Physico-mechanical Properties of Paper Sludge–Thermoplastic Polymer Composites

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ABSTRACT: This study investigates the effect of paper sludge's mixing ratio and the types and concentrations of coupling agents on the physical and mechanical properties of paper sludge–thermoplastic polymer composites. In the experiment, four levels of mixing ratios of paper sludge to thermoplastic polymer (10 : 90, 20 : 80, 30 : 70 and 40 : 60) and three levels of coupling agent (Epolene G-3003$^{\text{TM}}$) content (1, 3, and 5 wt.%) were designed to discuss the physical and mechanical properties of composite. Composite density, as expected, increased but melt flow index decreased when the paper sludge content increased. Thickness swelling and water absorption of composites was slightly improved by the addition of paper sludge compared with control specimens. Tensile properties of composites significantly increased as the mixing ratio of paper sludge increased. Especially, tensile modulus improved with the increase of paper sludge content. Flexural strength and modulus showed similar trends to that of the tensile properties. Notched and unnotched Izod impact strengths lowered by the addition of paper sludge.

With the addition of coupling agent, G-3003$^{\text{TM}}$, tensile and flexural properties improved considerably compared with control specimens (without any coupling agent). Epolene G-3003$^{\text{TM}}$, with high molecular weight, was effective in the improvement of the composites' tensile and flexural properties.

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INTRODUCTION

THE U.S. PULP and paper industry generates approximately 45 kg of sludge per ton of pulp. An annual pulp production of 80 million tons produces 4 million dry tons of sludge per year [1]. The vast majority of sludge is now being land-filled (70% in 1988), but environmental concerns and governmental regulations have made landfills more expensive to operate and much harder to site [1].

On the other hand, waste wood fibers separated from paper sludge, besides conventional inorganic reinforcing fillers such as clay, talc, calcium carbonate, and so forth, also have the feasibility of being effective fillers in manufacturing thermoplastic polymer composites. The use of reinforcing fillers for the reduction of material cost and improvement of composite performance is constantly increasing in the area of thermoplastic polymer composites.

Cellulose fibers attract considerable interest as reinforcing fillers for thermoplastic polymers especially those with a relatively lower melting point like polypropylene, high and low density polyethylene. Sludge from paper mills consists mainly of two components, fine cellulose fiber and inorganic materials, and can offer a number of benefits, as a substitute for the typical inorganic reinforcing fillers in manufacturing thermoplastic polymer composite.

These benefits, in comparison with typical inorganic fillers, include its low hardness and the resulting minimal abrasion of processing equipment, relatively low composite density, and low production cost on the unit volume basis. But cellulose fibers are unique in their response to moisture. Water absorption constitutes a major problem for users of reinforced plastics comprising cellulose fibers because cellulose fibers swell in water and cause a drop in both tensile strength and modulus [6]. Moreover, in some industries, particularly marine and chemical industries, absorbed water can cause damage to composite structures [16].

In this study, the effect of the paper sludge content on the physical (dimensional stability) and mechanical properties (tensile, flexural and impact properties) of the composites was determined. Also, the use of a maleated polypropylene (Epolene G-3003$^{\mathrm{TM}}$) to improve the fiber–matrix interaction and adhesion is discussed.

EXPERIMENTAL

Materials

Thermoplastic polymers were supplied by Daelim Chemicals Ltd., which is located in South Korea. The polypropylene was homopolymer spheres with a density of 0.91 g/cm^3 and a melt flow index of 12 g/10 min (230°C/2160 g). The high impact polypropylene (HIPP) was an ethylene–polypropylene random copolymer spheres with high impact strength and a low melt flow index of 0.5 g/10 min. The high-density polyethylene (HDPE) was homopolymer spheres with a density of 0.957 g/cm^3 and a melt flow index of 15 g/10 min. The low-density polyethylene (LDPE) was homopolymer spheres with a density of 0.918 g/cm^3 and a melt flow index of 20 g/10 min. Coupling agent was obtained from Eastman Chemical Products, Inc.; Epolene G-3003^{TM} has an acid number of 8, and molecular weight (M_w) of 103,500. The reinforcing filler in the composites was paper sludge from a newsprint mill; the particle sizes were 0.42–0.84 mm.

