

## Composites Prepared from Rice Husk and Recycled/Virgin HDPE with Addition of Coupling Agent

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**Abstract.** Composites were made from recycled HDPE and virgin HDPE as matrix and rice husk as filler and also added with polyethylene-graft-maleic anhydride (MAPE) as a coupling agent to improve the physical and mechanical properties of composites. The aim of study is to find the optimum condition of the type of used matrix and the percentage of added coupling agent on the quality of the produced composites. Composites were prepared by hot press method. Hot press process was performed at a temperature of 150 °C for 30 minutes. After cooling to room temperature, the product was tested for tensile strength, bending strength, thermal test and FTIR. The results show that composites prepared by virgin HDPE have much better physical and mechanical properties compared to composites prepared by recycled HDPE. The highest tensile strength value of 5.69 MPa was found on composite with matrix of virgin HDPE and addition of 4 wt% MAPE. While the highest bending strength value of 0.35 Mpa was obtained on composite with matrix of recycled HDPE and addition of 2 wt% MAPE. The presence of a number of MAPE concentration in the mixture resulted in increased adhesion properties between rice husk and HDPE thereby increasing the physical mechanical properties of composites.

**Keywords:** composite, rice husk, plastics waste and coupling agent

### Introduction

Nowadays, the use of wood for building materials or other applications has been increasing sharply, thus the production of composites as a substitute timber is a solution that can be applied. Preparation of composites by using recycled plastic and biomass can reduce the environmental load of the huge amount of plastic wastes in our atmosphere and also produces innovative products as a substitute for wood. The advantages of biomass-based composite products, among others, low density, the production cost is more economical, readily available raw materials, flexible in its construction and other better properties.

Province of Aceh as an agricultural based region has a lot of biomass that has not been fully utilized such as sawdust, coconut fiber, rice husk, straw and so forth. That biomass can be processed to be new materials by mixed with plastic in order to obtain a material that has different properties with its basic property, (Roger, 2007). Biomass-based materials such as sawdust, coconut fiber, rice husks or straw are hydrophilic, rigid and can be biologically degraded. Those specific properties of the material causes less suitable when combined with non-organic material such as plastic that is hydrophobic without addition of coupling agent that improve material interaction between matrix and fillers. With addition of coupling agent then it will improve the adhesion properties between matrix and filler, and finally improve physical and mechanical properties of composites.

It is well known that a lot of coupling agents can be used to produce wood polymer composites such as organic coupling agent, inorganic and organic-inorganic coupling agent. To enhance bonding interaction between matrixes with inorganic filler, some previous researchers have used various types of the coupling agents. Bledzka *et al.* (1998) and Farid (2012) using Maleic Anhydride as a coupling agent, Pickering (2003), Qiu *et al.* (2005), and Shuang Li (2006) added isocyanate coupling agent while John Z. L., *et al.*, 2005 using Maleic anhydride based polymers such as maleic anhydride polyethylene (MAPE) and maleic anhydride polypropylene (MAPP) in their research. The applicability of the coupling agent of maleic anhydride based polymers provides the best results where MAPE can increase phase inter bond between polar filler and a non-polar polyethylene effectively.

The aim of study is to investigate the matrix type effect of virgin HDPE or recycled HDPE and the amount of polyethylene-graft-maleic anhydride (MAPE) that is used as a coupling agent on the quality of produced composites.

## **Materials and Methods**

### **Materials**

The materials used in the study are: rice husk as filler, recycled polyethylene and virgin polyethylene as a matrix, xylene 20 % as a plastic solvent and polyethylene-graft-maleic anhydride (MAPE) with density 0.92 g/ml, 12 mesh and MW 15,000 as a coupling agent. Rice husk was obtained from paddy field in Aceh Besar region, the same type and color of recycled plastics was collected from recycled collection point in around of Banda Aceh City, while virgin HDPE plastic was purchased commercially. The used tools are: stirred reactor consisting of a three-neck flask (Pyrex), motor with stirrer (Fisher Scientific, maximum speed of 250 rpm), oil bath (Corning), Hot press (hand made, temperature range of 29-300 °C), Crusher and 100-200 mesh size sieve (Macross Testing sieve), Oven with temperature range 25-400 °C (Gallenkamp), Digital scales, 0-1000 gram (METLER Toledo). Thermometer (0 °C - 200 °C), temperature control (50-500 °C).

