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High Density Polyethylene/Paper Fiber Composites: Measuring the Impact of Additives on Their Physical and Mechanical Properties

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Susan E. Selke

Major professor

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HIGH DENSITY POLYETHYLENE / PAPER FIBER COMPOSITES: MEASURING THE IMPACT OF ADDITIVES ON THEIR PHYSICAL AND MECHANICAL PROPERTIES

By

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ABSTRACT

HIGH DENSITY POLYETHYLENE / PAPER FIBER COMPOSITES: MEASURING THE IMPACT OF ADDITIVES ON THEIR PHYSICAL AND MECHANICAL PROPERTIES

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In this particular study, virgin high density polyethylene (HDPE), and certain additives were combined with recycled newspaper fiber in a twin screw extruder. The extrudate was later compression molded. The additives used were: maleic anhydride modified HDPE (MAHDPE), low molecular weight polypropylene (Proflow 1000), and low density polyethylene (LDPE) with a high melt flow index. The fiber loading level remained at approximately 35%. Tensile, Izod impact, and water absorption tests were conducted to determine the effect which these additives had on the composite's physical and mechanical properties. The effects of MAHDPE were studied at 3%, 6%, and 10%. The effects of Proflow 1000 and LDPE were studied at 5% and 10%, while keeping the MAHDPE at 6%. The additives had no significant effect on modulus of elasticity, percent elongation, and Izod impact strength. MAHDPE was found to improve yield strength (at 10%) and tensile strength (at 3%), and appeared to decrease debonding in water (at 3%, 6%, and 10%).

To my loving wife, Susan

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INTRODUCTION

My initial interest in recycling was sparked when I visited a landfill in southern Idaho in early 1993. The landfill was actually a canyon set back in the mountains, and it was slowly filling up with people's trash. When we reached our designated dumping point at the landfill, I was amazed at all of the garbage: newspapers, plastic bottles, corrugated boxes, an expired toaster oven, etc., I asked myself, "What can I do to help reduce some of this waste?". The answer came six years later in the form of this thesis topic, which is part of an on going investigation into a composite material constructed of recycled high density polyethylene (HDPE) and recycled newspaper. I chose to conduct my research in this area of composites, because it is my hope that I will someday be able to say that I contributed to the development of a material which helps to relieve pressure on our nation's landfills instead of adding to it.

The purpose of this particular investigational study was to determine the effect of additives on the physical and mechanical properties of a fiber reinforced composite consisting of an HDPE matrix and recycled newspaper fibers

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as the reinforcement. These additives include: maleic anhydride modified HDPE (MAHDPE), low molecular weight PP (Proflow 1000), and low density polyethylene (LDPE). To determine the effect of these additives, tensile testing, impact testing, and water absorption tests were undertaken.

According to the Environmental Protection Agency (EPA), municipal solid waste (MSW) includes wastes such as durable goods, nondurable goods, containers and packaging, food scraps, yard trimmings, and miscellaneous organic wastes from residential, commercial, institutional, and industrial sources (EPA, 1998). The amount of MSW generated has decreased by two million tons since 1995 to 209.7 million tons of MSW generated in 1996 (EPA, 1998). Paper and paperboard products made up the largest component of MSW, about 38.1%, in 1996. As of 1996, plastics comprised only 9.4% of total MSW. Containers and packaging contributed to 33% of the total MSW weight in 1996, while nondurable goods contributed 26.5%. On a per person basis, generation of nondurable paper products (newspapers, office papers, mail, and other printed products) has been about constant since 1990 (EPA, 1998). Products made of paper and paperboard comprise the largest portion of nondurable goods. Newspapers are the largest single component of the

nondurable goods category with its 5.9% contribution to MSW. This is not surprising since it has been observed that in one year a single subscription to the New York Times uses about 520 lbs of paper (Rodriguez, 1996).

Once generated, MSW is dealt with by either recycling, composting, combustion, or placement in a landfill. Landfills managed 55% of all MSW generated, while combustion facilities managed 17% in 1996. Recycling (including composting) recovered 27% of MSW in 1996 (EPA, 1998). This is an increase of 1% since 1995. Recovery of paper and paperboard reached 41% in 1996, accounting for more than half of the total MSW recovered (EPA, 1998). 54% of all newspapers generated were recovered for recycling. Plastics are a rapidly growing segment of MSW and their overall recovery is only 5.4% of all of the plastics generated in 1996. However, the recovery of some plastic containers has increased. For example, in 1996 PET soft drink bottles were recovered of a rate of 40%. HDPE milk and water bottles were recovered at 30.8% in 1996 (EPA, 1998).

Recycled materials can have various uses. For example, the majority of recycled newspapers are used for the manufacture of newsprint, at 34% of the total recovered

(EPA, 1998). Other uses include recycled paperboard, construction products, molded pulp products, cellulose insulation, and animal bedding. The largest use of recovered HDPE bottles is for the production of new bottles (EPA, 1998). In addition, recovered HDPE is used for drainage pipe, plastic lumber, pallets, crates, and totes. It is my hope that in the future, recycled HDPE and newspaper may also be used to construct composites which can be used to manufacture consumer and industrial products.

A composite is constructed when two or more materials are combined to achieve a performance which is unable to be rendered by the individual parts if they were utilized alone. Composites have grown more prevalent throughout history as the demands on materials became so severe that individual materials alone were unable to perform or have the desired properties (Richardson, 1987). Therefore, people have found it necessary to combine materials to achieve the needed results. In fact, this was practiced thousands of years ago as the Old Testament of the Bible records the use of straw reinforced bricks by the Egyptians. Today, composites are present as materials like fiberglass for boats and cars. In addition, high strength composites are now being developed out of carbon fiber, Kevlar, as well

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as carbon/carbon, metal/matrix, and ceramic/matrix composites. New composites are also being created out of a variety of thermoplastics, thermosets, and fiber reinforcements.

The technology of composite materials has experienced a rapid development in the last two decades. This can be attributed to some distinct reasons. First, important progress has been made in materials science and technology in the area of fibers, polymers, and ceramics. Second, requirements have been present for high performance materials in aircraft and aerospace structures. Third, developments have been made in structural analysis, using modern computer technology and the availability of powerful desktop computers in the science and engineering community. Technology development was initially pushed forward in the search of weight savings. This was later accompanied by other factors like quality assurance, reproducibility, predictability of behavior over the lifetime of the material, and cost competitiveness (Daniel, 1994).

In short, fiber reinforced composites are a good alternative structural materials to monolithic materials. The advantages of composite materials appear when the

modulus per unit weight (specific modulus) and strength per unit weight (specific strength) are considered. This means that one will need less material, thus less weight, to attain the needed performance (Hull, 1981). This is especially important in the packaging industry, because reusable totes, crates, pallets, etc., will be able to be made stronger with less weight. This will enable companies to save money in terms of both product life cycle and transportation costs. In addition, natural fibers offer an advantage of cost and biodegradibility over other reinforcements like glass or graphite fibers. Also, conventional materials are more sensitive to their microstructure and local irregularities, which influence the brittle or ductile behavior of the material (Daniel, 1994).

LITERATURE REVIEW

General Information

Structural composites can be broken down into three main phases. First, the "reinforcement" refers to a phase that is usually discontinuous, stiffer, and stronger. It can consist of fibers, which are the principal components in fiber reinforced composite materials. The second phase is the "matrix", which is usually less stiff, weaker, and continuous. It provides a means to transfer stresses applied to the composite to the fibers, while also providing local stress transfer from one fiber to another. Most of these stresses are transmitted to each individual fiber's ends. It is assumed that these stresses gradually rise within the fiber as they move to the fiber's center. The other stresses are transmitted to the cylindrical surface of the fibers. Also, the usually low fracture toughness of the fibers is enhanced by the energy dissipation at the fiber/matrix interface and matrix ductility (Daniel, 1994). The matrix protects the fibers from environmental effects like moisture, temperature, and abrasion. It also keeps the fibers from buckling and bending. The third phase refers to the "interphase" (or interface) which sometimes exists due to chemical interactions or other effects. The interphase,

although small in size, can play an important role in controlling the failure mechanisms, fracture toughness, and overall stress-strain behavior of the material (Daniel, 1994). In the case of low to medium performance composite materials, the reinforcement, usually in the form of short fibers or particles, provides some stiffening but only local strengthening of the material. In contrast, the matrix is the main load bearing component governing the mechanical properties of the material. In the case of high performance structural composites, the usually continuous fiber reinforcement is the backbone of the material that determines its stiffness and strength in the direction of the fibers (Daniel, 1994). The paper fiber composites which were constructed for the purpose of this thesis would therefore fall under the category of low to medium performance due to the use of short paper fibers which are discontinuously and randomly distributed within their HDPE matrix. The orientation of the fibers in this way affects the composite's properties. For example, the mechanical properties of the composite will only be maximized if the fibers are parallel to the loading direction and if the fibers are uniform in their strength values. Also, the transfer of stress from matrix to fibers will be less efficient with misoriented fibers (Childress, 1991). For a

material to be an acceptable composite material for use in structural applications it should meet the following criteria: 1) It consists of two or more physically distinct and mechanically separable materials. 2) It can be made by mixing the separate materials in such a way that the dispersion of one material in the other can be done in a controlled way to achieve optimum properties. 3) The properties are superior, and possibly unique in some specific respects, to the properties of the individual components (Hull, 1981).

The lengths of the reinforcing fibers in a composite are important because they can affect the performance of the composite. For example, according to Hull (1981), the reinforcing efficiency decreases as the average fiber length decreases because a greater portion of the total fiber length is not fully loaded. In fact, it is possible to calculate the critical length of a fiber (Lc), which is the minimum length of fiber required for the stress to build up to the fracture strength of the fiber (ÓF) (Hull, 1981). It is at this point that it could be assumed that the fibers exhibit their maximum reinforcing effect. However, it is important to note that for composites where the fiber length (l), $l > l_c$, the stresses transmitted to unoriented fibers

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are much lower than those transmitted to oriented fibers (Berlin, 1986). In addition, a short fiber will not fracture under any load if it is below its critical length. This means that the stress cannot build up to the fiber's fracture strength, thus prohibiting the fibers from offering their full reinforcing potential.

The critical fiber length can be calculated using an analytical model based on a composite consisting of continuous aligned short fibers:

$$Lc = (r)(\acute{O}F)(T) \qquad \text{(EQ \#1)}$$

where (2r) is the diameter of the fiber and (T) is the shear stress parallel to the fiber resisting pull-out, and is related either to the shear strength of the matrix or the strength of the fiber-matrix interface (Hull, 1981). According to Berlin (1986), the maximum stress in a fiber will occur at the middle section of the fiber, and for a plastic matrix it is:

$$(\acute{O}\ max) = (2)(T)(\ell)/(d) \qquad \text{(EQ \#2)}$$

where (T) is the shear stress, (ℓ) is the length of the fiber, and (d) is the diameter of the fiber. Berlin (1986), also said that the average stress transmitted to the fiber of length $\ell \leq$ Lc is equal to half the maximum stress as

follows:

$$Ó F = 1/\ell \; Ó\int \ell \; Ó(x)dx = (T)(\ell)/(d) \qquad \text{(EQ \#3)}$$

and thus the reinforcement provided by very short fiber would be:

$$(Óc) = (Óm)(Vm) + (Óf)(Vf) \qquad \text{(EQ \#4)}$$

In equation #3, at $\ell \simeq d$, the stress transmitted to a filler particle is equal to the shear stress (T) generated in the matrix. Since (Tm) = (Óm)/2, the strength of the composite will, in this case, be lower than that of the matrix (Berlin, 1986).

It is important to note that both Hull and Berlin used continuous aligned fiber composite materials to generate the mathematical expressions above. They did this because generating mathematical expressions for a composite consisting of discontinuous fibers poses a high degree of difficulty due to the large number of geometrical and material variables which are possible. Similar approaches will be found throughout this paper for the same reason.

