

Rice Husk–Polyester Composites: The Effect of Chemical Modification of Rice Husk on the Mechanical and Dimensional Stability Properties

H. D. Rozman, L. Musa, A. Abubakar

School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia

Received 9 February 2004; accepted 30 June 2004

DOI 10.1002/app.21268

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Rice husk was used as filler in the production of rice husk (RH)–polyester composites and was subjected to three types of chemical modification. The chemical reagents employed in this study were glycidyl methacrylate (GMA), maleic anhydride (MAH), and succinic anhydride (SAH). This study revealed that the chemical modification of RH with GMA and MAH resulted in the enhancements of tensile and flexural properties of RH–polyester composites. The reduction in these properties with respect to those modified with SAH were attributed to the absence of C = C unsaturated groups. Water immersion test showed that

chemical modification of the RH improved the dimensional stability of the composites. This was shown in the GMA- and MAH-modified RH–polyester composites. The modification increased the hydrophobicity as well as the crosslinking between the RH and matrix in the composites. The lower performance demonstrated by the SAH-modified composites was due to the inability of the SAH to form crosslinking with the matrix. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1237–1247, 2005

Key words: rice husk; composites; lignocellulosics; polyester

INTRODUCTION

Recently, utilization of biomass resources has been the subject of various studies. In Malaysia, rice husk (RH) is one of the biomass materials, which is a by-product from the rice industry. Many studies have been carried out on the utilization of biomass, in general, such as particleboard,¹ medium-density fiberboard,² pulp,³ and composites.^{4–8} Utilization of biomass in lignocellulosic composites has been attributed to several advantages such as low density, greater deformability, less abrasiveness to equipment, biodegradability, and low cost. However, in producing a good lignocellulosic composite, the main obstacle to be resolved is the compatibility between the fiber and matrix. The properties of the lignocellulosic composites are dominated by the interfacial interaction between the lignocellulosic filler and polymer matrix. Generally, there are two types of interaction at the interfacial region, i.e., primary and secondary bondings. Primary and secondary bondings include covalent and hydrogen bondings, respectively. While covalent bondings at the interfacial region exist in thermoplastic–wood

composites with the incorporation of a coupling agent, such bondings are more prevalent in the thermoset–lignocellulosic composites. This is because lignocellulosic hydroxyl (OH) groups could serve as reaction sites with various functional groups in the thermoset system.

In this study, attempts to enhance the reaction between RH and the thermoset matrix have been carried out through the chemical modification of the former. RH was subjected to three types of chemical modification by reacting with maleic anhydride, glycidyl methacrylate, and succinic anhydride. Both maleic anhydride and glycidyl methacrylate possess C = C, which would provide additional sites for the crosslinking reaction between RH and polyester resin (maleate residue and styrene). Succinic anhydride was used as a control and for comparison with those modified with maleic anhydride.

EXPERIMENTAL

Materials

The matrix material used was commercially available unsaturated polyester (USP) Reversol P-9728P with an acid value of 15–25 mg KOH/g, specific gravity 1.1, nonvolatile 52–56%, and gel time 24–30 min. The polyester was purchased from Euro Chemo-Pharma Sdn. Bhd. (Penang, Malaysia). RH, which was used as filler, was obtained from Bernas, Bertam (Penang, Malaysia) (refer to Table I). Glycidyl methacrylate (GMA), ma-

Correspondence to: H. D. Rozman (rozman@usm.my).

Contract grant sponsor: Ministry of Science, Technology, and Environment (MOSTE) and Universiti Sains Malaysia, Penang.

TABLE 1
Chemical Composition of Rice Husk⁹

Content	% Based on weight
Raw protein	1.5–7.0
Raw fiber	31.5–50.0
Nitrogen	24.5–38.8
Cellulose	16.0–22.0
Lignin	20.0–27.5
Pentosan	31.5–50.0
Raw fat	0.05–3.0
Ash	15.0–30.0

leic anhydride (MAH) and succinic anhydride (SAH) were purchased from Delima Manis Sdn. Bhd. (Penang, Malaysia).

Methods

Filler preparation

The Retsch Test Sieve Model 5667 (Germany) was used to separate RH filler into different sizes. The filler size used in this study was of mesh 35–60, that is, 270–500 μm .

Chemical modification with GMA, MAH, and SAH

The RH filler was extracted with a 1:1:4 part mixture of acetone:ethanol:toluene to remove organic soluble material. After extraction, the solvent was drained and the residual solvent was removed by evaporation at ambient temperature and then finally by heating at 105°C in an oven for several hours. The filler was then reacted at 90°C in batches of three reagents, GMA, MAH, and SAH, each of which was diluted in *N,N*-dimethylformamide (2:3, vol:vol ratio) for a selected period of reaction times. To minimize the risk of free radical reaction at the unsaturated ends of GMA and MAH during the reaction, hydroquinone (5% weight of GMA) was added. After reaction, the modified filler was separated from the

liquid reagents by filtration, rinsed with acetone, and refluxed with excess acetone for about 3 h. = to remove solvent, unreacted reagent, and any nonbonded polymer formed during the reaction. Chemical loadings of the reagents were calculated as

$$\text{Weight Percent Gain (WPG)} = \frac{W_1 - W_0}{W_0},$$

where W_0 = oven-dried (105°C) weight before reaction and W_1 = oven-dried (105°C) weight after reaction.

Small samples were withdrawn from these products, milled to fine flour, and examined in transmission as KBr discs using Fourier transform infra-red spectroscopy (FTIR). All recorded spectra comprised 200 scans using Nicolet Avatar 360, operating at 4 cm^{-1} resolution.

Compounding and processing

RH and USP were mixed using propeller mixer "Framo-Geratetechnik." The amount of RH (mesh 35–60) in the composite was 57% by weight. Other chemicals used were *tert*-butyl perbenzoate (1 part per hundred of resin, pphr), zinc stearate (6 pphr of resin), and MgO (6 pphr of resin). The mixing was carried out for 15 min at a rotor speed of 400–600 rpm. The compound was then transferred into a mold with dimensions of 155 \times 155 \times 12 mm^3 . The compound was heated at 135°C for 5 min at a pressure of 500 kg/cm^2 . Cooling was then carried out for 5 min under pressure.

