Property Comparison Before and After Electron Beam Irradiation of Recycled Polypropylene/Peanut Shell Powder (Rpp/Psp) Composites

N.F. Zaaba¹, H. Ismail¹

¹School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, Penang, Malaysia

Email: fasehazaaba@usm.my

Abstract. This study investigated the properties of recycled polypropylene (RPP)/peanut shell powder (PSP) composites under the effect of electron beam (EB) irradiation. RPP/PSP composites were prepared by melt-mixing and compression moulding with 0 to 40 wt. % of PSP loading. The fabricated composites were then irradiated using 2.0 MeV EB accelerator at a fixed dose of 40 kGy. The properties of non-irradiated and irradiated composites were compared and characterized by tensile properties, Fourier transform infrared (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The results in tensile strength and tensile modulus of irradiated RPP/PSP composites show an increment while decrement in elongation at break. The thermal stability of irradiated composites was also improved compared to non-irradiated composites. The enhanced interfacial adhesion between components was evidenced by SEM morphology.

1. Introduction

Presently, owing to the growing demand for ambient and social queries, natural fillers are chosen as an alternative to substitute those damaging synthetic fillers. In fact, due to low density and good mechanical resistance of natural fillers, the application of these materials as reinforcement in thermoplastic and thermosetting polymers are getting higher [1].

Though, like other natural plant based resources, natural fillers have high moisture absorption tendency and poor surface adhesion to hydrophobic polymers. Thus, it is not suitable for high temperature applications. In order to deal with the weak interfacial adhesion between natural fillers and polymer matrices, a number of filler surface modification techniques have been amplified to enhance the interfacial bond strength. Among all, the ionizing radiation is a process that capable to modify the properties of natural filler polymeric materials. It can be used as an alternative in the development of new polymeric materials by enhancing the interfacial adhesion between natural fillers and polymer matrix [2].

Moreover, the main effects triggered by the ionizing radiation in polymers are the chain scission and appearance of crosslinking. Once the crosslinking is in high proportion, it tends to create three-dimensional nets. The procedure take place by the recombination of radicals formed by irradiation of polymer. In the crossed linking, the polymeric chains attach themselves via covalent bond caused
by chemical joining or radiation. The crosslinked structure could reduce the interfacial tension and resulted in an improvement in material properties. [3].

Numerous studies have discovered that ionizing radiation have proficiently improve the material properties by introducing the cross linking and scission process throughout the polymer chains in multipurpose applications [4]. On the face of it, no attempt has been made to study the effect of EB irradiation on the physical, thermal, mechanical and morphological properties of recycled polypropylene (RPP)/peanut shell powder (PSP) composites. It is expected that, it could induce the formation of crosslinking network and enhance overall properties of the composites.

2. Experimental study

2.1 Materials

Recycled polypropylene (RPP) with melt flow index of 30 g/10 min, density of 0.896 g/cm$^3$, and tensile modulus of 900 MPa was purchased from Zarm Scientific and Supplies, Penang, Malaysia. Peanut shell powder (PSP) was also supplied by Zarm Scientific and Supplies, Penang, Malaysia. Prior to composite fabrication, the peanut shells were crushed to produce particle sizes in the range of 70 to 250 μm. Then, the PSP was dried for 3 h at 70 °C using a vacuum oven.

2.2 Composite preparation

RPP/PSP composites were prepared using an internal mixer (Rheomixmixer, Haake, Model R600/610) at 180 °C and 50 rpm to obtain a homogeneous sample. The RPP was placed in the mixer and melted for 4 min before the PSP was added. The composites were mixed for another 8 min until the mixing torque stabilized. The total mixing time was 12 min for all samples. The processed samples were compression molded into a 1-mm thick sheet by an electrically heated hydraulic press (Compression Machine, Kao Tiek Go Tech) at temperature of 180 °C. Table 1 shows the formulation of the composites.

| Composite         | RPP (wt.%) | PSP (wt.%) |
|-------------------|------------|------------|
| RPP               | 100        | -          |
| RPP + 10% PSP     | 90         | 10         |
| RPP + 20% PSP     | 80         | 20         |
| RPP + 30% PSP     | 70         | 30         |
| RPP + 40% PSP     | 60         | 40         |

2.3 Electron beam irradiation

The composite sheet produced through melt-blending and compression-molding as mentioned earlier were then irradiated using an electron beam (EB) accelerator (NHV EPS, Model-3000) facility installed at the Malaysian Nuclear Agency, Bangi, Malaysia at a fixed dose of 40 kGy. All samples were irradiated at room temperature with accelerator energy of 2.0 MeV and beam current of 2mA.