As mentioned earlier, the fiber-matrix interactions within a composite and their interface are also important factors to consider. For example, a tensile stress applied

to a continuously aligned fiber composite, along the fiber direction, would be distributed between the matrix and fiber according to the following expression:

$$(Ó c) = (Em)(Vm)(Sc) + (Ef)(Vf)(Sc) \qquad \text{(EQ \#5)}$$

where (Sc) is the strain in the composite, (Em) is the Young's modulus of the matrix, (Ef) is the Young's modulus of the fiber, (Vm) is the volume fraction of the matrix, and (Vf) is the volume fraction of the fibers (Berlin, 1986).

Hull (1981), developed two different possible failure conditions depending on the relative values of (T), (ÓF), and (Óm), the fracture strength of the matrix. These were also based on a composite consisting of continuous aligned short fibers. The first failure condition is when fiber fracture occurs before matrix fracture. Stress builds up in the fibers as the load on the composites is increased, and the stress for fiber fracture is reached before the stress needed for matrix failure. The average stress in the fiber is expressed by the following equation:

$$Ó^* = [(\ell - Lc) + .5\ (Lc)/\ 1]ÓF \qquad \text{(EQ \#6)}$$

The strength of continuous aligned fiber composite materials parallel to the fibers (Óp), under these conditions, can therefore be calculated as:

$$(Óp) = [1 - (ÓF)(r)/2(T)(\ell)](ÓF)(VF) + (Óm)[1 - VF] \quad \text{(EQ \#7)}$$

The second failure condition is when the build-up of stress in the fiber is insufficient to cause fiber fracture and fracture occurs when the matrix stress is reached and the average stress in the fiber is:

$$ÓF = (\ell)(T)/2(r) \quad \text{(EQ \#8)}$$

By assuming $\ell < \ell c$, the (Óp) for these conditions can be calculated as:

$$(Óp) = [(\ell)(T)/2(r)](Vf) + (Óm)[1 - Vf] \quad \text{(EQ \#9)}$$

The interface between fibers and the matrix is important because strong adhesion between them is necessary to solidly anchor the fibers within the matrix and transfer stress. It can be reasoned that the stronger the adhesion between the matrix and fiber, the higher the resistance to separation between them, and the higher the stresses that can be applied to the composite before separation takes place. Hull (1981), stated that adhesion between the fiber and the matrix can be attributed to five main mechanisms: absorption and wetting, interdiffusion, electrostatic attraction, chemical bonding, and mechanical adhesion.

Wetting is very important in composite material

fabrication, which requires resin impregnation into the fibers. Wetting can be understood in terms of two simple equations. The first is the Dupre' equation for the thermodynamic work of adhesion, Wa, of a liquid to a solid:

$$(Wa) = (\gamma 1) + (\gamma 2) + (\gamma 12) \qquad \text{(EQ \#10)}$$

where (γ1) and (γ2) are the surface free energies of the liquid and solid, and (γ12) is the free energy of the liquid-solid interface (Hull, 1981). The second equation is Young's equation which states:

$$(\gamma Sv) = (\gamma Sl) + (\gamma Lv) \cos \Theta \qquad \text{(EQ \#11)}$$

where (γSv), (γSl), and (γLv) are the surface free energies, or surface tensions of the solid-vapor, solid-liquid, and liquid-vapor interfaces respectively. Theta (Θ) is the contact angle (Hull, 1981). A measure of (γSv) can be obtained from the way liquids of known (γLv) wet the solid. Zisman introduced the concept of critical surface tension of wetting (γc) such that only liquids with (γLv) > (γc) will spontaneously spread on the solid. This is a useful parameter in considering the wetting of fibers by resins (Hull, 1981).

The presence of voids within a composite has a definite effect on a composite's properties. In fact, the presence of voids is considered the most critical defect in

influencing the mechanical properties of a molded composite. Hull (1981) also stated that regardless of resin type, fibre type, and fibre surface treatment, the interlaminar shear strength of composite materials decreases by about 7% for each 1% of voids, up to a total void content of about 4%. The most common causes for void formation are incomplete wetting out of the fibers by the resin, and the inability of the resin to displace air or other gases from the fiber surface during the time fibers are coated with the resin (Mallick, 1993). Air entrapment is more likely in systems where the dry fibers are closely spaced and the viscosity of the resin is high (Hull, 1981). Gas entrapment may also be affected by the resin and fibers' surface energies, and the mechanical manipulation of fibers in the liquid resin.

According to Mallick (1993), the volume fraction of voids may be calculated with the following mathematical expression:

$$Vv = Pc - p/pc \qquad \text{(EQ \#12)}$$

where: Vv = volume fraction of voids

Pc = theoretical density

p = actual density, measured experimentally on composite specimens

and

$$Pc = 1/(wf/pf) + (1 - wf)/pm \qquad \text{(EQ \#13)}$$

The fiber volume fraction (vf) may also be calculated with the following mathematical expression:

$$vf = (wf/pf) / (wf/pf) + [1 - (wf/pm)] \qquad \text{(EQ \#14)}$$

where for both equations #13 and #14:

wf = fiber weight fraction

(1 - wf) = matrix weight fraction

pf = fiber density

pm = matrix density

It is important to note that with a random distribution of fibers in the matrix, a direct consequence is a lower fiber volume fraction (vf), and large resin rich areas may also occur (Hull, 1981).

The modulus for a composite may be calculated in different ways, depending on the orientation of the reinforcing fibers. For example, the Halpin-Tsai equations may be applied to predict the longitudinal and transverse moduli of aligned short fiber composites. According to Zadorecki and Karnerfors (1986), the equations for longitudinal moduli (El), and transverse moduli (Et) can be written as:

$$(El)/(Em) = [1 + (G)(NL)(Vf)] / [1 - (NL)(Vf)] \qquad \text{(EQ \#15)}$$

and,

$$(Et)/(Em) = [1 + (2)(NT)(Vf)] / [1 - (NT)(Vf)] \qquad \text{(EQ \#16)}$$

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$$(NL) = [(Ef)/(Em) - 1] / [(Ef)/(Em) + (G)] \qquad \text{(EQ \#17)}$$

and,

$$(NT) = [(Ef)/(Em) - 1] / [(Ef)/(Em) + 2] \qquad \text{(EQ \#18)}$$

where, (Ef) and (Em) are the moduli of the fiber and matrix, respectively. (Vf) is the volume fraction of the fiber, and (G) is a measure of the geometry of the reinforcement. For fibers of rectangular cross section, (G) may be calculated as:

$$(G) = 2\ \ell/d \qquad \text{(EQ \#19)}$$

where ℓ/d is the rectangular cross section aspect ratio when the dimension ℓ is taken in the direction of the loading (Zadorecki and Karnerfors, 1986).

The modulus of a composite with a random orientation of its fibers in a plane may be calculated using Tsai and Pagano's equation as follows:

$$E\ random = (3/8)(EL) + 5/8\ (ET) \qquad \text{(EQ \#20)}$$

This equation is derived from orthotropic elasticity theory. (EL) and (ET) are the moduli of an aligned short fiber composite with the same aspect ratio and fiber volume as the random composite (Zadorecki and Karnerfors, 1986).

PRIOR RESEARCH

Felix and Gatenholm (1992) investigated the nature of the interphase in composites and how it changes when compatibilizing agents, such as maleic anhydride modified polypropylene (MAPP), of different molecular weights were used. They focused on the effect of the orientation of immobilized compatibilizer chains on the interphase thickness. The interphase thickness was determined by dynamic mechanical thermal analysis. The molecular weights of the MAPP's were 39,000 and 4,500, and both contained 6 weight percent maleic anhydride. All samples contained 40 weight percent of cellulose fibers. Some cellulose batches were surface-infused with silane.

Felix and Gatenholm (1992) stated that the theoretical lengths of the chain segments, in this case when fully stretched away from the cellulose surface, were a function of the molecular weight of the compatibilizer. Possible lengths of fully stretched chains increase with increasing molecular weight. They predicted that this would probably affect interphase thickness. They found in composites containing untreated fibers, the interphase was much thinner than in composites with treated fibers. Also, the thickest interphase was obtained when the compatibilizer of the

highest molecular weight was used. They also found that the interphases were always considerably thicker than the length of the compatibilizer chains. This probably means that the compatiblizer chains also restricted the mobility of the matrix chains with which they were not in direct contact. Their results also indicated that the stretching of compatibilizer chains away from the cellulose surface probably took place, thus yielding a brush-like interface. It is believed that the predominant factor for this is the effort of the hydrophobic compatibilizer chains to withdraw from the hydrophilic cellulose surface. Finally, it was mentioned that in a previous paper, they had proved that MAPP reacted with and became covalently bonded to a cellulose surface in use for their composite material.

Hon et al (1992) evaluated the interactions between various plastics and newspaper. The newspaper was first defibrillated in a mechanical blender. Composites with different mixing ratios of polystyrene (MPS), polypropylene (PP), high density polyethylene (HDPE) and newspaper were then constructed. The specific energy requirement for processing, and the mechanical and thermal dynamic properties of the composites were determined. Fracture surface morphologies were examined by Scanning Electron

Microscopy (SEM).

They found that the more rigid the material, the more specific energy was required for processing with the intensive-mixture-measuring heads of a Brabender PL2000 Plasti-Corder. Statistical analysis revealed that the effects of MPS, PP, and HDPE levels and the MPS*PP interaction on both the specific energy and tensile strength were highly significant at the 99% confidence level. They also found that the amount of newspaper fiber and the HDPE*fiber interaction were significant for specific energy, and the MPS*PE and MPS*PP fiber interactions significantly decreased tensile strength. SEM showed that the plastics were uniformly dispersed, but there was poor fiber/matrix adhesion. In addition, dynamic mechanical spectra further proved that chemical interaction did not take place between the individual components.

Felix and Gatenholm (1993) studied the mechanical properties of composites whose fiber surface properties had been modified by heat treatment, silane coupling agents, and by maleated polypropylene grafts. Various diagnostic methods, including inverse gas chromatography, contact angle measurements, and electron spectroscopy, were used to evaluate the effect of the modifications on the acid/base

properties of cellulose fiber surfaces. Mechanical properties of the composites were measured in order to clarify their importance, with regard to solid-state properties, in controlling acid/base interactions at the host polymer/fiber interface.

They found that the cellulose was amphoteric, with prevalent acidic properties. Heat and chloro-silane treatments accentuated acidity, while amino-silane treatments produced net basicity on the fiber surface. Modification with maleated polypropylene reduced specific interactions and converted the fiber to a predominantly dispersion-force solid. Different matrices were used, consisting of polypropylene (neutral), polystyrene (basic), and chlorinated polyethylene (acid). They also found that stress/strain and dynamic mechanical parameters varied with acid/base interactions between polymer and fiber. Significant improvements were noted in elastic and storage moduli, and in tensile strength and elongation. In polypropylene, properties were unaffected by acid/base considerations. They concluded that acid/base forces are not dominant; however, they do deserve attention when modifying the surfaces of materials in an attempt to improve the mechanical properties of composites.

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Belgacem et al (1994) investigated the effect of various corona treatment conditions on the mechanical properties of cellulose fiber/polypropylene composites. The cellulose fibers and polypropylene were modified using a wide range of corona treatment levels and concentrations of oxygen. Their recent work had shown that corona treatment improves the mechanical and rheological properties of cellulose/polyethylene composites. Such a treatment modifies the surface composition and, therefore, the surface properties of the composite components. In the case of cellulose fibers, corona treatment increases the surface energy and the acidity and basicity. The treatment level of the fibers was evaluated using the electrical conductance of their aqueous suspensions. The mechanical properties of composites obtained from different combinations of treated or untreated cellulose fibers and polypropylene were characterized by tensile stress-strain measurements. The mechanical properties improved substantially when either the cellulose fibers alone or both components were treated, although composites made from untreated cellulose fibers and treated polypropylene showed a relatively small improvement in their mechanical properties. The results they obtained indicated that dispersive forces are mostly responsible for the enhanced adhesion. They found that the work of adhesion

increases with the treatment level of cellulose. They stated that this fact confirms that the dispersive interactions play an important role in improving the mechanical properties.