Testing

The sheet produced was cut into four types of test samples, i.e., tensile, flexural, impact, and water immersion test samples. Tensile tests were carried out according to ASTM D3039 on samples with dimensions of 100 \times 12 \times 5 mm (length \times width \times thickness) at a crosshead speed of 2 mm/min. The flexural

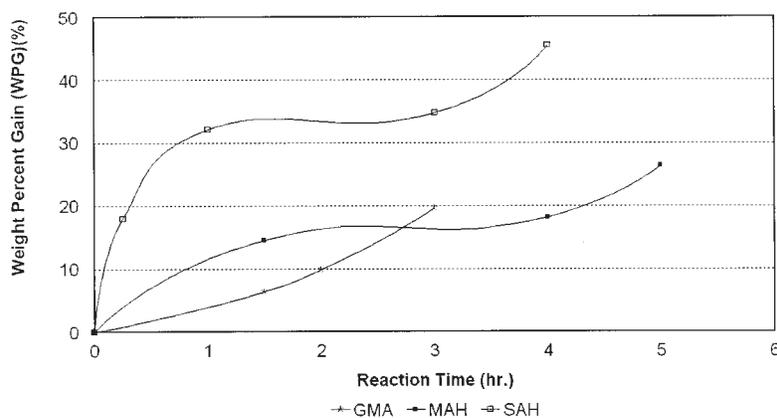


Figure 1 The reaction profile of GMA, MAH, and SAH with RH.

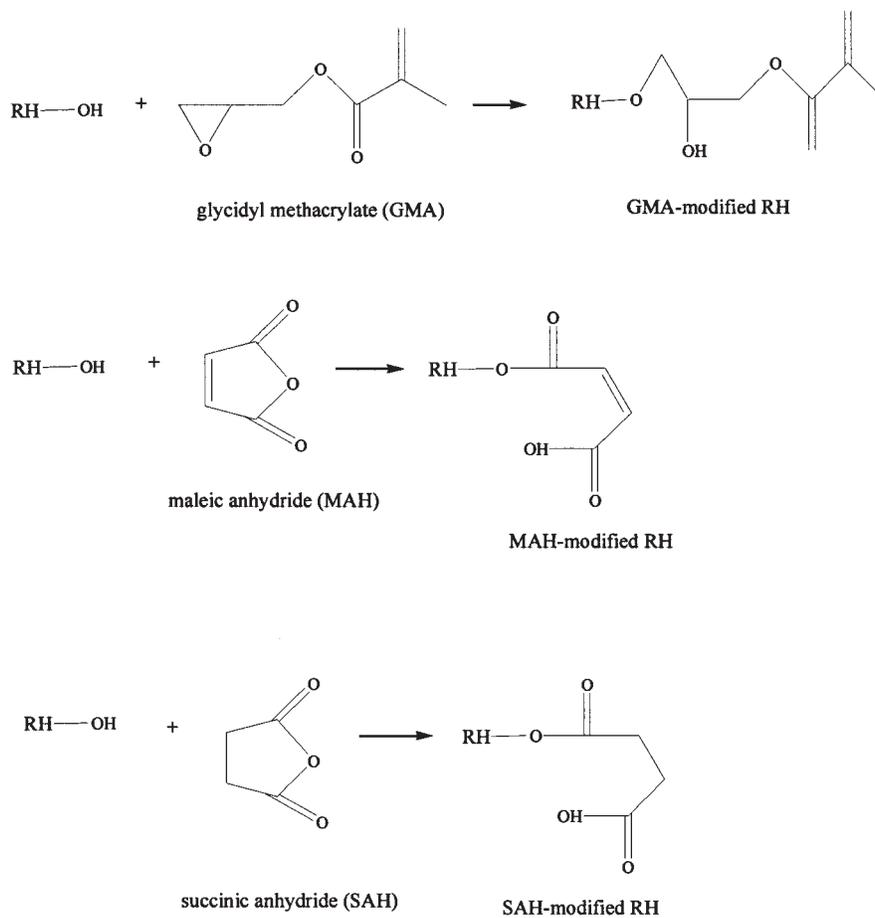


Figure 2 Possible reactions of RH with GMA, MAH, and SAH.

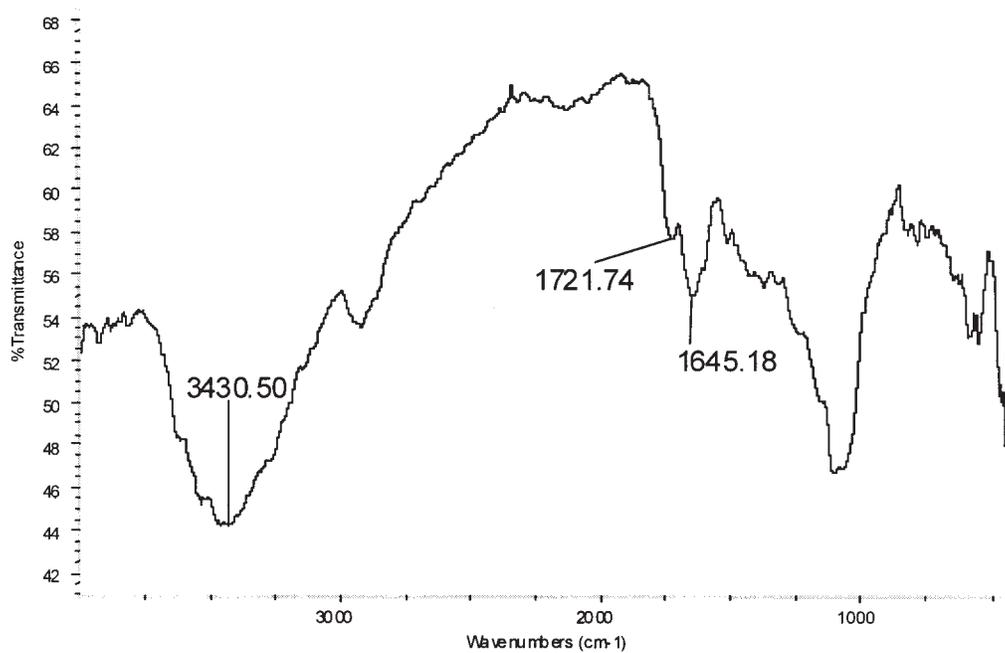


Figure 3 The FTIR spectrum of unmodified RH.

