held isothermally for 1 minute in a nitrogen atmosphere. The samples were then cooled at 10 °C/min to collect crystallization data, and heated again at 10 °C/min to observe the melting transition. The sample sizes were kept between 9 and 11 mg and all tests were run under nitrogen gas. The % crystallinity is determined as the heat of fusion of the sample relative to that of a 100% crystalline sample. The heat of fusion of pure crystalline isotactic PP is 209 J/g. Dynamic properties of the composites were measured using a Rheometrics DMTA MKIII. The samples were cut to size from the center of the boards. A single cantilever test was used for the testing with a span of 14 mm, and sample width and depth were about 5 mm and 1 mm, respectively. The deflection amplitude was 16 μm, frequency 1 Hz and the heating ramp rate was 2 °C/min and strain of 0.024%. Only specimen prepared using 2% by weight of glycerine were used in both DSC and DMTA analysis.

3. Results and Discussion

The effect of glycerine on board preparation was evaluated. It was only possible to prepare 85% by weight kenaf-PP boards without significant kenaf thermal degradation when glycerine was used. It appears that the glycerine broadens the processing window of compounding the fibers and polymer (Figure 1). The processing window is the temperature range over which the polymer has melted and is well dispersed and at the same time there is no fiber thermal degradation. There could be several reasons why the use of glycerine helped in preparing boards without kenaf fiber degradation. a) Heat developed during the compounding in the kenaf fiber is used to vaporize the glycerine present in the fiber and thereby dissipating heat and preventing the burning of the fibers; and b) Glycerine vapor may displace oxygen and reduce chances of fiber burning. The processing window could be very narrow when there is no glycerine and our control over the compounding stage was not good enough to make sample boards. The use of glycerine expands the processing window, Figure 1. The use of glycerine explains the shift of the upper end of the processing window to higher temperatures since its presence prevents the burning of the fibers.

We observed shifts in the processing window to lower temperatures when compounding typical 60% weight kenaf-PP composites while using glycerine. The use of glycerine resulted in the polymer having melted and well dispersed with fibers at temperatures of about 160 °C. The normal temperature when fibers are well dispersed and polymer is molten is about 190 °C. This is also true with the 85% kenaf boards, but this is hard to compare since boards without the use of glycerine could not be prepared without significant fiber thermal degradation. This is probably due to the plasticization and lubricant effect of the glycerine on the polymer and also the plasticization of the lignin and amorphous polymers present in kenaf.

![Figure 1. Schematic of processing window of fibers with and without glycerine. A) When no glycerine used, the processing window use is very narrow; and B) When glycerine was used it expanded the processing window.](image-url)
The flow of thermoplastic melts cannot be increased as desired (beyond practical limits) by raising the temperature: polymer molecular weight loss or crosslinking along with discoloration can occur due to the chemical instability of the macromolecule \(11\). Furthermore, in the case of lignocellulosic composites, fiber thermal degradation can take place at elevated temperatures. Higher processing temperatures require additional energy and could also lead to lower molding outputs through longer cool times. Furthermore, lignocellulosic fibers thermally degrade at higher temperatures. Polymer rheology is affected by several factors including stress, strain, time, temperature and additives such as plasticizers and lubricants. Several mechanisms can affect the characteristics of the polymer and thereby the compounding and blending of plastics, apart from the different mechanisms under which those plasticizers/lubricants function \(12\)–\(20\). It is well known that sorption of vapors or gases by polymers can cause significant plasticization resulting in a substantial decrease in the glass transition temperature \(11\). For example, the glass transition of PET decreased from about 80 to about 5 °C with about 0.10 mole fraction of CO\(_2\) gas \(\text{g}\) in the polymer. The presence of solvents and stresses can also decrease the surface energy required to form a craze and/or decrease the flow stress due to plasticization at the craze tips. For example, solvent crazing of glassy polymers (e.g., polycarbonate) can create a bulk plasticization effect due to the stress-induced adsorption \(21\)–\(23\).

In the case of wood, moisture or other plasticizers drastically affect the glass transitions of the amorphous parts (lignin and hemicellulose). Kelley, Rials and Glasser \(31\) have studied the transitions for wood. The glass transition temperature \(T_g\) of lignin can drop to about 70 °C in the presence of about 15% moisture, while that of hemicellulose can go below 0 °C at this moisture content. They also found that strong H-bonding solvents, such as formamide, could be effective plasticizers for the lignin and hemicellulose than weaker H-bonding solvents. Recent work has studied the plasticizing effect of various molecules on lignin \(2\)–\(4\) unfortunately the effect of glycerine was not studied. Furthermore, the structure of the lignin can also alter the molecular transitions of the lignin \(5\). Ralph \(6\) mentioned that kenaf has an unusual type of lignin, with extensive side chains that are acetylated, and this will change the transition of lignin compared to wood lignins. The transition of hemicelluloses are also affected by the type and amount of the plasticizer. Olsson and Salmen \(31\) have studied the transition behavior with respect to the amount of moisture.

