Effect of Surface Treatment on Mechanical Properties of Rice Husk Reinforced Recycled High Density Polyethylene (rHDPE) Composites.

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Abstract. The aim of this work was to investigate the effect of surface treatment on rice husk reinforced recycled high density polyethylene (rHDPE) composites. Three types of surface treatment on rice husk were carried out which were maleated treatment, alkaline treatment and acrylic acid treatment. The characteristics and mechanical properties of the composites were analysed. The results for all treatments showed that tensile strength and break elongation of composites decreased significantly when the rice husk filler loading increased. Further findings showed that maleated treatment on rice husk can further enhance the mechanical properties due to the present of ester bond formed in FTIR analysis.

1 Introduction

Recently, natural fiber reinforcements had been used in polymeric green composites to decrease environmental problems. Composite with natural reinforcements can decrease the environment burden, makes composite light in weight, economic and easy to process with comparable mechanical and thermal properties [1]. In early of the 1960s, the demand for high strength, tougher and low density materials for use in construction, transportation and aerospace industries becomes crucial. Due to the high demand on performance of products, extensive research and development had been carried out in the field of composite materials [2].

Nowadays, there has been increasing awareness of more sustainable and environmental friendly development, which has grown the interest of using agriculture waste as reinforcement in polymer composite [2]. Rice husk is one of the natural waste product which is widely available. It consists of 35% of cellulose, 25% of hemicellulose, 20% of lignin and 17% of ash content by weight. The rice husk ash with higher content of silica encourage the use of rice husk ash as inorganic reinforcement [3]. The rice husk is separated from the rice grain in the milling process. The function of rice husk is to provide the protection layer to the rice grain. It is the outermost which is cover the rice grain. Thus, many researchers are

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currently conducted on the studies of rice husk reinforced polymer composite to produce high performance natural fiber-reinforced composites.

In this research, the major concern is the poor compatibility between the hydrophobic thermoplastic matrix and hydrophilic fibers. This may cause to the poor dispersion of fibers into the matrix. Due to the hydrophilic nature of rice husk fiber, its highly moisture sensitivity causing swelling and delamination in composites. This is because there is a strong hydrogen bond exist between the fibers which is to hold them together. Weak interface will be resulted and cannot transfer stress from matrix to the fiber [4]. Therefore, chemical treatment and coupling agent is required to improve the adhesion of fiber and matrix interface. Surface modification is needed to modify the surface of rice husk in order to render the surface of rice husk to become more hydrophobic and more compatible to polymer matrix [5]. Chemical treatment is one of the mostly used for surface modification of natural fibers. Acrylic acid treatment and alkaline treatment are the common chemical treatment methods. This can help to enhance the adhesion properties between the matrix and fibers [6]. Maleic anhydride polyethylene (MAPE) is used as coupling agent in this polymer composite. The purpose of using coupling agents is to enhance the interaction between natural fibers and hydrophobic thermoplastic matrices. Hence, this research is intended to study the effect of chemical treatment on rice husk reinforced recycled HDPE and rice husk composites.

2 Materials and Methods

2.1 Raw Materials

The density of rHDPE is 923 kg/m³, melt flow index is 0.72 g/10min at 190 °C and melting point is 135 °C. The rHDPE was obtained from Nippon Pigmen (M) Sdn. Bhd with. While rice husk was sieved using 1mm of sieve which is 0.0394 inches. The rice husk was sieved to obtain an average size of rice husk and to remove the cadelle beetle in order to enhance the processing. Rice husk was oven dried at 80 °C for 24 h before use in order to reduce the moisture content.

