Evaluation of the Mechanical and Thermal Properties of Coffee Tree Wood Flour - Polypropylene Composites

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Columbian coffee trees are subject to frequent replacement plantings due to disease and local climate changes, which makes them an ideal source of wood fibers for wood plastic composites (WPC). Composites of polypropylene (PP) consisting of 25% and 40% by weight of coffee wood flour (CF) and 0% or 5% by weight of maleated PP (MAPP) were produced by twin screw compounding and injection molding. Composites containing MAPP had significantly improved tensile and flexural properties compared to neat PP or composites without MAPP. Excellent mechanical properties were obtained with CF relative to conventional wood fillers. IZOD impact resistances of CF composites were significantly lower than neat PP although WPC containing MAPP were superior to WPC without MAPP. Bio-based fiber composites made by mixing CF in equal portions with other fiber sources were evaluated to determine the compatibility of using CF with other sources of filler materials. Soaking of tensile bars of the various CF blends in distilled water for 35 days may alter their mechanical properties and result in weight gain. Differential scanning calorimetry and thermogravimetric analysis were conducted on the neat PP and bio-composites to evaluate their thermal properties as they relate to potential degradation during conventional thermoplastic resin processing.

Keywords: Mechanical properties; Flexural properties; Differential scanning calorimetry; Thermal properties; Injection molding

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INTRODUCTION

Coffee is the largest food commodity traded internationally and is the second most valuable commodity traded behind only crude oil (Café de Colombia.com 2012). The distinctive mild taste of Columbian coffee is obtained from the beans of *Coffea arabica* L. (family Rubiaceae) trees grown in equatorial regions lower than 10^{o} latitude at altitudes of 1000 to 1500 m (Wikipedia.com 2013). According to the National Coffee Association, USA (2013), Columbia is the fourth largest international supplier of coffee, ranking behind Brazil, Vietnam, and Indonesia. Colombia exported 9.5 million 60-kg bags of coffee in 2012 (Coffeereserach.org 2013). Coffee trees need to be replaced on a regular basis to

provide high and consistent yields due to "aging" and diseases (Guarin and Pachón 2012). In addition, coffee trees are susceptible to changes in climate. Between 1980 to 2010, the average temperature in Columbian coffee regions has risen one degree Celsius, but the average precipitation increased 25%; this in turn has severely disrupted the specific climatic requirements of the *Coffea arabica* bean harvest and encouraged coffee leaf rust infestation (Café de Colombia.com 2012; Birbragher and Rodriquez 2013). To address these situations, new productive and resistant varieties are being developed to renew existing crop acreage (Guarin and Pachón 2012). The frequent replacement of coffee trees is creating a massive biomass resource. As new and improved coffee varieties are developed, the replacement rates will become even more frequent, occurring every 7 years or less. Colombia Coffee Growers Federation/Coffee System Information (Sistema de Información Cafetera/SICA) provides data that during the last five years (2008 to 2012) more than 1.2 millions of acres were renewed. The coffee crop in Colombia consists of approximately 2.5 million acres, and the annual renewal capacity could be one-fifth of the total (*i.e.*, 500 thousand acres/year) depending on disease problems. Theoretically, this results in a minimum biomass equivalent of 3.2 million tons of dry wood per year (Café de Colombia.com 2012; Birbragher and Rodriquez 2013). This estimation is only for the stem biomass (approximately 23% from total dry plant material) from coffee trees and does not include the dry materials obtained from leaves and branches, which are 22% and 25%, respectively, of the dry tree weight (Riaño *et al*. 2004). Currently, most of this biomass, being unsuitable as lumber, is burnt on the spot to eliminate its obstruction to further coffee agricultural operations. However, higher value product utilization of this lignocellulosic source is sought.

The composite plastic industry is constantly seeking reinforcement materials that are more environmentally friendly, inexpensive, and improve the mechanical and physical properties compared to current products (Clemons *et al*. 2013). The global market for wood plastic composites (WPC), cellulosic plastics, plastic lumber, and natural fiber composites was 2.4 million metric tons (tonnes) in 2011 and by 2016 is estimated to grow to 4.6 million tonnes (Bccresearch.com 2011). From 2011 to 2016, the market for building materials and automotive applications are expected to grow 12.4% and 17.1% per yr, respectively (Bccresearch.com 2011). Because Colombia is a major oil producer and exporter in the world's economy, it is not unreasonable to suggest that the glut of coffee tree biomass could be utilized as a wood fiber source for the manufacture of thermoplastic WPC. Coffee tree cellulosic fibers may provide a perennial supply of fibers for "sustainable exploitation" of an available natural resource without causing severe strain on the natural environment (*i.e.*, the rain forest). For any long-term commercial development of a WPC, there must be a guaranteed supply of both the plastic and wood resources (Kim and Pal 2010). It is essential that both the thermoplastics and the filler materials used in the WPC be locally available, abundant, and inexpensive in order to be utilized. Unless a particular fiber has some advantage in the market, the lignocellulosic fibers used in WPC are those based on their availability at the locale they are manufactured (Kim and Pal 2010). Market advantage is based on availability, price, and performance of the fiber in the WPC. For example, jute fibers are commonly employed in eastern India and Bangladesh as an inexpensive source of reinforcements in polymer composites (Kim and Pal 2010). However, although jute fibers used at high fiber levels result in higher performance characteristics like modulus and recyclability, it is usually economically infeasible to export jute fibers to other countries as a WPC component (Kim and Pal 2010). One of the

reasons that wood is the major source of agro-based fibers is its cost versus other agro-fibers. Wood has a higher density than other agro-fibers and is less expensive to grow than materials obtained from seasonal crops.

