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Performance of Paper Sludge/Polypropylene Fiber/ Lignocellulosic Fiber Composites

Byoung-Hoo Lee, Hyun-Joong Kim†, and Hee-Jun Park*

Lab. of Wood-based Composites and Adhesion Science, School of Biological Resources & Materials Engineering, Seoul National University, Suwon 441-744, Korea
**Field of Engineering, Iksan National College, Iksan 570-752, Korea*

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Abstract: The effectiveness of the coupling agent addition and the paper sludge addition on the performance of the paper sludge/polypropylene fiber/lignocellulosic fiber composites was investigated. In the experiment, two addition levels of the paper sludge and four addition levels of the coupling agent, and an emulsion of maleic anhydride modified polypropylene (MAPP) were designed to discuss the physical and mechanical properties of the composites. Water absorption and thickness swelling decreased with increasing the paper sludge and MAPP addition. Also, modulus of rupture (MOR) decreased with 30 wt% paper sludge addition. But no significant effect of the paper sludge addition appeared by 30 wt%, compared to 0 wt%. MOR increased slightly as MAPP addition level increased. The greatest observed change was an increase in MOR with 1 wt% MAPP addition. Internal bond strength generally increased with increasing in the paper sludge and MAPP addition. It is due to the improved interaction and interfacial adhesion between the hydrophilic and polar lignocellulosic fiber with the hydrophobic and non-polar polymer. 1 wt% MAPP addition only produced a significant improvement on internal bond strength. Notched Izod impact strength decreased with an increase in the paper sludge and MAPP addition. All notched Izod impact strength of the composites was higher than that of the control board.

Keywords: *paper sludge, lignocellulosic fiber, polypropylene, maleic anhydride modified polypropylene, nonwoven web*

Introduction

Large amounts of waste such as the paper sludge and the waste plastic etc. are generated in the world annually. Especially, the U.S. pulp and paper industry generates approximately 45 kg of sludge per ton of pulp. With an annual pulp production of 80 million tons, this works out to 4 million dry tons of the sludge per year [1]. The disposal of the paper sludge from the production of pulp and paper, as well as the waste plastics from the plastics industry and the wide variety of the solid waste, is a serious problem. Most of them, however, has been landfilled and incinerated [2]. It has been raised the environmental pollution, the increase of the disposal costs and the shortage of landfills.

According to the previous research, it is virtually certain that the constituent of the wood-based composites can be totally or partially replaced by both the paper sludge and the recycled waste plastic in melt blending and nonwoven web formation for many application [3-6].

The recycling of the sludge and the waste plastics represents a significant opportunity to reduce the volume of the landfilled materials and the environmental pollution.

Generally, the lignocellulosic fiber/plastic composites are classified by their manufacturing process as either melt-blended or air-laid [3-6]. The latter process is also referred to as nonwoven web formation. Melt-blended composites typically consist of 40 ~ 60 wt% cellulose pulp fibers or lignocellulosic flours or a powdered or pelletized thermoplastic such as polypropylene or polyethylene. Limits on the melt viscosity of the mixture restrict the amount of fiber or flour (to about 50 wt%) as

† To whom all correspondences should be addressed.
(e-mail: hjokim@snu.ac.kr)

well as the length of the fiber.

For the nonwoven web composites, the lignocellulosic fiber (or even fiber bundle) is air-mixed with the thermoplastic fiber. With the technology, the amount of the lignocellulosic fiber can be greater than 90 wt% [3,4,7-9].

However, the lignocellulosic fiber/plastic composites has several problems due to a lack of interfacial adhesion between the lignocellulosic fiber and the plastic. The apparent lack of compatibility between the lignocellulosic fiber and the plastic comes from differences in the polarity of the hydrophilic lignocellulosic fiber and the hydrophobic plastic polymer chain. Several attempts have been made to overcome this problem. The addition of the coupling agent belongs to the most extensively used methods for improvement of the compatibility and bonding of the lignocellulosic fiber and the polymer chain [10-13].

