Effect UV/O_3 Modified Rice Husk on the Mechanical Properties of Recycle HDPE Rice Husk Composite

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ABSTRACT

Modifications of rice husk (RH) surfaces by ultraviolet-ozonolysis (UV/O_3) treatment were carried out in order to study the effects on the mechanical properties. The untreated and treated RH was characterized by FTIR, TGA and SEM. Recycled HDPE/RH composites were prepared with five different loading of RH fibers (10, 20, 30, 40 and 50 wt %) using the twin-screw extrusion method. Maleic anhydride grafted polyethylene (MAPE) was added as a coupling agent. Tensile modulus shows an increase trend while tensile strength shows a decline trend with addition of RH loading regardless of treatments. However, composites filled with UV/O_3-treated RH give a better result in comparison with composites filled with untreated RH. UV/O_3 treatment removes lignin, hemicellulose, fats and waxes from RH surfaces thus giving a rougher surface on RH. Therefore, UV/O_3 treatment can be used as an alternative method to modify RH surface in order to improve the adhesion between hydrophilic RH fibre and hydrophobic recycled high-density polyethylene (rHDPE) polymer matrix.

Keywords*: Surface Modification, UV/O3 Treatmen,; Tensile Properties*

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Introduction

There are an increasing number of research studies and developments of the use of natural fibers to reinforce polymers in the wood plastic composite (WPC) technology recently. This is due to their biodegradability, low costs, environmental friendly, low density, non-hazardous, nonabrasive nature and wide variety of fiber types [1]. Rice husk (RH) is one of the agricultural waste materials that acts like a cellulose-based fibre. It is estimated that RH of approximately 20% is obtained from the total rice by the milling process. Generally, rice husk contains 35% cellulose, 25% hemicellulose, 20% lignin and 17% ash (94% silica) by weight depends on the geographic location [2]. Many researches are currently interested on rice husk reinforced thermoplastic composites. The main problem of the broad usage of these fibres in thermoplastic polymers is the poor incompatibility between the hydrophilic natural fibres and the hydrophobic thermoplastic matrices. This leads to undesirable properties of the composites. It is therefore necessary to modify the fibre surface by employing chemical modifications to improve the adhesion between fibre and matrix [3]. There is many researches on the types of surface modifications of RH reported typically the alkali treatment but few reported on the alternative ozone surface modification method. In the ozonolysis process, the biomass is treated with ozone, which causes degradation of lignin by attacking aromatic rings structures, while hemicellulose and cellulose are not damaged [4]. It can be used to disrupt the structure of many different lignocellulosic materials, such as wheat straw, bagasse, pine, peanut, cotton straw and poplar sawdust [5]. Therefore, the main objective of this study is to explore an alternative approach to modify the rice husk surface using the ultra-violet/ozone (UV/O_3) treatment. Also, the effect of untreated RH and UV/O_3 treated RH composites on the tensile strength is being reported here.

Methodology

Rice husk (RH) were supplied by DinXings (M) Sdn Bhd with mesh size 212 µm while recycled HDPE is used as a matrix in the biocomposites. Maleic anhydride grafted polyethylene (MAPE) is used as coupling agent. Rice husk was oven dried at 80°C for 24 h in order to reduce the moisture content and then stored in sealed plastic bag before compounding. For surface modification of UV/O_3-treatment, the RH is exposed to a self-made in-house UV/O_3 system for 30 min exposure time and 10 Lm^{-1} ozone flow rate.

