

The Effect of the Chemical Modification of Wood Fibre Using Salicylic Acid and Ethanol on the Properties of Recycled High Density Polyethylene/Wood Fibre Composites

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Abstract: *The effect of the chemical modification of wood fibre (WF) using salicylic acid/ethanol on the tensile properties, water absorption, thermal degradation and morphology of recycled high density polyethylene/WF (rHDPE/WF) composites was studied. Both of the composites: rHDPE/WF and rHDPE/WF_M (modified with salicylic acid and ethanol) were prepared using a Brabender Plasticorder at 160°C with a rotor speed of 50 rpm. The results indicate that the rHDPE/WF_M composite has a greater tensile strength, a higher modulus of elasticity, greater thermal stability, greater resistance to water absorption and a lower elongation at break than the rHDPE/WF composite. SEM micrographs show that better interfacial adhesion occurs between the WF phase modified with salicylic acid and ethanol (WF_M) and the rHDPE phase in the rHDPE/WF_M composite.*

Keywords: Recycled high density polyethylene, wood fibre, salicylic acid, polyethylene, ethanol

1. INTRODUCTION

Renewable natural organic fibres that are biodegradable and ecofriendly act as reinforcing materials for glass or carbon fibre and as inorganic fillers. These fibres have high specific strengths and elastic moduli, low cost and low densities, and are renewable organic, non-hazardous, malleable, widely available and relatively unabrasive.^{1,2} Yazid et al.³ showed that the elastic moduli of rHDPE/NR/CFF composites increased with the fibre load in the blend, but the tensile strength and elongation at break decreased. Through studies and research, thermoplastic or natural fibre composites such as wood plastic composites (WPC) have been shown to have excellent qualities for technical applications such as load bearing.⁴ Polyethylene, which is a polymer, has numerous applications in our modern world. Such polymers are frequently used in thermoplastics for the

production of natural fibres to prepare composites. The addition of natural fillers and coupling agents improve their properties.⁵

In the modern age, the commercial use of natural fibres in plastics has been limited to wood fibre because its use as filler in a composite increases the composite's stiffness and reduces its toughness. The resulting composites are brittle due to stress concentrations at the ends of fibres and poor interfacial adhesion between the wood and the synthetic polymer. Research into new coupling agents, compatibilisers⁶ and the improvement of improve processing methods has been conducted.^{7,8} John et al.⁹ reported that wood fibre has good interfacial adhesion with HDPE and better thermal stability after the addition of a coupling agent. This article describes the effect of chemical modification of wood fibre with salicylic acid and ethanol on the tensile properties, morphology, water absorption and thermal degradation of rHDPE/WF composites.

2. EXPERIMENTAL

2.1 Materials

rHDPE with a melt flow index of $0.7 \text{ g } 10 \text{ min}^{-1}$ at 160°C and a density of 939.9 kg m^{-3} was supplied by Mega Makmur Sdn. Bhd., Penang, Malaysia. WF with an average fibre diameter of 177 microns was obtained from Titan Petchem (M) Sdn. Bhd., Pasir Gudang, Johor, Malaysia. Salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$ with a molar mass of $138.12 \text{ g mol}^{-1}$) and ethanol ($\text{C}_2\text{H}_5\text{OH}$ with a molar mass of 46.07 g mol^{-1}) were obtained from AR Alatan Sdn. Bhd., Alor Setar, Kedah, Malaysia.

2.2 Preparation of the Modified WF_M

The WFs were chemically modified by adding salicylic acid to ethanol. The WFs were dipped into a salicylic acid/ethanol solution containing 1.5 Molar salicylic acid for 2 h at 60°C , following Supri et al.¹⁰ The WFs were then decanted and dried in an oven at 70°C for 4 h. After that, the modified wood fibres (WF_M) were used as filler in the rHDPE composites. The formulations of the rHDPE/WF composites with and without the salicylic acid/ethanol solution are given in Table 1.

Table 1: Formulations of rHDPE/WF composites and rHDPE/WF_M composites.