Karmaker et al (1994) studied the influence of water uptake on the mechanical properties of jute fiber reinforced polypropylene. As the polypropylene melt cools during processing, it undergoes thermal shrinkage, which leaves some gaps between it (the matrix) and the jute fibers. Jute fibers absorb high amounts of water due to their hydrophilic nature. This absorption of water causes them to swell. Karmaker et al investigated whether these gaps could be filled by the swelling of the wetted jute fibers. They found that the swelling, due to water absorption of an individual fiber embedded in polypropylene, is able to fill the gap between the fiber and the matrix. The result was an increase in shear strength. In the case of jute yarn, the swelling of individual fibers could not increase the shear strength, because all of the voids couldn't be filled due to the highly viscous polypropylene melt. They concluded that if the individual fibers were embedded in the matrix polymer, water uptake by the composite wouldn't be as harmful to the composite's mechanical properties.

Schneider and Karmaker (1995) investigated the use of kenaf fibers and jute Bast fibers as fiber reinforcements in melt processed polypropylene composites. The fibers were chopped and mixed with polypropylene in a high intensity thermokinetic mixer. This mixture was then injection molded into test specimens. Tests for strength, stiffness, and Izod impact strength were conducted. Blends of 50/50 weight percent kenaf/PP (12 melt flow index (MFI)) and jute/PP (12 MFI) were prepared, with and without coupling agents (MAPP). In addition, blends of 40/60 weight percent kenaf/PP with coupling agent were prepared using two different types of PP: PP-L (12 MFI) and PP-H (50 MFI, nucleated, high stiffness).

They found that the jute fiber had better mechanical property values than the kenaf fiber. Also, the use of a coupling agent significantly increased the strength and impact properties of the composites, while elongation was decreased. Finally, compared to low MFI PP, high MFI PP had a minimal effect on most mechanical properties.

Karmaker and Youngquist (1996) studied the effect of fiber attrition, which occurred during injection molding, on the mechanical performance of jute/PP composites. In

addition, they studied the effect that MAPP had on jute/PP composites. The maleic anhydride grafted PP (MAPP), was added as a coupling agent to improve the adhesion between the jute fiber and PP. High fiber attrition was noted during injection molding, which had negative effects on the mechanical properties of the composites. The high fiber attrition was present for formulations with or without coupling agent. The coupling agent improved the tensile and bending strengths. However, the elastic and bending moduli were found not to be influenced by the coupling agent. In addition, the improved adhesion partially offset the fiber attrition and the associated strength loss that resulted from injection molding.

Karnani et al (1997) utilized matrix and fiber surface modification methods in an attempt to improve the mechanical properties of polypropylene (PP) composites reinforced with kenaf fibers. Both maleic anhydride modified PP (MAPP) and siloxane were used to improve the interfacial adhesion. The MAPP was added to the PP resin before it was fed into the twin screw extruder, to modify the PP matrix. The surfaces of the Kenaf fibers were modified by reacting them with siloxane in an aqueous reaction system. The modified fibers were extruded from a twin screw extruder with the modified

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PP matrix to form the compatibilized composite. The blends were then injection molded for mechanical characterization.

SEM observations showed a considerable difference in the fiber-matrix interaction between the compatibilized and uncompatibilized composites. The addition of MAPP resulted in a significant improvement in the wettability of the kenaf by the polymer. Also, the compatibilized PP-kenaf composites exhibited greater tensile strength and elongation than the uncompatibilized composites. This is accompanied by an increase in the toughness of the composite. In addition, there was a significant mechanical property improvement after surface modification of kenaf fibers with silane. Specifically, they said the increase in notched impact strength was remarkable. They also said that this indicated that long siloxane chains formed a ductile interface along with good fiber-matrix interfacial adhesion.

Gauthier et al (1998) discussed issues relating to the interface of polyolefin and cellulosic fibers in fiber reinforced composites. They stated that chemical modification of the cellulose is performed to allow good compatibilization. The most efficient compatibilizing agents must possess: 1) a function highly reactive with the

OH groups of the cellulose and, 2) a non-polar chain with preferably a polymeric structure. Also, smaller compatibilizing agents, especially if reacted with cellulose in a swelling media like water, can react with the bulk of the fiber and lead to dimensional stability. All treatments, even when performed with low degrees of grafting or small alkyl chains, significantly modify the hydrophilicity of the cellulose surface and play a role in a better wettability of the fiber by the matrix leading to improved adherence. Interestingly, they found that the morphology of the matrix in the vicinity of the non-treated fiber showed that, in some cases, the fiber acted as a nucleating agent involving the formation of a transcrystalline phase. However, only a small increase in the degree of crystallinity was observed. Also, the effect of this transcrystalline phase was not found to be either favorable or unfavorable to adherence characteristics. Finally, the effect of moisture can be limited by chemical treatment of the reinforcing fibers.

Luo and Netravali (1999) studied the mechanical and thermal properties of unidirectional, degradable composites made from pineapple fibers and poly (hydroxybutyrate-co-valerate) (PHBV) resin. They found that, compared to those

of virgin resin, the tensile and flexural strengths of the pineapple fiber composites were significantly higher in the longitudinal direction, while they were lower in the transverse direction. They also found that the mechanical properties were lower than those predicted in their models. This may be due to a higher void content and low interfacial shear strength, which resulted in less efficiency of load transfer. The thermal behavior, studied by thermogravimetric analysis (TGA), showed that the pineapple fibers did not affect the non-isothermal crystallization kinetics, crystallinity, and thermal decomposition of the PHBV resin.

METHODS

Conditioning of Paper Fiber

To condition the paper fiber, corrugated trays measuring 3.5 ft x 3.5 ft were constructed and then filled with the paper fiber to a depth of 2 inches. The trays were then placed in a conditioned room at 72 degrees F, 50% humidity for two weeks. After the first week, the paper fiber was stirred around to insure that all of the fibers were conditioned equally.

Determining Paper Fiber Moisture Content

The ASTM Standard D644-55, Standard Test Method for Moisture Content of Paper and Paperboard By Oven Drying, was followed. Eight aluminum trays were weighed and their weights recorded. They were then filled with conditioned paper fiber and weighed again. They were placed in a drying oven (National Vacuum Oven) for 24 hours at 50 +/- 3 degrees C. They were then removed and allowed to cool in a glass vessel whose bottom was filled with desiccant. The trays were then reweighed. The empty tray weights were deducted from the filled tray weights to determine the actual moisture loss from the paper fiber. The percentage of the moisture based on the original weight was calculated using

the following equation:

$$\text{Moisture, Percent} = [(W1 - W2)/W1] \times 100 \qquad \text{(EQ\# 21)}$$

where: W1 = original weight of the specimen

W2 = weight of the specimen after oven drying

Extruding the Composites

Before extruding the composites, preliminary steps were taken. First, the Zone 3 cover was removed from the co-rotating twin screw extruder (Werner-Pfleiderer 25k 30). Preheating the extruder was necessary to remove the cover. This is where the paper fiber was introduced into the barrel for mixing. The feeders were then set up and calibrated. The K-Tron Feeder was used to feed the HDPE resin and additive mixtures. A metal foil cone was fashioned to help direct the resin into the extruder's main feed hopper. The MDII-2000/BDFM Gravimetric Feeder was used to feed the paper fiber. A metal foil cone and paperboard chute were also made to facilitate easy feeding of the paper fiber.

When calibrating the feed rates of the machines, it was important to remember that the feed rates are impacted by the maximum amount of fiber one is able to push down into the extruder's zone 3 orifice, without overflow. Zone 3 was chosen as the place for fiber feeding, because this location

would facilitate mixing of the paper fiber and HDPE as they moved through zones 1 and 2. Zone 1 was closest to the die. In addition, the limited time in the barrel would limit thermal and physical damage to the fibers, which would have a detrimental effect on their performance. During calibration trials, it was found that 18.5 grams/minute of paper fiber was close to the maximum amount one could feed without overflow. The 18.5 grams/minute was set by using a bulk density of 13 and a set point of 13.3. The percent fiber loading level was then set using the following equation:

$$18.5/18.5+x = .35 \qquad \text{(EQ\# 22)}$$

where: x = 13.4 = feed rate of the resin (g/min.)

.35 = the chosen percent fiber loading of the composite

18.5 = feed rate of paper fiber (g/min.)

As will be discussed in the materials section, the 35% loading level was chosen because it was in the middle of the 30-40% fiber loading levels where ideal material properties were obtained in previous research. This would allow room for error in the paper feeding process. The 18.5 grams/minute of paper fiber feeding was utilized because it was found that the 34.4 grams/minute of resin feeding

calculated provided sufficient polymer/fiber extrudate flow out of the extruder at an extruder RPM setting of 120 RPM. The RPM of 120 was chosen because it has been used in previous research. The resulting torque percent hovered around 45%. The extruder could withstand a maximum torque of 90%.

The amount of resin planned for each production run was calculated using 1800 grams of HDPE as a base. It was found that this amount was excessive, and 1300 grams, or lower, of HDPE may be satisfactory for successful production runs in the future. The amount of additives used were all calculated as a percentage of the HDPE weight only. They were all then carefully mixed together with a mixer, and then mixed by hand in the composite lab.

Before each production day, conditioned paper fiber was placed in buckets and sealed in the conditioning room and then brought over to the lab. The extruder was preheated to 165 degrees C. This temperature is above the melt temperature of the HDPE and additives, but not too hot to cause thermal degradation during the processing. Pure HDPE was used before each production run to purge the extruder. During production, one person scraped the paper fiber into

the zone 3 orifice, and another person used a wooden plunger to push the paper fiber and paper fiber/HDPE chunks down into the barrel of the extruder. Paper fiber/HDPE chunks would often emerge out of the barrel. A third person was also needed to cut the extrudate into 6 inch pieces and lay them on sheet metal trays to air cool. During the production runs, there was variance in the zone temperatures and RPM readings. This could not be controlled. The die temperature was also unable to be controlled. However, the following readings are indicative of a typical production run:

Paper Feeder Settings

Bulk Density = 13

Set Point = 13.3

Resin Feeder Settings

9 RPM/HI SET/LOCAL/SP DISPLAY

Extruder Zone Temperature (degrees C)

Zone #1) 163

Zone #2) 164

Zone #3) 165

Zone #4) 172

Zone #5) 166

Zone #6) 165

Extruder Die Temperature (degrees C)

Die Temp. = 183

Extruder Settings

RPM = 121

Torque% = 45

Compression Molding

The extruded material was later compressed into plates using a Carver Laboratory Press, Model-M 25 Ton Capacity. To make plates from which tensile pieces would be machined, three 6 inch pieces of extrudate would be placed in a "sandwich". This "sandwich" would consist of, in the following order: chrome plate - Mylar sheet - frame - three 6 inch pieces of extrudate - Mylar sheet - chrome plate. The dimensions of the frame were 15 x 15 x .25 cm for tensile pieces and 12.7 x 12.7 x .3175 cm for impact and water absorption tests. Only two pieces of 6 inch extrudate were needed to make plates for impact and water absorption tests. For both types of plates, it is important to note the machine direction of the pieces and the corresponding

plates. The Mylar sheets were able to be used for the production of three plates. After three plates, the Mylar would begin to degrade, thus causing inconsistencies in the plates' surfaces.

Before each "sandwich" was made, the press was preheated to 165 degrees C. Once this temperature was attained, the "sandwich" was placed between the platens and the following procedure for opening the platens, applying hydraulic pressure, dwell time, and temperature settings were followed:

1) Apply hydraulic pressure to just above zero psi for 3 minutes.
2) Release pressure.
3) Apply hydraulic pressures at 600 psi for 1 minute.
4) Allow pressure to fall and release pressure (carefully lift top plate and Mylar sheet to vent steam).
5) Apply hydraulic pressure to 600 psi for 1 minute.
6) Allow pressure to fall and release pressure(vent steam).
7) Apply hydraulic pressure to 600 psi for 1 minute
8) Allow pressure to fall and release pressure(vent steam).
9) Apply hydraulic pressure to 600 psi for 1 minute.
10) Allow pressure to fall and release pressure.

11) Apply hydraulic pressure to 12,000 psi for 30 seconds.
12) Allow pressure to fall and release pressure.
13) Apply hydraulic pressure to 18,000 psi for 1 minute.
14) Allow pressure to fall and release pressure.
15) Apply hydraulic pressure to 30,000 psi for 8 minutes and maintain pressure.
16) Release pressure.
17) Apply hydraulic pressure to 30,000 psi for 7 minutes and maintain pressure.
18) Turn off heat, start cooling water, and maintain pressure for 10 minutes.
19) Place tape on plate showing machine direction of extrudate pieces.
20) Pop the plate out of the frame.