2.4 Measurement of tensile properties

Tensile tests were carried out using a universal testing machine (Instron, Model 3366) according to ASTM D638. Dumbbell specimens of 1 mm thickness were cut from the compression molded sheets with a Wallace die cutter. A crosshead speed of 5 mm/min was used, and the tests were performed at 25 ± 3 °C.
2.5 Thermogravimetric analysis

A Perkin Elmer Pyris TGA analyser was used to determine the TGA of non-irradiated and irradiated RPP/PSP composites. About 10 mg of samples required in this analysis under a nitrogen atmosphere at 50°C to 600°C and 20°C/min heating rate.

2.6 Fourier transform infrared spectroscopy analysis

The functional groups and chemical characteristics of the composites were obtained by FTIR (transmission mode method) with a Perkin Elmer System 2000 at a resolution of 4 cm\(^{-1}\) in a spectral range of 4,000 to 550 cm\(^{-1}\), using 32 scans per sample.

2.7 Morphology evaluation

The microstructure of the tensile fractured surfaces of the RPP/PSP composites were compared using a SEM ZEISS Supra, Model 35 VP operating at 5 kV. The samples were first sputter-coated with a thin layer of carbon, which provides an electron-transparent (low atomic number), conductive coating.

3. Results and Discussion

3.1 Tensile properties

Figures 1-3 demonstrate the results of tensile strength, elongation at break and tensile modulus of non-irradiated and irradiated RPP/PSP composites at different PSP loading, respectively. Obviously from Figure 1, the tensile strength of both non-irradiated and irradiated RPP/PSP composites decreased with an increase in PSP loading. The decline was due to the incompatibility between hydrophilic PSP and hydrophobic RPP. Owing to the different polarities, there was a weak interfacial adhesion between PSP and RPP. As comparing both composites, the irradiated RPP/PSP composites showed a higher tensile strength than the non-irradiated composites. The increment in tensile strength can be related to the formation of crosslinking during the EB irradiation [5].

![Figure 1. Tensile strength of non-irradiated and irradiated RPP/PSP composites at different PSP loading](image)

Figure 2 shows the elongation at break of non-irradiated and irradiated RPP/PSP composites at different PSP loading. The elongation at break of both composites lessened with a rise in PSP loading. The lessening was due to the decrease in polymer chain mobility or deformability of a rigid interface between the PSP and the RPP matrix. Again, when comparing both composites, the irradiated RPP/PSP composites showed a lower elongation at break than the non-irradiated composites. The reflection is accredited to the existence of irradiation which had persuaded the crosslinking in the irradiated RPP/PSP composites [6].
Likewise, the tensile modulus of non-irradiated and irradiated RPP/PSP composites is also shown in Figure 3. Apparently, the presence of PSP was discovered to increase the tensile modulus of RPP/PSP composites. This can be accredited to the composite stiffness increases as the filler content increased. [7]. Conversely, when comparing both composites, the irradiated composites showed a higher tensile modulus than the non-irradiated composites. The formation of crosslink network structure upon exposure to irradiation caused improvement of interfacial adhesion between filler and matrix [8]. Eventually, leads to the enhancement of tensile modulus of irradiated composites.