Blend composition	rHDPE (phr)	WF (phr)	WF treated with salicylic acid/ethanol (phr)
rHDPE/WF-0	100	–	–
rHDPE/WF-5	100	5	–
rHDPE/WF-10	100	10	–
rHDPE/WF-15	100	15	–
rHDPE/WF-20	100	20	–
rHDPE/WF-30	100	30	–
rHDPE/WF _M -5	100	–	5
rHDPE/WF _M -10	100	–	10
rHDPE/WF _M -15	100	–	15
rHDPE/WF _M -20	100	–	20
rHDPE/WF _M -30	100	–	30

2.3 Composite Preparation

The composites were compounded using a Brabender Plasticorder at a temperature of 160°C and a rotor speed of 50 rpm. Two composites were prepared, the rHDPE/WF and rHDPE/WF_M composites. The rHDPE composite was first put into the Brabender Plasticorder to begin the melt mixing process. The rHDPE composite was preheated for 2 min the mixing chamber. Next, WF with or without salicylic acid modification was added to the softened rHDPE composite. The mixing process continued for 8 additional min to produce homogeneous composites. The composites were discharged from the mixing chamber and pressed into thick round moulds. The discharged composites were then allowed to cool at the ambient temperature.

2.4 Compression Moulding

The specimens of the rHDPE/WF and rHDPE/WF_M composites were compressed using an electrically heated hydraulic press to produce plates. The temperatures of the top and bottom plates of the hot and cool press were set to 160°C. Then, the composites were put into the moulds, preheated for 6 min, compressed for 2 min at the same temperature and subsequently, cooled under pressure for 4 min.

2.5 Tensile Tests

Tensile tests were conducted based on ASTM standard D638 using an Instron 5569 system. Dumbbell-shaped specimens were conditioned at the ambient temperature (25 ± 3)°C and relative humidity (30 ± 2)% before testing. Five dumbbell-shaped samples of each composite were used. The tensile strength, modulus of elasticity, and elongation at break of each composite were obtained from the tests.

2.6 Water Absorption Tests

The kinetics of water absorption was studied using a water absorption test. The samples had dimensions of 40 mm × 20 mm × 2 mm based on ASTM standard D471-79. Before the test began, the samples were dried in oven at a temperature of 50°C for 30 min to remove the water in them. Then, the samples were completely immersed in distilled water for 42 days. After immersion in distilled water, the samples were removed at fixed time intervals, wiped with filter paper to remove surface water and weighed with an analytical balance with 0.1 mg resolution. The water absorption (%) was calculated using the following equation:

$$\text{Water absorption (\%)} = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)$$

where W_1 is the weight of the dry sample and W_2 is the weight of the sample after immersion.

2.7 Scanning Electron Microscopy (SEM)

The morphologies of the tensile-fractured surfaces of the rHDPE/WF and rHDPE/WF_M composites were analysed using a JEOL JSM-6460 LA scanning electron microscope. The samples were coated by sputtering before the SEM analysis was performed. A thin layer of palladium that was approximately 12 μm thick was applied using an auto-fine coater to avoid electrostatic charges during the analysis.

2.8 ATR-FTIR Spectroscopy

Spectra were obtained using Perkin-Elmer Spectrum One Series equipment, and the sample was prepared by grinding part of it with potassium bromide. The selected spectrum resolution and the scanning range were 4 cm⁻¹ and 650–4,000 cm⁻¹, respectively.

2.9 Thermogravimetric Analysis (TGA)

Thermogravimetric analyses of the rHDPE/WF and rHDPE/WF_M composites were performed using a Perkin-Elmer Pyris 6 TGA analyser. Samples of approximately 10 mg were scanned from 30°C to 650°C at a heating rate of 10°C min⁻¹ using a constant nitrogen gas flow of 50 ml min⁻¹ to prevent the thermal oxidation of the polymer sample. The temperature when 50% of its weight had been lost (T_{-50%WT}) and the residual mass of the TG curve were calculated.

3. RESULTS AND DISCUSSION

3.1 Tensile Properties

The effect of fibre loading on the tensile strengths of the rHDPE/WF and rHDPE/WF_M composites is shown in Figure 1. The results show that as the load on the fibres increased, the tensile strength of the rHDPE/WF composite decreased slightly due to the incompatibility of the rHDPE composite and WF. This incompatibility reduced the tensile strength because fractures were initiated at the weak interface between the composites due to their poor interfacial adhesion. It can be seen from Figure 1 that under a similar fibre load, the rHDPE/WF_M composite had a greater tensile strength than the rHDPE/WF composite. This was due to the presence of salicylic acid, which enhanced the interaction between the WF and rHDPE phases.

