UNITED STATES BASED AGRICULTURAL “WASTE PRODUCTS” AS FILLERS IN A POLYPROPYLENE HOMOPOLYMER

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Abstract

With the advent of modern coupling agents (MAPP or maleic arhythride grafted polypropylene), the potential use of various types of renewable, sustainable agricultural by-products as fillers in thermoplastics is explored. Over 7.7 billion pounds of fillers were used in the plastics industry in 1993. With sharp price increases in commodity thermoplastics (i.e. approximately 25% in 94'), the amount of fillers in thermoplastic materials will increase throughout the 90s. Various types of agricultural fibers are evaluated for mechanical properties vs. 50% wood flour and 40% talc filled polypropylene (PP). The fibers included in this study are: kenaf core, oat straw, wheat straw, oat hulls, wood flour (pine), corncob, hard corncob, rice hulls, peanut hulls, corn fiber, soybean hull residue, and jojoba seed meal. Composite interfaces were modified with MAPP to improve the mechanical properties through increased adhesion between the hydrophilic and polar fibers with the hydrophobic and non-polar matrix. The agro-waste composites had compositions of 50% agro-waste / 48% PP / 2% MAPP.

All of the agricultural waste by-products were granulated through a Wiley mill with a 30 mesh screen and compounded in a high intensity shear - thermo kinetic mixer. The resultant blends were injection molded into ASTM standard samples and tested for tensile, flexural, and impact properties. This paper reports on the mechanical properties of the twelve resultant composites and compares them to wood flour and talc-filled polypropylene composites. The mechanical properties of kenaf core, oat straw, wheat straw, and oat hulls compare favorably to the wood flour and talc-filled PP, which are both commercially available and used in the automotive and furniture markets.
Introduction

Lignocellulosic fibers (wood flour) have been used in the plastics industry for almost 90 years. Bakeland used wood flour to both extend and improve the processability of thermosetting resins in 1907. The use of fillers and reinforcements in plastics has changed the face of the industry. Over 500 million pounds of fibrous material (mostly glass) is being used in the plastics industry yearly (Ref. 1). The total amount of fillers being used is estimated at 7.7 billion pounds in 1993. As the plastics industry grew and developed, the cost of introducing and marketing new polymers became cost prohibitive. So, the industry turned to the idea of using existing plastics and filling / reinforcing them to close the performance gap between the new and more expensive engineered polymer resins. The need for polymer composites to perform in service applications require certain levels of strength, stiffness, and fracture toughness, in various conditions (i.e. high temperature, indoor / outdoor applications, etc.). In the 60’s and 70’s, the plastics industry began using more fillers / reinforcements to improve performance as well as reduce the overall cost of production. The use of fillers and reinforcements in the plastics industry have seen a steady growth throughout the past 30 years and this trend will continue into and beyond the 90’s.

As commercial industry seeks to offset price increases in base resin costs, increase product recyclability, and maintain composite performance, they will search for new materials to fill existing product niches and create new products for developing countries. China and India have over two billion potential buyers of goods and services in the global marketplace. These newer materials must be economically and more environmentally friendly then in previous years. Recent research into the use of annual growth lignocellulosics as reinforcing fillers in thermoplastics suggests they have high potential for industrial end uses. Results indicate that the mechanical properties of agro-waste / PP composites compare favorably to talc, calcium carbonate, and wood flour filled PP for certain applications (Ref. 2,3) where water absorption is not a problem. Furthermore, due to the softer non-abrasive nature of the agro-wastes it is possible to obtain a higher loading (by volume) of agro-wastes in the composites than other more traditional inorganic fillers (talc and calcium carbonate). As a result of the lower densities, more finished products are possible with a ton of agro-waste thermoplastic composites then are possible with a ton of conventional filler / thermoplastic composites.

Twelve different agro-wastes have been compatibilized with a polypropylene homopolymer. This study included the following agro-wastes: kenaf core, oat straw, wheat straw, oat hulls, wood flour (pine), corncob, hard corncob, rice hulls, peanut hulls, corn fiber, soybean hull residue, and jojoba seed meal. The tensile, flexural, and impact toughness properties are compared by the type of fiber and the fiber loading level. The fiber loading is based on the dry weight of the fibers. Also, the effect on the mechanical properties of the composites due to the modification of the interphase / interface region with MAPP coupling agent is evaluated. MAPP has been shown to improve the surface adhesion between the hydrophilic and polar lignocellulosic fibers and the hydrophobic and non-polar PP (Ref. 4). All twelve agro-waste composite systems had the following composition of 50% agro-waste / 48% PP / 2% MAPP.