2.2 Chemicals

MAPE was used as maleated agent to produce composite with a melting temperature of 135.2 °C. MAPE used is supplied by ALDRICH Chemistry. Its density is 0.92 g/mL at 25 °C. Acrylic acid was used to carry out the acid treatment on the rice husk. The molar weight of acrylic acid is 72.063 g/mol with a clear and colorless liquid. The melting and boiling point of acrylic acid is 14°C and 141°C respectively. Sodium hydroxide (NaOH) was used in the process of alkaline treatment on the rice husk, supplied by HmbG Chemicals Company. It may be corrosive to metals. The molar mass of NaOH is 40.00 g/mol.

2.3 Procedures

2.3.1 Acrylic Acid Treatment of Rice Husk

Acrylic acid solution was used in acid treatment of rice husk. Acrylic acid solution was prepared by mixing acrylic acid (10 vol. %) with 800ml of water in a 1000ml glass beaker. 150g of rice husk were stirred completely with acrylic acid in the beaker for 10 minutes. Soaking of rice husk was carried out for 4 hours. The treated rice husk was then washed by
tap water to completely remove the acid over the surface of rice husk until it reached pH 7. The wet rice husk was spread and lay over a tray and dried in an oven overnight at 60 °C. The dried clumps was break using a roller. The acrylic treated rice husk then were kept in a moisture free sealed polybag.

2.3.2 Alkaline Treatment of Rice Husk

NaOH solution was used in alkaline treatment of rice husk. 80g of NaOH was mixed with 800ml of distilled water in a 1000ml glass beaker to produce aqueous solution of NaOH. 150gms of rice husk were mixed and stirred with NaOH solution for 10 minutes. The treatment were carried out at room temperatures for 4 hours. The treated rice husk was then washed with tap water, dried and rolled prior to store in a sealed polybag.

2.3.3 Maleated Treatment on Rice Husk

The weight of MAPE, rHDPE and rice husk were prepared by following the composites formulation as shown in Table 1. MAPE, rHDPE and rice husk were mix homogeneously before compounded by using twin screw extruder.

2.3.4 Composite Compounding

The rHDPE and rice husk were compounded by using a co-rotating twin screw extruder at 70 rpm speed. The temperature from the feeding zone to die zone were set at 185 °C, 215 °C, 195 °C, and 185 °C. Then the rHDPE and rice husk were compounded into long strand through the twin screw extruder. The polymer composite strand was later pelletized using a crusher. The pelletized compound was dried in the oven to eliminate the moisture before molded using a compression machine. The temperature of the hot press were set at 180 °C upper dan lower platen, respectively to produce the polymer composites. The period of preheating, venting and full pressing were set at 3, 2 and 10 minutes, respectively and cold press was set to 5 min to cool the samples. The pressure used to press the samples was set at 10 MPa for both hot and cool press.

| Surface Treatment | Sample Notation | rHDPE (wt%) | Rice Husk (wt%) | MAPE (php) |
|-------------------|-----------------|-------------|-----------------|------------|
| Maleated Treatment | M-10            | 90          | 10              | 3          |
|                   | M-20            | 80          | 20              | 3          |
|                   | M-30            | 70          | 30              | 3          |
| Acrylic Acid Treatment | AC-10        | 90          | 10              | 0          |
|                   | AC-20           | 80          | 20              | 0          |
|                   | AC-30           | 70          | 30              | 0          |
| Alkaline Treatment | AK-10           | 100         | 10              | 0          |
|                   | AK-20           | 80          | 20              | 0          |
|                   | AK-30           | 70          | 30              | 0          |
2.4 Testing

2.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was used to analyze the IR spectra of the samples formed. In this study, The Perkin Elmer Spectrometer 2000 was used to obtain the result. An infrared spectra represent the functional group of a sample with absorption peaks. 32 times of scan were carried out to obtain a better resolution on the reading. The transmittance spectra were obtained in the range of 4000 and 6000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\).

2.4.2 Tensile Test

Tensile test is one of the testing to determine the mechanical properties of composites. All samples were tested using the Instron tensile test machine. The standard method of tension test for plastic properties is ASTM D638. The testing was carried out at room temperature with a crosshead speed of 10mm/min. All the reported results of tensile tests are the average of five replicated for each formulation.