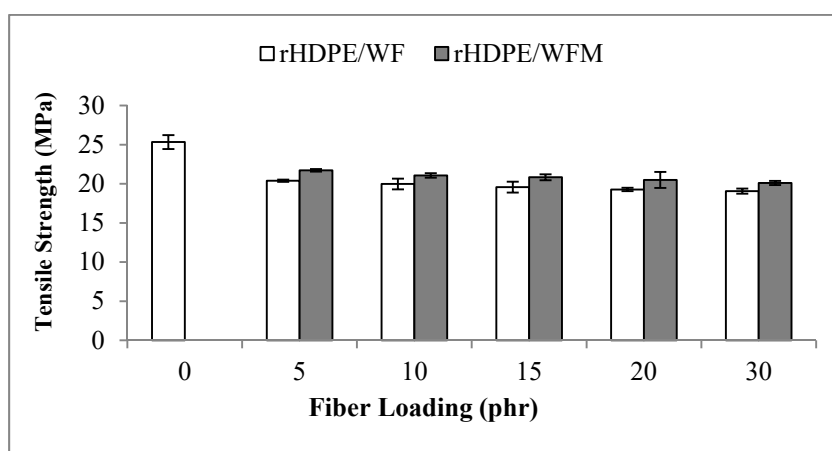


Figure 1: Effect of fiber loading on tensile strength of rHDPE/WF composites and rHDPE/WF_M composites.

Figure 2 also shows that under a similar fibre load, the elongation at break of the rHDPE/WF composite was greater than that of the rHDPE/WF_M composite. When the filler load increased, the ductility of the unmodified and modified rHDPE/WF composites decreased, indicating that the fillers had hardened the composites and reduced their ductility. John et al.⁹ also reported that the effect of a coupling agent on WF/HDPE composites was to decrease their ductility.

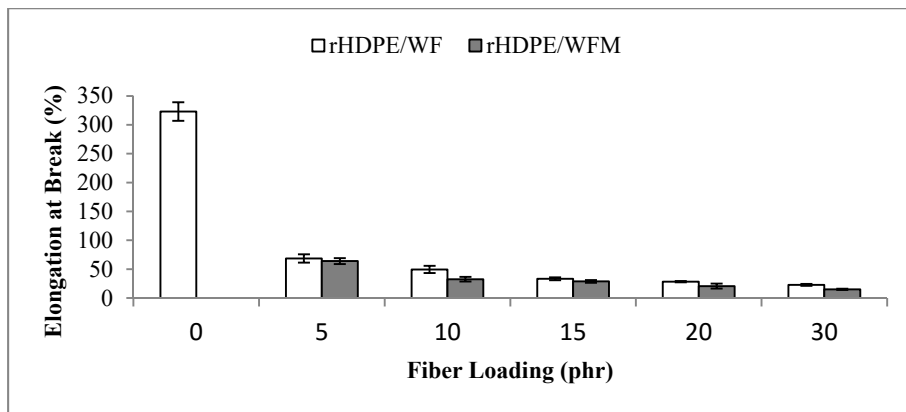


Figure 2: Effect of fiber loading on elongation at break of rHDPE/WF composites and rHDPE/WF_M composites.

The effect of fibre loading on the elastic moduli of the rHDPE/WF and rHDPE/WF_M composites is shown in Figure 3. The elastic moduli of the rHDPE/WF and rHDPE/WF_M composites tended to increase with the filler load. This was due to the presence of fibres, which stiffened and reduced the ductility of the composites. This result is in agreement with that of Viet et al.¹¹ This indicates that the presence of fibres reduced the ductility of the rHDPE/WF composite and increased its stiffness. It can be seen that the elastic modulus of the rHDPE/WF_M composite was greater than that of the rHDPE/WF composite. Again, this was due to the better interfacial adhesion between the rHDPE and WF_M phases when salicylic acid was present as a coupling agent.