During the past decade, urea formaldehyde and phenol formaldehyde resin binder have greatly contributed to the progress of wood industries. Formaldehyde is widely used as a major component in the production of building and furniture materials, such as medium density fiberboard (MDF), particleboard (PB), and polywood etc.

However, the emission of formaldehyde has been the major concern, associated with adhesively bonded wood products. Recently, interest has turned to other volatile organic chemicals (VOCs) that may be emitted from wood products [14,15]. The VOCs include chemicals naturally present in the wood as well as those added during processing. In new energy-efficient buildings, air exchange rates are low, permitting concentrations of VOCs to accumulate to detectable and possibly harmful levels.

According to the previous research [9], a variety of lignocellulosic fibers and synthetic fibers can be assembled into a web or mat using air-forming or nonwoven web technology. Fibers are initially held together by mechanical interlocking. The web is then fused or thermoformed into panels or various shapes. There is no formaldehyde emission from the lignocellulosic fiber/plastic composites. These must be economical and more environmentally friendly then in previous years.

In this study, we evaluated the physical and mechanical properties of the lignocellulosic fiber/plastic composites to determine the effects the paper sludge and the coupling agent.

Experimental

Materials

Radiata pine (*Pinus radiata* D. Don) wood fibers, obtained from Hansol Forem Co., Ltd, were thermomechanical pulp used for medium density fiberboard (MDF). The moisture content (MC) of the lignocellulosic fiber depended on the paper sludge addition and coupling agent addition level. The MC of mat was 10.5% for the composites, and 14% for the control board, based on the fiberboard.

The paper sludge in the shape of a cake, donated by SamPung Paper Co., was byproducts, which had 60 ~ 65% equilibrium moisture content (EMC), of the deinking for recycling of the waste paper and dried about 20 ~ 30% EMC with air drying for a few weeks. In order to produce materials with more uniform MC, the paper sludge was milled by the automatic screw miller with size controller and then dried to about 6% EMC. The paper sludge was milled by screw miller once more and run through the sieve shaker with under 10 and over 25 mesh screen. The paper sludge was about 2.00 mm ~ 0.70 mm in length. The ash content of the paper sludge was 46.3 wt%, performed in conformance with TAPPI T211 om-85 [16].

The thermoplastic polypropylene fiber was 3 denier with a melt flow index of 25 g/10 min and cutted with automatic paper cutter. The length was 10 mm ~ 12 mm and EMC was 1%. The coupling agent was obtained from Eastman Chemical Products, Inc.; Epolene E-43 has a acid number of 45, and approximate molecular weight (M_w) of 9100. The coupling agent was an emulsion of maleic anhydride modified polypropylene (MAPP) with solid content of 40 wt%.

The adhesive of the control board, provided by Dongwha Enterprise Co., Ltd, was a water-soluble liquid urea-formaldehyde resin with 46 wt% solids content. The curing agent (hardener) was a ammonium chloride (NH_4Cl) with 10 wt% water solution.

Manufacturing Processes of the Composites

The manufacturing process of paper sludge/propylene fiber/lignocellulosic fiber nonwoven web composites is shown in Figure 1.

In the composites without MAPP, the target specific gravity of the composites was 0.85. The composites were manufactured to be 250 mm × 150 mm × 3 mm. In the experiment, we replaced 15 wt% of the total composites

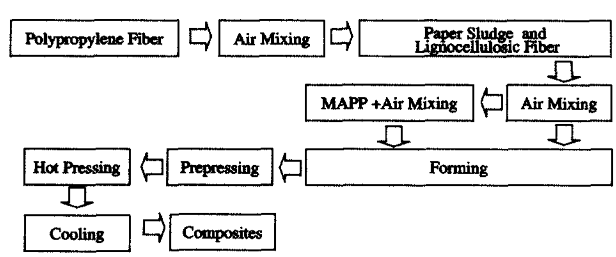


Figure 1. Manufacturing process of composites.

weight with equivalent weight (oven-dry weight) of the polypropylene fiber to bond mechanically between the paper sludge and the lignocellulosic fiber. The mixing ratio of the paper sludge to the lignocellulosic fiber was 0/100, 30/70 (based on oven-dry weight). We made the mat, after mixing the wood fibers, the paper sludge and the polypropylene fiber by the compressed air mixer and then prepressed the mat to 0.20 MPa at room temperature, because of the stability of the mat and the proper density gradient of the composites.