Processing

The paper sludge was dried at 80–100°C for 24 h to adjust it to a moisture content of 1–2% and then stored over desiccant in sealed containers. Four types of thermoplastic polymer were blended with paper sludge and coupling agents in a two-roll rheomixer. Mixing was continued at 200°C for 15 min with a rotor speed of 20 rpm. A laboratory-size single-screw extruder was employed to compound the paper sludge with the matrix resin. The extruded strand was pelletized and stored in sealed cans containing desiccant. Test specimens were prepared using an injection molding machine at 200°C, an injection pressure of 1200 psi, and a device pressure of 1500 psi. After molding, the specimens were stored over the desiccant at room temperature for at least 7 days before testing.

Testing

The density of paper sludge-reinforced composites was determined according to ASTM D 792. The melt flow index of paper sludge–thermoplastic polymer composites was determined according to ASTM D 1238-98 (210°C/2160 g).

Dimensional stability of composites was measured according to ASTM D 1037-95. Tensile tests were conducted according to ASTM D 638-91, flexural testing according to ASTM D 790-91, and Izod impact strength tests according to ASTM D 256-90. The crosshead speed during the flexural and tension testing was 2 and 5 mm/min, respectively.

RESULTS AND DISCUSSION

Density and Melt Flow Index of Composites by Paper Sludge Content

The densities of paper sludge–thermoplastic polymer composites are listed in Table 1. As expected, composite density increased with an increase in the paper sludge content. This is due to the apparently greater density of the paper sludge than that of the matrix polymer. Generally, the densities of composites decreased slightly, compared to the theoretical density of composites according to the rule of mixture [5]. The reason might be the less efficient dispersion of paper sludge and perhaps some porosity due to cellulose fine decomposition or vapor emission during processing [9].

According to Jacobson et al.'s research [4], the density of the lignocellulosic fiber-filled PP is about 1.4 g/cm^3 and that of the mineral-filled PP is about 2.5 g/cm^3. In other words, the density of lignocellulosic fiber-filled composites is much lower than the mineral-filled thermoplastic systems. The density of a 40% (by weight) paper sludge–PP composite in this study is about 1.08 g/cm^3 whereas, that of a 40% (by weight) glass fiber–PP composite is 1.23 g/cm^3. The density of the 40%-paper sludge-filled PP composites is comparatively lower than that of the 40%-$CaCO_3$-filled PP or 40%-talc-filled PP. Therefore, if we could use the paper sludge as a reinforcing filler in thermoplastic composites, we might obtain composites which have relatively low composite density and low production cost on a unit volume basis.

Table 1. Density and melt flow index of paper sludge (PS)–thermoplastic polymer (TPP) composite as a function of furnish mixing ratio.

	Filler Loading (wt.%)	PP	HIPP	HDPE	LDPE
Density (g/cm^3)	0	0.91	0.9	0.95	0.92
	10	0.95	0.94	0.99	0.96
	20	0.99	0.99	1.03	1.0
	30	1.04	1.03	1.08	1.05
	40	1.09	1.1	1.13	1.1
Melt flow index (g/10 min)	0	12.0	0.5	15.0	20.0
	10	11.0	0.5	14.0	18.0
	20	11.0	0.5	9.6	16.8
	30	7.2	0.4	5.8	12.7
	40	3.2	0.4	3.4	10.4

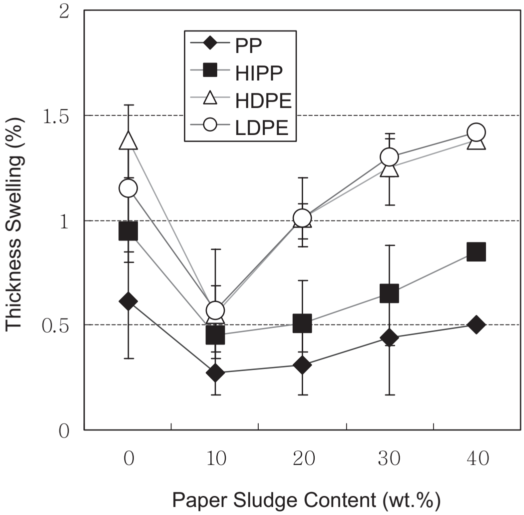

Figure 1. *Thickness swelling of paper sludge (PS)–thermoplastic polymer (TPP) composite as a function of furnish mixing ratio.*

The variation of melt flow index of the composites by furnish mixing ratio is also listed in Table 1. As listed in the table, the melt flow index decreased with increasing paper sludge content.