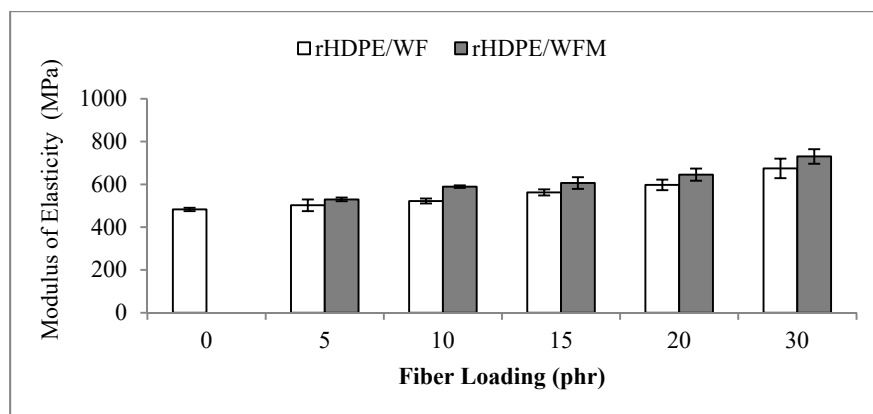


Figure 3: Effect of fiber loading on modulus of elasticity of rHDPE/WF composites and rHDPE/WF_M composites.

3.2 Morphology

The influences of WF loading on the morphologies of the rHDPE/WF and rHDPE/WF_M composites are shown in Figure 4(a–g). Figure 4(a) shows a smooth surface. As the fibre load increased, the micrographs show poor interfacial adhesion and more fibres pulling out of the matrix surface, i.e., Figures 4(b), 4(c) and 4(d). Figures 4(e), 4(f) and 4(g) show good interfacial adhesion and fewer fibres pulling out of the rHDPE/WF_M composite than the rHDPE/WF composite, shown in Figure 4(b), 4(c) and 4(d). This was due to the presence of salicylic acid, which acted as coupling agent that enhanced the interfacial adhesion between the fibres and the matrix. These morphological results are in agreement with the results of the tensile strength tests shown in Figure 1.

3.3 Infrared Spectroscopy

The FTIR spectra of the rHDPE/WF and rHDPE/WF_M composites are shown in Figure 5. Both of the spectra showed olefinic C-H stretching at approximately 2900 cm⁻¹–3100 cm⁻¹. CH₂ bending vibrations appeared at 1462 cm⁻¹, and the absorption at 668 cm⁻¹ showed the presence of C=C groups. However, the absorption peaks at 2360 cm⁻¹ and 2365 cm⁻¹ were attributed to C=C groups in the rHDPE and WF. This was due to the physical interactions between the WF and rHDPE phases. The peak that appeared at 717 cm⁻¹ was attributed to the mono-substitution of the benzene structure from the salicylic acid. An illustration of one possible mechanism behind the interaction between the salicylic acid-modified WF and rHDPE phases is shown in Figure 6.