The objective of this study was to evaluate the mechanical, physical, and thermal properties of WPC obtained from blending coffee wood flour (CF) with polypropylene (PP). It is particularly important to determine if CF functions as either a filler or a reinforcement material in WPC. Fillers generally do not improve the mechanical properties of the composite but are an inexpensive way to increase bulk. On the other hand, reinforcements improve strength and increase stiffness (Clemons *et al*. 2013). If a bio-fiber can be inexpensive and provide a notable improvement in the mechanical properties, then the benefit of replacing the neat resin with a bio-sourced material is not compromised. Further, there is a particular interest in the utilization of CF derived from terminated "replaced" trees from the high altitude regions of Colombia since such short-rotation woody crop trees will likely be a renewable source of woody biomass available for Colombia in the future. This biomass resource will not interfere with other agricultural or forestry operations in its production. Hence, this study was conducted utilizing CF derived from replaced tree biomass (*i.e.,* 7-year-old). In addition, because coupling agents have been commonly used for wood fiber PE composites (Carlborn and Matuana 2006; Lei *et al*. 2007; Clemons 2010), a maleated PP (MAPP) was employed as part of the scope of the project. Because CF is a bio-fiber and is subject to degradation by water, water immersion tests were administered on CF composites to evaluate their environmental durability. In the US, typical WPCs utilize commercial filler blends derived from various tree species (ash, oak, maple, birch). These blends are obtained by pulverizing and sieving lumber milling byproducts (wood shavings and sawdust). Therefore, tests were conducted to ascertain the potential compatibility value of mixing dissimilar fillers, *i.e.,* Osage orange wood (OOW), pine wood (PINEW), and Camelina press cake (CAM) with CF and PP. Finally, differential scanning calorimetry and thermogravimetric analysis were conducted on CF composites to evaluate their thermal properties and the implications these may have on selecting processing conditions for the bio-fiber use.

EXPERIMENTAL

Materials

The PP employed as the matrix material was Pro-fax SB891 (Lyondellbasell, Equistar Chemicals LP, Houston, TX). It had a melt-flow index of 35 g/10 min, a density of 0.90 g/cm^3, and a melt temperature of 165 ^{o}C. The coupling agent was a MAPP, supplied by Equistar Chemicals LP (product code NP 507-03). The MAPP had a melting point of 155 to 165^{o}C with approximately 1% maleic anhydride by weight grafted on the polypropylene.

Coffee tree wood was obtained from 7-yr-old trees grown in the Caldas region of Colombia. Osage orange (*Maclura pomifera* (Raf.) Schneid., Family Moraceae) wood was obtained from 20-yr-old trees grown in Missouri. White pine (*Pinus strobus* L., family Pinaceae) wood was obtained from packaged bedding shavings (American Wood Fiber, Schofield, WI). Camelina (*Camelina sativa* L. Crantz, family Brassicaceae) seeds were grown in Peoria County, Illinois. Camelina seeds were ground, and oils were extracted

with hexane and methanol using a Soxhlet extractor. Subsequently, bio-filler materials were milled with a Thomas-Wiley mill grinder, (Model 4, Thomas Scientific, Swedesboro, NJ). Each bio-fiber material was milled successively through 4-, 2- and 1-mm diameter stainless screens. Particles were then sized through a Ro-Tap™ Shaker (Model RX-29, Tyler, Mentor OH) employing 203 mm diameter stainless steel screens. Sieve/Screens employed were #30, #40, #50, #60, #80, #140, and #200 US Standards (Newark Wire Cloth Company, Clifton, NJ). Bio-fiber mixtures composed of #40 mesh and finer were employed in the extrusion operation. The bio-fiber particle size composition of these mixtures for each species is shown in Table 1.

Table 1. Sieve Information and Particle Distribution Percentages

Sieve #	Opening Size (µm)	Particle Sizes (µm)	CF (%)*	PINEW (%)	OOW (%)	CAM (%)
40	425	425-600	15.93	15.81	1.60	17.81
50	300	300-425	28.86	40.20	12.67	31.20
60	250	250-300	11.12	8.17	9.44	15.47
80	180	180-250	14.41	14.27	19.60	16.15
140	106	106-180	15.20	16.80	36.36	13.14
200	75	75-106	3.65	3.73	18.39	2.59
>200	≤75	≤75	10.82	0.90	1.93	3.64

*Distribution of particles sieved from 1-mm Wiley Milled Screen.

Preparations

Table 2 summarizes the various treatments conducted in this research project.

Table 2. Weight Percentages in Test Formulations

Formulation Code	PP/CF/Non-CF fiber/MAPP (wt.%)*
PP	100/0/0/0
PP-MAPP	95/0/0/5
PP-25CF	75/25/0/0
PP-25CF-MAPP	70/25/0/5
PP-40CF	60/40/0/0
PP-40CF-MAPP	55/40/0/5
PP-25PINEW-MAPP	70/0/25/5
PP-12.5CF/12.5PINEW-MAPP	70/12.5/12.5/5
PP-25OOW-MAPP	70/0/25/5
PP-12.5CF/12.5OOW-MAPP	70/12.5/12.5/5
PP-25CAM-MAPP	70/0/25/5
PP-12.5CF/12.5CAM-MAPP	70/12.5/12.5/5

*non-CF fibers include PINEW, OOW, and CAM.

Composite blends were compounded and extruded into strands using a Micro-18 30/l L/D co-rotating twin-screw extruder (American Leistritz Extruder, Branchburg, NJ). The barrel had six different zones, each 90 mm long, which were controlled at the following temperatures (°C): 40, 75, 125, 175, 175, and 175, respectively. The strand die temperature was set at 175 °C. Premixed weight fractions of CF, PINEW, OOW, or CAM were fed into zone 1 using a feeder (Model 15C-CM plus/R1.0, Brabender Technologies, Mississauga, Ontario, Canada), while at the same time, premixed quantities of PP and MAPP were fed into the extruder in zone 1 using a twin-screw gravimetric feeder (Model KCL24K520, K-tron, Pitman, NJ). The compounding screw speed was set at 200 rpm. Extruded strands were cooled on a conveyor belt equipped with an air stream (Model 2100, Dorner Mfg. Corp., Hartland, WI) and were processed into pellets with a strand pelletizer (Model 4, Killion, Cedar Grove, NJ).

Test specimen pellets were injection molded using an ASTM test specimen mold that included cavities for an ASTM D790 flexural testing bar (12.7 mm W × 127 mm L × 3.2 mm thickness), an ASTM D638 Type I tensile testing bar, and an ASTM D638 Type V dynamic tensile testing bar. Molding was conducted with a 30-ton molding machine (Engel ES 30, Engel Machinery Inc., York, PA) with set point temperatures (°C) for the four zone injection molding barrel set at: feed = 160; compression = 166; metering = 177, and nozzle = 191. The mold temperature was 37 °C. The Type I bars were used for the tensile strength property tests. The flexural bars were used to evaluate flexural properties and also used to make impact resistance measurements. The Type V bars were used to evaluate changes due to prolonged exposure to water: weight change, color change, and changes in tensile mechanical properties of the composites.

Mechanical Property Measurements

Samples were conditioned for approximately 240 h at standard room temperature and humidity (23 °C and 50% RH) prior to any test evaluations. The ASTM D638 Type I tensile bars were tested for Young's or tensile modulus (E), tensile strength (σ_u), and elongation at break (%El) using an Instron universal testing machine, Model 1122 (Instron Corporation, Norwood, MA). The speed of testing was 50 mm/min. Three point flexural tests were carried out according to ASTM-D790 specification on the Instron Model 1122.