It was extremely important in the first eight steps to vent the steam! If it wasn't released, bubbles would form in the polymer upon cooling. This would weaken the composite and cause erroneous results.

Specimen Preparation

Once the plates were made, they were cut into pieces for tensile, impact, and water absorption tests. When cutting, the machine direction was noted and kept consistent

for all of the test pieces. The tensile pieces were first cut into dimensions of .75 inches wide, and 5.5 inches long. They were then machined into a Type I dumbbell configuration using the Tensilkut equipment. The impact and water absorption pieces were both cut into dimensions of .5 inches wide and 2.5 inches long. The impact pieces were later notched using the TMI Notching Cutter. The angle of the notch was 22.5 degrees +/- .5 degree and the notch depth was .1 inch.

Tensile Properties

The tensile pieces were conditioned at 23 +/- 2 degrees C and 50 +/- 5% RH for not less then forty hours before being tested on the United Calibration Corporation Model SFM-20, tensile tester. The ASTM Standard D638-98, Standard Test Method for Tensile Properties of Plastics, was followed to conduct the tests. A laser extensometer was also utilized. Two pieces of reflective tape were applied on the test piece so that their furthest edges were exactly two inches apart. A special die for applying the tape was used to facilitate this procedure. The following parameters were followed:

1) Laser Extensometer Utilized

2) Gauge Length = 2 inches

3) ASTM - Type I specimen

4) Crosshead Speed = .2 in./min.

5) Load Cell Capacity = 1000 lbs

6) Pre-Load Value = 5 lbs

If the specimens didn't break within the narrow section, they were discarded, as outlined in the ASTM standard. The results for percent elongation at break, modulus of elasticity, tensile strength, and yield strength, were calculated as follows:

1) Percent Elongation at Break = peak extension/original gage length x 100
2) Modulus of Elasticity = stress/strain in initial linear portion of behavior
3) Stress = force/original minimum cross sectional area
4) Strain = change in length/original gage length
5) Tensile Strength = maximum force/original minimum cross sectional area

Izod Impact Strength

The Izod impact pieces were conditioned at 23 +/- 2 degrees C, and 50 +/- 5% RH for not less than 40 hours. The

pieces were then tested following ASTM Standard D256-97, Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics, using a TMI 43-Izod Impact Tester with a 5 pound pendulum. The impact tester was first calibrated for each group of pieces with a single swing of the pendulum with no test pieces in place. Then, a test piece was placed in the clamp with a special jig provided with the tester. The pendulum was released, breaking the test piece, and the TMI impact tester would give the impact strength in ft. lb./in. This value was recorded, along with the break type as: complete, hinge, partial, or non-break. This was repeated for each group of test pieces.

Water Absorption

Water absorption by the test pieces was found by using ASTM Standard D570-98, Standard Test Method for Water Absorption of Plastics. The test pieces were first placed in aluminum trays and dried in a National Vacuum Oven for 24 hours at 50 +/- 3 degrees C. They were then allowed to cool in a desiccator, and were weighed to the nearest .001 gram. All of the test pieces were then placed together in a beaker of boiling distilled water and kept totally immersed for two hours. A Bunsen burner was used to administer the heat. After two hours, the test pieces were dried and immediately

reweighed to the nearest .001 g with the same scale. The increase in weight by the absorption of water was calculated with the following equation:

Percent Water Absorption =

(gain in weight (g)/conditioned weight (g)) x 100 (EQ# 23)

Statistical Methods

A significant part of statistical methods was the design of the experiment. A control was established, consisting of HDPE and recycled newspaper fiber. The ratios of these materials were then kept consistent in the other treatments. The first three treatments consisted of increasing percentages (3%, 6%, 10%) of MAHDPE additive. In treatments four and five, the MAHDPE additive was kept consistent at 6%, while the Proflow additive was varied at 5% for treatment four and 10% for treatment five. Treatments six and seven also had 6% MAHDPE additive. However, the LDPE additive was set at 5% for treatment six and 10% for treatment seven.

The data for this investigational study was analyzed by fitting it to a model for a "Completely Randomized Design". A completely randomized design is the name given to a design in which the experimenter assigns the experimental units to

the treatments completely at random, subject only to the number of observations to be taken on each treatment. Also, a model is an equation that shows the dependance of the response variable upon the levels of the treatment factors (Dean and Voss, 1999).

For this particular investigational study, pure HDPE and recycled newspaper fiber were designated as the control. The pure HDPE and recycled newspaper fiber were then subjected to seven different treatments. The possible effects of the treatments were then determined according to the following model for a Completely Randomized Design:

	1	2	3	4	5	6	7	8
A	#	#	#	#	#	#	#	#
B	#	#	#	#	#	#	#	#
C	#	#	#	#	#	#	#	#
D	#	#	#	#	#	#	#	#
E	#	#	#	#	#	#	#	#
	Y1	Y2	Y3	Y4	Y5	Y6	Y7	Y8

(NOTE: 1 is the control, and # represents a measured value)

where, Response = constant + effect of treatment + error

or, $Y_{ij} = M + R_i + E_{ij}$

and, i = treatments 1-8

j = observations A-E

The variable Y_{ij} represents all of the observations, M represents the constant or overall mean, R_i represents the effect of the treatments, and E_{ij} represents the experimental error which is assumed to be mutually independent and normally distributed with a mean of 0 and variance $Ó^2$. It is also assumed in this model that the specimens are homogeneous and the variance is constant. It is also important to note that this model is a linear model, and it was fitted to a General Linear Model (GLM) in the SAS software. According to Dean and Voss (1999) the method of Least Squares is used to obtain estimates and estimators for estimable functions of parameters in linear models. The expression $Y_{ij} = M + R$ is then used to determine the Least Squared Means (LSM) of each group. The difference between each groups' LSM is then calculated. These differences are tested, F-values and T-values are found, as well as the corresponding probability values Pr > F for the "F" values, and Pr > | T | for the observed "T" values.

These steps were all taken by the SAS software. However, in order to interpret the data, several steps had to be taken. First, the null and alternative hypotheses had

to be established. These were used to show if certain treatments had an effect or not. The null hypothesis stated that there was no significant difference between the means of the groups, and the alternative hypothesis was set up contrary to this by stating that there was a significant difference. If a significant difference was found, it meant that a particular treatment had a significant effect.

Another step was the establishment of an alpha. An alpha is known as the probability of a type 1 error. A type 1 error occurs when one rejects the null and says there is a significant difference when actually there is no significant difference. The most important probability in hypothesis tests is usually the alpha (Watson et al, 1993). In this study, the alpha was set at 5%. This means there was only a 5% chance of a type 1 error. With the alpha set at 5%, a comparison was first made between it and the probability value Pr > F. If that value was less than 5%, the null hypothesis would be rejected and the statistical model for that particular trial would be statistically significant. If the model for that trial was found to be statistically significant, one could look at the probability values Pr > | t |, for the different treatments. If the probability value Pr > | t | was less than 5% for a treatment, the null

hypothesis was rejected. As mentioned earlier, this meant that a particular treatment had a significant effect.

MATERIALS

High density polyethylene (HDPE) is an addition polymer based on ethylene, and it is a semicrystalline thermoplastic. Thermoplastics will repeatedly melt when heated and harden when cooled. In contrast, thermosets cannot be remelted and reshaped once they have cured. If this is attempted with sufficient heat, they will degrade, char, or burn. This is due to their cross-linked structure. Thermoplastics are, therefore, ideal for recycling.

The HDPE used in this study was provided by Exxon Chemical Corporation. Its product name was AD60-007. The HDPE was used to form the matrix of the composites. In some previous studies, recycled milk bottles were cut into chunks and then granulated into the HDPE resin which was used as the matrix.

HDPE's high crystalinity is due to its regular placements of atoms in its polymer chains (Hernandez and Selke, 1998). In fact, its chains are very linear without any substantial branching. This enables the chains to pack closely together in a regular, parallel array, thus facilitating crystal growth. This close packing of the

molecules and resultant crystal growth is responsible for HDPE's high density characteristics. According to ASTM, HDPE is a Type III polyethylene with its density in the range of 0.941-0.959 g/cc. In contrast, low density polyethylene (LDPE) is a Type I polyethylene and its density is in the range of 0.910-0.940 g/cc. The high crystallinity and density of HDPE has an impact on its properties. For example, as the crystallinity and thus density increases, stiffness, tensile strength, and creep resistance increase. However, impact strength, elongation, flexibility, toughness, and ductility decrease.

In addition, HDPE is non-polar, and thus, hydrophobic because of the basic structure of the molecule. The structure of HDPE may be found in Appendix C. HDPE's melt temperature is between 130-135 degrees C and its glass transition temperature is -120 degrees C.

The additives used in this study were maleic anhydride modified HDPE (MAHDPE), Proflow 1000, and LDPE. The MAHDPE was provided by Uniroyal Chemical, Inc. Its product name was Polybond 3009 and its melting point was 127 degrees C. MAHDPE is a coupling agent, and its purpose is to couple the non-polar HDPE with the polar paper fiber reinforcement.

According to Childress (1991), very small amounts of coupling agent can produce significant improvements in mechanical properties. Childress (1991), stated that only a monolayer of coupling agent is sufficient to improve the bond between the fiber and matrix. This is important because it is known that the hydrophilic cellulosic fibers have no adhesion to hydrophobic thermoplastic matrices such as polyethylene (Herrara-Franco and Aguilar-Vega, 1997).

Proflow 1000 was another additive used in this study. It was provided by Polyvisions Inc. Proflow 1000 is an isotactic homopolymer of polypropylene with a melting point of 161 degrees C. The structure of Proflow 1000 may be found in Appendix C. At this melt temperature, the Proflow 1000 would rapidly transform to a low melt viscosity, allowing it to be readily dispersed into other plastics (Childress, 1991). This is important because it is known that the high viscosity of the matrix during composite fabrication hinders the paper fiber dispersion, and, therefore, results in a poor fiber-matrix interaction (Herrera-Franco and Aguilar-Vega, 1997). It was hoped that the Proflow 1000 would decrease the viscosity of the mix facilitating fiber wetting and a more homogeneous dispersion within the matrix.

Another additive used was low density polyethylene (LDPE). It was supplied by the Dow Chemical Company, and its product name was DOW LDPE 993I. LDPE is a thermoplastic homopolymer of ethylene. It is fabricated under high pressure and temperature conditions by a free radical polymerization process (Hernandez and Selke, 1998). Its structure differs from HDPE because it has extensive chain branching. These branches inhibit the polymer chains from packing close together, thus preventing extensive crystal growth as seen with HDPE. The crystallinity of branched polyethylene is in the range of 40-60%, while its density ranges from 0.910-0.940 g/cc. Its melt temperature is in the range of 105-115 degrees C, while its glass transition temperature is -120 degrees C. It was hoped that the LDPE would also aid in fiber wetting and dispersion by decreasing the viscosity of the mix and improving its flow.

Recycled newspaper fiber was used in this study as the fiber reinforcement. It was provided by Interfibe. Paper fibers are a hygroscopic material. This is due to the presence of hydroxyl groups and C-O-C links in their structure. (Please refer to Appendix C for its molecular structure.) A cross section of a paper fiber looks somewhat like a hollow tube of irregular shape (Hanlon, 1992).

Externally, they are observed to be of an elongated shape with closed pointed ends. The open center portion is called the lumen, and this is surrounded by a wall made up of layers, or lamellae, of fibrils. These fibrils, which have diameters of about 0.000001 inch, are made up of microfibrils about one-tenth this size and about .00005 inch long. These, in turn, are composed of chains of cellulose molecules, about 3 million in each microfibril, along with short chain hemicellulose molecules and other residues (Hanlon, 1992). During the paper-making process, individual fibrils extend out and interlock with other fibers. It has been discovered that a fiber's tensile strength decreases rapidly with increasing fibril angle. The fibril angle is measured from the longitudinal axis of the secondary cell wall (Biermann, 1996).