Figure 2 shows the hot pressing schedule. The mat was hot-pressed to 3 mm, the thickness of the stops, at 190 °C. The closing pressure was 2.96 MPa. Two caul plates were used to sandwich the mat during hot-pressing for 9 minutes of the press time. And then the composites were cold-pressed by 40 °C because of the spring back in the thickness direction, due to the release of residual compressive stresses imparted to the composites during the pressing of the mat in the hot press, and the keeping of the target thickness of the composites.

In the composites with MAPP, we used a rotary drum blender with the compressed air sprayer in order to apply MAPP to the mixing compound of the lignocellulosic fiber, the paper-sludge and the polypropylene fiber. The addition levels of coupling agent, MAPP, were 1, 2.5 and 4 wt%, based upon the total mixing compound weight (oven-dry weight basis).

Manufacturing Processes of the Control Board

The control board (fiberboard) was also manufactured for performance comparison with the composites. The target specific gravity and the size of the control board were consistent with the composites.

The control bod was manufactured by the wood fiber using the urea-formaldehyde resin (UF) commercially used. The wood fiber was loaded in a drum blender and then the a ammonium chloride (NH_4Cl) as a curing agent was added into the resin to give 1 wt% curing agent content, based upon the total resin solids content as a percent of the oven-dry weight. The UF resin was sprayed over the wood fibers to give 10 wt% resin content, based upon the total wood fiber weight as a percent of oven-dry weight. On adding the curing agent, the wood fiber was sprayed with the resin in the drum blender rotated. The mat was made and then hot-pressed to stops at 140 °C for 3 min, after this had been prepressed. The closing pressure was 3.43 MPa.

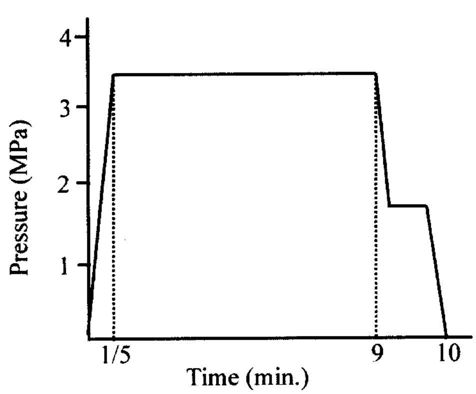


Figure 2. Hot pressing schedule.

Mechanical & Physical Properties of the Composites

Specimens were conditioned at 65±3% relative humidity and 20±1 °C for at least 2 weeks by constant weight before testing. Water-absorption and thickness swelling were performed according to ASTM D 1037 [17]. Specimens were immersed in water at 20±1 °C and then the change of the thickness and weight for each specimen were measured after 24 h immersion. Also, tensile strength was performed according to ASTM D-1037 [17]. The crosshead speed during tensile testing was 2 mm/min (UTM at NICEM, Seoul National University). Notched Izod impact strength was measured in conformance with KS M-3055, 2-A specimen [18].

Results & Discussion

Physical Properties

The values of air-dry specific gravity of the composites are ranged 0.79~0.82 and oven-dry specific gravity is from 0.83 to 0.86. The values are nearly consistent with the target oven-dry specific gravity, 0.85. EMC of the composites is 5.73~7.05%.