For the composite processing of raw and surface modified RH, five different RH fibre loadings (0, 10, 20, 30, 40, 50 wt. %) were used. A laboratory scale counter-rotating twin screw extruder (Thermo Prism TSE 16PC) was employed for compounding RH fibers and rHDPE with the coupling agent. The barrel temperatures of the four zones were 180 ºC, 190 ºC, 200 ºC and 190 ºC. The screw speed was 30 rpm. The extrudates were collected, cooled and granulated into pellets. In the second stage, compression moulding process was used to make the specimen panels for testing. Pellets were put into mould of 14 mm x 14 mm x 3 mm thick. The temperature of the hot press was set at 180 °C for both upper heater and lower heater. The period of preheating, venting and full pressing was set to 3, 2 and 5 minutes respectively. The cold press was set to 5 minutes to reduce temperature and minimize/eliminate residual stress of the specimens. The pressure used to press the samples was set at 1000 psi.

The raw and surface modified RH were analyzed using FTIR, scanning electron microscope (SEM). Thermal stability of untreated and treated rice husks were studied using a Thermal Gravimetric Analyser (TGA Q500 V20). This was performed under inert conditions in order to obtain pure thermal degradations of the rice husks by heating the samples under N_2 gas at a flow rate of 10°C/min and temperature range from 25°C to 600°C. Prepared composite specimens were characterized by tensile tests according to ASTM D 638-03 using Materials Testing Machine, model: M350-10CT with the speed of 5 mm/min. Flexural test was performed according to ASTM D 790-03 using Materials Testing Machine, model: M350-10CT. Ray-Ran Universal Pendulum Impact System was used to determine the impact strength of the specimens.

Results and Discussion

FTIR Analysis

Figure 1 shows the FTIR spectra of untreated RH and UV/O_3-treated RH. It can be seen that there are significant changes between untreated RH and UV/O_3-treated RH in the spectrum of 3200–3400 cm^{-1}, which represents the stretching vibration of intermolecular hydrogen-bonded -OH groups in the cellulose fibers. UV/O_3-treated RH shows a broader peak at 3318 cm^{-1} compared to the peak at 3294 cm^{-1} from untreated RH which indicates higher concentration of hydroxyl group which contributed by ozone. Ozone exists as both molecular and atomic oxygen on the surface of carbon. Atomic oxygen is a powerful oxidizing agent, which oxidizes the carbon surface into acidic functional groups such as carboxylic, ketonic and phenolic on ozone treatment [6]. All these peaks from surface modification result for making more adhesive surface on treated RH so there will be improved bonding between the polymer matrix and the RH filler for composite processing.

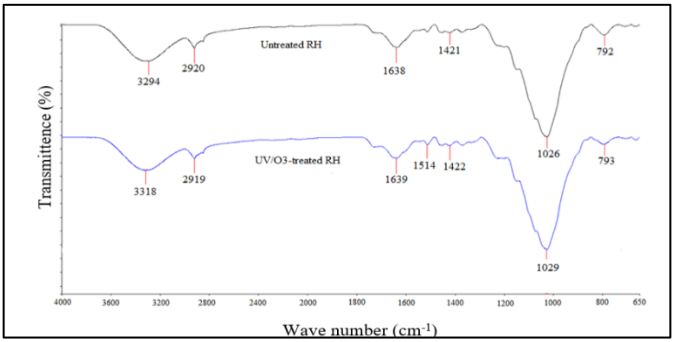
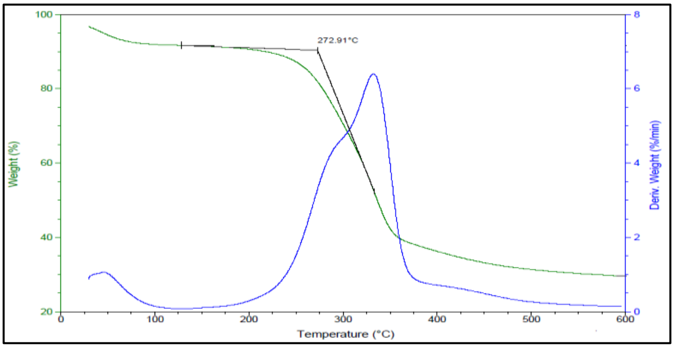