The flexural strength or maximum fiber stress (σ_{fm}) and flexural modulus of elasticity (E_b) were calculated. The flexural tests were carried out using Procedure B with a crosshead rate of 13.5 mm/min. However, even Procedure B failed to achieve a maximum bending force within the required 5% of strain. The maximum bending load typically occurred between 5.5 to 8% of strain, and the calculated flexural strength reported in this study is based upon the maximum load. IZOD impact tests were conducted with a pendulum impact tester, Model Resil 5.5, P/N 6844.000 (CEAST, Pianezza, Italy) according to ASTM D256-84. Impact test specimens were obtained by cutting the flexural specimens in half to 12.7 mm W × 64 mm L × 3.2 mm thickness and then notched. Each mechanical test involved testing five specimens of each formulation. The average values and standard errors were reported. Following impact testing, the fractured surfaces of specimen bars were examined using a Wild Heerbrugg M5 Stereo dissecting microscope (Leica Microsystems GMbH, Wetzlar, Germany) to evaluate the dispersion of the wood flour particles in the PP matrix.

Water Absorption

The Type V tensile bars injection molded for each composite were dried in an oven for 24 hours at 100 ± 2 ºC and weighed. Tests were conducted in an incubator at 25 ± 2 ºC under a photosynthetic photon flux density of 180 μmol·m^{2}·s^{-1} using a photoperiod of 12 h light/12 h dark. Tensile bars were placed in distilled water at room temperature for 872 h. At predetermined time intervals the specimens were removed from the distilled water, the surface water was blotted off with paper towels, and their wet mass and thickness were determined. Water absorption, measured as weight gain percentage, was computed using the following formula,

$$\text{Weight gain (\%)} = (m_t - m_o)/m_o \times 100 \quad (1)$$

where m_o denotes the oven-dried weight and m_t denotes the weight after soak time t.

Thermal Properties

Differential scanning calorimetry (DSC) of molded specimens was conducted with an Auto DSC-7 calorimeter with a TAC/DX controller (TA Instruments, New Castle, DE). Samples of 5 to 7 mg were weighed and sealed hermetically in aluminum DSC pans. First, the calorimeter was programmed to increase the temperature from 0 to 180 ºC at a rate of 10 ºC/min, then kept isothermal for 3 min. Second, the samples were cooled to -50 ºC at a rate of 10 ºC/min. Finally, the samples were heated to 180 ºC from -50 to 180 ºC at the same rate. Data from the second heating cycle were used to determine the melting temperature (T_m) and enthalpy of melting (ΔH_m) for PP-CF blended samples. The heat flow rate corresponding to the crystallization of PP in composites was corrected for the content of the WF and MAPP. The value of crystallization heat was also corrected for the crystallization heat of MAPP. The degree of crystallinity (χ_c) of the PP matrix was evaluated from the following relationship (López *et al*. 2012),

$$\chi_c = (\Delta H_{exp}/(W_f * \Delta H) * 100 \quad (2)$$

where ΔH_{exp} is the experimental heat of fusion (ΔH_m) or crystallization determined by DSC, ΔH is the assumed heat of fusion or crystallization of fully crystalline PP (204 J/g), and W_f is the weight fractions of PP in the composites.

Thermogravimetric analysis (TGA) was performed to determine the thermal characteristics of the composites. The TGA was conducted using a Model 2050 TGA (TA Instruments) under nitrogen at a scan rate of 10 ºC/min from room temperature to 600 ºC. A sample of ≈7.5 mg was used for each run. Data were analyzed using the TA Advantage Specialty Library software (TA Instruments). The derivative TGA (wt %/min) of each sample was obtained from the software.

RESULTS AND DISCUSSION

Mechanical Properties of CF Blends

The mechanical properties of the various composite blends are shown in Fig. 1. Pearson correlation coefficients comparing the mechanical properties for the composites

conducted in this study are presented in Table 3. High positive correlations occurred between σ_u and σ_{fm} (0.951), E and E_b (0.992), and %El and impact resistance (0.964). In addition a negative correlation occurred between E and %El (-0.770).

Table 3. Pearson Correlation Coefficient Values for the Mechanical Properties of the Blends Conducted in this Study

Correlations:	σ_u*	E	%El	σ_{fm}	E_b	Impact resistance
σ_u	--	0.460	-0.282	0.951*	0.516	-0.091
E	0.460	--	-0.770*	0.551	0.992*	-0.711
%El	-0.282	-0.770*	--	-0.383	-0.702	0.964*
σ_{fm}	0.951*	0.551	-0.383	--	0.592	-0.168
E_b	0.516	0.992*	-0.702	0.592	--	-0.632
Impact resistance	-0.091	-0.711	0.964*	-0.168	-0.632	--
*Values with asterisks were significant at P=0.05 employing 5 observations.						

The blending of 25% CF with PP produced a formulation (PP-25CF) that had a slightly lower or on par strength (σ_u and σ_{fm}) values to neat PP. The σ_u of PP-25CF was 7% lower that of neat PP, and the σ_{fm} of PP-25CF was 3% greater than neat PP, referring to Fig. 1. Modulus (E and E_b) values, however, increased significantly with the addition of CF. The E was improved by 72%, and the E_b was increased by 33% compared to neat PP, as shown in Fig. 1. The dramatic improvement of the composite modulus was due to the presence of the higher modulus wood fiber that impeded the relatively small scale deformation of the matrix. As with other fiber fillers, however, the addition of CF dramatically lowered the %El, a 91% reduction, and also lowered the impact resistance, a 65% reduction, compared to neat PP. These trends continued in blends containing 40% CF. The PP-40CF composite exhibited σ_u, E, %El, σ_{fm}, E_b, and impact resistance values that were -9, +125, -94, +1, +121, and +70%, respectively, compared to neat PP. Other investigators have observed that the inclusion of wood or lignocellulosic flour into thermoplastics such as PLA, PE, or PP results in a significant decrease in σ_u and %El values but increases E values (Stark and Berger 1997; Julson *et al.* 2004; Febrianto *et al.* 2006; Li and Sun 2011). Poor interfacial adhesion between the wood flour and the thermoplastic resin is responsible of decrease in the σ_u and %El values (Petinakis *et al*. 2009). However, other investigators have been able to obtain σ_u values in PLA-wood composites without the use of coupling agents comparable to neat PLA which suggests good interfacial adhesion is possible without coupling agents (Petinakis *et al*. 2009). CF formulations showed only a slight reduction in σ_u values ($\geq$10%) compared to neat PP, which can be attributed to relatively good interfacial compatibility occurring between the CF and PP.