3 Results and Discussion

3.1 Fourier Transform Infrared (FTIR)

Fig. 1 shows the structural analysis and structural comparison of rice husk reinforced rHDPE composite. The FTIR spectra showed the composite of M-20, AK-20 and AC-20. From Figure 1, there are a few of same peaks in these three spectra. The absorption band at the range of 3350 cm\(^{-1}\) to 3430 cm\(^{-1}\) attributed to carboxylic group in the rice husk filler and rHDPE. While the absorption at around 2905 cm\(^{-1}\) and 2860 cm\(^{-1}\) were indicated to the vibration of carbon-hydrogen (CH) bonds, which is present in three types of surface treatments. Besides, at the absorption ranges of between 2024 cm\(^{-1}\) to 2026 cm\(^{-1}\) showed the stretching of aromatic carbon upon C=C. Another carbonyl vibration was found at 1660 cm\(^{-1}\), which could be attributed to the stretching vibration of carboxylic groups or the interaction of cell window. Another peak which showed at 1452 cm\(^{-1}\) attributed to the vibration of carbon-hydrogen bonds [7].

For the M-20 which is shown in red line, there is one weak absorption band at 1031 cm\(^{-1}\) appeared in the spectrum which is absent in alkaline treatment and acrylic acid treatment. This peak showed the carbonyl stretching vibrations of the ester, ether and aldehyde groups in the hemicellulose, lignin and natural fats and wax. Esterification reaction occurred in maleated treatment due to the ester bond form between the hydroxyl groups on the surface of rice husk and the ahydride group of coupling agent [8]. This can enhance the interfacial adhesion of the composite. Esterification reaction happened due to the presence of MAPE, therefore when after the alkali treatment and acrylic acid treatment, this peak was disappeared. The function of alkaline treatment and acrylic acid treatment are to remove the hemicellulose, lignin and wax. Furthermore, the absorption band showed at 1660 cm\(^{-1}\) which indicated the presence of grafted maleic anhydride group in the polymer matrix due to the C=O stretching.

Next, for the AK-20 which is showed in blue line, the FTIR spectrum showed one extra absorption band at 3630 cm\(^{-1}\) which is –OH vibration. This peak occurred after the alkaline treatment on rice husk due to the removal of surface impurities from the rice husk filler. Therefore, the –OH groups are increasingly exposed on the rice husk filler surfaces.
Fig. 1. Structural comparison of M-20, AK-20 and AC-30 of rice husk loading.

3.2 Tensile Test

3.2.1 Tensile Strength

Fig. 2 shows the result of tensile strength of different loading of rice husk with different surface treatment on rice husk. The tensile strength of rice husk reinforced rHDPE composite are influenced by the content of rice husk loading and the surface treatment on rice husk. Based on the Figure 2, 10% loading of rice husk in this composite showed the highest tensile strength value among these three content of rice husk. The content of rice husk resulted in significant effect on the tensile strength.

For the maleated treatment on rice husk, 10% loading of rice husk (M-10) had the highest tensile strength which is 16.544 MPa. This is because the rice husk fillers were effectively transfer the stress applied due to the better interfacial bonding between the hydrophilic group in fillers and the hydrophobic group in matrix modified with MAPE [9]. The higher loading of rice husk content attributed to the lower the tensile strength of the rice husk reinforced rHDPE composite. The value of tensile strength of M-20 reduced to 13.902 MPa and tensile strength of M-30 reduced to 13.545 MPa.