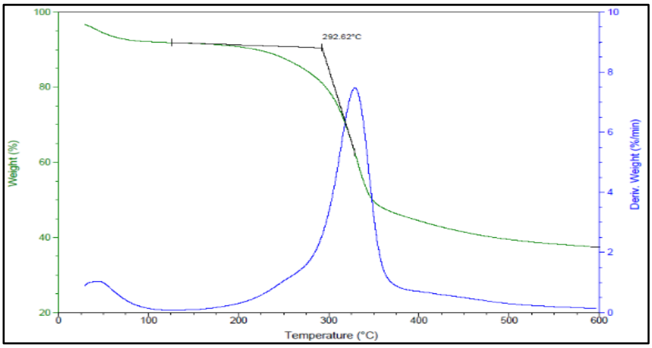
Figure 1: FTIR spectra of untreated and UV/O_3-treated rice husk

TGA Analysis

The thermal stability of the untreated RH and UV/O_3 modified RH was investigated and the results are shown in Figure 2(a) and 2(b). Both rice husk undergo initial weight loss between 60~200 °C, irrespective of their treatment condition. The weight loss is due to the removal of water and other primary volatile substances [7]. Most of the thermal degradation takes place in between 260 °C ~ 360 °C where decomposition of secondary volatile substances such as primary hemicelluloses and cellulose [8]. The degradation of UV/O_3-treated RH was more significant at 292.62°C, as shown by the sharp peaks as shown on the derivative thermal gravimetric curve (DTG) compared to untreated RH at 272.91°C. The decomposition of UV/O_3-treated RH involve only one step, in contrast to that of untreated RH which was preceded by decomposition of volatile materials until 300°C before undergoing further weight loss after that [7]. The one step decomposition confirms that removal of lignin, hemicelluloses, cellulose and wax during the surface treatment.

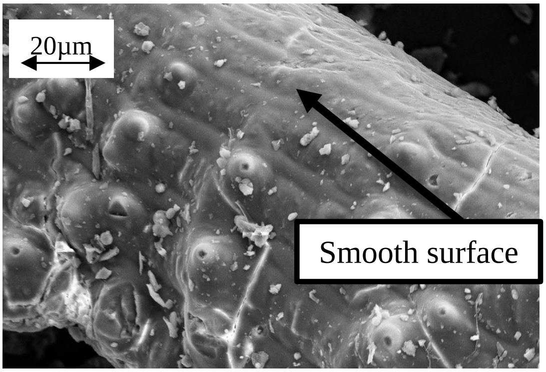


(a)

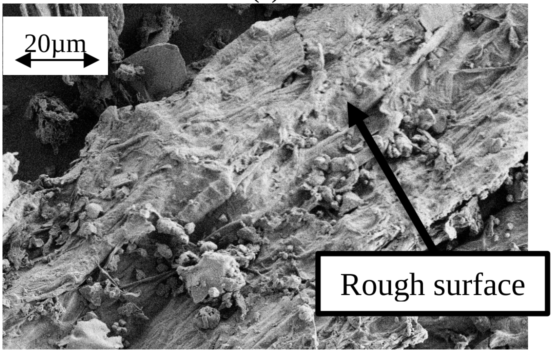


(b)

Figure 2: TGA degradation curve of (a) Untreated RH and (b) UV/O_3-treated RH



(a)



(b)

Figure 3: SEM image of (a) Untreated and (b) UV/O_3-treated rice husk under 500x magnification

SEM Analysis (RH)

The scanning electron (SEM) micrographs of untreated and UV/O_3-treated rice husk are shown in Figure 3. Untreated RH possess a smooth, flat and cloudy surface due to the presence of lignin, wax and hemicelluloses [9]. However UV/O_3-treated RH possess a rougher surface. The rougher surface is allow to improve the compatibility between fibers and matrix [10].