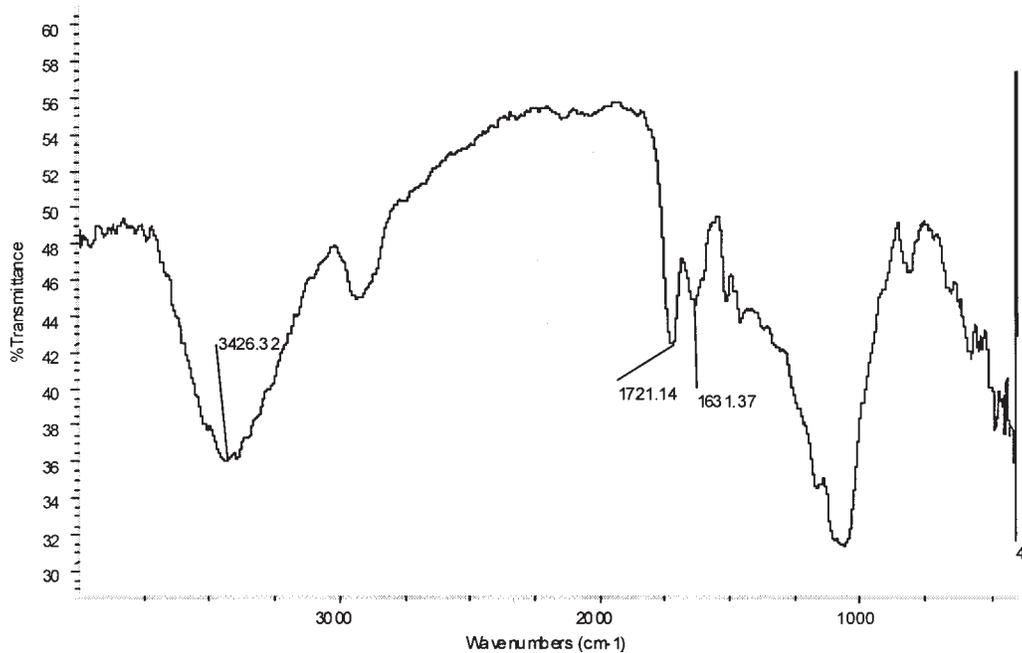


Figure 4 The FTIR spectrum of GMA-modified RH.

test (three-point bending) was conducted according to ASTM D790. The samples with dimensions of $80 \times 12 \times 12$ mm (length \times width \times thickness) were tested at a crosshead speed of 2 mm/min. All tensile and flexural tests were conducted using an Instron machine Model 1114. The Charpy impact test was carried out according to ASTM D256 on samples with dimensions of $65 \times 12 \times 12$ mm using a Ray-Ran Universal

pendulum impact system. A minimum of seven samples were tested in each case.

Water absorption and thickness swelling test

Samples were immersed in distilled water at 30°C. Water absorption was determined by weighing the specimens after immersion in water for a specific time.

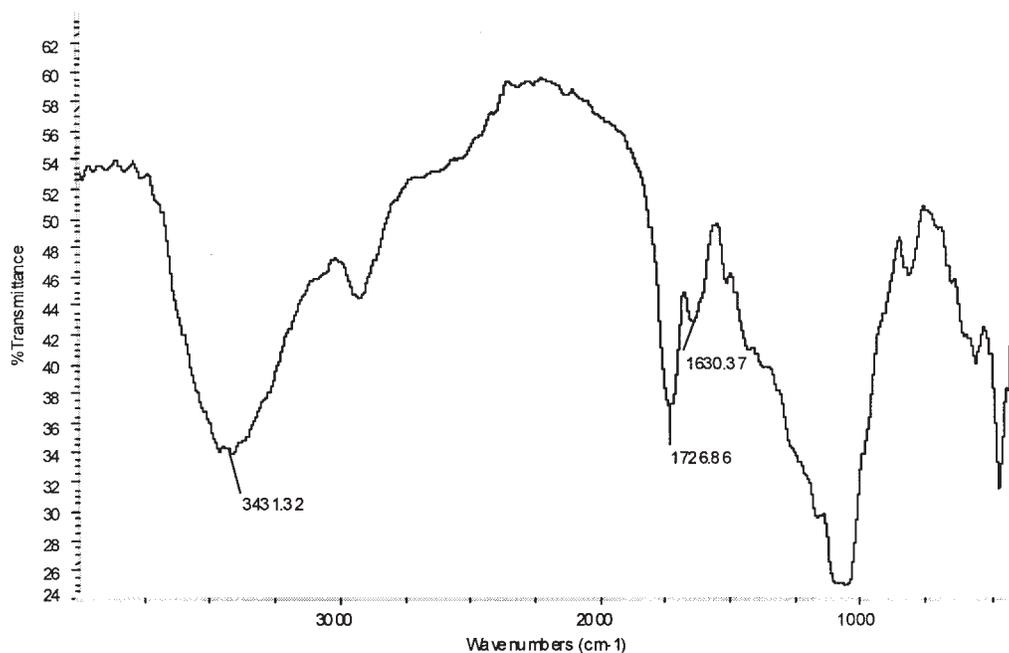


Figure 5 The FTIR spectrum of MAH-modified RH.