The addition of MAPP in the PP-CF formulations significantly improved the strength, impact, and elongation properties, but did not significantly alter the modulus values. The MAPP had a pronounced effect on the strength, elongation, and impact properties because MAPP works to minimize the creation of microcracks between the dissimilar polar wood material and the nonpolar PP matrix (Myers *et al*. 1991; Clemons 2010; Rodríquez-Llamazares *et al*. 2011; Clemons *et al*. 2013; Ehrenstein 2001; Lopez *et al*. 2012; Tisserat *et al*. 2013). The ultimate strength and elongation are large-scale

deformation processes that are disrupted by the formation of cracks (Ehrenstein 2001). The stress field that can be generated in a composite is a function of how well the composite can hold together during increased loading. If microcracks are present at the onset of loading, then higher stresses will function to open the cracks and lead to premature rupture of the composite. In effect, this lowers the σ_u of the composite compared to neat resin. This trend is seen by comparing PP-25CF to PP in Fig. 1. The addition of MAPP reduces the potential for small cracks to form and thus helps to maintain the integrity of the composite during higher loading. This results in an increase σ_u compared to non-MAPP composites. Impact strength is a measure of how well a material can minimize the propagation of a crack during dynamic loading. The addition of MAPP functions to better bind the polar and non-polar components of the composite. This works to minimize the creation of cracks and thus retards crack propagation during impact thus improving impact strength. However, modulus (E and E_b) values are a measure of a small scale deformation processes thus the development of cracks have less effect on these properties.

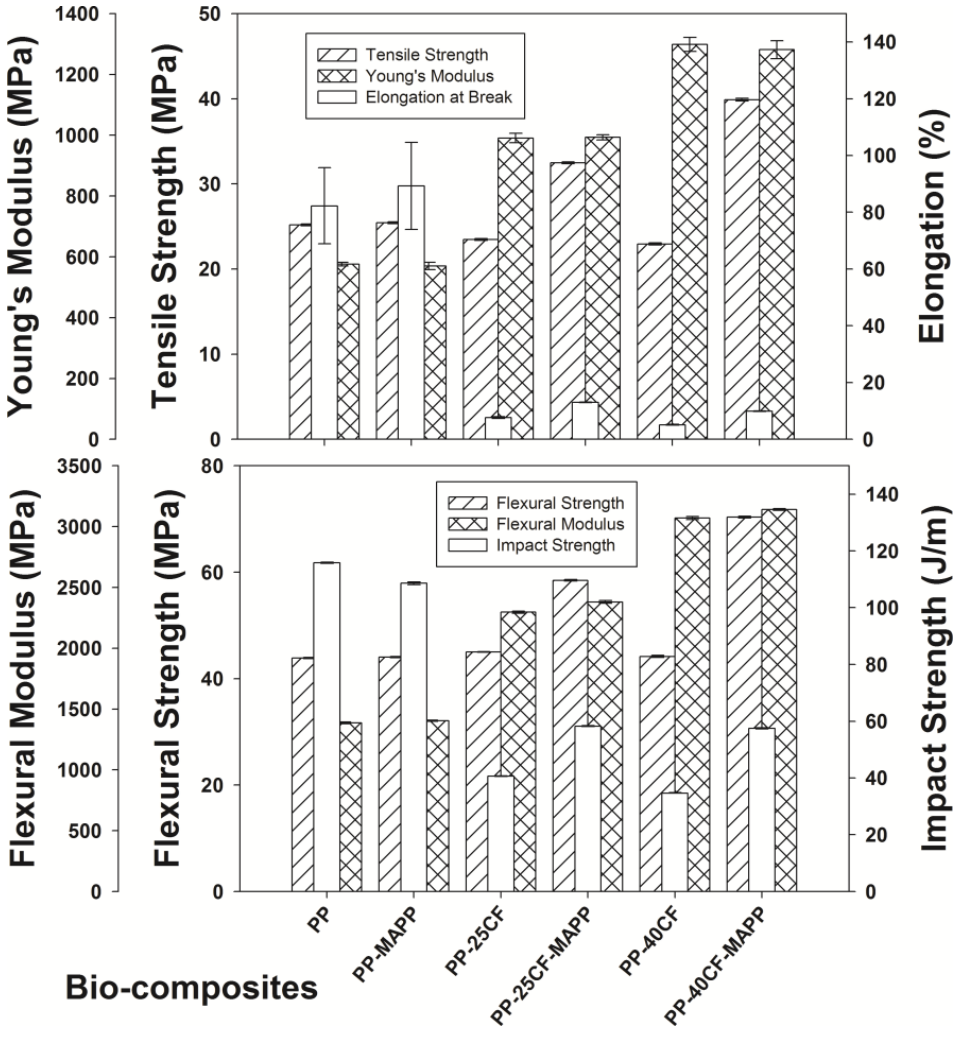

Fig. 1. Effect of coffee wood concentrations with and without coupling agent (MAPP) on the mechanical, flexural, and impact resistance properties in coffee composites and compared to PP and PP-MAPP controls

The effect of MAPP is accentuated with increased loading of CF, as shown in Fig. 1. The 40% loading of CF has greater changes in σ_u, %El, σ_{fm}, and impact resistance when MAPP is added compared to similar changes 25CF to 25CF-MAPP. The mechanical properties of σ_u, E, %El, σ_{fm}, E_b, and impact resistance of PP-40CF-MAPP were 74, 1.3, 94, 59, 2, and 66% higher than the same mechanical values of the PP-40CF formulation, referring to Fig. 1.

Generally, those composites that exhibit high σ_{fm} also will exhibit high E_b (Zabihzadeh 2010a,b). This was similarly observed in the present study (Fig. 1). Flexural strength of the PP-25CF composite was statistically identical to neat PP. However, the E_b for the PP-25CF composite was greatly improved over the neat PP. Adding MAPP in the PP-25CF and PP-40CF formulations continued to improve the σ_{fm} and E_b values compared to neat PP. Impact strengths of neat PP or PP-MAPP were significantly higher than any PP-CF formulation tested. Notched impact resistances of PP-CF formulations containing MAPP were significantly higher than the PP-CF formulations without MAPP. For example, the formulation PP-25CF-MAPP exhibited an impact energy that was 43% higher than PP-25CF formulation.