Effect of Paper Sludge Content on Dimensional Stability

The dimensional stability of paper sludge–thermoplastic polymer composites is shown in Figure 1. Generally, thickness swelling of composites is increased with an increase in the paper sludge content, but paper sludge had no significant effect on the dimensional stability of composites. Moisture absorption of the fibers can be significantly reduced by the acetylation of the hydroxyl groups present in the fiber, although at some increase in cost [10].

Thickness swelling of paper sludge-filled PE composites was higher than that of paper sludge-filled PP composites. This is attributed to the weak interfacial adhesion among polyethylene chain–paper sludge's fiber interactions, judging from mechanical property data of paper sludge–thermoplastic polymer composites [15].

Effect of Paper Sludge Content on Mechanical Properties

The simplest theory describing the mechanical properties of composite materials is the rule of mixtures. This states that the modulus of a composite is the volume-weighted average of the moduli of the components:

$$M_c = \sum V_i M_i \tag{1}$$

where M_c is the composite modulus, V_i is the volume fraction of component i, M_i is the modulus of component i

And we have for stiffness:

$$E_L = V_m E_m + V_f E_f \tag{2}$$

And for strength:

$$\sigma_L = V_m \sigma_m + V_f \sigma_f \tag{3}$$

where L is the composite modulus in the longitudinal direction (along the fiber axis), m is the matrix, f is the fiber

Since there are only two phases:

$$V_m + V_f = 1 \tag{4}$$

Equations (2) and (3) may then be written as:

$$E_L = E_m + V_f(E_f - E_m) \tag{5}$$

$$\sigma_L = \sigma_m + V_f(\sigma_f - \sigma_m) \tag{6}$$

Equations (5) and (6) may be "reduced" by dividing by the matrix modulus to give:

$$E_L/E_m = 1 + V_f[(E_f/E_m) - 1] \tag{7}$$

$$\sigma_L/\sigma_m = 1 + V_f[(\sigma_f/\sigma_m) - 1] \tag{8}$$

Plots of reduced composite modulus versus V_f will then have an intercept of 1 and a slope proportional to the inherent properties of the components. The use of reduced moduli allows the comparison of different systems on a more even basis.

The elastic moduli for tensile and flexural tests of thermoplastic polymer filled with paper sludge are shown in Figures 3 and 5, respectively. The stiffness of composites significantly increased as the mixing ratio of paper sludge increased. In other words, the use of paper sludge as reinforcing filler gave an increase in stiffness for the composites. The results suggest that cellulose fibers in paper sludge significantly enhance the stiffness of composites.

The effect of paper sludge content on the flexural strength of paper sludge-filled thermoplastic polymer composites is graphically represented in Figure 4. As shown in this figure, the flexural strength generally increased with a rising content of paper sludge.

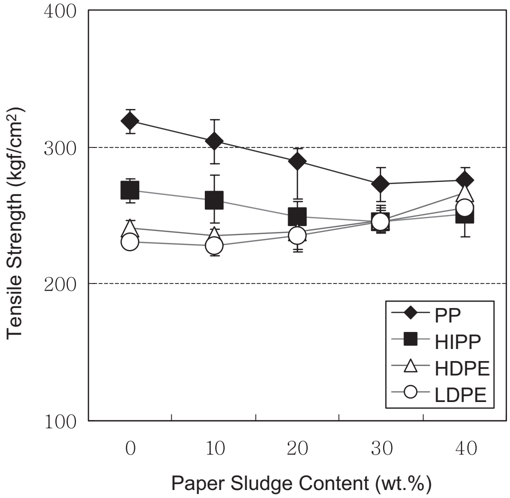

Figure 2. *Tensile strength of paper sludge (PS)–thermoplastic polymer (TPP) composite as a function of furnish mixing ratio.*

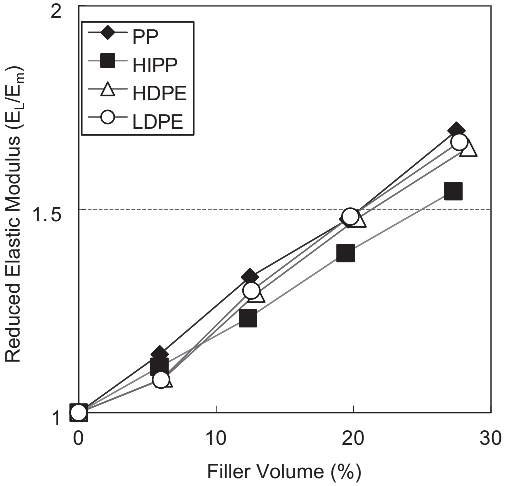

Figure 3. *Elastic moduli of paper sludge (PS)–thermoplastic polymer (TPP) composite by tensile test.*