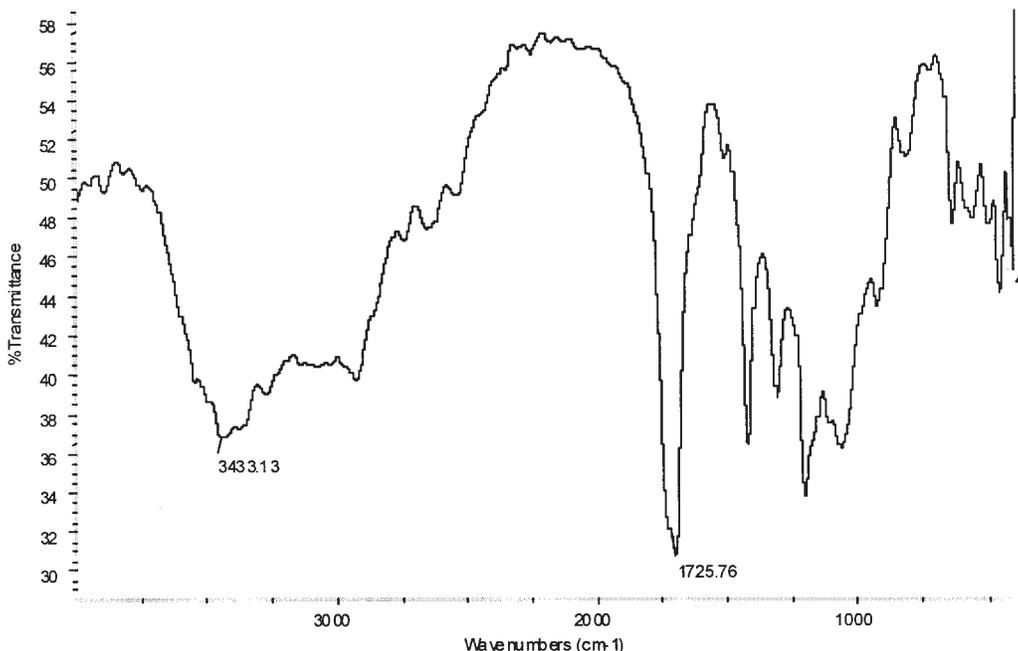


Figure 6 The FTIR spectrum of SAH-modified RH.

A Mettler balance, type AJ150, was used, with a precision of 1 mg. The water absorption at any time t (M_t) was calculated from the expression

$$M_t = \frac{W_w - W_d}{W_d},$$

where W_d and W_w are the original dry weight and the weight after exposure to water, respectively. The

thickness swelling (T_t) was calculated according to the formula

$$T_t = \frac{T_w - T_d}{T_d},$$

where T_d and T_w are the original dry thickness and the thickness after immersion, respectively.

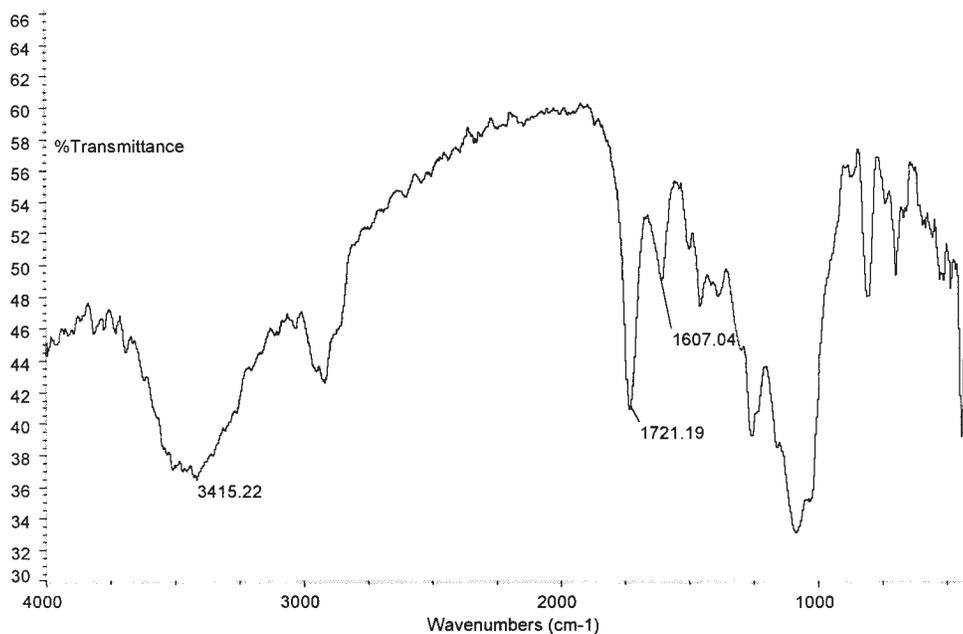


Figure 7 The FTIR spectrum of GMA-modified RH—polyester composite.

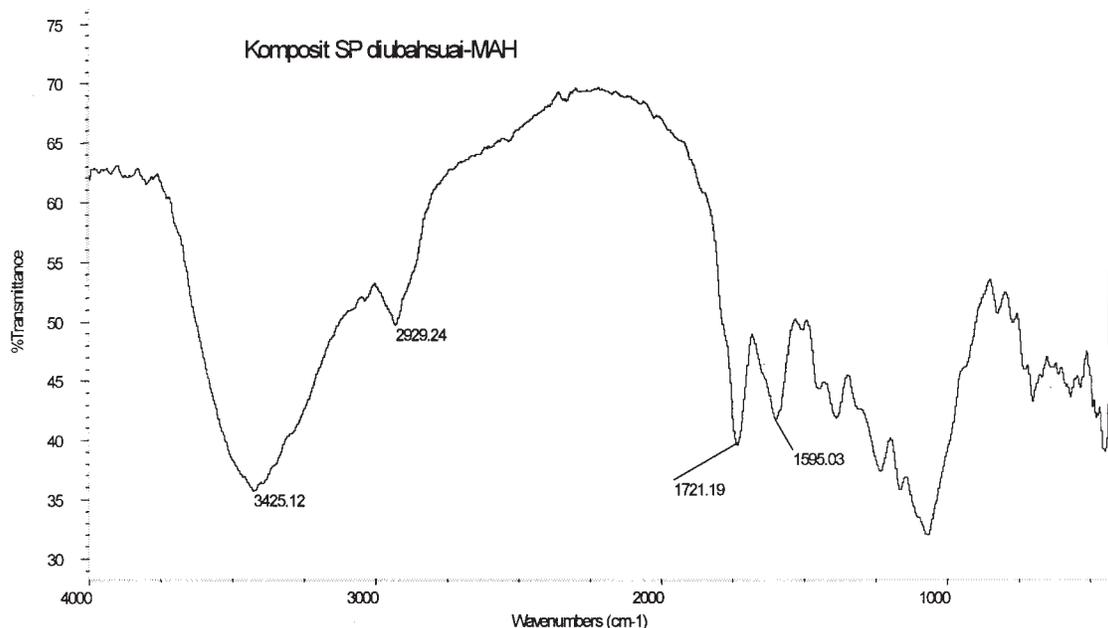


Figure 8 The FTIR spectrum of MAH-modified RH-polyester composite.