### **Preparation of composites**

#### *Preparation of matrix and filler*

Rice husks previously were soaked in hot water at a temperature of 100 °C for 2 hours (while mixed). The purpose of soaking is to eliminate the extractive substances contained inside. After soaking, the rice husk was dried up to air dry. Later rice husk was grinded and sieved with size of 100-200 mesh and then dried again using the oven at temperature of 105 °C for 24 hours until it reaches the water content of 2% - 3%, (Harper and Charles, 1999). After that, the rice husk was kept in a desiccator to prevent contact with the outside air and also to absorb the remaining water contained in rice husks before composites manufacturing process.

Recycled HDPE was cut to small size then washed with detergent to clean recycled HDPE from contaminants. After that, recycled HDPE was rinsed with water and dried in the sun and in oven at temperature of 105 °C for 24 hours, (Harper and Charles, 1999).

#### *Production of composites*

Recycled HDPE or virgin HDPE as much as 40 grams incorporated into the three-neck flask and added with 200 ml of xylene as solvent to melt HDPE (Carrollet *al.*, 2001). Furthermore turned on the bath and set the temperature around 145 °C. Then as much as 60 grams of rice husk was added inside the flask and stirred until homogeneous condition for about 20 minutes with the addition of MAPE coupling agent as much as 1, 2, 3, 4% by weight and without addition of MAPE. Homogeneous mixture was removed from the flask and allowed to cool to evaporate the solvent for 24 hours. Further compression process is carried out by hot press at a temperature of 150 °C for 30 min (Prasetyawan, 2009). Composites then were cooled naturally and later were tested.

### **Analysis and testing**

Tests that conducted in this study were: tensile strength that tested in accordance with ASTM 638-99 Type I in Laboratory of Research Center, Faculty of Mathematics and Natural Sciences University of North Sumatra; Bending strength using a Universal Testing Machine Electronic System Type: SC-2DE Japan in Laboratory of Research Center, Faculty of Mathematics and Natural Sciences University of North Sumatra. Thermal test using a Shimadzu DSC-60 in Laboratory of Catalysis and Reaction Engineering Chemical Engineering Syiah Kuala University. FTIR using Shimadzu Prestige-21 in Environmental Laboratory of Chemical Engineering Syiah Kuala University.

## **Results and Discussion**

It is cited in literature that mechanical and thermal properties and bonding types of produced composites would be affected by the type of used matrix and also depends on the amount of added coupling agent. One of the coupling agent is polyethylene-graft-maleic anhydride (MAPE) that is an effective and suitable coupling agent to produce composites based on a matrix of HDPE polymer. MAPE has been used as a coupling agent to improve

the adhesion bonding between ligno-cellulosic fiber derived from biomass-based filler and plastics based matrix (Sameniet *et al.*, 2004).

### **Mechanical properties**

The mechanical properties of composites are properties that associated with ability of composite to resist external forces that acting on the composite. Mechanical properties that were tested in this study is tensile strength and bending strength. Test results from this study were then compared to the standard SNI 03-2105-1996 and JIS A5908.

### **Tensile strength**

The results testing of tensile strength for composites with matrix of recycled HDPE and virgin HDPE are shown in Figure 1.