While for the alkaline treatment and acrylic acid treatment, there was a slightly difference with maleated treatment which is there is a slightly decrease in tensile strength of the composite when the rice husk loading increase from 10% to 20%. The decrease in tensile strength with the rice husk fillers loading may be due to the increase in weak interfacial area between the rice husk fillers and rHDPE matrix [10]. This also might be due to too much loading of rice husk loading and causing insufficient wetting of rice husk by the polymer matrix. This will lead to the filler agglomeration and hence affecting the stress transfer.
Maleated treatment of rice husk reinforced rHDPE shows the highest tensile strength compared to alkaline treatment and acrylic acid treatment. Maleated coupling agent is widely used to enhance the strength of composites which consists of fillers and polymer matrix. Maleated treatment is different with other chemical treatment. This is because the maleic anhydride is not only modify the surface of rice husk but also the PE matrix in order to obtain better interfacial bonding in composites [11]. Therefore, maleated coupler forms carbon-carbon bond to the polymer chain with the matrix. This covalent bonding between the hydroxyl groups of the fibre and the anhydride groups of the maleic anhydride make the bridge interface for efficient interlocking [12]. This had proved by the result of FTIR before which is showed in Figure 1. The absorbance band which show at 1660 cm\(^{-1}\) proved the presence of grafted maleic anhydride group in the composite, therefore, maleated treatment had the highest tensile strength.

![Graph showing tensile strength of biocomposite with different rice husk loading and surface treatments.](image)

**Fig. 2.** Tensile strength biocomposite with different rice husk loading and surface treatments.

### 3.2.2 Elongation at Break

Figure 3 shows the elongation at break of the composite with different rice husk loading and surface treatments. The elongation at break tend to reduce when the loading of rice husk increases. AK-30 and AC-30 had the lowest value of elongation at break which is 3.9%. This happened due to the brittle properties of rice husk in the composite and this can reduce the ductility of the polymer matrix [13].

Besides, based on the Figure 3, maleated treatment composite has the highest elongation at break compared to alkali treatment and acrylic acid treatment. M-10 of rice husk loading shows the highest value which is 9.5%, while M-20 loading of rice husk is 6.6% and M-30 is 4.8%. For alkaline treatment on rice husk, AK-10 of rice husk loading shows 9.3% of break elongation while AK-20 rice loading is 4.5% and AK-30 of rice husk loading is 3.9%. Acrylic acid treatment has a lower break elongation compared to maleated treatment and alkaline treatment. AC-10 of rice husk loading with acrylic acid treatment shows 7.9% of break elongation while AC-20 is 5.2% and AC-30 is 3.9%.

According to Jia Ying Tong et al., maleic anhydride grafted matrices used as coupling agent are able to improve the elongation at break of the composite. This is because the formation of ester bonds between anhydride groups of coupling agents entered into an esterification reaction with the surface hydroxyl groups of rice husk. This can be proved by the result in FTIR. The peak of 1031 cm\(^{-1}\) was detected and this showed the formation of
ester bond. The hydrophilic group in rice husk is chemically bonded by coupling agent. Coupling agent was blended by wetting in the polymer chain. Therefore, maleated treatment composite had the highest elongation at break among the three surface treatment [8].

![Fig. 3. Elongation at break of biocomposite with different rice husk loading and surface treatment](image)

### 4 Conclusion

In a conclusion, the FTIR shows the spectrum of M-20, AK-20 and AC-20. The peak of carbonyl stretching vibrations of ester, ether and aldehyde groups appeared in spectrum of maleated treatment. The peak was disappeared after the alkaline and acrylic acid treatments. Due to the ester bond formed in the maleated treatment composites, the reading of tensile strength and break elongation were the highest among the three surface treatments. The spectrum of alkaline treatment shows one extra peak which is –OH vibration. This is resulted by increasingly exposure of –OH groups on the rice husk surface after the alkali treatment which removed the surface impurities. In addition, the higher the loading of rice husk filler, the weaker the tensile properties of the rice husk reinforced rHDPE composites. 10% of rice husk loading shows the optimum tensile strength and break elongation due to the effective transfer of applied stress. The higher the loading of rice husk, the lower the tensile strength and break elongation achieved by the composite. This is because of the insufficient wetting of rice husk by the polymer matrix.

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