RESULTS AND DISCUSSION

Figure 1 shows the reaction profile of GMA, MAH, and SAH with RH. Generally, it can be seen that the rate of reaction follows the order of SAH > MAH > GMA. GMA is a larger molecule (molecular weight of 142) than both MAH and SAH (molecular weights of 98 and 100, respectively). Since the reaction requires the chemical reagent to enter the cell wall and react with the accessible OH groups, the molecular size of the reagent is the deciding factor. Hence, the reaction with OH groups of RH would favor the two anhydrides. Being unsaturated, the MAH molecule is "stiffer" than SAH. Thus, the reaction of MAH with OH groups of RH may be somewhat inhibited compared to SAH. Under the conditions described (with base catalyst and inhibition of free radical processes), the possible reactions are presented in Figure 2.

Infra red spectra for the solvent-extracted control (unmodified) and the chemically modified filler are presented in Figures 3–6. Comparison of Figures 3 and 4 for unmodified and GMA-modified filler, respectively, shows that there is an increase in absorption in the C = C region (at about 1630 cm^{-1}). This is probably due to the absorption of the C = C unsaturated group of GMA. Since the samples for infrared study were extracted exhaustively with solvent to remove free reagent and homopolymer, this suggests that GMA reacts with RH filler and introduces terminal C = C on the surfaces.

Inspection of Figure 5 (reaction with MAH) shows a significant increase in absorption at about 1726 cm^{-1} , suggesting increased carbonyl content. This is consistent with the reaction to form an ester attachment. There is also evidence of increased absorption at 1630

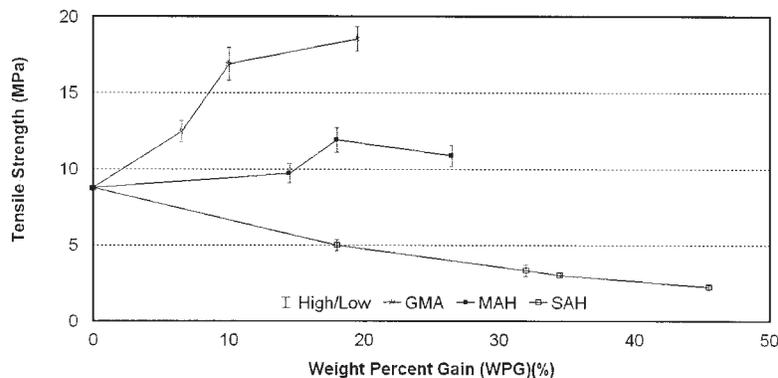


Figure 9 The effect of WPG on the tensile strength of composites.

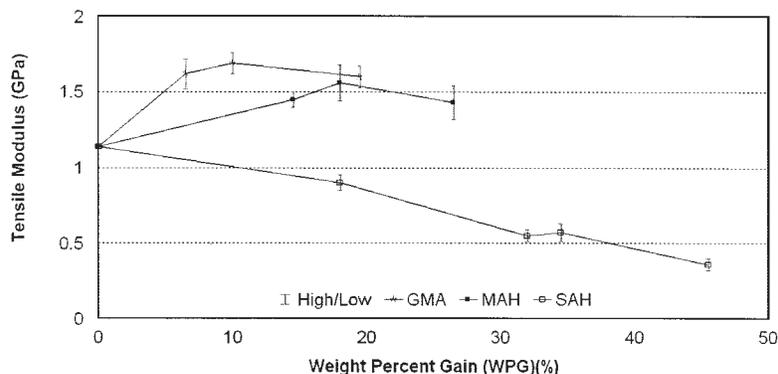


Figure 10 The effect of WPG on the tensile modulus of composites.

cm^{-1} . This feature is a characteristic of $\text{C} = \text{C}$ group, associated with the maleate ester.

The IR spectrum of the SAH-modified filler is shown in Figure 6. Here, the most obvious feature is increased absorption at 1726 cm^{-1} . This is a characteristic of saturated ester $\text{C} = \text{O}$. As expected, there is no evidence of $\text{C} = \text{C}$ enhancement by this reaction. These results are in line with studies by Banks et al.¹⁰ and Rozman et al.¹¹

Comparison of Figures 7 (IR spectrum of GMA-modified RH-polyester composite) and 4 (GMA-modified RH) shows a disappearance of peak at 1630 cm^{-1} after the addition of polyester resin in the process of composite making. This indicates the reaction of $\text{C} = \text{C}$ from GMA with $\text{C} = \text{C}$ sites along polyester chains. A similar phenomenon is observed by comparing the IR spectrum of MAH-modified RH-polyester composite (Fig. 8) and MAH-modified RH (Fig. 5). Thus, the results are consistent with the secondary reactions of $\text{C} = \text{C}$ groups either from GMA or MAH through radical process with $\text{C} = \text{C}$ groups from polyester.

Figure 9 depicts the effect of WPG of the chemically modified filler on the tensile strength of composites. Both composites with GMA- and MAH-modified filler show an increasing trend as the WPG increases. How-

ever, composites with SAH-modified filler show a decreasing trend. Thus, the results indicate that in the composites with GMA- and MAH-modified RH, the stress distribution is more efficient than in composites with SAH-modified RH. This is probably due to the ability of the $\text{C} = \text{C}$ groups in GMA and MAH to copolymerize through a radical process with $\text{C} = \text{C}$ sites along polyester chains and/or with styrene. These would create a better and longer bridging linking together RH and polyester chain compared to shorter ester linkages as the result of OH groups from unmodified RH and carboxylic acid groups from polyester resin. GMA with a longer chain and a terminal $\text{C} = \text{C}$ group makes it more accessible for the copolymerization with $\text{C} = \text{C}$ on polyester chains and/or styrene. Hence, more bridging would be formed compared with MAH. This is reflected in the value of tensile strength, where at about the same WPG (approximately at around 20 WPG) the composites with GMA-modified RH display higher tensile strength than with MAH. For the composites with SAH-modified RH, the results show that the introduction of the anhydride does not impart any improvement in the tensile strength; in fact, the strength reduces as more SAH is introduced on the surface of RH. Thus, this indicates that the introduction of SAH on the RH