1 The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin. This article was written and prepared by U.S. Government employees on official time, and it is therefore in the public domain and not subject to copyright laws.
Experimental Procedures

Materials

The base resin was a polypropylene homopolymer, Fortilene 1602 (generously donated by Solvay Polymer, Houston, TX.) with a melt flow index of 12 gr. / 10 min. at 230 °C (ASTM - D1238). A maleic anhydride grafted polypropylene (MAPP) modifier, Epolene G3002 (donated by Eastman Chemical, Kingston, TN.) was used to enhance the surface adhesion between the agro-wastes and the PP matrix. The agro-wastes used in this study were kenaf core from AG-Fibers Inc., corncob, hard corncob from Composition Materials Inc., corn fiber from Cargill, Inc., oat hulls from Quaker Oats Co., rice hulls from Busch Agricultural Resources Center, peanut hulls from Seminole Peanut Co., and soybean hull residue from WI Soybean Assoc., oat / wheat straw, wood flour, and jojoba seed from other sources.

Methods

The agro-wastes were run through a Wiley mill with a 30 mesh screen. The agro-wastes, PP, and MAPP were compounded in a 1 liter - high intensity shear - thermokinetic mixer (Synergistic Industries Ltd., Canada). No external heat sources are required due to the high shearing / smearing of the PP which produces friction and generates heat. The shearing action causes softening and flow of the composite system. A thermally controlled monitor regulated the dump temperature at 168 °C (360 °F) to 199 °C (390 °F) depending on the fiber type. The composites were compounded at 5000 rpm (tip speed = 32.9 m/s) and 150 gram batches were standard. Directly after reaching the dump temperature, the material was pressed flat to enhance cooling and prevent fibers in the core of the composite from burning.

The resultant composite blends were then granulated and dried at 105 °C for 4 hours to drive off residual fiber moisture in preparation for injection molding. A 33-ton Cincinnati Milacron injection molder was used to produce standard ASTM tensile, flexural and impact specimens. Samples were placed in a controlled humidity room for three days prior to testing to assure complete thermal stability of the test samples. Test conditions were performed according to the following ASTM standards: tensile testing (ASTM D638), flexural testing (ASTM D790), impact testing (ASTM D256).

Results and Discussion

In the United States alone, there is approximately 120,000,000 metric tons (Ref. 5 - 1982 data) of non-wood plant straws available as raw materials for industry. Wheat straw, oat straw, and barley straw compose the largest volumes. Other crops, such as corn stalks and sorghum stalks, are available in the 190,000,000 metric ton (Ref. 5) range. There is approximately 2,000,000 metric tons of rice straw and rice hulls are available in the range of 1,000,000 metric tons that are located at point sources in the southern regions. Peanut hulls are located mainly in the southwestern states, such as, Georgia. The availability of potential fibers to be used by the United States plastic industry is governed by the location of the fiber sources. Each geographical region has its own type of fiber supply.
Farmers of fledgling non-food crops, such as, kenaf, jojoba seed, guayule, and milkweed, search for innovative applications for use in industrial applications. Currently, there is approximately 4,000-6,000 thousand acres of kenaf grown in the U.S. from California to Mississippi. As more potential markets are created, the acreage of these non-food crops will increase. The potential for using agro-wastes as fillers in commodity thermoplastics (i.e. PP, PE, PS, and PVC) is enormous if markets are developed and expanded over the next decade. Certain restrictions do apply for lignocellulosic reinforced polymers in terms of applications were moisture adsorption and creep resistance are required.

**Tensile Strength and Modulus**

Figures 1 and 2 show the tensile strength and tensile modulus properties of the agro-waste polypropylene based composites. For purposes of comparison, 100% PP, 40% talc, and 50% wood flour composites are included because they are commercially available products. The figures show that the tensile strength properties of kenaf core, oat straw, wheat straw, and oat hulls compare favorably to both wood flour and talc filled PP composites. All other fillers have mechanical properties which are slightly less then the 50% wood flour, but still compare favorably to 40% talc filled PP. The 50% corncob-un is an uncoupled system (i.e. no MAPP) and is used for comparison vs. the 50% corncob. The tensile strength of the un-coupled system increased 95% with the addition of 2% MAPP for the coupled corncob composite. All of the filler systems will react in a similar fashion when no MAPP is used during the compounding stage.