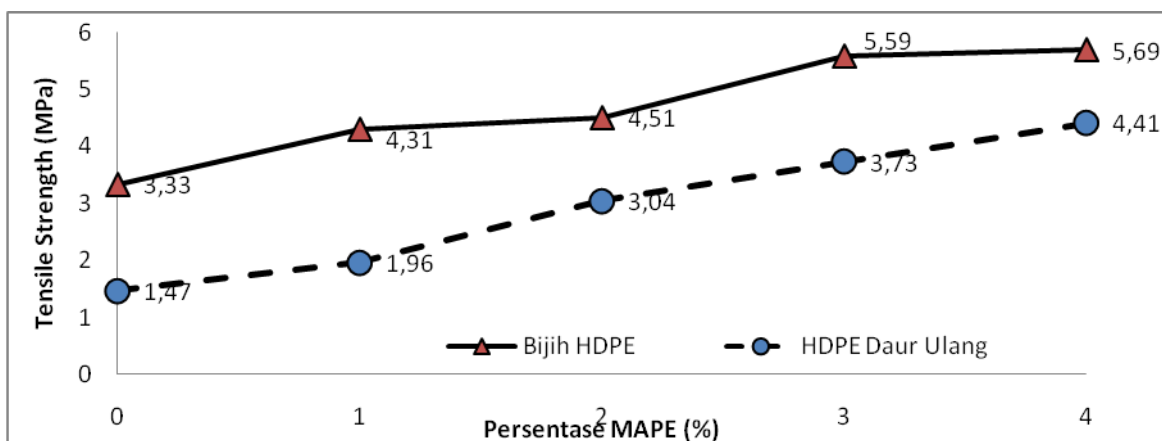


Figure 1. The relationship between the percentage of MAPE as a coupling agent with tensile strength

From the figure it is known that tensile strength value increased with increasing percentage of MAPE for composite with the matrix recycled HDPE and virgin HDPE. The optimum tensile strength value of virgin HDPE based composites that obtained at addition of 3% wt of MAPE was 5.59 MPa, while the optimum tensile strength value of composites with recycled HDPE matrix that obtained at addition of 4 wt% MAPE was 4.41 MPa. Composites that using virgin HDPE as matrix, tensile strength value was much greater than composites based on recycled HDPE in all conditions performed. This can be caused by surface pore of virgin HDPE is not too wide compared to the surface pore of recycled HDPE and also during mixing it was found that samples using virgin HDPE were more thicker than composites prepared from recycled HDPE and also took long time for melting of virgin HDPE. It also suggests that a more homogeneous mixing occurred on composite prepared from virgin HDPE.

Prachayawarakorn *et al.* (2008) also found a decline in tensile strength value after addition of excess coupling agent caused low blending component interface interaction, which would lead to the outbreak of the mechanical structure of the mixed interface. Kamal *et al.*, 2008 found that an increase of tensile strength due to the formation of ester bonds between carbonyl groups of the anhydride of coupling agent and the hydroxyl groups of the filler. In addition, Fatih *et al.*, 2008 found that the type of plastic used does not significantly affect the quality of the composite. However, the amount of coupling agent had a significant effect on tensile strength value, which means that the addition of coupling agent increases the tensile strength value due to an increase of adhesion bonding between the matrix and the filler.

From the above results, it is known that tensile strength value of virgin HDPE-based composites and recycled HDPE meets the standards according to SNI 03-2105-1996 where the value of the required minimum tensile strength is 0.15 MPa - 0.29 MPa. (SNI, 2006)

### **Bending strength**

The test results of bending strength for composites with matrix of recycled HDPE and virgin HDPE were shown in Figure 2.

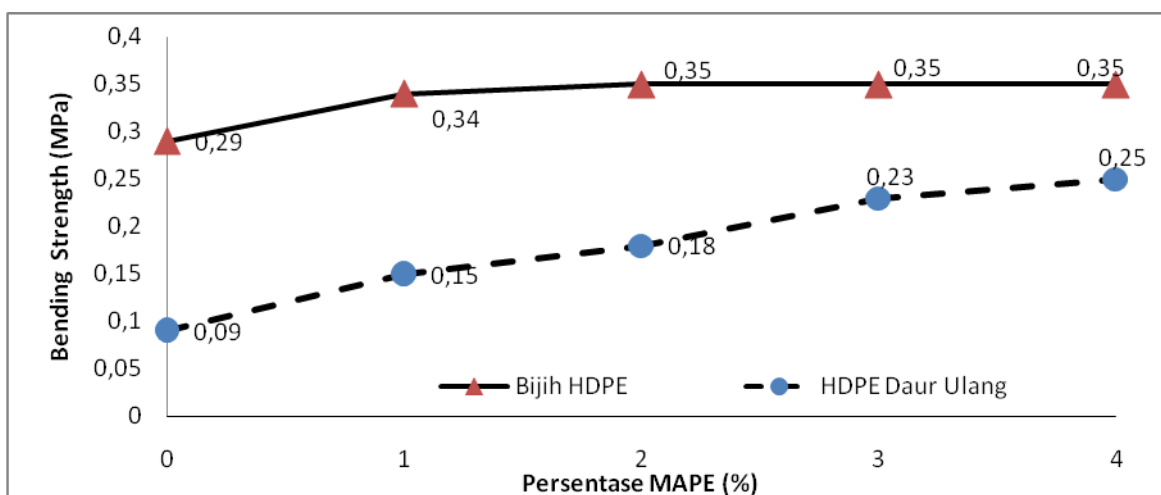


Figure 2. The relationship between the percentages of MAPE as a coupling agent with bending strength value.