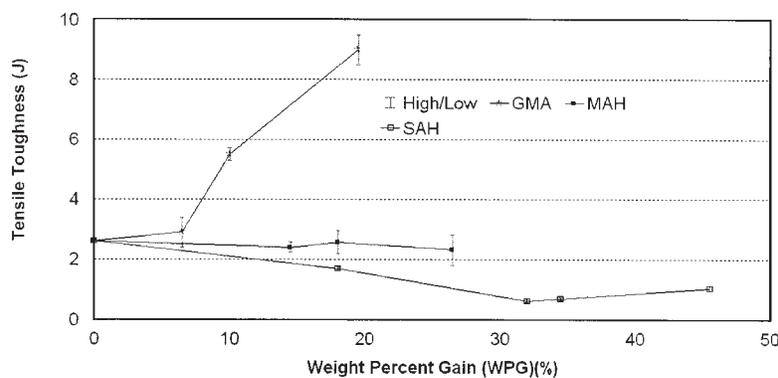


Figure 11 The effect of WPG on the tensile toughness of composites.

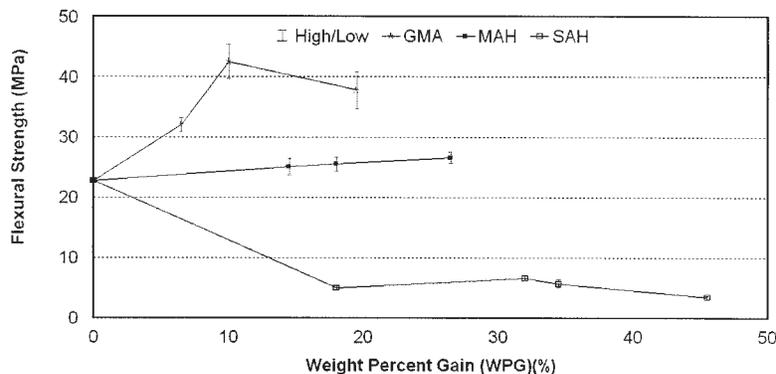


Figure 12 The effect of WPG on the flexural strength of composites.

surfaces may produce a plasticizing effect, allowing movements between the surface and polyester.

Results of tensile modulus (Fig. 10) follow the same trend as tensile strength results. The composites with GMA- and MAH-modified RH show an increasing trend as the WPG increases. However, the tensile modulus of composites with SAH-modified filler decreases as the WPG increases. Thus, the results show that the modification of RH with GMA and MAH has converted the composites into stiffer materials. This may indicate that the bridging formed between RH and polyester as the result of modification may restrict movements of RH in relation to matrix polyester. As mentioned earlier, the bridging maybe produced from the reaction of C = C groups in GMA and MAH with C = C groups along polyester chains and/or with styrene. For the composites with SAH-modified RH, the results show that the introduction of the anhydride decreases the modulus of the samples. This may be attributed to the absence of C = C groups compared to MAH.

Figure 11 shows the results of tensile toughness. It is obvious that only composites with GMA-modified RH display an improvement in the tensile toughness as the WPG is increased. The composites with MAH-modified RH show no changes while those with SAH-

modified RH show a decreasing trend. Thus, it is clear that with GMA-modified RH, more energy is required to bring the sample into failure. This maybe attributed to the more bridging between the terminal C = C of GMA with C = C sites along the polyester chain. As mentioned earlier, since the copolymerization between C = C of MAH is believed to be not as efficient as GMA, it is expected that the energy required to break the sample is accordingly lower.

Figure 12 shows the results of flexural strength. The results follow a similar trend as the tensile strength. The flexural strength of composites with GMA-modified RH increases as the WPG increases. The composites with MAH-modified RH only show a marginal increase. As shown by tensile strength results, those with SAH-modified RH show a decreasing trend as the WPG increases. Both composites with GMA-modified and MAH-modified RH show an increasing stiffness as the WPG increases (Fig. 13). This indicates that the bridging formed between C = C groups of GMA and MAH with matrix and/or styrene restricted the mobility of the RH in the flexural direction. Similar to tensile modulus results, for the composites with SAH-modified RH, the results show that the introduction of the anhydride decreases the modulus of the samples. This may be attributed to the absence of C = C groups

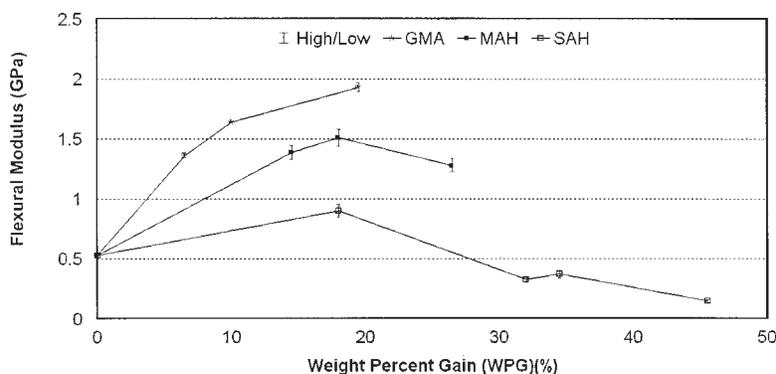


Figure 13 The effect of WPG on the flexural modulus of composites.

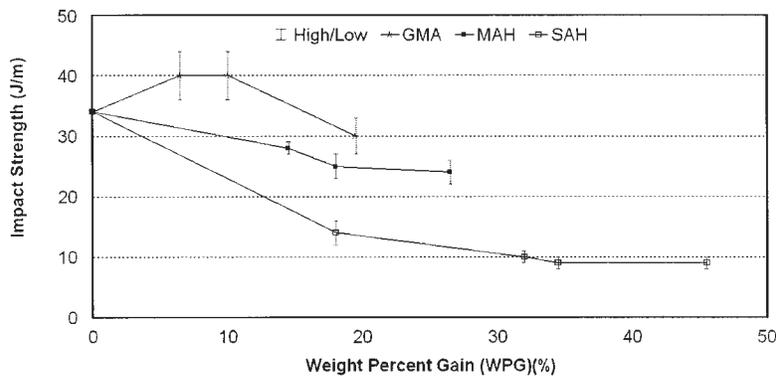


Figure 14 The effect of WPG on the impact strength of composites.