In past studies, mixed paper and high grade deinked newspaper were used to determine the optimum fiber loading level for paper fibers in HDPE. It was determined that ideal material properties were obtained between 30-40% of paper fiber loading (Chotipatoomwan, 1998). A 35% fiber loading level was chosen for this investigational study.

RESULTS AND DISCUSSION

Results - Izod Impact Strength

Results determined from the Izod impact strength tests are given in Table 1, and presented graphically in Figure 1. It was observed during testing that all of the samples broke in a brittle manner. All of the test pieces broke with a clean fracture, perpendicular to their lengths. Statistical analysis was conducted, and the Pr > F value, .0784, was greater than the alpha of .05. This meant that the statistical model for the Izod impact strength data was not statistically significant. In other words, there was no statistically significant difference, at the chosen confidence level, between the means of the different treatments. Therefore, no further comparisons were made between the results of these treatments.

Table 1. Izod Impact Strength Results

Izod Impact Strength, (Ft-lb/in)		
Materials	**Mean**	**Std. Dev.**
NO ADDITIVES - HDPE/FIBER	0.666	0.019
3% MAHDPE	0.728	0.040
6% MAHDPE	0.715	0.053
10% MAHDPE	0.665	0.057
6% MAHDPE, 5% PROFLOW	0.667	0.063
6% MAHDPE, 10% PROFLOW	0.644	0.021
6% MAHDPE, 5% LDPE	0.693	0.043
6% MAHDPE, 10% LDPE	0.723	0.066

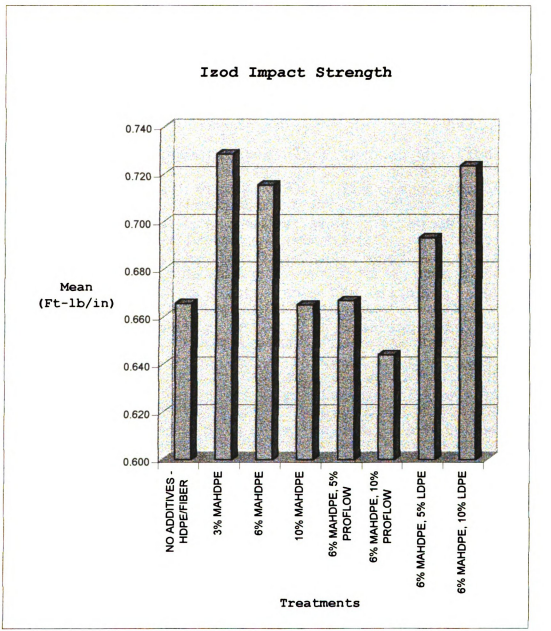

Figure 1. Izod Impact Strength

Dicussion - Izod Impact Strength

According to Mallick (1993), the impact properties of a material represent its capacity to absorb and dissipate energies under impact or shock loading. In most fiber filled composites, a significant part of the energy absorption during impact takes place through the fiber pullout process (Devi et al, 1997). The energy involved, and hence toughness, are greatest when the length of the fibers is less than the critical fiber length of the fiber reinforcement. Fibers shorter than the critical length are pulled out of the matrix rather than breaking when a crack passes through the composite as a result of the impact. The resulting fracture energy is a combination of the work needed to debond the fibers from the matrix and the work done against friction in pulling the fibers out of the matrix (Devi et al, 1997). Devi et al (1997) also stated that a decrease in impact strength is found for fiber lengths above the critical fiber length, because only a proportion of the fibers will pull out.

Unfortunately, the critical fiber length of the particular paper fibers used in this study has not yet been established. Thus, the fracture energy arising from fiber

pull-out cannot be calculated according to the formula given by Devi et al(1997), for fibers whose length is shorter than (Lc):

$$U = (V)(Is)(\ell)^2/12(d) \qquad \text{(EQ \#24)}$$

or, for fibers greater than (Lc):

$$U = (V)(Is)(\ell c)^3/12(d)(\ell) \qquad \text{(EQ \#25)}$$

where,

U = the fracture energy arising from fiber pull-out

V = the volume fraction of the fiber

Is = the interfacial friction stress

ℓ = the length of the fiber

ℓc = the critical length of the fiber

d = the diameter of the fiber.

However, it is important to see that this fracture energy is influenced by the strength of the fiber-matrix interface, which has to be debonded. The use of MAPP in this study was intended to improve the fiber-matrix adhesion at this interface. According to Mallick (1993), the failure mode of a composite is brittle and relatively little energy is absorbed when there is a high level of adhesion. If there had been a significant difference between the results of the impact data from the various trials in this study,

this might have been a good explanation of that finding. It is important to note that the control and all of the different trials were similar because they all had similar fiber loading. Chotipatoomwan (1998) found that the inclusion of paper fibers into the HDPE matrix caused the composite to be brittle. This would explain the homogeneity of the different trials and the control, with respect to their brittleness. In addition, Kalyankar (1989) stated that with a ductile matrix, like polyethylene, the triaxial restraint of the matrix between fibers limits the elongation of the matrix, and reduces the toughness of the composite.

Results - Yield Strength

The yield strength results are given in Table 2, and presented graphically in Figure 2. Statistical analysis was conducted, and the Pr > F value, .0345, was less than the alpha of .05, indicating a statistically significant difference between treatments. The 3% MAHDPE and 10% MAHDPE treatments had significantly higher yield strengths than the control. In addition, a statistically significant difference was found between the 3% MAHDPE and the 6% MAHDPE treatments. The yield strength of the 3% MAHDPE composite was 725 psi higher than the yield strength of the 6% MAHDPE composite. The 3% MAHDPE treatment had the highest yield strength at 3271 psi. The second highest yield strength was with the 10% MAHDPE treatment, at 2978 psi.

Table 2. Yield Strength Results

Yield Strength, (psi)		
Materials	**Mean**	**Std. Dev.**
NO ADDITIVES-HDPE/FIBER	2,134.16	285.93
3% MAHDPE	3,271.64	664.54
6% MAHDPE	2,546.36	366.05
10% MAHDPE	2,978.58	810.60
6% MAHDPE, 5% PROFLOW	2,516.98	267.06
6% MAHDPE, 10% PROFLOW	2,376.47	801.95
6% MAHDPE, 5% LDPE	2,294.93	103.31
6% MAHDPE, 10% LDPE	2,513.18	385.86

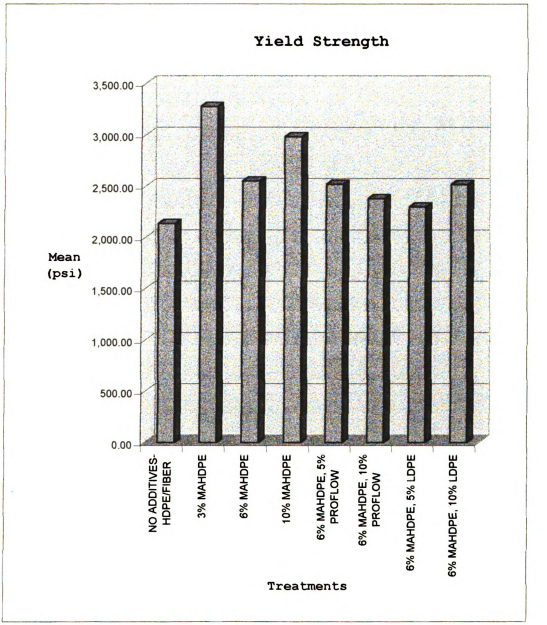

Figure 2. Yield Strength

Results - Modulus of Elasticity

The results determined for the modulus of elasticity are given in Table 3, and presented graphically in Figure 3. Statistical analysis was conducted, and the Pr > F value, .3808, was greater than the alpha of .05. This meant that the statistical model for the Modulus of Elasticity data was not statistically significant. In other words, there was no statistically significant difference, at the chosen confidence level, between the means of the different treatments. Therefore, no comparisons were made between the results of these treatments.

Table 3. Modulus of Elasticity Results

Modulus of Elasticity, (kpsi)		
Materials	**Mean**	**Std. Dev.**
NO ADDITIVES - HDPE/FIBER	232.00	72.33
3% MAHDPE	233.80	25.03
6% MAHDPE	213.40	13.35
10% MAHDPE	232.00	24.47
6% MAHDPE, 5% PROFLOW	218.00	29.99
6% MAHDPE, 10% PROFLOW	225.40	48.31
6% MAHDPE, 5% LDPE	183.60	7.33
6% MAHDPE, 10% LDPE	200.80	36.99

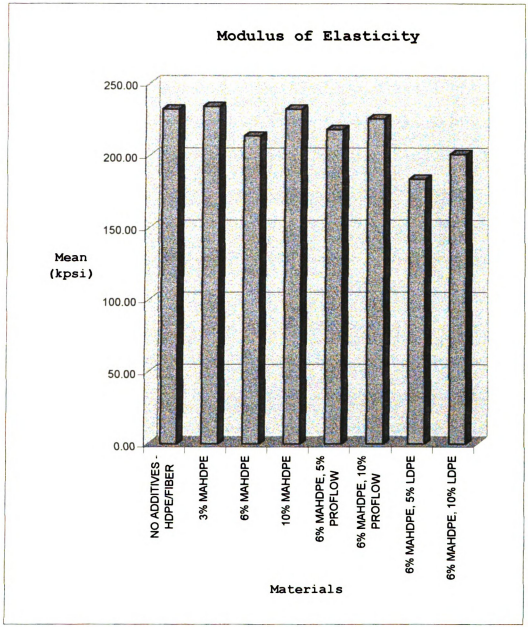

Figure 3. Modulus of Elasticity

Results - Tensile Strength

The tensile strength results are given in Table 4, and presented graphically in Figure 4. Statistical analysis was conducted, and the Pr > F value, .0079, was less than the alpha of .05, indicating a statistically significant difference between treatments. All of the different treatments, except treatment six, had significantly higher tensile strengths than the control. In addition, a statistically significant difference was found between the 6% MAHDPE and the 10% MAHDPE treatments. The tensile strength of the 10% MAHDPE composite was 654 psi higher than the tensile strength of the 6% MAHDPE composite. In fact, treatment three, with the 10% MAHDPE, had the highest tensile strength at 3774 psi. The second highest tensile strength was with the 3% MAHDPE treatment, while treatment seven, with 6% MAHDPE and 10% LDPE, had the third highest tensile strength. The fourth highest tensile strength belonged to the 6% MAHDPE and 10% Proflow treatment. In contrast, the second lowest tensile strength belonged to the 6% MAHDPE and 5% LDPE treatment.

Table 4. Tensile Strength Results

Tensile Strength, (psi)		
Materials	**Mean**	**Std. Dev.**
NO ADDITIVES - HDPE/FIBER	2,359.40	366.65
3% MAHDPE	3,461.40	421.46
6% MAHDPE	3,120.40	691.77
10% MAHDPE	3,774.80	452.98
6% MAHDPE, 5% PROFLOW	3,153.20	410.41
6% MAHDPE, 10% PROFLOW	3,199.80	614.69
6% MAHDPE, 5% LDPE	2,916.60	497.00
6% MAHDPE, 10% LDPE	3,345.60	487.31

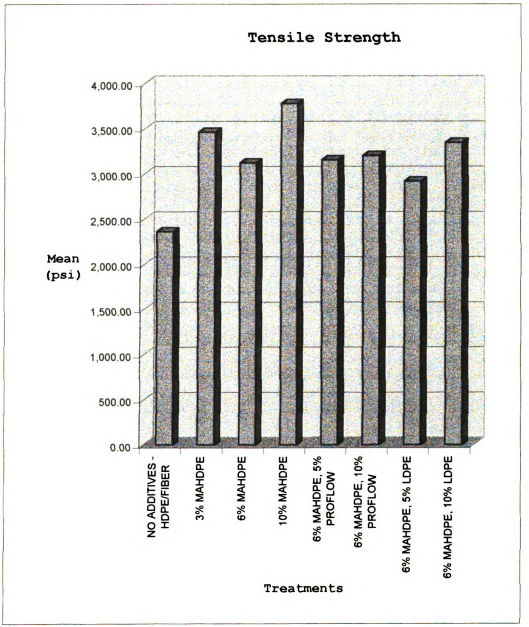

Figure 4. Tensile Strength

Results - Percent Elongation at Break

The results determined for percent elongation at break are given in Table 5, and presented graphically in Figure 5. Statistical analysis was conducted, and the Pr > F value, .2297, was greater than the alpha of .05. In other words, there was no statistically significant difference, at the chosen confidence level, between the means of the different treatments. Therefore, no comparisons were made between the results of these treatments. However, it is important to note that the percent elongation was very small, with 2.5% being the largest mean percent elongation for the 6% MAHDPE and 10% LDPE treatment.