Figure 2 shows that the optimum of bending strength value for virgin HDPE-based composites that obtained at addition of 3 wt% MAPE is equal to 0.35 MPa. While on composites prepared by matrix of recycled HDPE, it was found that the increasing of percentage of MAPE would also increase the value of the bending strength where the maximum value of 0.25 MPa was obtained at addition of 4% wt MAPE. The presence of MAPE content in the mixture resulted in increasing of adhesion properties between rice husk with HDPE due to the esterification process between the anhydride groups of MAPE with the hydroxyl group of rice husk.

Kamal *et al.*, (2008) also found that the addition of coupling agent increase bending strength and composites stiffness significantly. Bending strength value in composite with MAPE coupling agent increased if compared with composites without using MAPE. This is because the addition of MAPE has improved compatibility between filler and HDPE which in this case also reduces the absorption of water and increase the stability and mechanical properties of composites.

From the results above, it was found that bending strength of composites either by using recycled HDPE and virgin HDPE does not meet the standard of JIS A5908 and SNI 03-2105-1996. Based on JIS A5908 and SNI 03-2105-1996, minimum standard of bending strength was 8.04 MPa and 9.81 Mpa, respectively.

#### **Thermal test**

It can be seen in Figure 3 the number of heat needed to melt the composite prepared by recycled HDPE and virgin HDPE. The largest amount of heat to melt the virgin HDPE-based composites found at addition of 4% wt MAPE is 788 J/g. While the lowest amount of heat obtained for the composites prepared by virgin HDPE without addition of coupling agent is 172 J/g. In general, the more amount of added coupling agent, then the greater heat required to melt composites. This can happen due to the increasing number of added coupling agent then the interaction between the bonding of rice husk and HDPE became stronger so it also takes a greater heat to melt composites. Generally the amount of heat of composites prepared by virgin HDPE was higher than that of composites prepared by recycled HDPE. This is because a reduction of energy required to melt recycled HDPE-based composites because for this type of plastic most properties have been degraded after first moulding and addition of other additives into materials during previous process. The melting temperature ( $T_m$ ) of each composite was found different each other. Composite with recycled HDPE matrix has a melting temperature averages about 132.76 °C while composite with virgin HDPE matrix has a melting temperature average of 134.69 °C.