Tensile Analysis (RH/rHDPE Composite)

Tensile test was performed to measure the response of a material to slowly applied uniaxial force according to ASTM D 638-03. Figure 4 and Figure 5 illustrates the results obtained from tensile modulus and tensile strength for untreated and UV/O_3-treated rice husk reinforced rHDPE composite. For tensile modulus, both results shows increase of composite stiffness as the RH filler increases [11]. However, UV/O_3-treated RH reinforced rHDPE composite shows better results compared to the untreated RH composite. This supports that ozone treatment removes lignin, hemicellulose, fats and waxes from RH surfaces thus giving a rougher surface on RH. Therefore, UV/O_3-treated RH improves the compatibility between hydrophobic polymer and hydrophilic rice husk [4,5,6]. After UV/O_3 surface treatment, tensile strength increased slightly due to removal of impurities from the rice husk surface like lignin, hemi-cellulose, fats and waxes thus revealing chemically reactive functional groups like –OH. UV/O_3 treatment gave the rough surface on RH filler which increased the interfacial interaction between filler and matrix [9].

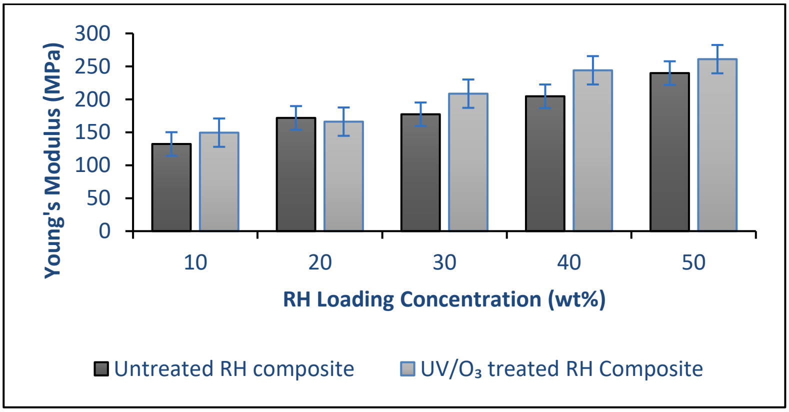


Figure 4: Tensile Modulus of untreated and UV/O_3-treated rice husk composites

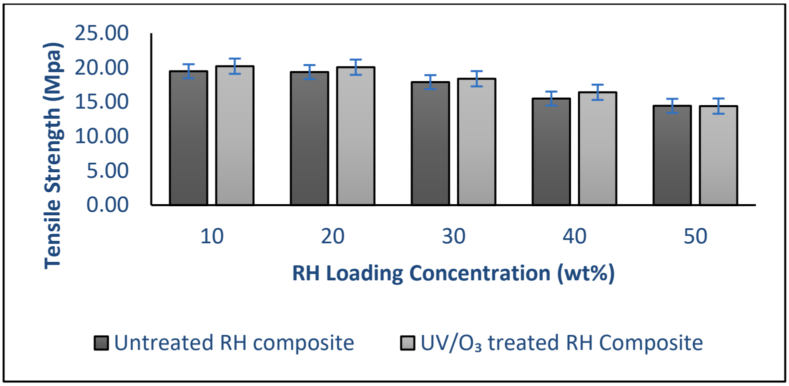


Figure 5: Tensile strength of untreated and UV/O_3-treated rice husk composites

Impact Analysis (RH/rHDPE Composite)

Impact test is was done to measure the ability of a material to absorb the sudden application of a load with breaking according to ASTM D 256-05. Figure 6 shows the results of the impact strength of composites of untreated and UV/O_3-treated RH. The impact strengths of the untreated RH composites shows low result due to the poor interfacial bonding between the filler and the matrix. This poor interfacial bonding resulted in an increased in the number of micro voids, causing increased in water absorption [12]. Upon UV/O_3 treatment, it showed a significant improvement in impact strength of RH/rHDPE composite. The removal of surface impurities on RH surface seems beneficial in enhancing filler-matrix adhesion and increasing the toughness.