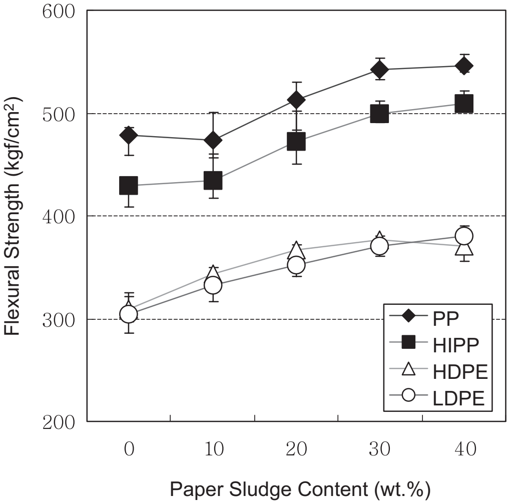

Figure 4. *Flexural strength of paper sludge (PS)–thermoplastic polymer (TPP) composite as a function of furnish mixing ratio.*

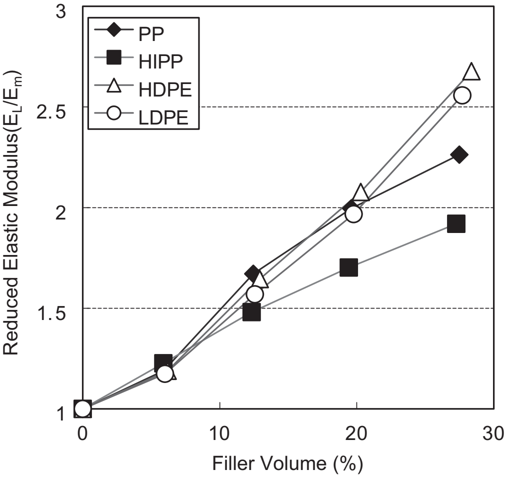

Figure 5. *Elastic moduli of paper sludge (PS)–thermoplastic polymer (TPP) composite by flexural test.*

As shown in Figure 2, however, tensile strength decreased slightly with low paper sludge content (10–20%). Thus flexural strength was still higher than tensile strength. This is because of the orientation of cellulose fibers in the outer skin of the specimens during injection molding as reported by Woodhams et al. [17].

Typically, the strengths of filled thermoplastics fall into two general classes. Fillers are incorporated into polymer matrices mainly to achieve improvement of service properties (reinforcing filler) or to reduce the material cost (nonreinforcing filler). Reinforcing fillers show increasing strength with increasing filler content, while particulate fillers show decreasing strength [14]. The data obtained in this research, with some exceptions (tensile strength of paper sludge–polypropylene composites), showed increasing strengths with increasing paper sludge content. Generally, the studies show that paper sludge can be used as reinforcing filler for thermoplastic polymer composite.

The tensile strength and modulus of the paper sludge system is about equivalent to that of the 40%-$CaCO_3$-filled or 40%-talc-filled PP composite [12]. The tensile and flexural properties of the paper sludge system is also almost equivalent or superior to that of wood flour-filled PP [7]. According to Son et al.'s research [15], the ash content of the paper sludges were about 73.7, 46.2, and 38.1% in particle sizes below 0.15, 0.18–0.25, and 0.42–0.84 mm, respectively, which meant a lower ash content and thus a higher cellulose fiber content with the larger particle size of the paper sludge. So this is attributed to the reinforcing effect of fine cellulose fiber in paper sludge.