Optical observations of impacted tested fractured specimens provides information concerning the interaction of the matrix and filler components in response to a physical stress. It should be noted that the differences between composite blends were subtle. However, the fractured surface morphology of the PP-40CF-MAPP composite appeared more homogenous than that of the PP-40CF composite which was considerably rougher in appearance (Fig. 2).

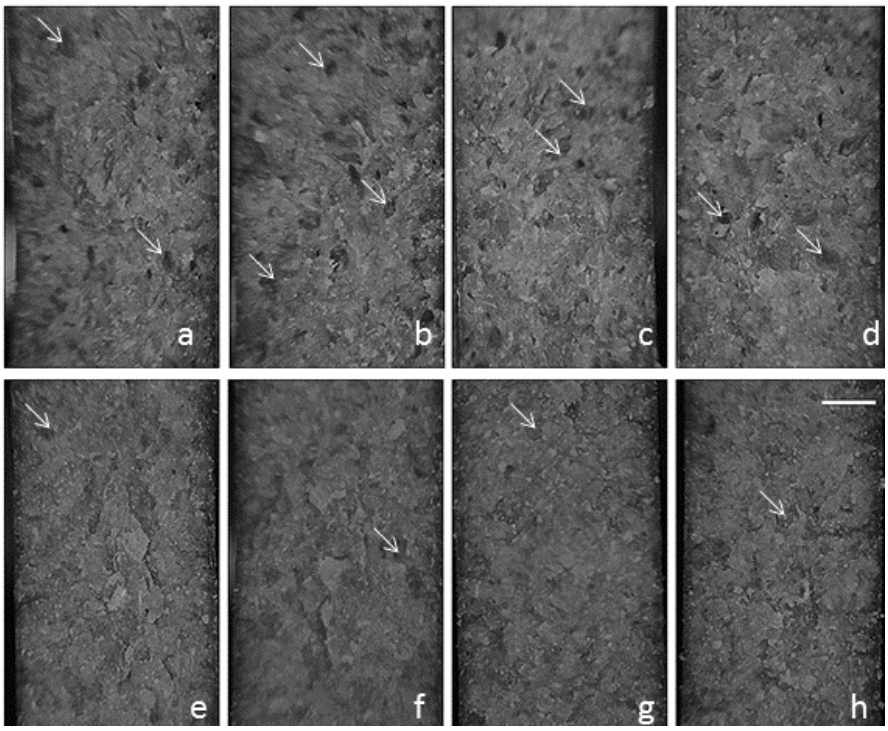

Fig. 2. Optical microscope images of the PP-40CF (a-d) and PP-40CF-MAPP (e-h) composites following impact strength tests. Arrows designate visible wood particles and the bar in image h represents 1 mm.

This roughness was attributed to matrix disruption and higher occurrence of visible "uncoated" wood flour particles. We did not note any wood flour particle clumping in any composite blends examined but rather a random dispersion of wood flour particles throughout the matrix.

Wood particles were not as apparent in the PP-40CF-MAPP composite as they were in the PP-40CF composite. This suggests that greater coating of the wood flour particles by the PP matrix occurred in the PP-40CF-MAPP composite than in the PP-40CF composite.

Evidently, there was greater interfacial adhesion between PP matrix and the CF wood particles in composites containing MAPP than in composites without MAPP. Similar observations were made for CF composites containing lower filler loadings (i.e. PP-25CF versus PP-25CF-MAPP).

Overall, CF showed promising results when blended with PP, since the resulting formulations exhibited mechanical properties (*i.e.*, σ_u, E, σ_{fm}, and E_b) that significantly exceeded that of neat PP. These observations suggest that CF materials can be considered to be reinforcement in WPC.

Comparing CF to Other Fillers

The mechanical properties of the PP-25CF-MAPP formulation compared well to other wood (PP-25PINEW-MAPP and PP-25OOW-MAPP) and press cake (PP-25CAM-MAPP) formulations (Fig. 3). Pine wood flour is a common commercial wood filler material employed in WPC and was included as an appropriate comparative filler/reinforcement source. OOW flour was included because it is a readily available hardwood tree common to the Midwest, USA where this study was conducted. Similarly, the CAM filler was included because it is also readily available in the Midwest. The σ_u, E, %El, σ_{fm}, E_b, and impact resistance values of PP-25CF-MAPP were -1, -6, +32, +13, -7, and +30%, respectively, of that of the PP-25PINEW-MAPP formulation (Fig. 3). Likewise, CF formulations compared well to the OOW and CAM composites.

Every bio-polymeric material has its own unique set of chemical and physical properties which, when combined with thermoplastic resins, correspondingly results in a unique bio-composite. For example, wood fillers are composed primarily of cellulose (40 to 45%) and lignin (20 to 30%), and have some protein (~1 to 2%) and solvent extractables (~3 to 12%).

In contrast, press cakes are primarily composed of protein (20 to 35%), vegetable oils (~8 to 12%), and have much lower cellulose (11 to 25%) and lignin (3 to 15%) levels (Tisserat *et al*. 2013). Although press cakes are relatively abundant and inexpensive, few studies have been conducted attempting to employ them as a bio-filler with thermoplastic resins (Tisserat *et al*. 2013). Clearly, they provide an inferior filler compared to wood (Fig. 3).

The high concentration of protein and residual oils are probably undesirable characteristics of press cake fillers and interfere with binding with thermoplastic resins (Finkenstadt *et al*. 2007; Reifschneider *et al*. 2013). Nevertheless, mixture of CF and CAM in equal proportions improves the mechanical properties and suggests that CAM filler could be employed commercially.