Water-absorption and thickness swelling is shown in Figures 3 and 4. The values of water-absorption and thickness swelling are 55.2%~67.5% and 35.5%~19.6%, respectively. Water-absorption and thickness swelling of control board are 71.2% and 35.6%, respectively. Water-absorption and thickness swelling decrease slightly with 30 wt% addition of the paper sludge. A

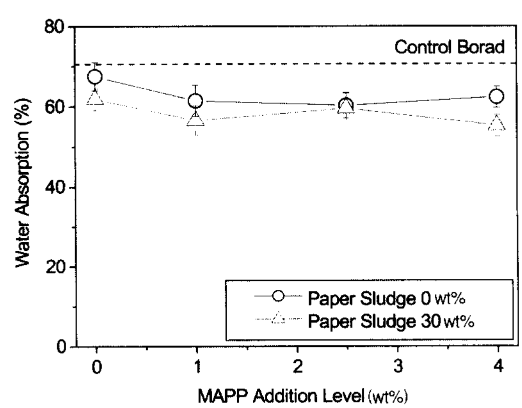


Figure 3. Water-absorption as a function of MAPP addition levels (0, 1, 2.5 or 4 wt%) at paper suldge additions (0 or 30 wt%).

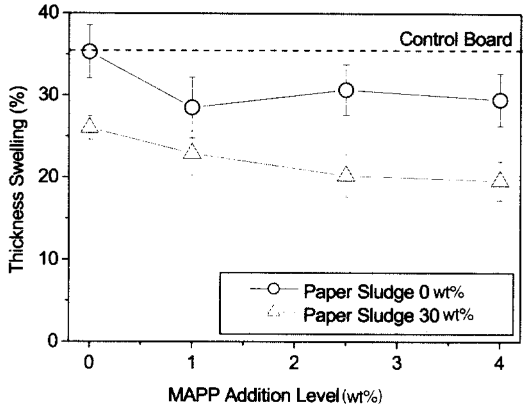


Figure 4. Thickness swelling as a function of MAPP addition levels (0, 1, 2.5 or 4 wt%) at paper suldge addition (0 or 30 wt%).

decrease in water-absorption and thickness swelling may be due to the hornification of the paper sludge, related to the included fine fiber, thus limiting the water uptake by the paper sludge.

According to the previous research [19], hornification occurs in the cell wall matrix of recycling fibers. During drying, delaminated parts of the fiber wall, i.e., cellulose microfibrils, become attached as the Figure 5 shows. Hydrogen bonds between those lamellae also form. Reorientation and better alignment of microfibrils, which are the constituent of the fiber wall, also occur. All this causes an intensely bonded structure. In immersion in water, the fiber cell wall microstructure remains more resistant to delaminating forces because some hydrogen bands do not reopen. Also, according to Nelson's research [20], water absorption and thickness swelling on the medium-density, dry-hardboard were significantly decreased by decreasing the fiber size of the wood and the pulp. Our observed decrease on water absorption attributable to the paper sludge consisted of most fine recycling fibers.

As shown in Figure 3 and 4, water-absorption and thickness swelling decrease with increasing MAPP addition level. Felix and coworkers [11] showed MAPP-treated fibers had become totally hydrophobic. Also, the hydrophilic lignocellulosic fiber is able to be encapsulated by the thermoplastic polypropylene fiber during hot-pressing, thereby reducing exposure of the lignocellulosic fiber to the moisture [3,4].

Mechanical Properties

Modulus of rupture (MOR) and modulus of elasticity (MOE) of the composites are shown in Figures 6 and 7. The values of MOR are 30.21 MPa to 39.13 MPa, while MOR on the control board is 45.90 MPa. As illustrated in Figure 6, MOR generally decreases with 30 wt% paper sludge addition. But all values of MOR satisfied with

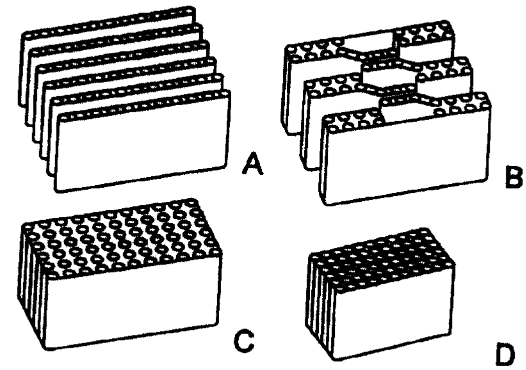


Figure 5. Changes in fiber wall structure (A→B→C→D). [19]