The tensile modulus of agro-waste composites show dramatic property improvement characteristics vs. 100% PP. Wood flour shows a 225% increase in modulus, while kenaf core, oat straw, and wheat straw shows a 200% increase in modulus vs. 100% PP. Other systems, such as, oat hulls, corncob, hard corncob, and rice hulls show an increase in modulus of 100% vs. virgin PP. For coupled and uncoupled systems, there is little change in the tensile modulus properties between 50% corncob and 50% corncob-un. Previous work at the Forest Products Laboratory (Ref. 6) indicates that some fiber systems will show a decrease in tensile modulus with a coupled system. Therefore, no discussion of the other fiber systems will be presented until further testing is done.

The addition of MAPP has the most dramatic effect on the tensile strengths of agro-waste composites. The uncoupled fiber systems have strengths approximately half that of coupled systems. MAPP migrates to the interface between the non-polar PP and polar fiber surfaces. In addition, the maleic anhydride present in the MAPP can covalently link to the hydroxyl groups on the lignocellulosic fibers (Ref. 7). Under a tensile load, the improved adhesion at the fiber / matrix interface results in a more efficient stress transfer from the matrix to the reinforcing fillers. As a result, strength properties of agro-waste composites can be improved with small additions of MAPP.

**Flexural Strength and Modulus**

Figures 3 and 4 show the flexural strengths and flexural moduli for the agro-waste polypropylene based composites. The addition of MAPP increases the flexural strengths of these agro-waste composites by approximately 50% of the value of un-coupled systems. Values for the 50% corncob-un and 50% corncob in Figure 3 shows an increase of 57% for a coupled system and is an indication of how the other composite systems flexural strengths would be if no MAPP were present in the composites. Increased adhesion between the lignocellulosic fibers and the matrix provides for increased stress transfer from the matrix to the filler. This results in an increased stress at failure and the higher values
for flexural strengths in the coupled systems verses un-coupled systems. The flexural strengths of composite systems composed of kenaf core, oat straw, wheat straw, and oat hulls are equivalent or superior to both wood flour and talc filled polypropylene composites. The kenaf core composite shows an increased flexural strength of 75% vs. 100% PP. Other systems, such as, corn cob, hard corn cob, and rice hulls have flexural strengths slightly less then wood flour and talc filled composites. These systems still show an increase in flexural strengths of approximately 50% over virgin PP.

In terms of the flexural modulus, Figure 4 shows that wood flour has the highest flexural modulus with an increase of 270% over 100% PP. On average, the top eight agro-waste composites show an increase in flexural modulus of 200% over virgin PP. The kenaf core, oat straw, and wheat straw composites have flexural moduli between wood flour and talc filled composites, while all other agro-waste / PP composites have flexural moduli less than talc and wood flour.

Notched and Unnotched Izod Impact

Figures 5 and 6 show the notched and unnotched Izod impact properties for the agro-waste composites. The commercially available 40% talc / PP has a notched impact toughness of 26.7 J/M, while 100% PP has a value of 24 J/M. Various types of talc filled PP is available and the notched Izod impact toughness can range up to 75 J/M. The mechanism for the toughness is due to the plate-like particles of talc which have a higher aspect ratio than the finely ground (i.e. 30 mesh) agro-wastes. Overall, the top eight agro-waste composites notched Izod impact toughness equals 22.1 J/M (i.e. average) and compares favorably to the wood flour. In comparing the agro-wastes composites to the talc filled PP and 100% PP, there is an 8-10% decrease in the notched toughness.

Figure 6 shows the unnotched Izod impact toughness of 100% PP equals 640 J/M, while the 40% talc filled PP equals 240 J/M. The average value for the agro-waste composites is approximately 95 J/M. The addition of MAPP results in a 100% increase in the unnotched toughness over un-coupled systems. The 50% corn cob-un has a value of 40 J/M, while the 50% corn cob has a value of 80 J/M. Further research and development involving impact copolymers will improve the toughness of these composites, but at a loss in strength properties (Ref. 8).

Conclusions

- With the addition of a maleic anhydride grafted PP to agro-waste composites, the tensile strength, flexural strength and un-notched impact toughness values are shown to improve substantially over un-coupled systems.

- Twelve different agro-waste composites have been successfully compatibilized with a polypropylene homopolymer. Results indicate that kenaf core, oat straw, wheat straw, and oat hulls have equivalent mechanical properties to commercially available wood flour and talc filled polypropylene composites.

- Continued research and development of agro-waste composites will show that these material systems are viable alternatives to commercially available wood filled and talc filled PP systems.
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Figure 1 - Tensile Strength (MPa) Properties.

Figure 2 - Tensile Modulus (GPa) Properties.
Figure 5 - Notched Izod Impact (J/m) Properties.

Figure 6 - Unnotched Izod Impact (J/m) Properties.

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