3.2 Thermogravimetric decomposition behaviours

As can be seen in TG thermograms in Figure 4, all composites experienced the three stages of weight losses; first region (130-170 °C), second region (200-400 °C), and third region (above 400 °C). Around 130-170 °C, the TGA result shows the removal of absorbed water in the composites [9]. Also, the decomposition temperature in the range 200-400 °C validates the thermal degradation of hemicellulose and cellulose while above 400 °C goes to the decomposition temperature of lignin and RPP [10].
3.3 Fourier transform infrared spectroscopy

Figure 5 exhibits the FTIR spectroscopy of non-irradiated and irradiated RPP/PSP composites at 10 wt.% PSP loading. The comparison of chemical change that might be occurred after being subjected to EB irradiation could be determined through this spectroscopy. After the EB irradiation, some changes in the absorption bands which were related to chemical reaction occurred in the blends can be observed in Figure 5(b). As can be seen in the figure, there was an increase in the intensity of the O-H stretching absorption bands at 3000-3600 cm\(^{-1}\). This band was associated to the formation of oxidative products during the irradiation. This result is in agreement with Sam et al. in their study on LLDPE/soya powder blend [11]. In addition, there is a slightly increase and broad peaks existed at 1600-1800 cm\(^{-1}\) implied the formation of carbonyl group (like carboxylic acids at 1713 cm\(^{-1}\), ketones at 1718 cm\(^{-1}\) and esters at 1741 cm\(^{-1}\)) whereas an oxidative product generated during irradiation [5]. Figure 6 shows the proposed crosslinking between propylene chains of RPP after being subjected to EB irradiation.

![Figure 5. FTIR spectra of (a) non-irradiated and (b) irradiated RPP/PSP composites at 20 wt. % PSP loading and a zoom at C=O band.](image1)

![Figure 6. Proposed crosslinking between propylene chains of RPP.](image2)

3.4 Morphological properties

Figure 7 demonstrates the morphology of RPP/PSP composites before and after being subjected to EB irradiation process. As shown in Figure 7(a), (b) and (c), for non-irradiated composites, the micrograph of tensile fractured surface presented a distinguish filler pulled out as well as filler tearing. As PSP loading increased, the presence of filler pulled out or remained loosely within the RPP matrix was more visible. More voids were also distinguished, indicated the places where the fillers were pulled out. Furthermore, the voids also reveal the poor adhesion of the filler to the matrix, where it acts as stress concentration points and contributes to the decrement of mechanical properties. Hence, lower tensile strength and elongation at break were obtained for non-irradiated composites.

While for irradiated composites, a considerable improvement in adhesion between filler and matrix can be observed in Figure 7(d), (e) and (f). The filler coated within the RPP matrix and the absence of the voids were an evidence of the improvement in adhesion mechanism [12]. The PSP filler surface is coated with RPP matrix indicated the good adhesion between them whereas the voids that being detected earlier are almost covered up after subjected to the EB irradiation. Therefore, the tensile properties of irradiated RPP/PSP composites were improved.
4. Conclusion

The overall results have shown that there is an improvement in the tensile strength and tensile modulus of irradiated RPP/PSP composites while decrement in elongation at break. The thermal stability of irradiated composites was also improved compared to non-irradiated composites. The enhanced interfacial adhesion between components of irradiated composites was evidenced by SEM morphology.

References
[1] Mohanty A K, Misra M, and Hinrichsen G 2000 Macromol Mater Eng 1 276.
[2] Ismail H, Galpaya D, and Ahmad Z 2010 Journal of Vinyl Additives and Technology 16 141-146.
[3] Nordin R, and Ismail H 2013 International Journal of Engineering Research and Application 3 1820.
[4] Choi H Y, Han S O, and Lee J S 2008 Applied Surface Science 255 2466.
[5] Murray K A, Kennedy J E, McEvoy B, Vrain O, Ryan D, and Cowman R 2013 Nuclear Instruments and Methods in Physics Research B 297 64-74.
[6] Sabet M, Hassan A, and Ratnam C T, Polymer Bulletin 68 2323.
[7] Ismail H, Abdullah A H, and Bakar A A 2011 Journal of Vinyl and Additive Technology 17 132.
[8] Ibrahim N A, Ahmad S N A, Yunus W M Z Y, and Dahlan K Z M 2009 eXPRESS Polymer Letters 3 226.
[9] Ma X, Yu J, and Kennedy J 2005 Carbohydrate Polymers 62 19-24.
[10] Liang J 2018 Journal of Thermoplastic Composite Materials 31 246-264.
[11] Sam S T, Ismail H, Ahmad Z, and Ratnam C T 2012 Journal of Applied Polymer Science 124 5220.
[12] Youssef H A, Ismail M R, Ali M A M, and Zahran A H 2009 Journal of Elastomers and Plastics 41, 245.