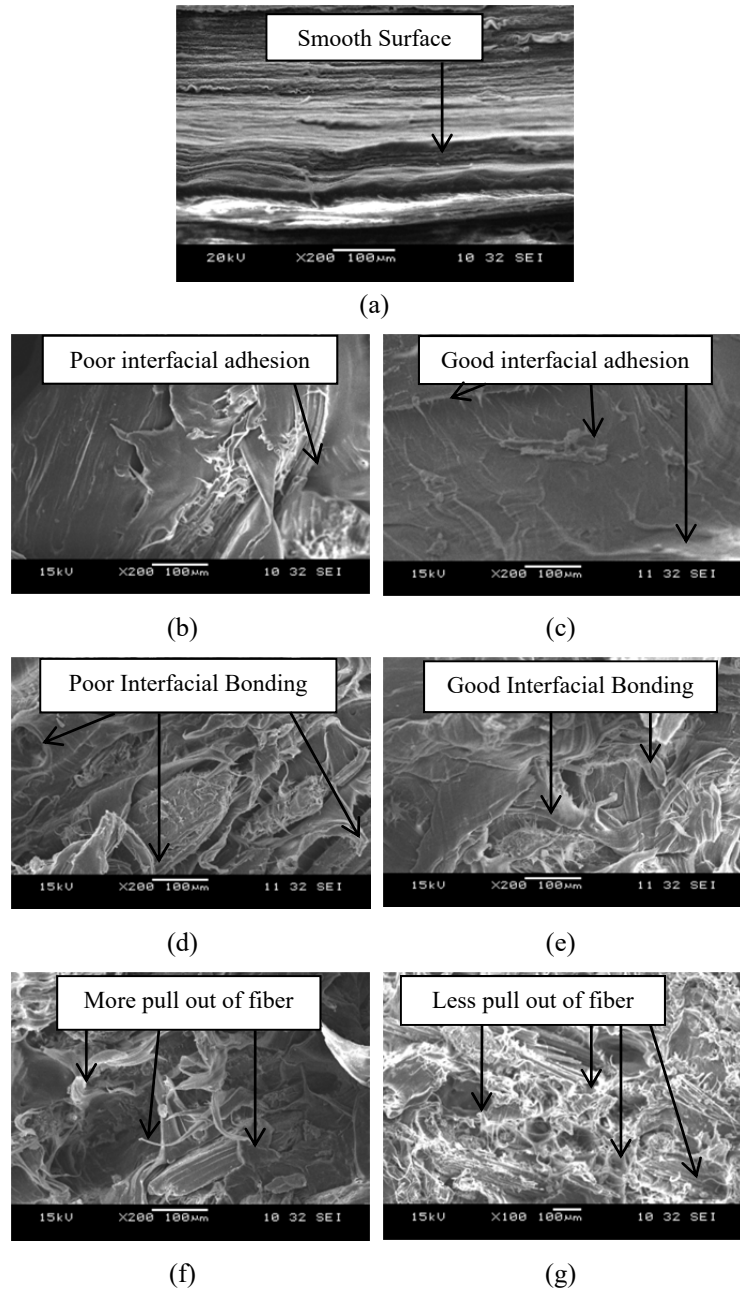


Figure 4: SEM micrographs of tensile fracture surfaces of rHDPE/WF composites of (a) rHDPE/WF 0phr, (b) rHDPE/WF 5phr, (c) rHDPE/WF 15phr, (d) rHDPE/WF 30phr, (e) rHDPE/WF_M 5phr, (f) rHDPE/WF_M 15phr and (g) HDPE/WF_M 30phr.

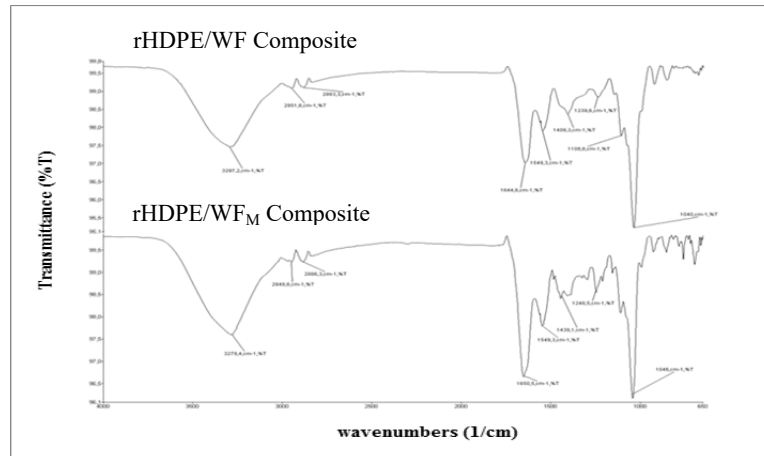


Figure 5: FTIR spectrum of rHDPE/WF and rHDPE/WF_M composites.

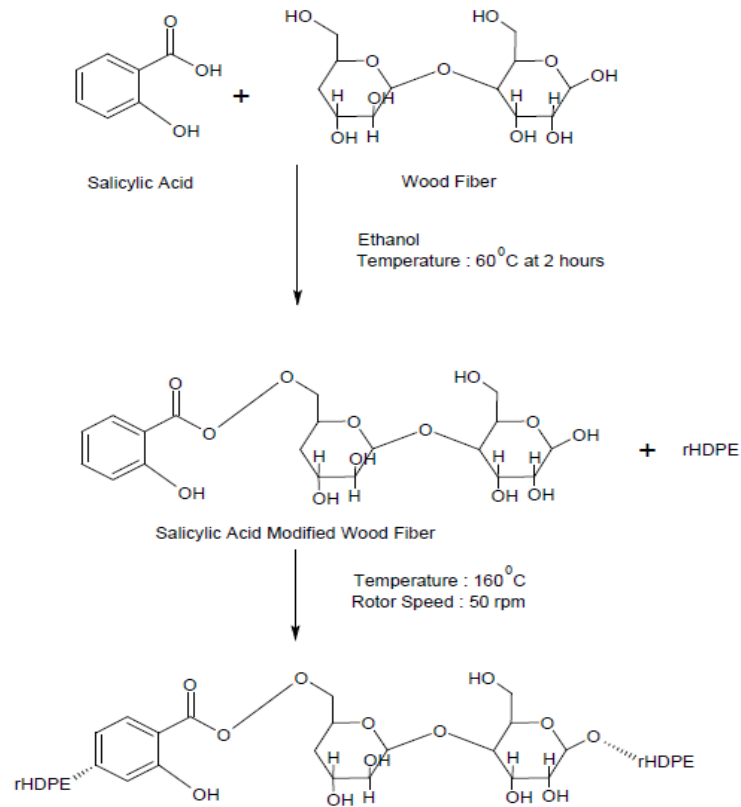


Figure 6: Propose interaction of salicylic acid modified WF with rHDPE phases.