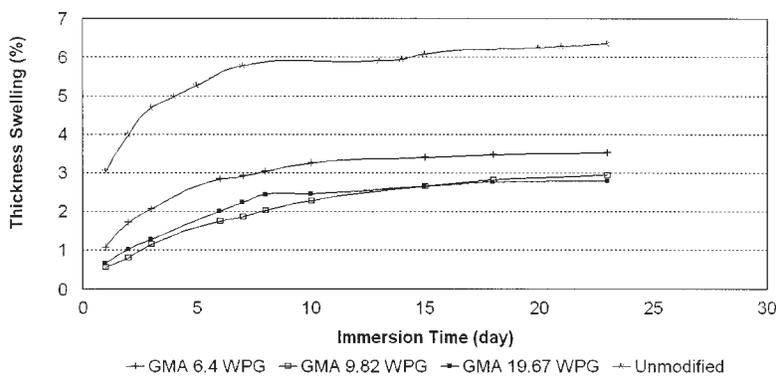


Figure 15 Thickness swelling of composites at various chemical loadings (WPG) of GMA.

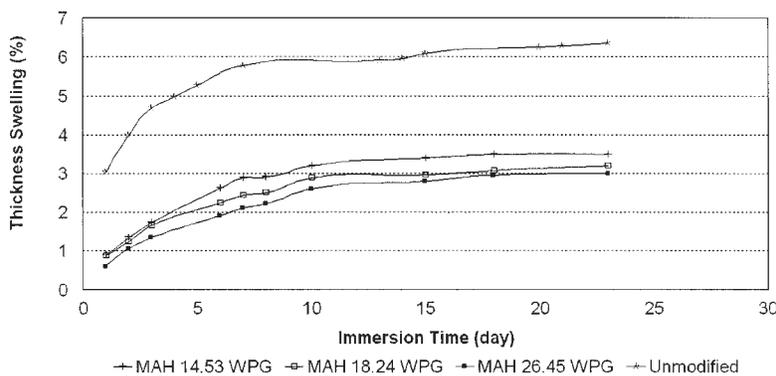


Figure 16 Thickness swelling of composites at various chemical loadings (WPG) of MAH.

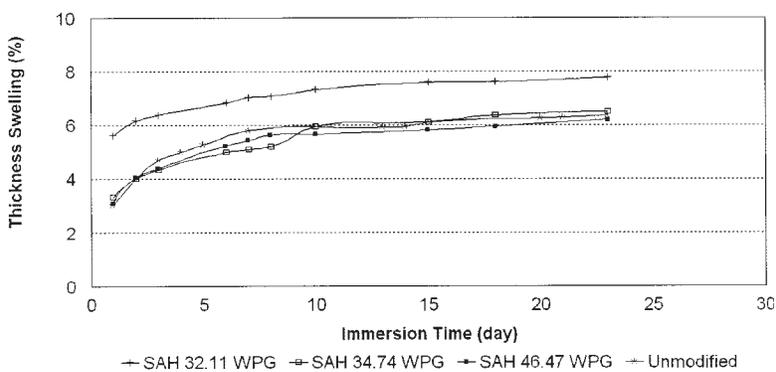


Figure 17 Thickness swelling of composites at various chemical loadings (WPG) of SAH.

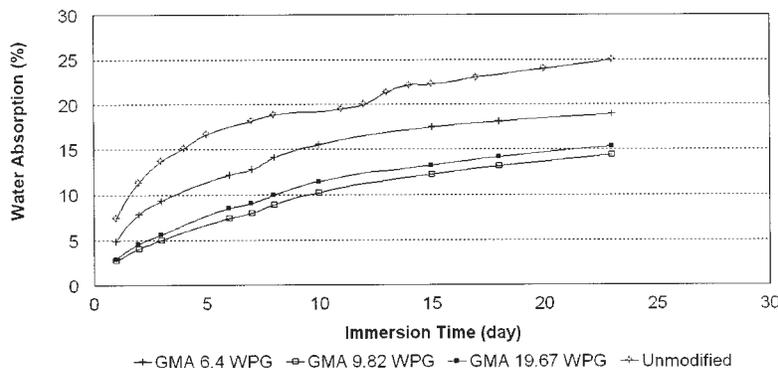


Figure 18 Water absorption of composites at various chemical loadings (WPG) of GMA.

compared to MAH. In general, Figure 14 shows that the impact strength is reduced as the WPG increases. This shows that although composites fair well with regard to tensile and flexural tests, especially those with GMA-modified and MAH-modified RH, it seems that the bridgings formed are not able to transfer efficiently the high-speed stress generation from the matrix to RH.

Figures 15–17 show the results of thickness swelling. In general, lignocellulosic material is hydrophilic with the presence of OH groups in the cell wall which comes from cellulose, hemicellulose, and lignin. These groups absorb water through the formation of hydrogen bonding. This results in the increase in weight and change in dimension.¹² The conversion of hydrophilic OH to a more hydrophobic group reduces the formation of hydrogen bondings, thus reducing the increase in weight and change in dimension. This effect is clearly shown in this study where those modified with GMA and MAH resulted in the reduction of water absorption and thickness swelling. Regarding the effect of water on this lignocellulosic–polyester composite, it is believed that there are two important phenomena that take place. First, water may enter the cell wall and swell it. This would subsequently increase the weight and result in dimensional changes of the com-

posites. However, these effects would be reduced if the interfiller bondings are sufficiently strong and hydrophobic to accommodate the stress generated by the swelling of the cell wall. Without these properties, the swelling of the composites in water is unhindered. For unmodified and modified composites, the RH fillers are bonded together by polyester matrix. In the unmodified composites, while the bonding is able to hold the RH filler together, it fails to prevent the cell wall from swelling, which would subsequently swell the composite. However, by converting RH hydrophilic OH into a more hydrophobic ester through the reaction with anhydride groups, the swelling of the cell wall and composite would be reduced. These phenomena are clearly demonstrated in composites modified with GMA and MAH. However, by looking at the behavior of SAH-modified composites, it is clear that the deciding factor that differentiates the behavior between GMA/MAH and SAH samples is the ability to form extra crosslinking through the reaction of C = C bonds introduced by GMA and MAH on the RH. Although the introduction of SAH increases the hydrophobicity of the RH, it reduces the availability of OH from RH for the reaction with COOH from the polyester resin to form crosslinking. Thus, the swelling of the composites is less hindered and greater than

