Isotactic Poly(propylene)/Wood Sawdust Composite: Effects of Natural Weathering, Water Immersion, and Gamma-Ray Irradiation on Mechanical Properties

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Summary: Isotactic poly(propylene) (iPP)/wood sawdust composite containing 30 wt.% of the natural fibers was first prepared by melt-mixing in a twin screw extruder and later molded into various shaped specimens by injection molding machine. The effect of natural weathering, water immersion, and gamma-ray irradiation on mechanical properties of the specimens were studied. All of the tensile properties were improved with initial increase in the exposure time of natural weathering of up to 30 days and decreased afterwards. Similarly, the tensile strength and the Young's modulus of the composite increased with initial increase in the radiation dosage and decreased afterwards. On the contrary, the tensile strength and the elongation at break of the composite were unchanged after having been immersed in water for the first 15 days, but increased slightly afterwards. The alteration in these properties were postulated to be a result of the interplay between the cross-linking and the chain scission reactions that occurred during natural weathering and gamma-ray irradiation and the plasticizing effect of the absorbed water molecules during water immersion.

Keywords: cellulose; composites; irradiation; mechanical properties; poly(propylene); sawdust; weathering

Introduction

Studies on the use of various kinds of reinforcing fillers to improve mechanical properties of a polymeric material with an aim to obtain a composite with specific properties are prevalent in the open literature.[1] Among the various fillers, lingo-cellulosic materials in their native fibrous form have received much attention for being used as reinforcing materials in place of some synthetic fibers of the same sort. Two most important reasons for the popularity of these natural fibers as reinforcing materials for the production of polymeric composites are the inexpensiveness of the materials that help reduce the final costs of the composite products and the biodegradability of the materials that help alleviate the environmental concerns.[2–4]

The use of wood sawdust as a filler offers an economical solution for the increasing costs of wooden products and construction materials. However, the often poor mechanical integrity of the polymer/wood sawdust composites are somewhat inherent, as the poor mechanical properties are mainly attributed to the poor compatibility between the two constituents (i.e., due to the difference in the hydrophobicity/

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hydrophilicity of the two materials). The disparity in their chemical functionalities also results in the poor environmental and dimensional stability of the finished products. For examples, absorption of water of the wood sawdust leads to micro-crack formation of the composites when they are in contact with water for a lengthy period of time, hence the poor mechanical integrity of the products. Therefore, water uptake is one of the most serious concerns that limit the use of such materials.[5]

In order to study the durability of polymeric composites containing wood sawdust, the weathering characteristics much be thoroughly evaluated. Joseph et al.[2] investigated the water absorption and UV degradation of sisal fiber-reinforced isotactic poly(propylene) (iPP) composites and reported that both the water absorption and the UV irradiation adversely affected a great deal the mechanical properties of the materials. Irradiation of such composites with gamma ray, on the other hand, proved to be an alternative method to compatibilize the two constituents.[6] Basically, irradiation of the composites lead to the formation of excited species to the polymer matrix, which later cause the breakage of bonds and/or the production of free radicals. Basically, both the chain scission and the cross-linking reactions of the polymer matrix occur simultaneously after gamma-ray irradiation. The treatment of polymeric composites with gamma-ray irradiation, therefore, offers a number of advantages, e.g., no involvement of chemical reagents and simplicity.

The potential for use of iPP/wood sawdust composites in an outdoor application requires the assessment of their mechanical properties under a long-term weathering condition. In the present contribution, the effects of water immersion and water immersion on the mechanical properties of such a composite having a fixed composition of the constituents of 70/30 w/w were evaluated. Additionally, the effect of gamma-ray irradiation on the mechanical properties of the iPP/wood sawdust composite was also evaluated.

Experimental Part

Materials

Isotactic poly(propylene) (iPP; P 700 J-P; pellet form) was donated by Thai Polyethylene Co., Ltd. *Hevea brasiliensis* wood sawdust (35 mesh particles) was practically the waste from a furniture-making company, Universal Para Wood Co., Ltd. (Thailand). The wood sawdust was dried at 80 °C for 6–8 h in a hot-air oven to adjust the moisture content of ca. 1–2% and was stored in polyethylene bags prior to further use.