3.4 Water Absorption

Figure 7 shows the effect of fibre loading on the equilibrium water absorption (after 42 days) of the rHDPE/WF and rHDPE/WF_M composites. As seen from Figure 8, the water absorption of the rHDPE/WF and rHDPE/WF_M composites increased with the filler load. Note that the equilibrium water absorption also generally increased when more reinforcing materials were used, which can be attributed to the hydrophilic nature of lignocellulose-based materials. This result agrees with the finding of Ahmad et al.,¹² who used bagasse flour to reinforce rHDPE to make composite material. Because they are lignocellulosic, natural fibres are highly hydrophilic in nature and are permeable to water. Incorporating lignocellulosic filler into polymeric composites generally increases the rate of water sorption by causing the formation of hydrogen bonds between water and the hydroxyl groups of the cellulose, hemicellulose and lignin in the cell wall.¹³ The rHDPE/WF_M composite absorbed less water than the rHDPE/WF composite. As a result of the chemical coupling agent, the hydroxyl (O-H) groups of the WF reacted with the salicylic acid, which, in turn, interacted with the polymer matrix and, therefore, a good fibre/matrix interaction was established.

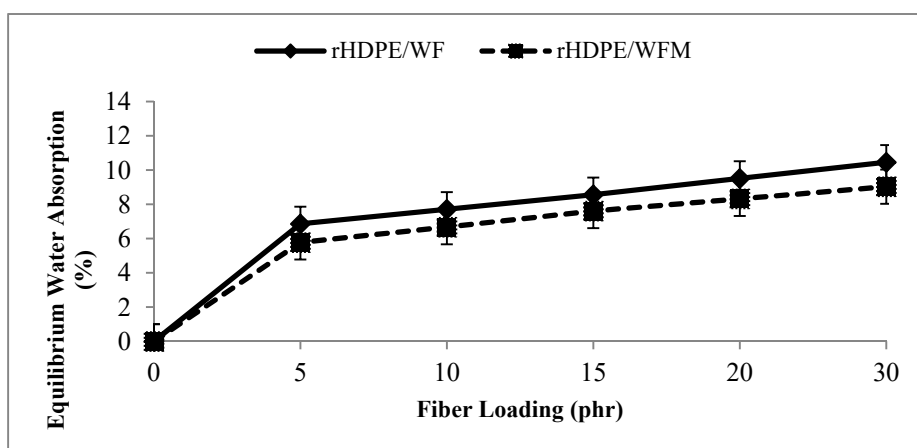


Figure 7: Effect of filler loading on equilibrium water absorption of rHDPE/WF composites and rHDPE/WF_M composites.

3.5 Thermal Degradation using TGA

Figures 8 and 9 show the thermogravimetric curves of the rHDPE/WF and rHDPE/WF_M composites (treated with salicylic acid and ethanol) under different fibre loads. Table 2 shows the temperature at which 50% of the weight is lost ($T_{-50\%wt}$) and the residual mass for both of the composites. The degradation

temperatures of both of the composites were lower when 50% of their weight had been lost than that of the rHDPE matrix due to the degradation of the WF at a lower temperature. However, the residual mass of the rHDPE/WF and rHDPE/WF_M composites increased with the WF load, indicating that the residue consisted primarily of the decomposition products of the wood fibre. When the two composites were compared under the same fibre load, the rHDPE/WF_M composite had a higher T_{-50%wt} because WF treated with salicylic acid and ethanol has better thermal resistance than untreated WF. The higher residual mass also indicated that the rHDPE/WF_M composite was more thermally stable than the rHDPE/WF composite. This might be due to the presence of good interfacial adhesion between the fibre and rHDPE phases as a result of the uniform dispersion of the fibres throughout the rHDPE matrixes. Well-dispersed fibres create a barrier against the release and volatilisation of gases during thermal degradation. This result may also be attributed to an adsorption effect of these gases at the fibre surface, which slowed the composites' decomposition. The presence of salicylic acid had a considerable effect on the thermal degradation behaviour of the composites; it promoted and increased their thermal stability due to better interactions in the rHDPE/WF_M composite, which is evident from the SEM observations.