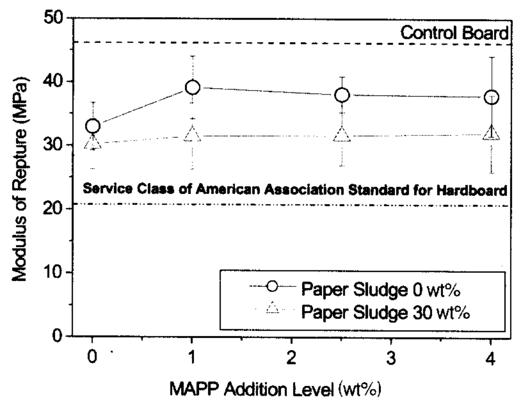


Figure 6. MOR as a function of MAPP addition levels (0, 1, 2.5 or 4 wt%) at paper suldge additions (0 or 30 wt%).

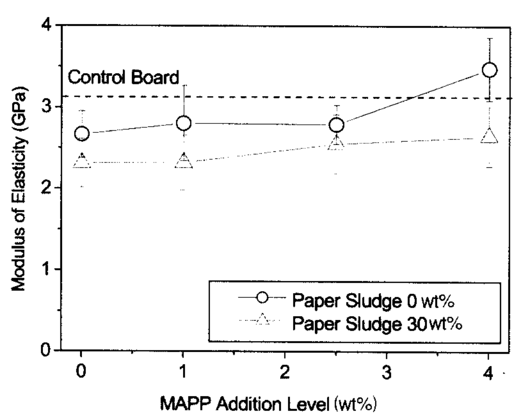


Figure 7. MOE as a function of MAPP addition levels (0, 1, 2.5 or 4 wt%) at paper suldge additions (0 or 30 wt%).

service class (20.69 MPa) of American Association Standard for Basic Hardboard [21]. Therefore, the composites can be produced using the paper sludge by 30 wt%.

Also, MOR increases slightly as MAPP increased. 1 wt% MAPP addition to the composites increases slightly MOR, compared to 0 wt% MAPP. However, no significant increases is observed in 2.5 wt% and 4 wt% MAPP addition, compared to 1 wt% MAPP. Little or no advantage is to be gained by using 1 wt% MAPP. Beyond 1 wt% MAPP, the addition of MAPP exerts only a small effect on MOR.

Generally, a wide variety of lignocellulosic materials and thermoplastic fibers can be assembled into a web or mat using air-forming or nonwoven web technology. The components of composites are initially held together by mechanical interlocking. The web is then fused or thermoformed into panels with a variety of shapes.

However, poor attraction and low interfacial adhesion between the hydrophilic lignocellulosic materials are serious drawbacks to achieving composite materials with the improved mechanical property [22].

In this study, the modification of the lignocellulosic materials' surface either by chemical coupling agents or grafting to enhance the compatibility between lignocellulosic materials and thermoplastic fibers, has proven to be beneficial in improving the strength.

According to the previous research [11,13], two factors need to be considered. Firstly, MAPP present near the fiber surface should be strongly interacting with OH groups on the fiber surface through covalent bonding and hydrogen bonding. Actually, the maleic anhydride present in the MAPP can covalently bond to the hydroxyl group on both the lignocellulosic fiber and the paper sludge. This is to ensure that the fiber surface-interaction is strong. Secondly, the polymer chain of the MAPP should be long enough to permit entanglements with the polypropylene fiber in the interphase. As illustrated in Figure 8, the reaction between lignocellulosic materials (lignocellulosic fiber or paper sludge) and coupling agent may occur, in agreement with Felix and coworkers, who showed the peak of ester bonds (1746 cm^{-1}) between the cellulosic fiber and MAPP with FT-IR [11].