Table 5. Percent Elongation at Break Results

Percent Elongation at Break, (psi)		
Materials	**Mean**	**Std. Dev.**
NO ADDITIVES - HDPE/FIBER	1.66	0.54
3% MAHDPE	2.19	0.59
6% MAHDPE	1.90	0.87
10% MAHDPE	2.42	0.36
6% MAHDPE, 5% PROFLOW	1.79	0.37
6% MAHDPE, 10% PROFLOW	1.88	0.60
6% MAHDPE, 5% LDPE	1.87	0.66
6% MAHDPE, 10% LDPE	2.50	0.43

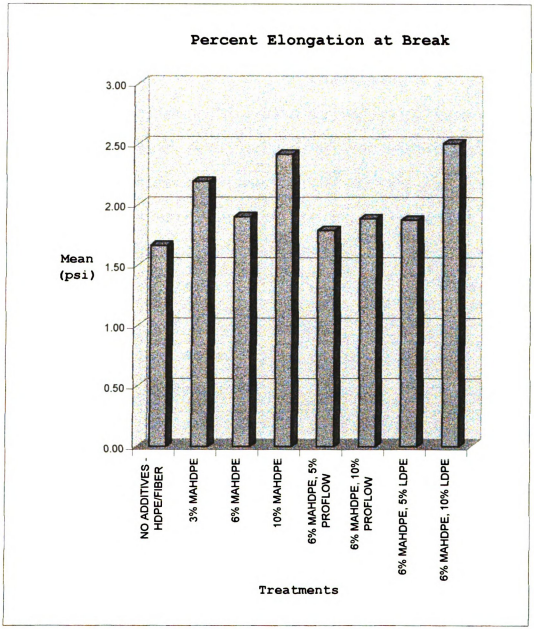

Figure 5. Percent Elongation at Break

Discussion - Tensile Properties

A material's tensile properties are indicative of its mechanical strength. Each test specimen's yield strength, modulus of elasticity, tensile strength, and percent elongation at break were found by conducting a tensile test of each test specimen. This data is important because it helps to characterize each composite test sample modified by a particular treatment. However, the statistical models for yield and tensile strength were the only ones found to be statistically significant. The outcome of these tests were impacted by various factors. For example, all of the test specimens failed with a brittle fracture, and a very small percent elongation. As mentioned in the discussion of test results impact, the composite's brittle nature is due to fiber loading of the HDPE matrix. The composite's brittleness reduced its percent elongation. In addition, MAHDPE was used to improve the interfacial adhesion between the hydrophilic paper fiber reinforcement and the hydrophobic HDPE matrix. This results from the anhydride groups present in the MAHDPE providing polar interaction, or even covalently bonding to the hydroxyl groups of the fiber surfaces (Rowell et al, 1997). Hull (1981) stated that composite materials with weak interfaces have relatively low strength and stiffness, but high resistance to fracture,

whereas materials with strong interfaces have high strength and stiffness but are very brittle. This effect is related to the ease of debonding and pull-out of fibers from the matrix during crack propagation, as mentioned in the Izod impact strength discussion. This point is reinforced as Rowell et al (1997), discovered that a small amount of MAPP (0.5% by weight) improved the flexural and tensile strength, tensile energy absorption, and Izod impact strength of kenaf/PP composites. They stated that improving the vending at the fiber matrix interface with MAPP increased the resistance to crack initiation at the fiber-matrix interface. Also, the improved interaction and adhesion between the fibers and the matrix lead to better matrix-to-fiber stress transfer.

In this particular study, the addition of MAHDPE was found to improve tensile strength and yield strength. The 10% MAHDPE treatment had the highest tensile strength, while the 3% MAHDPE treatment had the highest yield strength. It can be assumed that the other treatments were found to have statistical significance with regards to tensile strength, because of the presence of the 6% MAHDPE, which was held consistent through treatments 4-7. The inclusion of the 6% MAHDPE in these treatments allowed for greater adhesion than

the control, which didn't have any MAHDPE. However, only the 6% vs. 10% MAHDPE treatment comparison was found to be statistically significant for tensile strength. The 10% MAHDPE treatment had a higher tensile strength due to improved adhesion, which the higher concentration of MAHDPE was able to produce. It is surprising that only the MAHDPE was found to be statistically significant, since additives like the Proflow 1000, or LDPE were expected to produce better flow characteristics than HDPE. According to Mallick (1993), proper flow of resin through fiber networks or lay ups is critical in producing void-free parts and good fiber wet out. Without effective wetting of the fiber, strong interfacial adhesion cannot exist (Bledzki et al, 1996). This is important because, as mentioned earlier, interfacial adhesion affects the matrix to fiber stress transfer. Karnani et al (1997) stated that stress transfer efficiency plays a dominant role in determining the mechanical properties of a composite. It is probable that the Proflow 1000 and LDPE had difficulty in wetting the paper fiber. According to Bledzki at al (1996), wettability is impacted not only by a polymer's viscosity, but also the surface tension of both the polymer and the material it is intended to wet. The surface tension of the polymer should be as low as possible, at least lower than the surface tension of the

fiber. There are different methods of modification to change the surface energy of the fiber and the polymer. This is something which can be explored in the future.

Results - Water Absorption

The water absorption results are given in Table 6, and presented graphically in Figure 6. Half way through the test, the water in the beaker started to turn green and debris began to collect at its surface. By the end of the experiment, the amount of the floating debris had intensified and the water became a darker green color. Also, all of the test pieces' outer surfaces had changed from smooth to rough, and they had experienced discoloration. It was apparent that debonding of the paper fibers from the matrix had occurred. Most of the debonding must have occurred with the control, since it lost a substantial amount of weight. The data also shows that all of the other treatments had gained weight. However, meaningful measurements were not able to be made for water absorption, since all of the test pieces may have simultaneously lost weight from debonding, but also gained weight from water absorption. Therefore, a discussion involving statistical analysis for this particular test is irrelevant since the measurements made were not meaningful.

Table 6. Water Absorption Results

Water Absorption, (g)	*Mean,*	
Materials	*% Change*	*Std. Dev.*
NO ADDITIVES - HDPE/FIBER	-0.4147	0.5693
3% MAHDPE	0.5525	0.0593
6% MAHDPE	0.9167	0.1439
10% MAHDPE	0.8917	0.2624
6% MAHDPE, 5% PROFLOW	0.7941	0.1195
6% MAHDPE, 10% PROFLOW	0.6499	0.1674
6% MAHDPE, 5% LDPE	0.6987	0.0825
6% MAHDPE, 10% LDPE	0.6664	0.2085

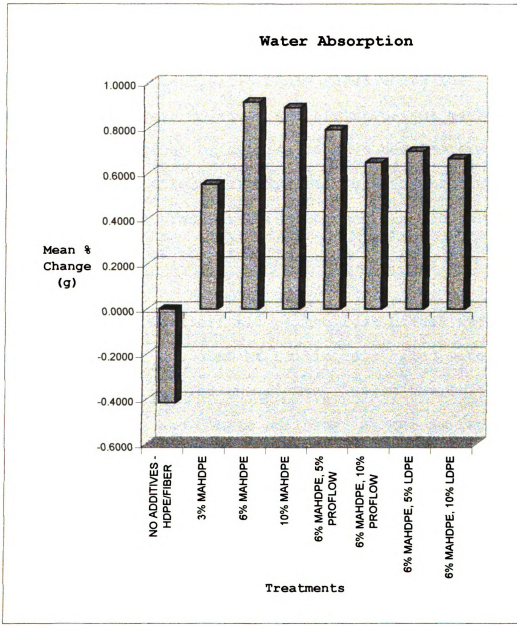

Figure 6. Water Absorption

Discussion - Water Absorption

According to ASTM, D570-98, the Standard Test Method for Water Absorption of Plastics, has two chief functions: first, as a guide to the proportion of water absorbed by a material and consequently, in those cases where the relationships between moisture and electrical or mechanical properties, dimension, or appearance have been determined, as a guide to the effects of exposure to water or humid conditions on such properties; and second, as a control test on the uniformity of the product.

As mentioned earlier, all of the test pieces were placed together in a beaker of boiling distilled water and kept totally immersed for two hours. During the test, the water turned green and debris collected at the surface of the water in the beaker. It was clear that the water had interacted with the hydrophilic paper fibers. This is possible due to the polar nature of water and the chemical structure of cellulose, which has many hydroxyl groups which are available for interaction with the water molecules by hydrogen bonding (Gauthier et al, 1998). The control had lost substantial weight due to debonding, and Bledzki et al (1996) explained why this could happen. They said that the absorption of moisture by untreated fibers, poor

wettability, and insufficient adhesion between the polymer matrix and fiber leads, in time, to debonding. They also said that the lack of interfacial interactions leads to internal strains, porosity, and environmental degradation. It is possible for that to happen with the treatments as well as the control, but their weight loss due to debonding may have been masked by their weight gain due to moisture absorption. In the control, the weight loss was larger and may have masked any weight gain from moisture absorption.

Results & Discussion - Fiber Moisture Content

In order to calculate the moisture content in the paper fibers, ASTM Standard D644-55 was followed. The initial and final weights were recorded and then used in the calculations, to find this value. The fiber moisture content is expressed as the percentage of moisture contained by the fibers based on the original weight. The average percent moisture was found to be 5.0295%

The percent moisture is important, because during processing it can vaporize and be trapped in the resin or fibers. According to Mallick (1993), trapped air, or other gasses can exist in the cured composite as micro voids, which can affect its mechanical properties. He also stated that a high void content (over 2% by volume) usually leads to lower fatigue resistance, greater susceptibility to water diffusion, and increased variation in a composite's mechanical properties.

Discussion - Variability

Unfortunately, the results obtained in this study were plagued with variability from various sources. For example, the MDII-2000/BDFM Gravimetric Feeder did not have a consistent output of paper fiber into the extruder. Its output would oscillate. This may have been due to bridging of the fiber inside the apparatus, which would cause the machine to speed up its output in an attempt to reach the desired average output. Bridging results when the fiber becomes clogged above the auger. Once the bridge would break, and the average was met, it would slow down until another bridge would form. Another source may have been inconsistent mixing of the fiber within the extruder. Variability may have also been introduced when the plates were pressed with the Carver Laboratory Press. When the resin melted and flowed to fill the frame, the fibers may not have filled that area in a homogeneous manner. These sources may help to explain the clumping of fibers which could be visually recognized in the samples. Finally, variability may be due to the presence of gases during extrusion or plate pressing. These gases were evident when they were vented while pressing plates with the Carver Laboratory Press. The gases may have been moisture from the fibers, or other volatiles. This is important to note,

because gases can be caught in the fibers or resin and form voids. These voids will weaken the composite. It is important to discuss these potential sources of variability, because they may cause one to determine that a particular treatment is not statistically significant when it actually does have an effect.

SUMMARY

This investigational study succeeded in fulfilling its purpose of determining the effects of certain additives on the physical and mechanical properties of a fiber reinforced composite consisting of an HDPE matrix and recycled newspaper fiber as the reinforcement.

The control for this study consisted of HDPE and recycled newspaper fiber. The fiber loading level was set at 35%. This loading level remained throughout the study. The first three treatments consisted of increasing percentages (3%, 6%, 10%) of MAHDPE additive. MAHDPE was kept constant at 6% for the remaining four treatments. Proflow 1000 was varied at 5% for treatment four, and 10% for treatment five. LDPE was set at 5% for treatment six, and 10% for treatment seven. To determine the effect of these additives, tensile testing, Izod impact tests, and water absorption tests were conducted.