An interesting point to note is that the glycerine plasticizes the amorphous components (lignin and hemicellulose) of the kenaf fibers by breaking some of the H-bonds present. Kenaf fibers have a significant amount of amorphous lignin (15-19%) and amorphous hemicellulose (22-23%) along with crystalline cellulose (44-57%) \(13\)–\(22\). The amorphous content then accounts for about 40% of the material in kenaf. A highly filled kenaf-PP board can thus have a significant amount of amorphous polymers in the composite. Thus in the kenaf fiber the amorphous component (lignin and hemicellulose) can vary from 43 to about 56%. Since the boiling point of glycerine is very high, the plasticization can occur well above the boiling point of water, and during the compounding of the kenaf boards. The presence of glycerine may permit the kenaf fibers to deform without extensive breaking during the high intensity of mixing also during the hot press cycle. It is not inconceivable that the lignin can be plasticized to make binderless fiberboards and research is being done in this area to understand the plasticization process \(23\). This along with understanding the plasticization process of hemicelluloses \(23\) could help in developing a new generation of panel boards using thermoplastic (linear) polymers as binders.

The effect of the amount of glycerine in the fibers also is important (Table 1). Sufficient glycerine is needed to prevent thermal degradation and also help plasticize the amorphous material at high temperatures. A 2% by weight of glycerine based on the dry weight of the fiber gave the best results. At higher glycerine loadings there was a drop in both strength and modulus.

Figure 2 shows scanning electron microscopy of the fracture surfaces 85% kenaf fiber-PP/MAPP boards (using 2% glycerine) showed that the bonding between the fiber and polymer appears to be good. The orientation of the fibers seemed random (Figure 2a) and this makes sense when one compression molds the blended mass that

| Kenaf content | Glycerine (%) | Flexural strength (MPa) | Flexural modulus (GPa) | Specific gravity |
|---------------|--------------|------------------------|-----------------------|-----------------|
| 85            | 1            | 68 (7)                 | 6.2 (0.4)             | 1.235           |
| 85            | 2            | 75 (9)                 | 6.8 (0.5)             | 1.234           |
| 85            | 4            | 64 (9)                 | 6.1 (0.6)             | 1.241           |

Figure 2. a) Shows the fracture surface of an 85 % by weight kenaf-PP/MAPP board. (Note several fibers appear well bonded and the fibers have themselves between torn apart.) Some voids can also be seen; and b) A close-up of an 85 % weight composite shows polymer adhering to the fiber surface. This indicates good bonding between the fiber and the PP/MAPP.
comes out of the thermokinetic mixer. Quite a few voids can also be seen indicating that the PP/MAPP acts as an adhesive between the fibers rather than as a continuous mass as in the case of a typical fiber reinforced composite. This is in opposition to typical kenaf-PP composites reported (prepared by extrusion and injection molding) where there are practically no voids. Furthermore, when composites are injection molded as in earlier studies, the fibers are preferentially aligned in the direction of the molding axis. The interface between the PP/MAPP and the fiber surface appears to be good. Figure 2b shows a fracture surface where one can see polymer adhering to the fiber surface which indicates that the adhesion is good.

An 85% by weight kenaf board has a theoretical kenaf volume fraction of about 78% assuming fiber specific gravity of 1.4. It is theoretically not possible to have “true” fiber composite (i.e., with a continuous matrix phase with embedded fibers and with no voids) with a fiber volume fraction of 78% when the fibers are randomly distributed. Thus the polymer molecules act as binders in the 85% kenaf boards and this is similar in function to phenol formaldehyde in typical wood panel boards.

DSC results indicate there is a little difference in the onset and peak crystallization and the melting temperatures between the kenaf composites (Table 2). The percent crystallinity of polymer present in the 85% boards (PP/MAPP mixture) was however marginally lower than of a typical 60% kenaf-PP/MAPP injection molded fiber reinforced composite. These data were from an average taken from two samples. The value of the crystallization enthalpy for pure PP was 209 J/g. There is a difference in the onset Tc and peak Tc between the pure PP and kenaf-PP composites (60% kenaf) and boards (85% kenaf). It is believed that the fiber surface nucleates the crystallization of PP at higher temperatures. The 85% kenaf boards had a larger percent of MAPP (5% of composite weight) than 60% kenaf-PP composite (2%) and this can also affect the amount of crystallinity being measured. The difference in crystallinity could be due to the glycerine present, but the higher MAPP content can also explain the difference. It should be noted that the 85% boards has a significantly higher surface area exposed to the PP than the 60% composites. Further studies need to be conducted to determine the primary reason.