The greatest observed change is an increase in MOR with 1 wt% MAPP. As noted for a trend of MOR, a similar trend is repeated for those of MOE in Figure 7. Figure 9 shows a typical stress-strain curve of composites for tensile test. As shown in Figure 9, coupling agent improves the strength and modulus of the composites.

Internal bond strength is presented in Figure 10. The values of internal bond strength of composites are 0.33 MPa ~ 0.56 MPa. Internal bond strength of the control board is 0.40MPa. Internal bond strength increases with 30 wt% paper sludge addition, as shown in Figure 10. Also internal bond strength increases with an increasing MAPP, except for the composite with 2.5 wt% MAPP at 30 wt% paper sludge addition. As noted previously, the interface of the composites is modified with MAPP to improve the mechanical properties through increased adhesion between the hydrophilic and polar lignocellulosic fiber with the hydrophobic and non-polar polymer chain. An increase in internal bond strength may reflect the positive effect with the addition of MAPP. Moreover, only 1 wt% MAPP addition produces a significant improvement of internal bond strength, compared to control board.

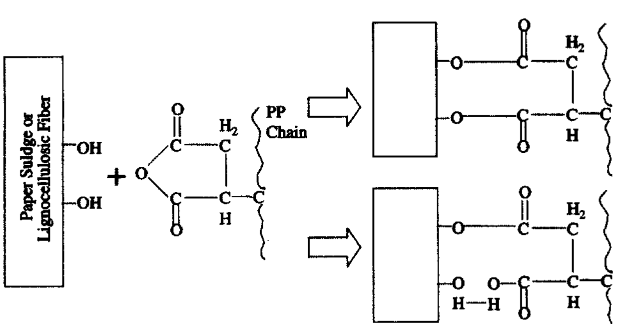
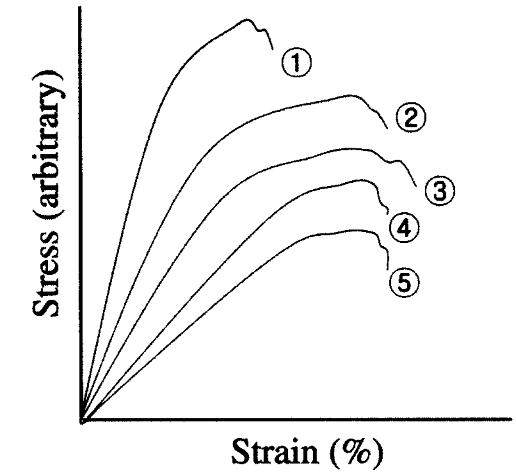


Figure 8. Schematic reactions between lignocellulosic materials (lignocellulosic fiber or paper sludge) and coupling agent .[11]



① Fiberboard (control board), ② Polypropylene fiber/lignocellulosic fiber composites + coupling agent, ③ Polypropylene fiber/lignocellulosic fiber composites, ④ Paper sludge/polypropylene fiber/lignocellulosic fiber composites+coupling agent, ⑤ Paper sludge/polypropylene fiber/lignocellulosic fiber composites

Figure 9. Stress-strain curves of each composites obtained from tensile test.

Notched Izod impact strength is shown in Figure 11. The values of notched Izod impact strength are 43.69 J/m ~80.63 J/m. In contrast to the internal bond strength data, notched Izod impact strength decreases with 30 wt% paper sludge addition and an increase in MAPP addition level. Notched Izod impact strength on the control board is 25.36 J/m. All notched Izod impact strength of the composites is higher than that of the control board.

Figure 12 shows the sacrifice in notched Izod impact strength that would accompany the improvements in strength and modulus with the addition of MAPP. Loss in impact energy may reflect the greater strength and stiffness of the composites due to some loss in the polymer mobility and impact energy absorbing ability,

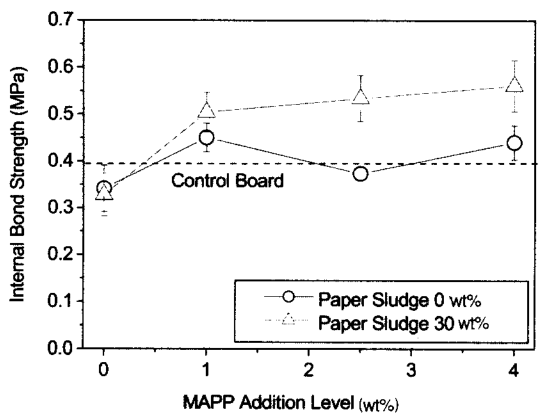


Figure 10. Internal bond strength as a function of MAPP addition levels (0, 1, 2.5 or 4 wt%) at paper suldge additions (0 or 30 wt%).