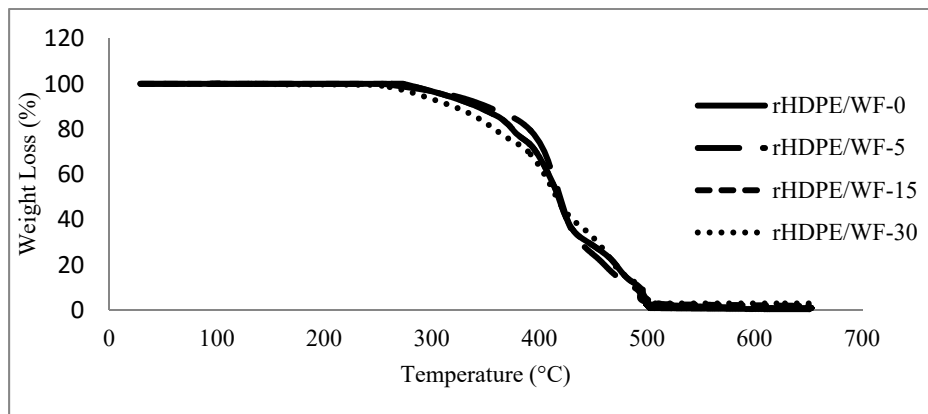


Figure 8: TG thermogravimetric of rHDPE/WF composites at different fiber loading.

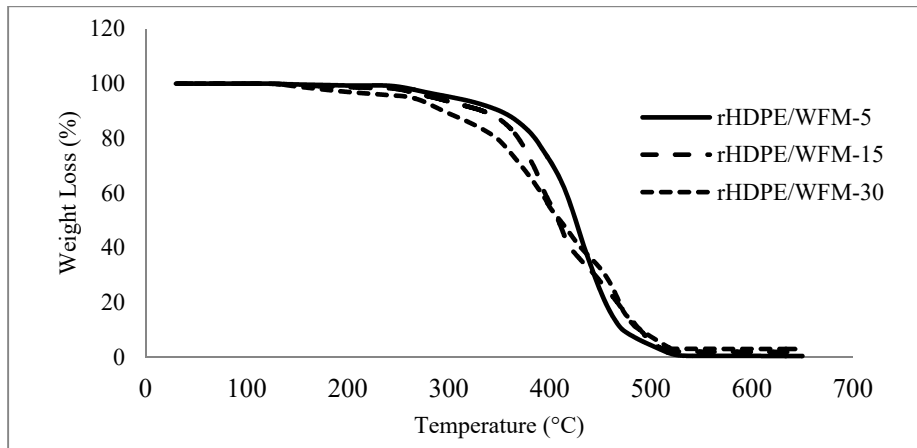


Figure 9: TG thermogravimetric of rHDPE/WF_M composites at different fiber loading.

Table 2: Data of T_{-50%wt} and residual mass of rHDPE/WF composites and rHDPE/WF_M composites with different of fiber loading.

Blend composition	T _{-50%wt} (°C)	Residual mass (%wt)
rHDPE	434.52	0.269
rHDPE/WF-5	419.17	0.284
rHDPE/WF-15	417.59	0.604
rHDPE/WF-30	415.86	1.063
rHDPE/WF _M -5	425.57	0.451
rHDPE/WF _M -15	418.33	1.066
rHDPE/WF _M -30	416.13	1.364

4. CONCLUSION

The effects of the chemical modification of WF with salicylic acid and ethanol on the tensile properties, water absorption, morphology, and thermal degradation of rHDPE/WF composites were evaluated. The rHDPE/WF_M composite had a higher tensile strength, elastic modulus, resistance to water absorption, and thermal stability and a lower elongation at break than the rHDPE/WF composite. These results were due to the better interfacial adhesion between the wood fibre and rHDPE phases observed in the SEM-based studies of their morphologies.

5. ACKNOWLEDGEMENT

The authors would like to thank Universiti Malaysia Perlis for financial support provided through University Fund 9007-00201.

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