The impact strength was also measured with notched and unnotched specimens in this study. Izod notched and unnotched impact strength values of paper sludge–thermoplastic polymer composite as a function of furnish mixing ratio are shown in Figures 6 and 7. Notched and unnotched Izod impact strengths were lowered by the addition of paper sludge. In the case of

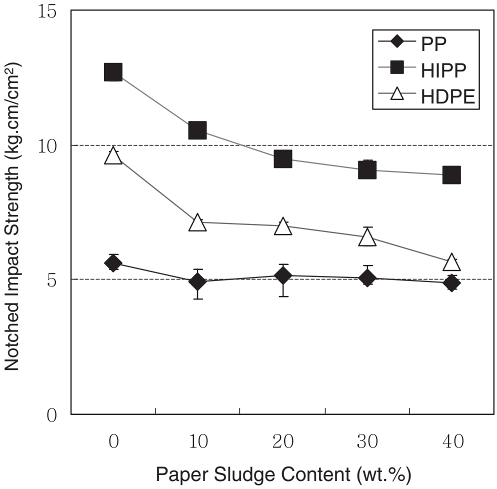

Figure 6. *Notched impact strength of paper sludge (PS)–thermoplastic polymer (TPP) composite as a function of furnish mixing ratio.*

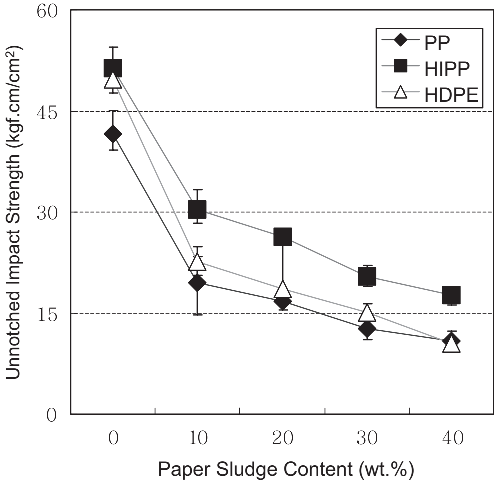

Figure 7. *Unnotched impact strength of paper sludge(PS)–thermoplastic polymer (TPP) composite as a function of furnish mixing ratio.*

notched samples, the impact strength decreases with the amount of cellulose fibers added until a plateau is reached at about 45% fiber weight, irrespective of whether coupling agents were used or not. The cellulose fibers in paper sludge bridge cracks and increase the resistance of the propagation of the crack. Contribution from fiber pullout is limited since the aspect ratio of the fibers in the system is well below the estimated critical aspect ratio of about 0.4 mm [11].

As can be seen by comparing Figures 6 and 7, unnotched Izod impact energies are considerably larger than notched Izod impact energies. This is due to different fracture processes for notched and unnotched specimens. The existence of different trends for the two measurements of the impact strength was not surprising. According to Nielsen [8] and Clemons [2], the unnotched impact behavior is controlled to a considerable extent by fracture initiation processes that, in turn, are controlled by stress concentrations at defects in the system. Notched impact behavior is controlled to a greater extent by factors affecting the propagation of fracture initiated at the predominating stress concentration at the notch tip. In other words, unnotched Izod impact energies are not only a measure of crack propagation but also of crack initiation.

Effect of Coupling Agent Content on Mechanical Properties

In Figures 8 and 9, the tensile and flexural properties of paper sludge-filled thermoplastic polymer composites treated with coupling agent are

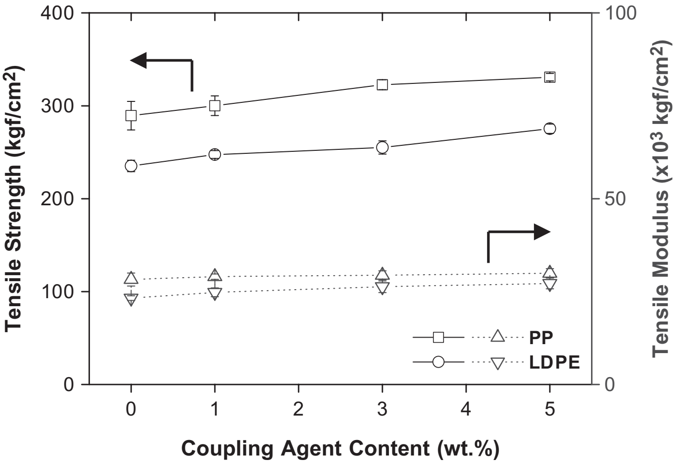

Figure 8. *Tensile strength and modulus of paper sludge–thermoplastic polymer (20%/80% wt.) composite as a function of coupling agent content.*