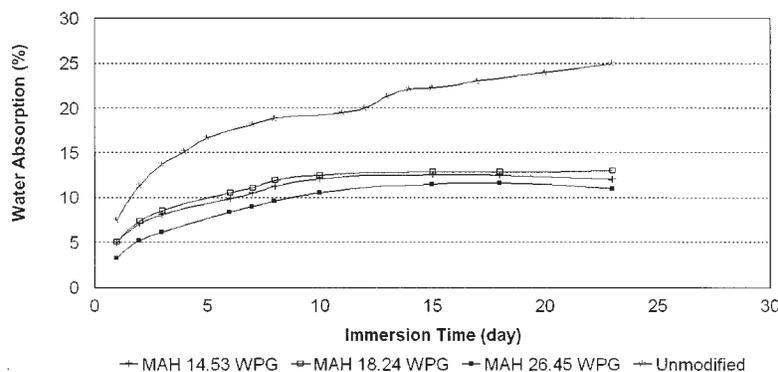


Figure 19 Water absorption of composites at various chemical loadings (WPG) of MAH.

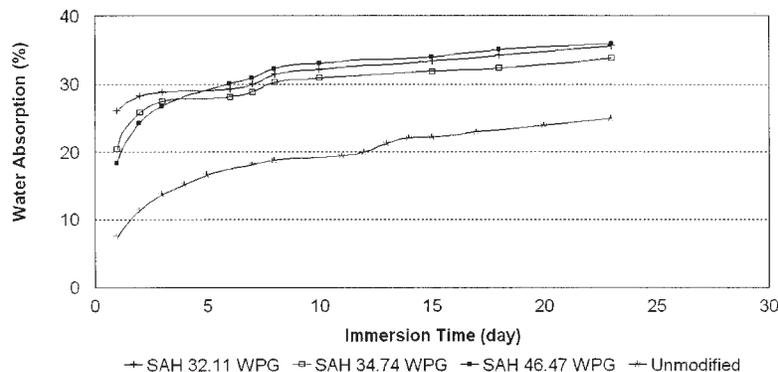


Figure 20 Water absorption of composites at various chemical loadings (WPG) of SAH.

that of those modified with GMA and MAH. A similar trend is shown for the results of water absorption (Figs. 18–20).

CONCLUSIONS

This study demonstrated that the chemical modification of RH with GMA and MAH resulted in the enhancements of tensile and flexural properties of RH-polyester composites. However, the reduction in these properties with respect to those modified with SAH were attributed to the absence of C = C unsaturated groups. Water immersion test showed that chemical modification of the RH improved the dimensional stability of the composites. This was shown in the GMA- and MAH-modified RH-polyester composites. The modification increased the hydrophobicity as well as crosslinking between the RH and matrix in the composites. The lower performance demonstrated by the SAH-modified composites was due to the inability of the SAH to form crosslinking with the matrix.

The authors thank Bernas Dominals for the free sample of rice husk.

References

- Harun, J.; Idris, H.; Mohd Yunus, N. Y.; Kasim, J. In Utilization of Oil Palm Tree. Oil Palm Residues: Progress Towards Commercialisation; Harun, J.; Mohmod, A. L.; Abdul Aziz, A.; Khoo, K. C.; Mohd. Yunus, N. Y.; Md. Tahir, P.; Abood, F.; Mohd. Yusof, M. N.; Husin, M., Eds.; Oil Palm Tree Utilisation Committee (OPTUC), 1997; pp 89–95.
- Chooi, S. Y.; Chan, K.W. In Utilization of Oil Palm Tree. Oil Palm Residues: Progress Towards Commercialisation; Harun, J.; Mohmod, A. L.; Abdul Aziz, A.; Khoo, K. C.; Mohd. Yunus, N. Y.; Md. Tahir, P.; Abood, F.; Mohd. Yusof, M. N.; Husin, M., Eds.; Oil Palm Tree Utilisation Committee (OPTUC), 1997; pp 96–105.
- Mott, L.; Sule, A.; Suleman, A.; Matthews, R. In: Utilization of Oil Palm Tree. Oil Palm Residues: Progress Towards Commercialisation; Harun, J.; Mohmod, A. L.; Abdul Aziz, A.; Khoo, K. C.; Mohd. Yunus, N. Y.; Md. Tahir, P.; Abood, F.; Mohd. Yusof, M. N.; Husin, M., Eds.; Oil Palm Tree Utilisation Committee (OPTUC), 1997; pp 131–140.
- Mohd Ishak, Z. A.; Aminullah, A.; Ismail, H.; Rozman, H. D. J Appl Polym Sci 1998, 68, 2189.
- Abdul Khalil, H. P. S.; Ismail, H.; Ahmad, M. N.; Ariffrin, A.; Hassan, K. Polym Int 2001, 50, 396.
- Abdul Khalil, H. P. S.; Rozman, H. D.; Ahmad, M. N.; Ismail, H. Polym-Plast Technol Eng 2000, 39, 757.
- Rozman, H. D.; Tay, G. S.; Kumar, R. N.; Abusamah, A.; Ismail, H.; Mohd. Ishak, Z. A. Polym-Plast Technol Eng 2001, 40, 103.
- Rozman, H. D.; Tay, G. S.; Kumar, R. N.; Abusamah, A.; Ismail, H.; Mohd. Ishak, Z. A. Eur Polym J 2001, 37, 1283.
- Lauricio, F. M. Introduction Manual on Rice Husk Ash Cements. UNDP/UNIDO Regional Network in Asia for Low Cost Building Materials Technologies and Construction System, Manila, 1987.
- Banks, W. B.; Din, R. H.; Owen, N. L. Holzforschung 1995, 49, 104.
- Rozman, H. D.; Banks, W. B.; Lawther, M. L. Int J Polym Mater 1994, 26, 19.
- Rozman, H. D.; Banks, W. B.; Lawther, M. L. J Appl Polym Sci 1994, 54, 191.