Compounding

A laboratory-sized twin-screw extruder was used to mix iPP pellets and the wood sawdust at the iPP/wood sawdust ratio of 70/30 w/w. The highest temperature of the last segment of the extruder barrel and the die was set at 190 °C. The iPP/wood sawdust extrudate was cooled in water and palletized. The composite pellets were dried at 80 °C for 6–8 h prior to being shaped into tensile and Izod impact test specimens by injection molding.

Weathering and Water Immersion Trials

Some of the tensile and the Izod impact test specimens were subjected to natural weathering and water immersion for a period of up to 3 months. For the natural weathering condition, the specimens were left exposed to the natural weather on an opened rooftop of a building in Bangkok, Thailand over the period of November 2005 to January 2006, while, for the water immersion condition, the specimens were immersed in water at ambient condition over the same period of time.

Gamma-Ray Irradiation Trials

Gamma-ray irradiation of the rest of the tensile and the Izod impact test specimens was carried out at the Office of Atomic for Peach (Thailand) using a ^{60}Co gamma ray source. Specimens had been sealed in glass tubes filled with oxygen, prior to being irradiated integral doses of 7.5, 15, 30, 45 and 60 kGay at 80 °C.

Characterization

A JEOL JES-6380 LV scanning electron microscope (SEM) was used to observed the fractured surface of a specimen. Tensile strength, Young's modulus, and elongation at break were studied using a SHIMADZU Autograph AG-1 universal tester. The tests were conducted at room temperature at a constant strain rate of 50 mm/min. Notched Izod impact and hardness tests were performed at room temperature using a Yasuda Impact Tester 258 and Durometer model 475 hardness tester (Shore D), respectively. Fourier-transformed infrared spectroscopic (FT-IR) measurements were performed on a Perkin-Elmer Spectrum 2000 infrared spectrometer.

Results and Discussion

Morphology

Injection molding was used to prepare the specimens of iPP/wood sawdust composite with a fixed compositional ratio of 70/30 w/w. Figure 1 shows a selected SEM image of a fractured surface of a specimen. According to the image, the wood sawdust particles were not homogenously dispersed and poor adhesion between the particles and the iPP matrix was evident. This is due to the presence of the hydrophilic, hydroxyl groups on the surface of lingo-cellulose, the major component of the wood sawdust, which resulted in agglomeration and the poor adhesion with the hydrophobic iPP matrix.

Weathering and Water Immersion Trials

To investigate the effects of natural weather and water immersion on the mechanical properties of the iPP/wood sawdust composite, some specimens were either left exposed to the weather or kept immersed in water for a period of up to 3 months. The tested results on the effect of natural weathering in terms of the tensile strength, Young's modulus, elongation at break, notched Izod impact strength, and hardness are shown graphically in Figure 2 to 4.

All of the tensile properties investigated were found to increase in their values with increasing the exposure time during the first 30 days and decrease with further increasing the exposure time. Due to the difference in the hydrophobicity/hydrophilicity of the two constituents, the composites of this sort usually fail at the interface between the wood fibers and polymer matrix. However, during the exposure to natural weathering, the iPP matrix could undergo both the cross-linking and the chain scission reactions. It is suspected that, during the first 30 days of natural weathering, cross-linking of the iPP matrix could be the major