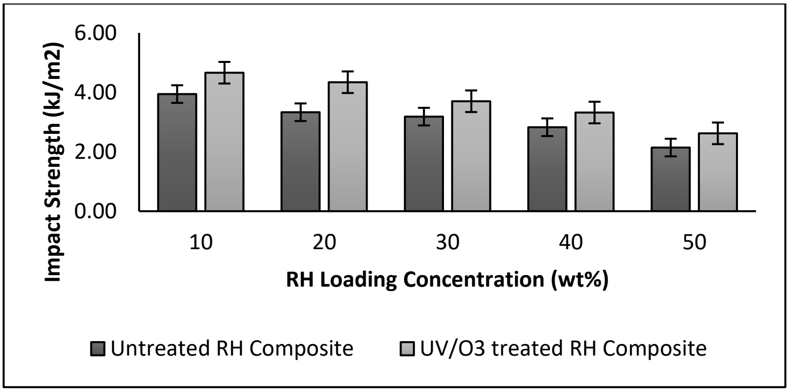
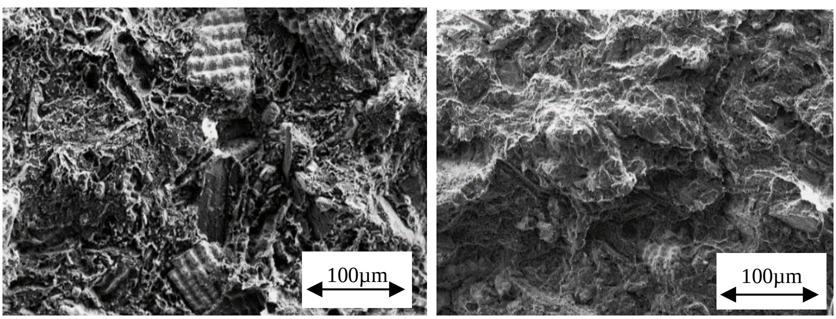


Figure 6: Impact Strength of untreated and UV/O_3-treated rice husk composites

SEM Analysis (RH/rHDPE Composite)

Scanning Electron Microscope (SEM) analysis determines the fracture surface of the RH. Figure 7(a) and 7(b) shows the SEM micrograph of Untreated and UV/O3-treated RH composites. Untreated-RH possess a smooth, flat and cloudy surface due to the presence of lignin, wax and hemicelluloses [9]. After surface treatment, the degradation of the wax, lignin and hemicellulose among the lignocellulosic matrix can be observed from the lighter color of the sample as shown in Figure 7(b). This was due to the lignin concentration of raw rice husks always presenting a really dark color [13].
On the other hands, UV/O_3-treated RH possess a rougher surface. Rougher surfaces improve the compatibility between fibres and matrix to obtain better bonding between the polymer matrix and the RH filler for composite processing. The SEM analysis proved that the rice husk morphology was significantly changed after being treated in UV/O_3 conditions, which confirmed the elimination of organic components (like hemicellulose and lignin) and the decrease in cellulosic crystallization. Also, the treated rice husk shows a brighter color and a more uniform fiber distribution [13].



(a) (b)

Figure 7: SEM image of (a) untreated and (b) UV/O_3-treated rice husk composite

Conclusion

This study investigates the modification of rice husk (RH) surfaces by ultraviolet-ozonolysis (UV/O_3) treatment method. FTIR and TGA results shows that UV/O_3 treated RH has higher or better results compared to untreated RH. UV/O_3-treated RH composite gives the highest tensile strength compared to the untreated RH composites. Impact test showed a significant improvement upon UV/O_3 treatment. Therefore, the UV/O_3 treatment can be used as an alternative method to modify RH surface in order to improve the adhesion between hydrophilic RH fibre and hydrophobic rHDPE polymer matrix.

Acknowledgement

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