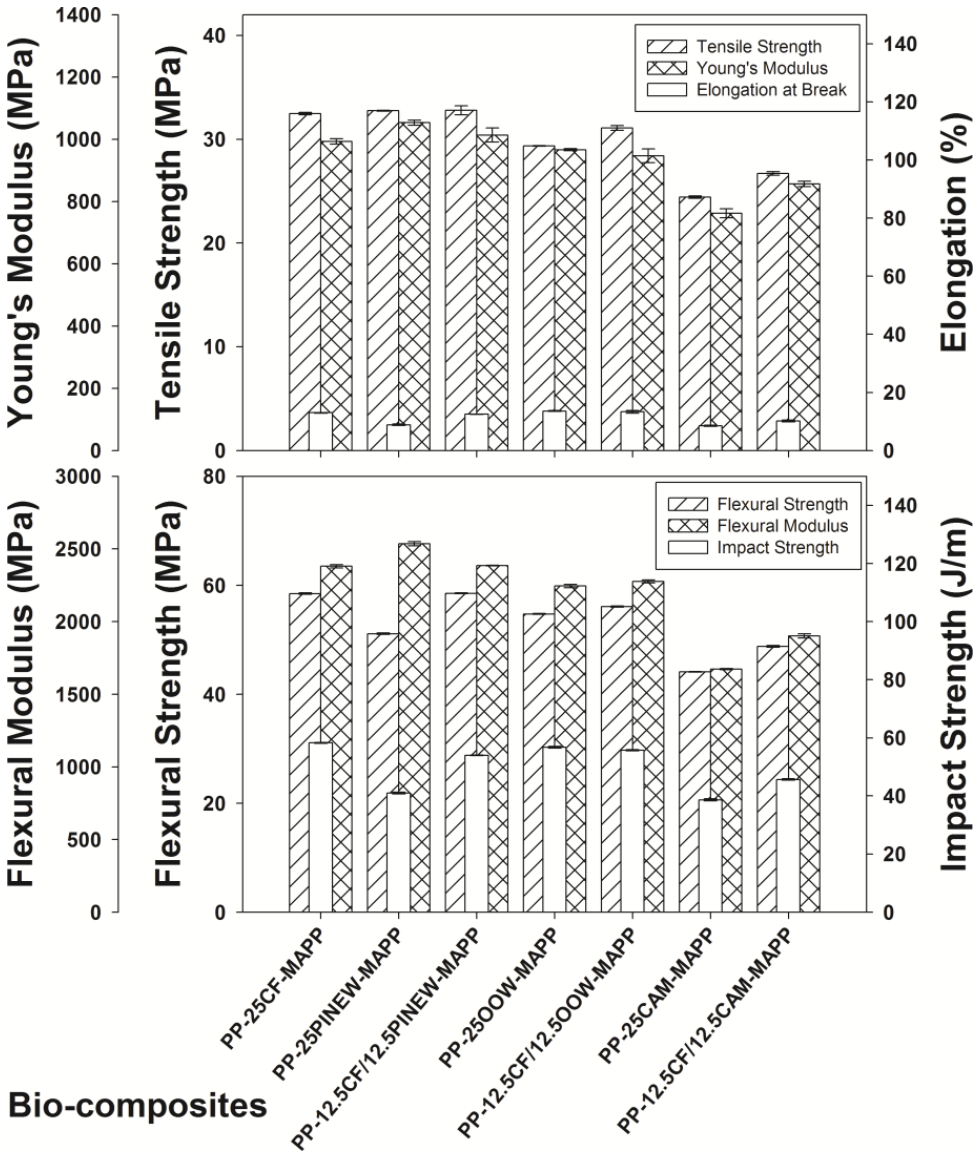

Fig. 3. Comparing the mechanical, flexural, and impact resistance properties of individual bio-fibers and mixtures

Water Absorption Responses

Figure 4 shows the long-term water absorption plots of WF-based composites at room temperature, where weight gain (%) (*i.e.*, water absorption) is plotted against immersion time (h). All composites absorbed water during the incubation period, and a saturation level did not occur for any of the fillers employed. PP and PP-MAPP exhibited less than a 1% increase in weight after the immersion incubation time (872 h). Inclusion of the MAPP coupling agent to the CF filler formulation produced a biocomposite that was more resistant to water absorption. For example, PP-40CF and PP-40CF-MAPP exhibited weight gains of 7.8 and 4.7%, respectively; inclusion of MAPP reduced weight gain by 40%. Others have reported that inclusion of maleated polyolefins in the composite

considerably reduces water absorption when using bio-fillers of popular wood, loblolly pine wood, sisal fiber, or wheat straw (Joseph *et al.* 2002; Zabihzadeh 2010a,b).

As shown in Fig. 4, the PP-25CF-MAPP absorbed more water (2.9%) than PP-25PINEW-MAPP (2.4%) or PP-25OOW-MAPP (1.6%). The PP-25CAM-MAPP formulation exhibited a higher absorption rate, 4% of which may be attributed to the high content of protein present. Mixing CF and non-CF fillers resulted in "mixed" formulations that exhibit absorption rates manifesting the mixing properties of the two fillers (Fig. 3). The response of bio-composites to water soaking is related to the bio-filler's chemical and anatomical properties (Joseph *et al.* 2002; Kord 2011; Zabihzadeh 2010a; Segerholm *et al.* 2012). Clearly, a species-related WF response to soaking was observed, since CF WPC exhibited a higher weight gain that PINEW or OOWF filler WPC. Absorption of water by composites is a crucial factor in determination of the ability of bio-composite to be commercially utilized (Zabihzadeh 2010a,b).