The interface between the matrix and the reinforcing fibers is crucial because it impacts the properties of the composite by influencing the transfer of stress from the matrix to the fibers. The additives used in this study were

chosen in an attempt to increase the performance of the composite by enhancing this interface. MAHDPE's purpose was to couple the non-polar HDPE with the polar paper fibers. Proper adhesion is essential to prohibit debonding of the fiber and matrix, as well as to decrease internal stresses and environmental degradation. Improved adhesion also leads to better matrix-to-fiber stress transfer. The Proflow 1000 and LDPE were added to decrease the viscosity of the mix within the extruder, facilitating fiber wetting and a more homogeneous dispersion within the matrix. Incomplete wetting of the fibers can cause voids which will weaken the composite. In addition, effective wetting leads to strong interfacial adhesion.

This study found that the various treatments had no statistical significance with respect to modulus of elasticity, percent elongation, and Izod impact strength. However, all of the test speciments broke in a brittle manner. In addition, the tensile test specimens had a very small percent elongation due to their brittleness. This is due to fiber loading and the triaxial restraint of the matrix between the fibers.

The addition of MAHDPE was found to improve tensile

strength and yield strength. The 10% MAHDPE treatment had the highest tensile strength, while the 3% MAHDPE treatment had the highest yield strength. The Proflow 1000 and LDPE were not found to have any significant effect on the composite's tensile properties. This may be due to incompatible surface energies with the paper fiber.

Also, most of the debonding observed during the water absorption test, must have occurred with the control, since the test data showed that it lost a substantial amount of weight. The test data also showed that all of the other treatments had gained weight. However, meaningful measurements were not able to be made for water absorption, since all of the test pieces may have simultaneously lost weight from debonding, but also gained weight from water absorption.

Finally, venting of released gas during compression molding is essential to minimize the formation of voids, which will weaken the composite.

RECOMMENDATIONS FOR FUTURE RESEARCH

A replacement for the MDII-2000/BDFM Gravimetric Feeder should be strongly considered. It has difficulty feeding paper fiber consistently. Another K-TRON Feeder with a larger hopper than the one presently in the lab would suffice. Its feed rate is controlled by an RPM setting, unlike the MDII-2000/BDFM Gravimetric Feeder. This would provide consistent feeding. Also, it is important for future researchers to vent the gases when using the Carver Laboratory Press. Future researchers may also want to granulate the extrudate from the twin screw extruder and try injection molding the test plates, instead of forming them with the Carver Laboratory Press.

Future studies could also focus on the fibers themselves. Tests could be done to determine their surface energy, stiffness, and strength. In addition, Zadorecki et al (1986) stated that a mechanical treatment of fibers in the presence of water (beating process) increases the fiber surface through fibrillation and makes fibers more flexible. Future studies could be conducted by investigating this effect on recycled newspaper fiber. If this treatment does have an effect, one could also determine at what point this

treatment ceases to be advantageous, by discovering when the average fiber length of the fibers drops below the critical length, due to fiber fracture. The fibers could also undergo surface treatments to change their surface energy to be more compatible with the HDPE matrix and additives like Proflow 1000. This could promote better adhesion and wetting. For example, the fiber surface energy could be increased to a compatible level with corona or cold plasma treatments. According to Bledzki et al (1996), the corona treatment works by surface oxidation activation. They also said that a variety of surface modifications can be achieved with cold plasma treatments depending on the type and nature of the gases used. Cold plasma can promote surface cross linking, produce reactive free radicals and groups, and increase or decrease surface energy. They stated that these methods have been very effective with polystyrene, polyethylene, and polypropylene polymer substrates. Herrera-Franco et al (1997), also stated that silane coupling agents have been shown to increase the strength of composites reinforced with cellulose by improving their fiber-matrix adhesion. This could also be applied to research involving composites consisting of an HDPE matrix reinforced with recycled newspaper fibers.

APPENDIX

Table 7. Izod Impact Strength Data

Izod Impact Strength, (Ft-lb/in)							
Materials	**Piece 1**	**Piece 2**	**Piece 3**	**Piece 4**	**Piece 5**	**Mean**	**Std. Dev.**
NO ADDITIVES - HDPE/FIBER	0.677	0.682	0.678	0.651	0.640	0.666	0.019
3% MAHDPE	0.662	0.760	0.722	0.749	0.749	0.728	0.040
6% MAHDPE	0.682	0.785	0.755	0.656	0.699	0.715	0.053
10% MAHDPE	0.736	0.602	0.713	0.635	0.639	0.665	0.057
6% MAHDPE, 5% PROFLOW	0.628	0.766	0.693	0.622	0.625	0.667	0.063
6% MAHDPE, 10% PROFLOW	0.628	0.667	0.633	0.625	0.667	0.644	0.021
6% MAHDPE, 5% LDPE	0.740	0.683	0.656	0.651	0.736	0.693	0.043
6% MAHDPE, 10% LDPE	0.748	0.722	0.683	0.645	0.819	0.723	0.066

Table 8. Yield Strength Data

Yield Strength, (psi)							
Materials	**Piece 1**	**Piece 2**	**Piece 3**	**Piece 4**	**Piece 5**	**Mean**	**Std. Dev.**
NO ADDITIVES-HDPE/FIBER	2,307.62	2,126.47	2,207.64	2,377.06	1,652.00	2,134.16	285.93
3% MAHDPE	3,713.59	3,523.16	2,629.52	3,985.63	2,506.29	3,271.64	664.54
6% MAHDPE	2,108.16	3,029.98	2,342.71	2,458.03	2,792.91	2,546.36	366.05
10% MAHDPE	2,929.54	2,340.74	4,360.76	2,448.03	2,813.82	2,978.58	810.60
6% MAHDPE, 5% PROFLOW	2,374.09	2,541.57	2,278.65	2,963.51	2,427.08	2,516.98	267.06
6% MAHDPE, 10% PROFLOW	1,114.12	2,623.72	2,264.38	2,572.60	3,307.51	2,376.47	801.95
6% MAHDPE, 5% LDPE	2,202.23	2,391.88	2,295.35	2,181.50	2,403.71	2,294.93	103.31
6% MAHDPE, 10% LDPE	2,209.88	3,170.28	2,268.52	2,513.25	2,403.98	2,513.18	385.86

Table 9. Modulus of Elasticity Data

Modulus of Elasticity, (kpsi)							
Materials	**Piece 1**	**Piece 2**	**Piece 3**	**Piece 4**	**Piece 5**	**Mean**	**Std. Dev.**
NO ADDITIVES - HDPE/FIBER	339.00	267.00	197.00	204.00	153.00	232.00	72.33
3% MAHDPE	223.00	218.00	229.00	278.00	221.00	233.80	25.03
6% MAHDPE	207.00	236.00	204.00	205.00	215.00	213.40	13.35
10% MAHDPE	249.00	231.00	263.00	213.00	204.00	232.00	24.47
6% MAHDPE, 5% PROFLOW	202.00	215.00	195.00	270.00	208.00	218.00	29.99
6% MAHDPE, 10% PROFLOW	199.00	201.00	187.00	306.00	234.00	225.40	48.31
6% MAHDPE, 5% LDPE	181.00	181.00	191.00	174.00	191.00	183.60	7.33
6% MAHDPE, 10% LDPE	193.00	257.00	169.00	216.00	169.00	200.80	36.99

Table 10. Tensile Strength Data

Tensile Strength, (psi) Materials	Piece 1	Piece 2	Piece 3	Piece 4	Piece 5	Mean	Std. Dev.
NO ADDITIVES - HDPE/FIBER	2,559.00	2,133.00	2,567.00	2,709.00	1,829.00	2,359.40	366.65
3% MAHDPE	3,718.00	3,525.00	3,015.00	3,990.00	3,059.00	3,461.40	421.46
6% MAHDPE	2,226.00	3,451.00	2,544.00	3,797.00	3,584.00	3,120.40	691.77
10% MAHDPE	4,087.00	3,491.00	4,364.00	3,237.00	3,695.00	3,774.80	452.98
6% MAHDPE, 5% PROFLOW	3,164.00	3,337.00	2,593.00	3,696.00	2,976.00	3,153.20	410.41
6% MAHDPE, 10% PROFLOW	3,350.00	3,296.00	2,630.00	2,619.00	4,104.00	3,199.80	614.69
6% MAHDPE, 5% LDPE	2,268.00	3,063.00	3,637.00	2,847.00	2,768.00	2,916.60	497.00
6% MAHDPE, 10% LDPE	2,834.00	4,040.00	2,952.00	3,571.00	3,331.00	3,345.60	487.31

Table 11. Percent Elongation at Break Data

Percent Elongation at Break, (psi)							
Materials	Piece 1	Piece 2	Piece 3	Piece 4	Piece 5	Mean	Std. Dev.
NO ADDITIVES - HDPE/FIBER	1.63	1.07	2.21	2.21	1.19	1.66	0.54
3% MAHDPE	2.94	2.60	1.53	2.15	1.74	2.19	0.59
6% MAHDPE	0.91	1.83	1.26	3.07	2.43	1.90	0.87
10% MAHDPE	2.48	2.34	2.53	1.87	2.86	2.42	0.36
6% MAHDPE, 5% PROFLOW	1.95	1.85	1.27	2.25	1.61	1.79	0.37
6% MAHDPE, 10% PROFLOW	2.33	1.99	1.40	1.15	2.55	1.88	0.60
6% MAHDPE, 5% LDPE	1.09	2.02	2.77	2.09	1.39	1.87	0.66
6% MAHDPE, 10% LDPE	2.05	2.76	2.01	2.84	2.86	2.50	0.43

Table 12. Water Absorption Data

Water absorption, (g)	*Initial Weight*					*Final Weight*			
Materials	**Piece 1**	**Piece 2**	**Piece 3**	**Piece 4**	**Piece 5**	**Piece 1**	**Piece 2**	**Piece 3**	**Piece 4**
NO ADDITIVES - HDPE/FIBER	2.5824	2.6936	2.5844	2.5400	2.6928	2.5926	2.6923	2.5656	2.5219
3% MAHDPE	2.5779	2.5310	2.7704	2.7763	2.5977	2.5915	2.5443	2.7886	2.7913
6% MAHDPE	2.5608	2.4653	2.6481	2.5638	2.6436	2.5896	2.4881	2.6738	2.5841
10% MAHDPE	2.5902	2.5543	2.5497	2.4792	2.5061	2.6110	2.5822	2.5813	2.4951
6% MAHDPE, 5% PROFLOW	2.5351	2.6101	2.6851	2.5322	2.6320	2.5553	2.6302	2.7060	2.5570
6% MAHDPE, 10% PROFLOW	2.5038	2.5270	2.6673	2.6452	2.5031	2.5133	2.5449	2.6896	2.6623
6% MAHDPE, 5% LDPE	2.6059	2.7711	2.6076	2.6097	2.6479	2.6261	2.7905	2.6230	2.6301
6% MAHDPE, 10% LDPE	2.8642	2.8507	2.6342	2.5651	2.5935	2.8930	2.8700	2.6480	2.5819

	% Change (g)					*Mean,*	
Piece 5	**Piece 1**	**Piece 2**	**Piece 3**	**Piece 4**	**Piece 5**	***% Change***	***Std. Dev.***
2.6664	0.3950	-0.0483	-0.7274	-0.7126	-0.9804	-0.4147	0.5693
2.6110	0.5276	0.5255	0.6569	0.5403	0.5120	0.5525	0.0593
2.6640	1.1246	0.9248	0.9705	0.7918	0.7717	0.9167	0.1439
2.5232	0.8030	1.0923	1.2394	0.6413	0.6823	0.8917	0.2624
2.6490	0.7968	0.7701	0.7784	0.9794	0.6459	0.7941	0.1195
2.5201	0.3794	0.7083	0.8361	0.6465	0.6792	0.6499	0.1674
2.6650	0.7752	0.7001	0.5906	0.7817	0.6458	0.6987	0.0825
2.6057	1.0055	0.6770	0.5239	0.6549	0.4704	0.6664	0.2085

APPENDIX B
Statistical Analysis

Figure 7. Izod Impact Strength

General Linear Models Prodecure

Dependent Variable: IZOD

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	0.03368858	0.00481265	2.05	0.0784
Error	32	0.07500120	0.00234379		
Cor Total	39	0.10868978			