The DMA spectra of the 85% kenaf boards (Figure 3) show some interesting features when compared to a typical 60% kenaf fiber reinforced composite that was injection molded. It should be noted that the 60% composites were injection molded, which results in significant amount of fiber alignment. This is as opposed to the compression molded 85% boards 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% boards have a higher modulus. The difference in storage moduli become even more pronounced as the temperature increases. The softening temperature of the 85% boards 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.

In terms of the loss modulus (E") spectra, two transitions can be clearly seen. The α transition, related to the glass-rubbery transition, is due to molecular motions associated with unrestricted amorphous PP. The β transition is related to the relaxation of restricted PP amorphous chains in the crystalline phase. The presence of crystals is necessary for this transition to occur.

The β transition, occurring at about 10 to 25 °C is associated with the glassy-rubbery transition of the amorphous chains of the polymer and the α transition is related to the crystallites, but the relaxation occurs due to the presence of “rigid” amorphous molecules present within the crystal. These regions disrupt the purity of the crystals and thus can be considered to be defects. The β relaxation for the 85% composite is much wider than the 60% composite. The wider relaxation and the shift to higher temperatures generally indicate that some of the amorphous molecules are more restricted. 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 in the 85% boards are further restricted in mobility due to interactions with the solid fiber surface since the distance between fiber surfaces is smaller (compared to 60% composite). Furthermore, since the 85% boards have a significantly higher fiber surface exposed to the polymer-the polymer molecules near the surface have restricted mobility and therefore result in higher β relaxation temperatures.

Table 3 compares the flexural strength and modulus of kenaf-PP boards (using 2% glycerine) with those of commercially available conventional wood based boards. Data of the wood based panel products were from the Wood Handbook. The strength of the kenaf-PP

| 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           |
boards was significantly higher than the standard high density hardboards and in the same range as tempered hardboards. The density of the kenaf-PP boards were in the same range as hardboards. The special densified hardboards had both higher properties and specific gravity as compared to the kenaf-PP composites. Due to the presence of the linear polymer binders, the wet mechanical properties of the kenaf-PP boards are expected to be higher than the hardboards, although we did not measure these properties for this study. Another advantage is that very complex shaped (Figure 4) can be made during the pressing cycle that may have implications in large volume indoor furniture applications since it reduces cost of the final product. In this case, a special mold with ribs was used instead of hot pressing between flat plates.

Both strength and modulus of the 85% boards are lower than 60% (injection molded) kenaf fiber reinforced PP composites (Table 3)\(^{19}\). This is not surprising since the 85% boards have randomly oriented fibers and the boards are hot pressed. In the case of the 60% composites the specimens were injection molded and tested along the direction of mold flow. In this injection molding process, the fibers align in the direction of the mold flow, resulting in high strengths and moduli which are higher than the randomly fiber oriented 85% boards.

### 4. Conclusions

A new technique of using glycerine to facilitate the preparation of highly filled natural fiber boards in PP was developed. Glycerine, to the amount of 2% by weight of dry kenaf fibers resulted in the better properties than 1 and 4% by weight glycerine. From SEM micrographs and visual observation the fibers appear to be randomly oriented in the boards. The PP acts like an adhesive that binds the fibers together similar to the way conventional formaldehyde based resins acts as in conventional wood based composites. DSC data indicate there is a small difference in the crystallinity of the PP when using glycerine, but this difference could be because of the high percent of low molecular eight MAPP (5%) used in preparing these boards. DMA data indicate that the 85% boards have much higher integrity at higher temperatures as compared to typical 60% kenaf-PP injection molded composites. The flexural strength, flexural modulus and specific gravity of the 85% boards compare well with high density hardboards. One advantage of the 85% kenaf-PP boards is that complex shapes can be molded during the hot press cycle. Furthermore due to the use of the thermoplastic PP, any excess material in the production cycle can be chipped and reused during the blending stage. These materials also have the advantage of being recyclable due to the use of PP. However, at this stage further studies need to be conducted on these new materials to evaluate properties such as toughness, creep, etc to get a better idea of the potential of these 85% boards.

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### Table 3

| Type of Board                              | Flexural modulus (GPa) | Flexural strength (MPa) | Specific gravity |
|--------------------------------------------|------------------------|-------------------------|-----------------|
| Standard high density hardboard            | 5.5                    | 48.3                    | 1.28            |
| Tempered hardboard                         | 7.5                    | 69                      | 1.28            |
| Special densified hardboard                | 8.6                    | 86                      | 1.44            |
| 60% injection molded Kenaf-PP composites   | 10.1                   | 110                     | 1.13            |
| 85% kenaf-PP boards from this work         | 6.8                    | 75                      | 1.24            |