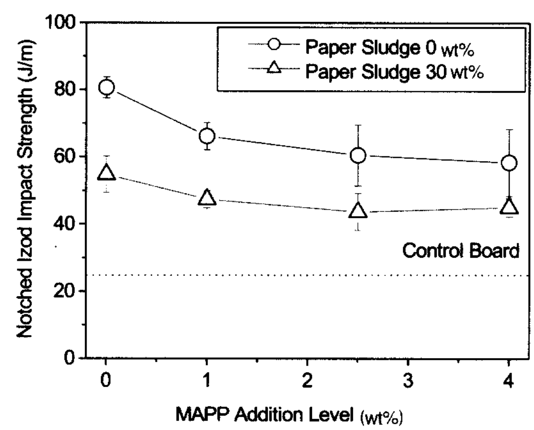


Figure 11. Notched Izod Impact strength as a function of MAPP addition levels (0, 1, 2.5 or 4 wt%) at paper suldge additions (0 or 30 wt%).

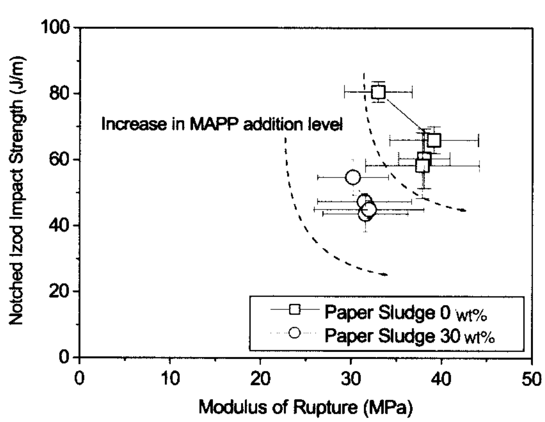


Figure 12. Plots of MOR vs. notched Izod impact strength.

caused by increased bonding between the lignocellulosic materials and the polypropylene fibers; additionally, lower impact energy may result from an increase in a short-length paper-sludge addition and an acidic nature of MAPP induced the degradation of lignocellulosic materials at high hot-pressing temperature [12,13].

Conclusions

A designed study was performed to determine the influence of paper sludge and MAPP addition on the physical and mechanical properties of lignocellulosic fiber/thermoplastic polymer composites.

The results obtained were summarized as follows :

1) Water absorption and thickness swelling decreased with 30 wt% paper sludge addition and an increase in MAPP addition level. This results may be reflect from the hornification of the paper sludge by the waste paper recycling and the capsulation of the lignocellulosic materials by the thermoplastic polypropylene fiber. Also, the decrease in water-absorption and thickness swelling of the composites after incorporating MAPP is due to the hydrophobic character of the MAPP-treated composites.

2) MOR and MOE decreased with 30 wt% paper sludge addition. But all values of MOR satisfied with service class of American Association Standard for Basic Hardboard. The greatest observed change on MOR and MOE was at 1 wt% MAPP addition.

3) Internal bond strength generally increased with 30 wt% paper sludge addition and an increase in MAPP addition level. It is due to the improved interaction and adhesion between the hydrophilic and lingocellulosic polar fibers, and the hydrophobic and non-polar polymer. But, 1 wt% MAPP addition only produced a significant improvement on internal bond strength.

4) Notched Izod impact strength decreased with 30 wt% paper sludge addition and an increase in MAPP addition level. But all notched Izod impact strength of the composites was higher than that of the control board.

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