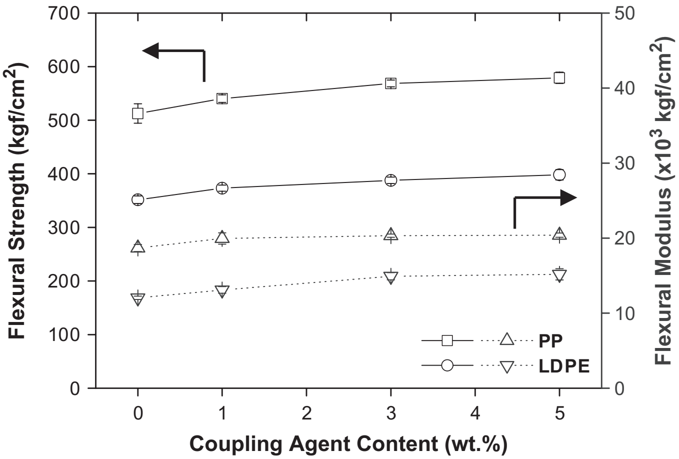

Figure 9. *Flexural strength and modulus of paper sludge–thermoplastic polymer (20%/80% wt.) composite as a function of coupling agent content.*

represented as a function of coupling agent content. Use of the Epolene G-3003^{TM} resulted in somewhat improved tensile and flexural properties over control specimens (without any coupling agent). The anhydride groups present in the coupling agent (maleated polypropylene) can covalently bond to the hydroxyl groups of the fiber surface of paper sludge. Any maleic anhydride that has been converted to the acid form can interact with the

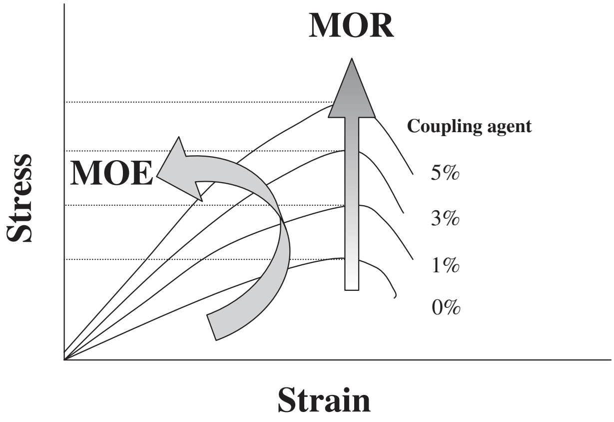

Figure 10. *Stress–strain curves of paper sludge–thermoplastic polymer (20%/80% wt.) composite with the amount of coupling agents varying from 1 to 5%.*

fiber surface through acid–base interactions. The improved interaction and interfacial adhesion between the fibers and the matrix leads to better matrix-to-fiber stress transfer. Also, the higher tensile and flexural strength of the G-3003 composite system is probably due to improved interphase properties. The longer molecular chains of Epolene G-3003^{TM} resulted in greater molecular entanglement that strengthens the interphase. It is important to recall that as the degree of polymerization increases, the mechanical properties of a polymeric material improve until a critical degree of polymerization, beyond which no significant effect on polymer mechanical properties occurs [13].

Figure 10 shows the stress–strain curves of paper sludge/thermoplastic polymer composites with varying amounts of coupling agents present, schematically. As shown in the figure, the tensile and flexural properties (MOR, MOE) of composites were improved with an increase of coupling agent content. The nonlinearity in the curves is mainly due to the plastic matrix deformation. However, the distribution of fiber lengths present in the composite can also cause the slope of the stress–strain curve to decrease with increasing strain. This is because the load taken up by the cellulose fibers of paper sludge and the efficiency of the fibers decreases as the strain increases [3].

CONCLUSIONS

The physical and mechanical properties of paper sludge–thermoplastic polymer composites were examined to determine the influences of paper sludge content (0, 10, 20, 30, and 40 wt.%) and concentrations (0, 1, 3, and 5 wt.%) of coupling agent, and some conclusions are as follows;

Composite density, as expected, was increased but melt flow index decreased with increasing of paper sludge content. Thickness swelling of composites was slightly improved by the addition of paper sludge compared with control specimens. Tensile properties of composites significantly increased as the paper sludge content increased. Tensile modulus improved with the increase of paper sludge content. Flexural strength and modulus showed similar trends to that of the tensile properties. Notched and unnotched Izod impact strengths lowered by the addition of paper sludge. By the addition of coupling agent, Epolene G-3003$^{\mathrm{TM}}$, its tensile and flexural properties improved considerably compared with control specimens (without any coupling agent).

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