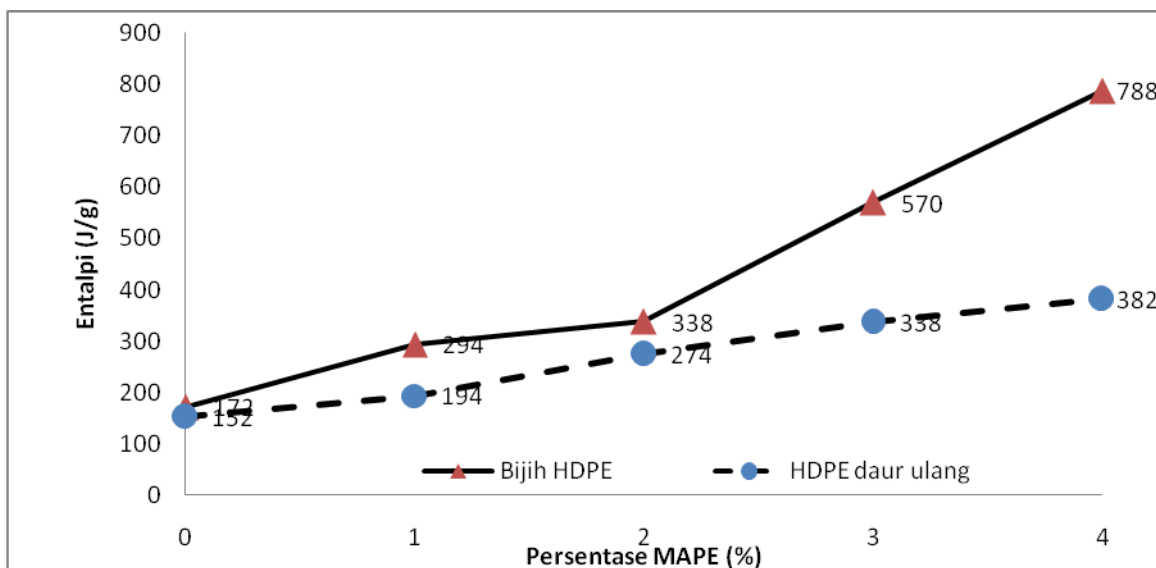


Figure3 The relationship between the percentage of MAPE as a coupling agent to the enthalpy of composite prepared by recycled HDPE and virgin HDPE.

#### Fourier Transform Infra Redtest

FTIR spectra of composites prepared by recycled HDPE were presented in Figure 4. There are similarity pattern of spectra in each composite with and without addition of MAPE. This shows that all types of functional groups of composite have a similar spectrum that is derived from the filler group of rice husk. However, it was also found a difference in the magnitude and peak height and that referring to difference of functional group substituents.

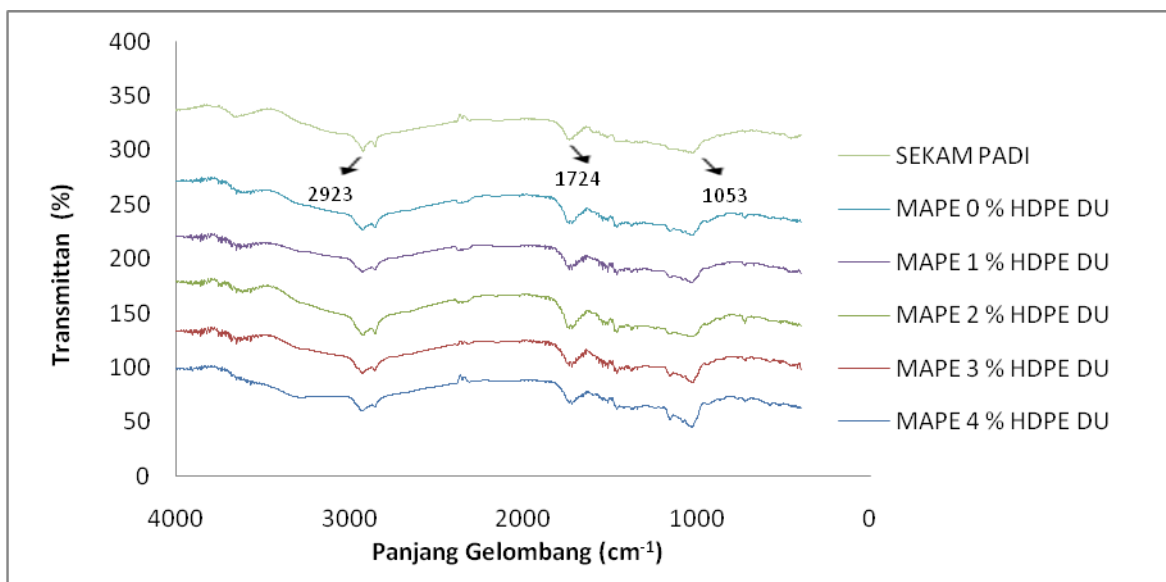


Figure 4 FTIR spectra of composites prepared by recycled HDPE.

Spectra of composites with MAPE composition from 0% to 4% wt show peak at 1053  $\text{cm}^{-1}$  that indicate the presence of -OH group which is the constituent cellulose contained in the rice husk filler. The absorption of water by cellulose depends on the number of free -OH groups. The increased of adhesion bonding between the filler and the matrix as shown in the increase of mechanical properties of composites due to the presence of hydrogen bonding (Balasuriya, P. W. *et al.*, 2002). According Basuki, 2005, cellulose content which has hydroxyl groups that can form hydrogen bonds can also be found at 3425  $\text{cm}^{-1}$ .