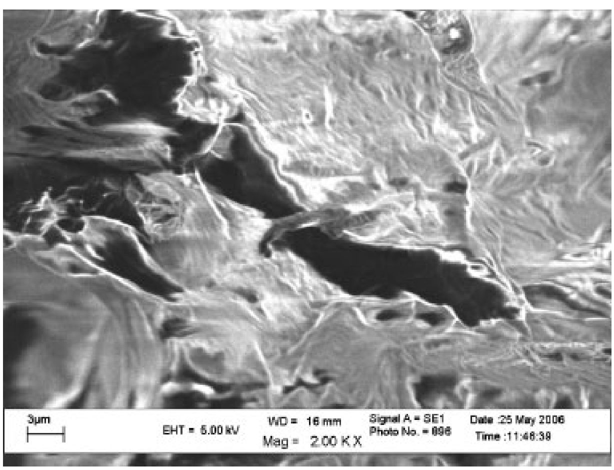


Figure 1.
SEM image of the fractured surface of an iPP/wood sawdust composite specimen.

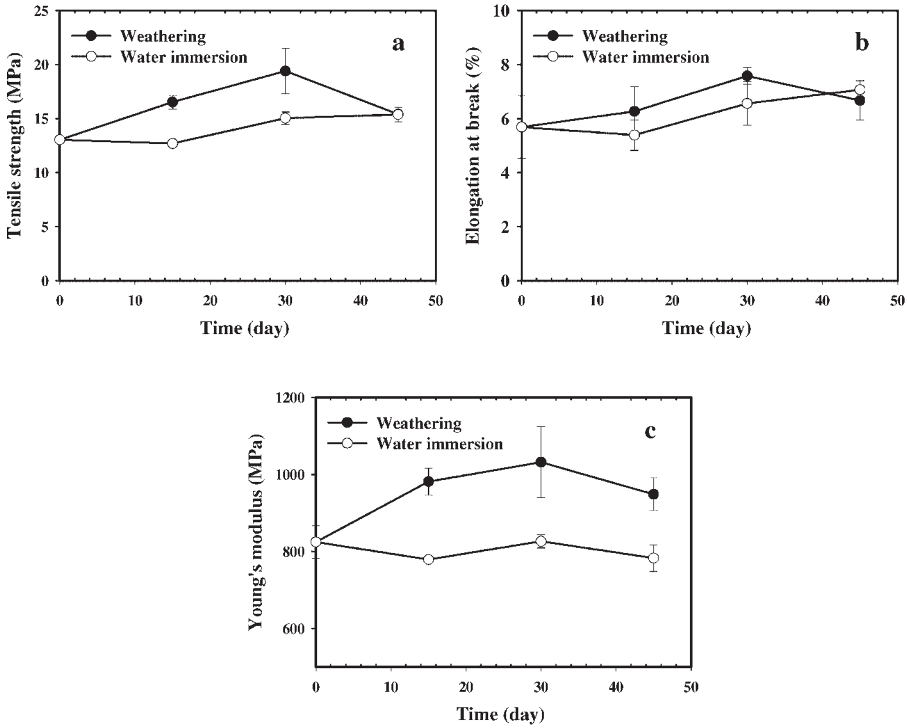


Figure 2.
Tensile properties in terms of (a) tensile strength, (b) Young's modulus, and (c) elongation at break of iPP/wood sawdust composite after being exposed to natural weathering for a period of up to 3 months.

reaction that occurred, which could lead to the observed increase in tensile property values. This postulation was accented by the observed decrease in the notched Izod impact property and the slight increase in the hardness of the composite during the first 30 days of natural weathering. After 30 days of natural weathering, chain scission reactions could become more significant that the deterioration of all the mechanical properties was evident.[7]

The tested results on the effect of water immersion in terms of the tensile strength, Young's modulus, elongation at break, notched Izod impact strength, and hardness are also shown graphically in Figure 2 to 4. Both the tensile strength and the elongation at break values were practically unchanged during the first 15 days of water immersion. After 15 days, the property values increased slightly afterwards. On the other hand, the Young's modulus was statistically the same during the first 30 days of water immersion, while the property value decreased slightly when the immersion time increased to 60 days. Since iPP is a non-hygroscopic material, submersion of the iPP/wood sawdust composite should only result in the water being absorbed into the hydrophilic entity of the wood fibers. During the