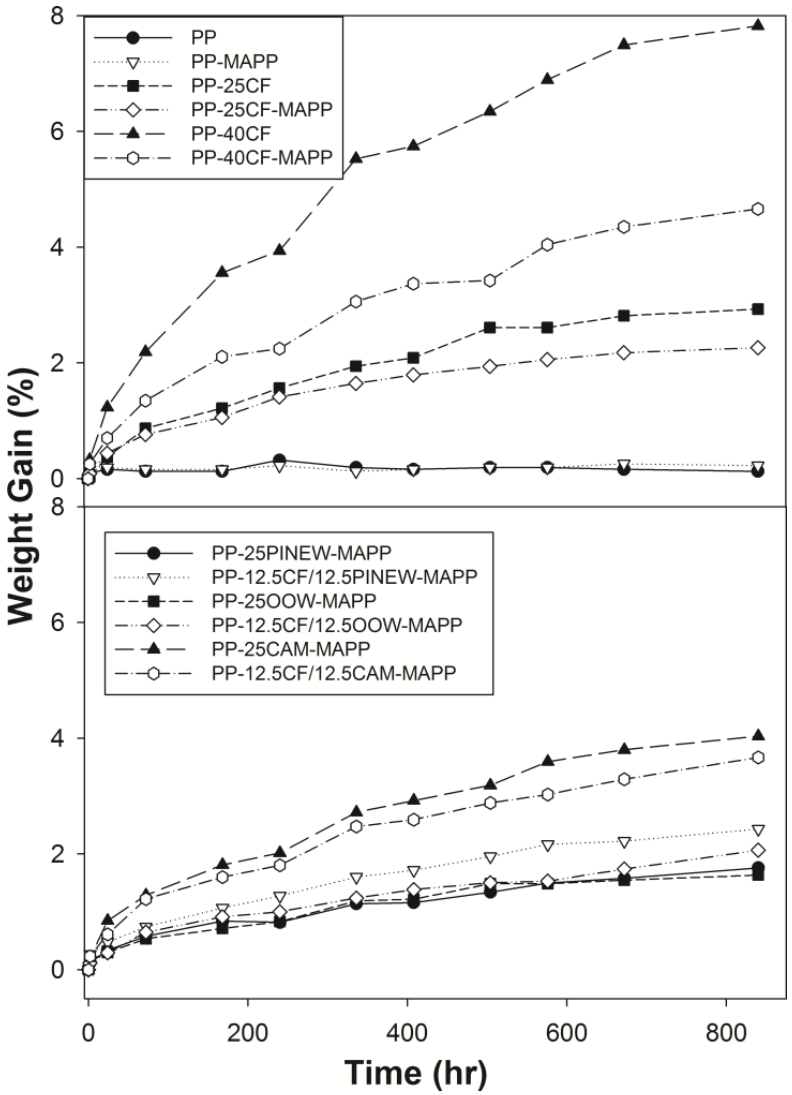

Fig. 4. Comparative water absorption plots for various WF composites for 872 h of soaking. A. Influence of concentration on weight gain and B. Influence of filler mixtures on weight gain.

Water soaking of bio-composites simulates a severe environmental stress that may cause changes in the mechanical properties to occur; such effects need to be determined in order to assess the potential commercial value of a composite (Thwe and Liao 2002; Lopez *et al.* 2006; Clemons and Stark 2009; Kord 2011; Zabihzadeh 2010a,b). For example, flexural properties have been reported to decrease when bio-composites are weathered (Thwe and Liao 2002; Lopez *et al*. 2006; Clemons and Stark 2009). The mechanical properties of Type V tensile bars that were soaked and not soaked for 872 h are shown in Fig. 5.

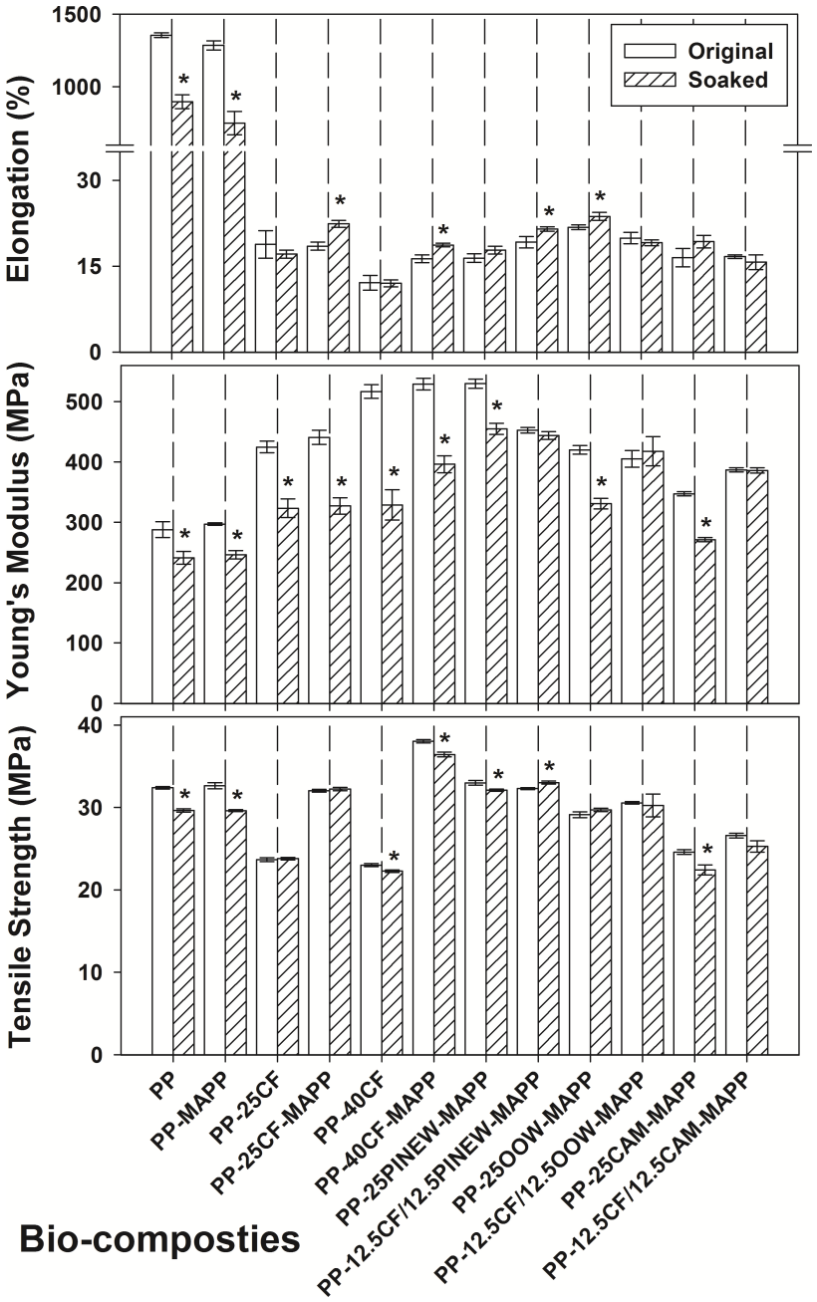

Fig. 5. Mechanical properties of original (unsoaked) and soaked composites. Asterisk indicates significant difference between the water soaking treatments ($P < 0.05$).

The mechanical properties of composites as well as neat PP and PP-MAPP were all affected by water soaking to some degree. PP and PP-MAPP blends exhibited significant reductions in σ_u, E, and %El values. Generally, the σ_u and E values for soaked bio-composites decreased, while the %El values were mainly retained, although some showed increases when compared to untreated controls (Fig. 5). The largest change in σ_u values occurred in the soaked PP-25CAM-MAPP formulation, which decreased 9%. It was interesting that two of the "mixed" formulations (PP-12.5CF/12.5OOW-MAPP and PP-12.5CF/12.5CAM-MAPP) retained their σ_u and E and %El values while composites containing the individual ingredient fillers showed greater variation in their mechanical properties. Further work needs to be conducted to determine if these situations can be duplicated with other filler mixtures.

Thermal Analysis

The thermal properties measured by DSC of the composite blends containing different concentrations of MAPP are shown in Table 4. T_m values varied among the bio-composites. All the composites examined exhibited a lower T_c than neat PP. These observations conform to others (Onwulata *et al*. 2009; Sutivisedsak *et al*. 2012).