Figure 4 show two prominent peaks at 2923  $\text{cm}^{-1}$  that are referring to vibration of CH stretching that indicating the formation of bonding between filler and matrix and at 1724  $\text{cm}^{-1}$  which is C = O carbonyl groups associated with group of lignin and cellulose. Mohanty, S. *et al.* 2006 confirmed that the carbonyl index for recycled HDPE showed some degradation. Recycled HDPE shows spectra range between 1740-1715  $\text{cm}^{-1}$  (due to carbonyl group) and 1640  $\text{cm}^{-1}$  (due to the double bond), which indicates degradation. Composites that modified with addition of coupling agent have a high concentration of carbon, but low oxygen concentrations. This indicates that the chemical composition of the interface is influenced by the type and structure of the coupling agent, coupling agent concentration, and reaction of coupling agents with fillers and the polymer matrix.

#### Effect of addition coupling agent

From some previous studies revealed that MAPE is more effective in improving the bonding between the filler surface and plastic matrix. Therefore, the mechanism of MAPE on the interface in the composites is shown in the following figure.

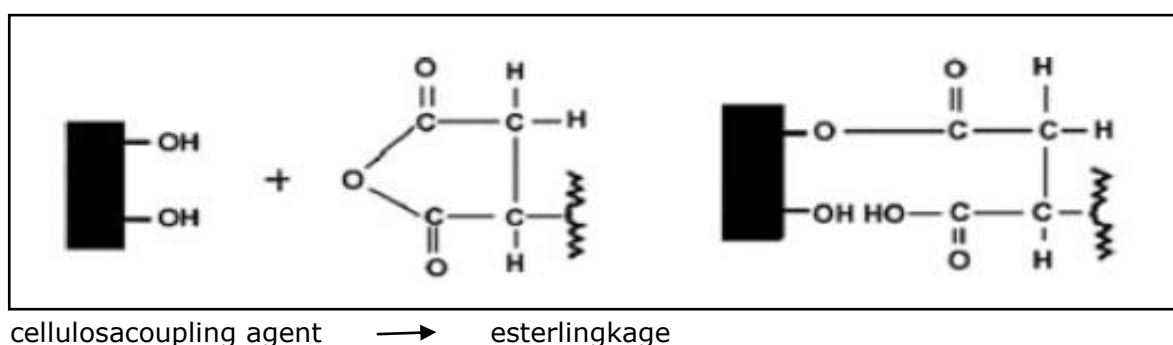


Figure 5. The mechanism of esterification reaction between hydroxyl groups of filler and anhydride groups of MAPE

The reaction is between the filler containing -OH groups with the anhydride groups of MAPE to form esters linkage. Moreover, part of the HDPE also tends to approach MAPE that has hydrophobic property so that the long chain of HDPE lowering the surface tension. Hydroxyl groups of filler that has hydrophilic properties are not easily mix with the hydrophobic HDPE matrix. Therefore, to reduce the surface hydrophilicity of filler thus rice husk surface have to be coated with coupling agent. MAPE with hydroxyl groups of filler to form an ester linkage. Furthermore, part of the nonpolar HDPE that combined with MAPE become compatible and also at the same time would reduce the surface energy of the filler, thus increasing the wetness and dispersion in the matrix completely. Mohanty *et al.*, 2007 also found that preparation of composite with MAPE coupling agent can improve mechanical properties compared to preparation of composite without addition of coupling agent. The increase of mechanical properties due to the increased surface adhesion between filler and matrix with the addition of MAPE.

#### Conclusions

From the above study, it is found that composites produced from rice husk and matrix of virgin HDPE give better mechanical properties compared to composites that were prepared by matrix of recycled HDPE. The highest tensile strength value of 5.69 Mpa was found on composite prepared by virgin HDPE plastic at addition of 4 wt% MAPE. While the highest bending strength value of 0.35 Mpa was obtained on composites with matrix of recycled HDPE and addition of 2 wt% MAPE. Tensile strength values of composites prepared by matrix of recycled HDPE and virgin HDPE has already met the minimum standards of SNI 03-2105-1996 but not for bending strength values. The presence of coupling agent content in composites resulted in increased adhesion properties between rice husk and HDPE thereby increasing the mechanical physical properties of composites.

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