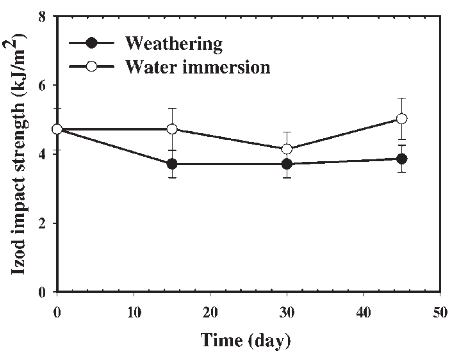


Figure 3.
Notched Izod impact strength of iPP/wood sawdust composite after being exposed to natural weathering for a period of up to 3 months.

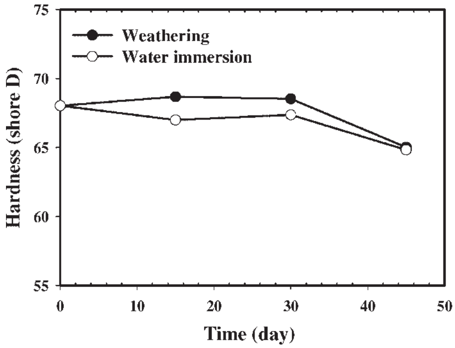


Figure 4.
Hardness of iPP/wood sawdust composite after being exposed to natural weathering for a period of up to 3 months.

first 15 days of water immersion, the absorption of water might not be significant enough to affect the tensile properties of the composite. With increasing the immersion time up to 60 days, the amount of water absorbed might result in the excessive swelling of the wood fibers, causing the fibers to swell against the iPP matrix. This, in turn, might enhance the mechanical interlocking, which could have a role in improving the tensile strength of the material. On the other hand, the excessive amount of absorbed water molecules in the free volume of the iPP matrix might act to plasticize the material, which could be used to explain the slight increase in the elongation at break and the slight decrease in both the Young's modulus and the hardness of the material during the final 30 days of water immersion.[7]

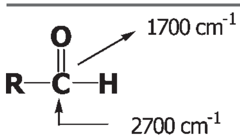
Interestingly, at any given time point investigated, the mechanical properties of the specimens that were subjected to natural weathering were greater than those of the specimens that were immersed in water, with an exception to the notched Izod impact strength which showed an opposite trend. As previously discussed, the observed greater mechanical property values (or lower values for the notched Izod impact strength) of the composite that were exposed to natural weathering should be due to the cross-linking reactions that occurred to the iPP matrix during its exposure to the sunlight and to the plasticizing effect of the absorbed water molecules in the free volume of the iPP matrix.

Gamma-Ray Irradiation Trials

To investigate the effect of gamma-ray irradiation on the mechanical properties of the iPP/wood sawdust composite, the rest of the specimens were exposed to gamma ray of various doses of up to 60 kGay. To clearly observe any change to the chemical integrity of the composite as a function of radiation dosage, FT-IR was employed and the results are shown in Table 1.

It is evident that, the signals associated with the aldehyde functional groups became stronger with increasing the radiation dosage. Specifically, the carbonyl stretching at around 1710 cm^{-1} and the C-H absorption in the range of 2700 to 2800 cm^{-1} were observed. The asymmetric stretching of C=C for both *cis* and *trans* isomers at about 1670–1675 cm^{-1} was also observed. In addition to these absorption peaks, typical absorption bands for iPP were observed over the wavenumber range of 1460–1450 cm^{-1} (for $-CH_2$) and 1380–1370 cm^{-1} (for $-CH_3$). The

Table 1.
Analysis of FTIR spectra of gamma-ray-irradiated iPP/wood saw dust composite at various radiation dosage.