Table 4. DSC Thermal Data for Composites

Composition	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	χ_c (%)
PP	122.3	91.8	164.4	84.8	41.6
PP-MAPP	122.8	95.6	164.1	85.7	42.0
PP-25CF	119.3	69.4	165.3	58.6	38.3
PP-25CF-MAPP	121.9	73.1	164.4	62.5	40.8
PP-40CF	120.2	53.6	165.2	44.3	36.2
PP-40CF-MAPP	122.2	58.5	165.7	47.6	38.9
PP-25PINEW-MAPP	120.0	67.6	164.7	54.1	35.4
PP-12.5CF/12.5PINEW-MAPP	120.1	70.9	166.5	63.2	41.3
PP-25OOW-MAPP	120.7	72.8	165.6	63.3	41.4
PP-12.5CF/12.5OOW-MAPP	121.2	71.6	164.7	65.8	43.0
PP-25CAM-MAPP	118.5	71.6	164.1	62.4	40.8
PP-12.5CF/12.5CAM-MAPP	119.3	67.4	164.0	56.9	37.2

Generally, one can attribute the variation in T_m in the composites to interaction of the PP crystal lattice network with the filler particles. The melting enthalpy of the bio-composites was significantly less than the neat PP or PP-MAPP formulations (Table 4). This suggests that filler material in the bio-composites absorbs more heat energy than the neat PP and MAPP formulations. Inclusion of MAPP in the CF bio-composites increased the melting enthalpy values compared to CF bio-composites without MAPP. The inclusion of fillers with PP resulted in composites with lower degree of crystallization levels than in the neat PP (Table 4). The lowered crystallization levels in CF composite blends roughly corresponded to the concentration of CF filler employed. For example, a blend containing 25% CF and 75% PP (PP-25CF) exhibited a crystallinity level 38.3%; and blend containing 40% CF and 60% PP (PP-40CF) exhibited a crystallinity level 36.2%. Other investigators have also observed a decrease in the crystallinity values associated with various

lignocellulosic plastic composites (Ayrilmis *et al*. 2013; Kalia *et al*. 2009). The presence of MAPP in the composite (PP-25CF-MAPP) slightly increased the degree of crystallinity compared to composites without MAPP (PP-25CF). Interestingly, the degree of crystallinity varied little among the bio-composites.

It is important to determine the thermal stability of CF fillers, because the temperatures employed in their processing (injection molding) may exceed 200 °C. The thermogravimetric curves are summarized in Table 5. The degradation of neat PP occurs in a single stage, beginning at 448.7 °C, with a maximum decomposition rate occurring at 463.3 °C. PP degradation was 99.1% complete at end of this stage. Similarly, the PP-MAPP blend mimics these parameters. In contrast, there are several degradation peaks for bio-composites. Early degradation peaks for PP-25CF were initiated around 240 °C and resulted in a prominent degradation peaks around 290 °C and 350 °C. These lower degradation peaks are associated with the decomposition of low molecular weight components such as hemicellulose, which degrades between 225 to 325 °C (Lee and Wang 2006; Clemons and Stark 2009). A second higher degradation peak occurred with a maximum at 316.2 °C. This degradation peak is associated with decomposition of cellulose which degrades in the 300 to 400 °C (Lee and Wang 2006). A third degradation peak corresponds to lignin decomposition is often reported occurring near 420 °C; however it was not readily seen in this study (Lee and Wang 2006). This peak was obscured by the decomposition of the PP. The PP-25CF composite has a residual weight of 5.9% due to the heterogeneous ingredients in the flour, which was considerably higher than residual weight of PP, 2.0%.

Table 5. TGA Data for Composites

Composition	1st	2nd	Peak Temp. (°C)**		Residual
	T_d (°C)*	T_d (°C)	Peak 1	Peak 2	(%)
PP	--	398	--	445	2.0
PP-MAPP	--	405	--	449	1.9
PP-25CF	240, 300	432	354	453	5.9
PP-25CF-MAPP	240, 300	433	355	456	6.1
PP-40CF	240, 299	431	354	455	10.0
PP-40CF-MAPP	240, 298	430	354	456	9.3
PP-25PINEW-MAPP	240, 314	437	359	456	17.8
PP-12.5CF/12.5PINEW-MAPP	240, 303	432	356	455	4.4
PP-25OOW-MAPP	240, 314	435	358	458	7.2
PP-12.5CF/12.5OOW-MAPP	240, 306	431	357	454	6.0
PP-25CAM-MAPP	220, 260	432	314	452	7.2
PP-12.5CF/12.5CAM-MAPP	220, 279	426	341	451	7.7
*Initial thermal degradation temperatures (T_d): 1st-hemicellulose, cellulose; 2nd-lignin/PP.					
**Maximum degradation temperature: 1st-cellulose; 2nd-lignin/PP.					

Differences among the bio-composite T_d values are due to the association of the filler material and the plastic resin. Higher T_d values and peak temperatures occurred for wood composites compared to the CAM composites; this can be attributed to the

occurrence of higher levels of low-molecular-weight organic compounds in CAM composites compared to wood composites. Similarly, other investigators report that addition of extractables (*e.g*. clay) causes decreases in T_d values to occur (Lei *et. al*. 2007). The addition of the coupling agent MAPP had little influence on the decomposing behavior the composites. Based on the TGA analysis and since the injection molding temperatures did not exceed 200 ^oC, the composites were relatively thermally stable for the temperatures they were subjected to in this study.

CONCLUSIONS

1. Replacement coffee trees provides a source of sustainable natural fiber that is an excellent reinforcement material for WPC based on its mechanical properties.
2. Adding a MAPP coupling agent to the WPC (PP-25CF-MAPP or PP-40CF-MAPP) improved the tensile strength, elongation at break, flexural strength, and modulus of elasticity compared to WPC without MAPP (PP-25CF-MAPP or PP-40CF-MAPP). However, Young's modulus was unaffected by the addition of MAPP in the WPC formulation.
3. PP-25CF-MAPP and PP-40CF-MAPP composites exhibited higher Young's modulus, tensile strength, flexural strength, and flexural modulus of elasticity than neat PP.
4. All WPC tested exhibited lower elongation at break and impact energy properties than neat PP.
5. The mechanical properties of WPC containing coffee wood compared well to WPC containing either Pine or Osage orange wood.
6. All composites soaked in water for 35 days exhibited an increase in weight gain and an alteration of their mechanical properties, especially Young's modulus.

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