R-Square	C.V.	Root MSE	IZOD Mean
0.309952	7.045175	0.0484127	0.6871750

Source	DF	Type I SS	Mean Square	F Value	Pr > F
GROUP	7	0.03368858	0.00481265	2.05	0.0784

Source	DF	Type III SS	Mean Square	F Value	Pr > F
GROUP	7	0.03368858	0.00481265	2.05	0.0784

Dependent Variable: IZOD

Parameter	Estimate	T for HO: Par.= 0	Pr>|T|	Std Error of Estimate
ctrl vs 3%mah	-0.05840000	-1.91	0.0655	0.03061887
ctrl vs 6%mah	-0.04980000	-1.63	0.1137	0.03061887
ctrl vs 10%mah	0.00000000	0.02	0.9845	0.03061887
ctrl vs 6%mah 5%pro	-0.00120000	-0.04	0.9690	0.03061887
ctrl vs 6%mah 10%pro	0.02160000	0.71	0.4856	0.03061887
ctrl vs 6%mah 5%ldpe	-0.02760000	-0.90	0.3741	0.03061887
ctrl vs 6%mah 10%ldpe	-0.05780000	-1.89	0.0682	0.03061887
3%mah vs 6%mah	0.00860000	0.28	0.7806	0.03061887
3%mah vs 10%mah	0.05900000	1.93	0.0629	0.03061887
6%mah vs 10%mah	0.05040000	1.65	0.1095	0.03061887
5%pro vs 10%pro	0.02280000	0.74	0.4619	0.03061887
5%ldpe vs 10%ldpe	-7.03020000	-0.99	0.3314	0.03061887
6%mah vs 5&10%pro	0.06000000	2.26	0.0306	0.02651672
6%mah vs 5&10%ldpe	0.00710000	0.27	0.7906	0.02651672

Figure 8. Yield Strength

General Linear Models Prodecure

Dependent Variable: YIELD

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	4841259.3724	691608.4818	2.53	0.0345
Error	32	8753801.3556	273556.2924		
Cor Total	39	13595060.7281			

R-Square	C.V.	Root MSE	YIELD Mean
0.356104	20.27990	523.02609	2579.0368

Source	DF	Type I SS	Mean Square	F Value	Pr > F
GROUP	7	4841259.3724	691608.4818	2.53	0.0345

Source	DF	Type III SS	Mean Square	F Value	Pr > F
GROUP	7	4841259.3724	691608.4818	2.53	0.0345

Dependent Variable: YIELD

Parameter	Estimate	T for HO: Par.= 0	Pr>|T|	Std Error of Estimate
ctrl vs 3%mah	-1137.48000	-3.44	0.0016	330.790745
ctrl vs 6%mah	-412.20000	-1.25	0.2218	330.790745
ctrl vs 10%mah	-844.42000	-2.55	0.0157	330.790745
ctrl vs 6%mah 5%pro	-382.82200	-1.16	0.2557	330.790745
ctrl vs 6%mah 10%pro	-242.30800	-0.73	0.4692	330.790745
ctrl vs 6%mah 5%ldpe	-160.77600	-0.49	0.6303	330.790745
ctrl vs 6%mah 10%ldpe	-379.02400	-1.15	0.2604	330.790745
3%mah vs 6%mah	725.28000	2.19	0.0357	330.790745
3%mah vs 10%mah	293.06000	0.89	0.3823	330.790745
6%mah vs 10%mah	-432.22000	-1.31	0.2007	330.790745
5%pro vs 10%pro	140.51400	0.42	0.6738	330.790745
5%ldpe vs 10%ldpe	-218.24800	-0.66	0.5141	330.790745
6%mah vs 5&10%pro	99.63500	0.35	0.7303	286.473188
6%mah vs 5&10%ldpe	142.30000	0.50	0.6228	286.473188

Figure 9. Modulus of Elasticity

General Linear Models Prodecure

Dependent Variable: MODULUS

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	10968.175000	1566.882143	1.11	0.3808
Error	32	45163.200000	1411.350000		
Cor Total	39	56131.375000			

R-Square	C.V.	Root MSE	MODULUS Mean
0.195402	17.28255	37.567938	217.37500

Source	DF	Type I SS	Mean Square	F Value	Pr > F
GROUP	7	10968.175000	1566.882143	1.11	0.3808

Source	DF	Type III SS	Mean Square	F Value	Pr > F
GROUP	7	10968.175000	1566.882143	1.11	0.3808

Dependent Variable: MODULUS

Parameter	Estimate	T for HO: Par.= 0	Pr>|T|	Std Error of Estimate
ctrl vs 3%mah	-1.80000000	-0.08	0.9401	23.7600505
ctrl vs 6%mah	18.60000000	0.78	0.4395	23.7600505
ctrl vs 10%mah	-0.00000000	-0.00	1.0000	23.7600505
ctrl vs 6%mah 5%pro	14.00000000	0.59	0.5598	23.7600505
ctrl vs 6%mah 10%pro	6.60000000	0.28	0.7830	23.7600505
ctrl vs 6%mah 5%ldpe	48.40000000	2.04	0.0500	23.7600505
ctrl vs 6%mah 10%ldpe	31.20000000	1.31	0.1985	23.7600505
3%mah vs 6%mah	20.40000000	0.86	0.3970	23.7600505
3%mah vs 10%mah	1.80000000	0.08	0.9401	23.7600505
6%mah vs 10%mah	-18.60000000	-0.78	0.4395	23.7600505
5%pro vs 10%pro	-7.40000000	-0.31	0.7575	23.7600505
5%ldpe vs 10%ldpe	-17.20000000	-0.72	0.4744	23.7600505
6%mah vs 5&10%pro	-8.30000000	-0.40	0.6894	20.5768073
6%mah vs 5&10%ldpe	21.20000000	1.03	0.3106	20.5768073

Figure 10. Tensile Strength

General Linear Models Prodecure

Dependent Variable: TENSILE

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	6031715.2000	861673.6000	3.40	0.0079
Error	32	8106236.4000	253319.8875		
Cor Total	39	14137951.6000			

R-Square	C.V.	Root MSE	TENSILE Mean
0.426633	15.89531	503.30894	3166.4000

Source	DF	Type I SS	Mean Square	F Value	Pr > F
GROUP	7	6031715.2000	861673.6000	3.40	0.0079

Source	DF	Type III SS	Mean Square	F Value	Pr > F
GROUP	7	6031715.2000	861673.6000	3.40	0.0079

Dependent Variable: TENSILE

Parameter	Estimate	T for HO: Par.= 0	Pr>|T|	Std Error of Estimate
ctrl vs 3%mah	-1102.00000	-3.46	0.0015	318.320522
ctrl vs 6%mah	-761.00000	-2.39	0.0229	318.320522
ctrl vs 10%mah	-1415.40000	-4.45	0.0001	318.320522
ctrl vs 6%mah 5%pro	-793.80000	-2.49	0.0180	318.320522
ctrl vs 6%mah 10%pro	-840.40000	-2.64	0.0127	318.320522
ctrl vs 6%mah 5%ldpe	-557.20000	-1.75	0.0896	318.320522
ctrl vs 6%mah 10%ldpe	-986.20000	-3.10	0.0040	318.320522
3%mah vs 6%mah	341.00000	1.07	0.2921	318.320522
3%mah vs 10%mah	-313.40000	0.98	0.3322	318.320522
6%mah vs 10%mah	-654.40000	-2.06	0.0480	318.320522
5%pro vs 10%pro	-46.60000	-0.15	0.8845	318.320522
5%ldpe vs 10%ldpe	-429.00000	-1.35	0.1872	318.320522
6%mah vs 5&10%pro	56.10000	-0.20	0.8400	275.673659
6%mah vs 5&10%ldpe	-10.70000	-0.04	0.9693	275.673659

Figure 11. Percent Elongation at Break

General Linear Models Prodecure

Dependent Variable: ELONGATION

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	7	3.28992000	0.46998857	1.43	0.2297
Error	32	10.55292000	0.32977875		
Cor Total	39	13.84284000			

R-Square	C.V.	Root MSE	ELONGATION Mean
0.237662	28.33072	0.5742637	2.0270000

Source	DF	Type I SS	Mean Square	F Value	Pr > F
GROUP	7	3.28992000	0.46998857	1.43	0.2297

Source	DF	Type III SS	Mean Square	F Value	Pr > F
GROUP	7	3.28992000	0.46998857	1.43	0.2297

Dependent Variable: ELONGATION

Parameter	Estimate	T for HO: Par.= 0	Pr>|T|	Std Error of Estimate
ctrl vs 3%mah	-0.53000000	-1.46	0.1425	0.36319623
ctrl vs 6%mah	-0.23800000	-0.66	0.5170	0.36319623
ctrl vs 10%mah	-0.75400000	-2.08	0.0460	0.36319623
ctrl vs 6%mah 5%pro	-0.12400000	-0.34	0.7350	0.36319623
ctrl vs 6%mah 10%pro	-0.22200000	-0.61	0.5454	0.36319623
ctrl vs 6%mah 5%ldpe	-0.21000000	-0.58	0.5672	0.36319623
ctrl vs 6%mah 10%ldpe	-0.84200000	-2.32	0.0270	0.36319623
3%mah vs 6%mah	0.29200000	0.80	0.4273	0.36319623
3%mah vs 10%mah	-0.22400000	-0.62	0.5418	0.36319623
6%mah vs 10%mah	-0.51600000	-1.42	0.1651	0.36319623
5%pro vs 10%pro	-0.09800000	-0.27	0.7890	0.36319623
5%ldpe vs 10%ldpe	-0.63200000	-1.74	0.0915	0.36319623
6%mah vs 5&10%pro	0.06500000	0.21	0.8376	0.31453716
6%mah vs 5&10%ldpe	-0.28800000	-0.92	0.3667	0.31453716

APPENDIX C
Chemical Structures

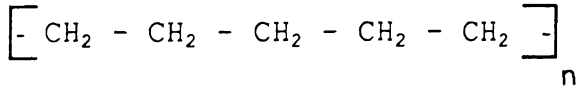

Figure 7. Chemical Structure of HDPE

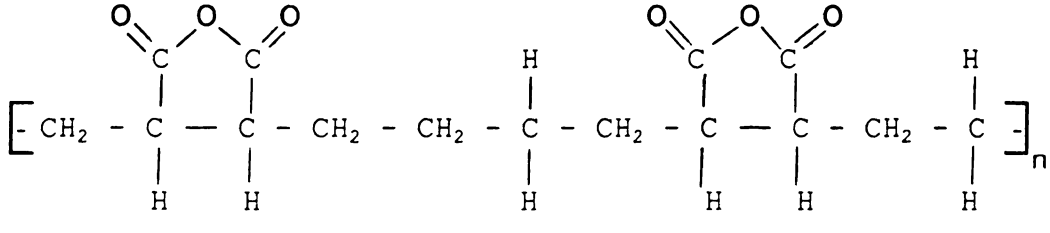

Figure 8. Chemical Structure of MAHDPE

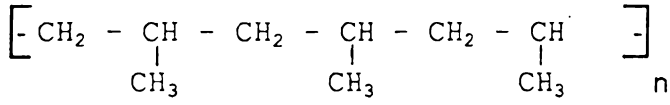

Figure 9. Chemical Structure of Proflow 1000

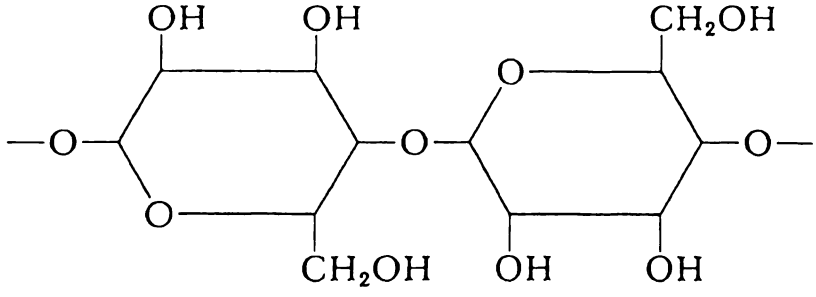

Figure 10. Chemical Structure of Cellulose
(Hanlon 1992)

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