Functional group	Wavenumber (cm^{-1})					
	0 kGay	7.5 kGay	15 kGay	30 kGay	45 kGay	60 kGay
	2713 1743	2721 1730	2725 1746	2725 1713	2729 1743	2724 1694
C=C	1594	1644	1588	1605	1595	1650
$-CH_2$	1459	1454	1460	1453	1473	1450
$-CH_3$	1371	1376	1373	1374	1376	1372

absorption band in the range of 3500–3100 cm^{-1} may be a result of the –OH stretching vibrations of wood sawdust and/or the hydroxyl groups which could be introduced on iPP molecules after gamma-ray irradiation in the presence of oxygen (in the air). FT-IR results confirmed that gamma-ray irradiation caused the formation of various functional groups.

The effect of gamma-ray irradiation on the tensile properties of the iPP/wood sawdust composite in terms of the tensile strength, Young's modulus, and elongation at break of the composite is graphically shown in Figure 5.

Apparently, the tensile strength at break, the ultimate strength, and the Young's modulus of the irradiated iPP/wood sawdust composite increased from those of the neat composite with the initial increase in the radiation dosage of up to about 30 kGay. Further increase in the radiation dosage to 60 kGay caused the property values to decrease. Various related studies[8–10] indicated that both cross-linking and chain scission reactions occurred when iPP had been irradiated with gamma ray. At low dosages, cross-linking reactions contributed more the observed increase in the tensile strength at break, the ultimate strength, and the Young's modulus of the irradiated composite in comparison with those of the neat one. It was also pointed out that enhancement of hydrophilicity was observed on gamma-ray irradiated iPP, due to the introduction of oxygen-containing functional groups, such as carbonyl, carboxylic, and ether, on to the iPP molecules.[11] The introduction of these functional groups may also help contribute to the observed increase in the mentioned tensile property values, as a result of the improvement of the interfacial adhesion between the wood fibers and the iPP matrix. At high dosages, the chain scission reactions caused a significant

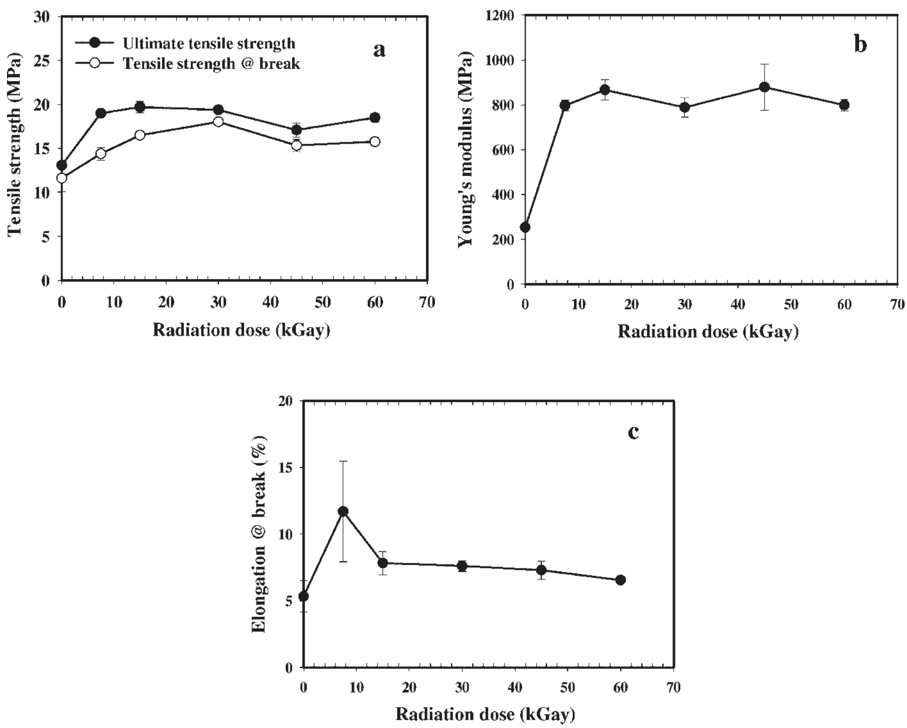


Figure 5.
Tensile properties in terms of (a) tensile strength, (b) Young's modulus, and (c) elongation at break of iPP/wood sawdust composite after being irradiated with gamma ray of up to 60 kGay.

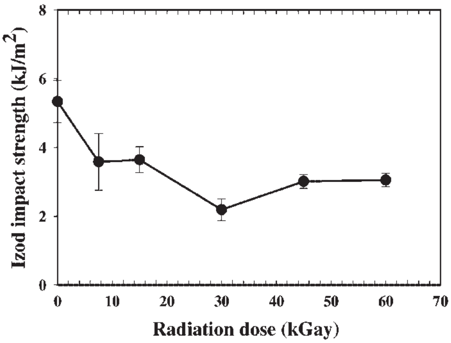


Figure 6.
Notched Izod impact strength of iPP/wood sawdust composite after being irradiated with gamma ray of up to 60 kGay.

decrease in the molecular weights of the iPP molecules, hence the observed decrease in the tensile property values.

The effect of gamma-ray irradiation on notched Izod impact strength and hardness of the iPP/wood sawdust composite was also evaluated and the results are shown graphically in Figure 6 and 7. The impact strength is a measurement of the ability of a material to absorb energy during an impact. Several factors influence the impact strength of a composite materials: they are, for examples, aspect ratio, particle size, rigidity, and content of the filler, interaction between filler and the polymer matrix, size and amount of crystalline entity of the polymer matrix, etc.[12] Clearly, the notched Izod impact strength of the composite at any given radiation dosage was lower than that of the neat material, with the property value tended to decrease with increasing the radiation dosage (despite it showing a minimum at 30 kGay). This should be a result of both the cross-linking and the chain scission reactions that occurred during irradiation. Unlike the impact strength, the hardness of the composite was not affected by the variation in the radiation dosage.

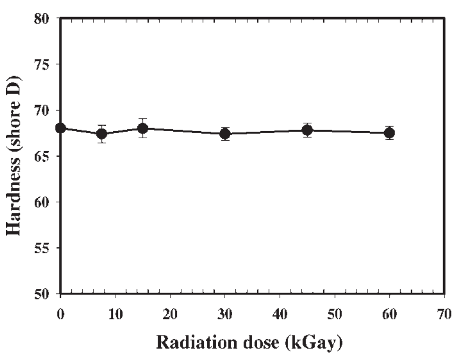


Figure 7.
Hardness of iPP/wood sawdust composite after being irradiated with gamma ray of up to 60 kGay.

Conclusion

Isotactic polypropylene (iPP)/wood sawdust composite was prepared by an extruder and fabricated into specimens for tensile, notched Izod impact strength, and hardness measurement by injection molding. The content of the wood sawdust was fixed at 30% by weight. The effects of natural weathering, water immersion, and gamma-ray irradiation on the mechanical properties of the composite were evaluated. All of the tensile properties were found to increase with initial increase in the exposure time of natural weathering of up to 30 days and decrease with further increase in the exposure time. Similarly, the tensile strength and the Young's modulus of the composite were found to increase with initial increase in the radiation dosage and decrease with further increase in the radiation dosage. On the other hand, the tensile strength and the elongation at break of the composite were unaffected by the immersion in water during the first 15 days, but slightly increase with further increase in the immersion time. While the notched impact strength of the composite was not significantly affected by the water immersion, the property values of the composite that was subjected to natural weathering and gamma-ray irradiation were lower than those of the neat ones. Lastly, the hardness of the composite was the lowest at 60 days of natural weather and water immersion, while it appeared not to be affected by the variation in the dosage of the gamma-ray irradiation.

Acknowledgements: The authors acknowledge Thai Polyethylene Co., Ltd. and Universal Para Wood Co., Ltd. for donating isotactic polypropylene resin and wood sawdust, respectively, used in this work. The Office of Atomic for Peach (Thailand) and the Department of Tool and Materials Engineering, King Mongkut's University of Technology Thonburi were also acknowledged for the assess to a ^{60}Co gamma ray source and the financial support, respectively.

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