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The Curing Characteristics and Mechanical Properties of Wood Sawdust/Carbon Black Filled Ethylene Propylene Diene Rubber Composites

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ABSTRACT

In this research work, ethylene propylene diene rubber (EPDM) composites were prepared by incorporating wood sawdust and carbon black on a 2 roll mill. The effect of wood sawdust content on the curing characteristics and mechanical properties of EPDM composites were studied. When the size of wood sawdust was fixed, it was found that wood sawdust content had no effect on scorch time. The cure time, minimum torque and maximum torque increased with increasing wood sawdust content. Increasing the wood sawdust content tended to increase the hardness of the composites, but the tensile strength and elongation at break decreased, heat ageing resistance and ozone resistance slightly decreased. Moreover, the types and concentrations of coupling agents were compared between silane Si69 and epoxidized natural rubber, ENR-50 (50 % mol epoxide groups) on the mechanical properties of EPDM composites. It was found that a silane Si69 concentration of 2.0 wt % of wood sawdust improved the mechanical properties of the EPDM composites but ENR-50 was not able to improve interfacial adhesion between the wood sawdust and EPDM matrix.

Keywords: Wood sawdust, ethylene propylene diene rubber, coupling agent, composites

INTRODUCTION

Manufacturers and engineers have researched new materials and improved processes to manufacture better products, and thus maintain their competitive edge and increase their profit margins. Wood-Polymer composites (WPC) are being used in a large number of applications in automotives. The WPC identified for the application of green-composites, the replacement of fiberglass and steels which are automotive components. They are used in under-the hood applications such as rubber fender aprons and mudguards. It has many advantages such as mechanical strength, reduced material weight, energy/fuel consumption and lower production costs. Furthermore they may improve passenger safety and shatterproof performance under extreme temperature change [1]. However, it is well known that a different surface property between the fibre and the matrix, i.e. the former is highly polar and hydrophilic while the latter is, generally, non-polar and relatively hydrophobic. The surface modifications of the fibres improve the fibre/polymer compatibility and their interfacial adhesion [2]. Several strategies for surface modification aimed at improving the compatibility between cellulose fibres and polymer matrices were recently reviewed [3]. The chemical modification using coupling agents bearing 2 reactive groups, 1 of which being likely to react with the OH functional group at the fibre surface, whereas the other one is left to copolymerize with the matrix, constituting a highly effective way of establishing covalent bonding between the fibres and matrix, thus leading to materials with high mechanical properties.

In this study, the composites of ethylene propylene diene rubber (EPDM) and wood sawdust were used as rubber mudguard application. They were prepared by varying the sawdust content in order to seek the automotive requirements by considering various properties such as cure characteristics, mechanical properties and morphological properties. A silane coupling agent and epoxidized natural rubber were used to improve the properties of the wood sawdust/carbon black filled EPDM rubber vulcanisates.

MATERIALS AND METHODS

Materials

Ethylene propylene diene rubber (Royalene 501) was purchased from the Cinnamon Co., Ltd. The average size of the wood sawdust used in this work was in the range of 150 - 250 μm which was obtained from wood-working process in Wood Science and Engineering Research Unit, Walailak University. The carbon black (GPF-N660) used in the form of fine powder was supplied by Thai Tokai Carbon Product Co., Ltd. Thailand. The silane coupling agent was a bifunctional silane, Bis(triethoxysilylpropyl) polysulfide (Si-69) was supplied by Behn Meyer Chemicals Co., Ltd. Thailand. The epoxidized natural rubber (50 % mol epoxide groups, ENR-50) was supplied by Dynathai Co., Ltd. Thailand. Parafinic oil (PHAZOL 7), ZnO (white seal), stearic acid, CBS and sulfur were purchased from the Cinnamon Co., Ltd. Processing aids (WB-215) were supplied by the Structol Company, America. TMTD and DPTT were purchased from the Reliance Technochem Co., Ltd.

Sawdust Treatment by Silane Coupling Agents

The silane concentration was 2.0 wt % and 5.0 wt % of sawdust and it was dissolved in ethanol. Wood sawdust fibres were dried prior to use by heating in oven at 80 °C for 24 h until the weight was constant with a moisture content about 3 %. They were mixed in silane solution for 2 h at 25 °C and were then dried at room temperature and heated at 80 °C for 24 h in order to promote the actual chemical coupling [4].

Compounding and Specimen Preparation

Wood sawdust fibres were dried in an oven at 80 °C for 24 h to expel moisture. Mixing was carried out on a conventional laboratory 2 roll mill (Yong Fong Machinery Co., Ltd. Thailand) according to ASTM D3184-80. The composites with various wood sawdust loadings and with different types and amounts of compatibilizers were prepared using the formulations given in **Tables 1** and **2**, respectively. The sheeted rubber compound was conditioned at a temperature of 23 ± 2 °C for 24 h in a closed container. The minimum torque, maximum torque, scorch time and cure time of the rubber compounds were determined using an Oscillating Disk Rheometer (GT7070S2 GOTECH Testing Machine, Inc., Taiwan) at a test temperature of 170 °C. The rubber compound was then compression moulded to a 90 % cure using a hydraulic press (Carver, Inc., USA) at 2500 kgf and 170 °C.

Mechanical Testing

The mechanical properties of the vulcanized rubber composites were estimated via tensile strength, elongation at break, hardness and compression set, in addition to thermal ageing resistance and ozone cracking resistance.

The tensile properties of vulcanized rubber composites were tested according to ASTM D412-98 using dumbbell-shaped specimens with a Universal Testing Machine (UTM) (model LR150K, Lloyd Instruments). The tensile testing speed was at 500 mm/min. A hardness durometer (Shore A) (model Digi test, Bareiss) was used for hardness tests in accordance with ASTM D2240-97. The compression set testing was conducted according to ASTM D395-03 method B. The thickness of the original specimen, before and after compression to 25 % of its original height at 125 °C for 22 h, was measured. The compression set was calculated using the equation below.

$$CS(\%) = \frac{t_0 - t_i}{t_0 - t_n} \times 100\,\% \qquad (1)$$

where

CS is the compression set as a percentage of the original
t_o is the original thickness of the specimen, mm
t_i is the final thickness of the specimen, mm
t_n is the thickness of the spacer bars used, 9.75 mm

Table 1 Formulation of composites.

Ingredient	Amount (phr, part per hundred rubber)							
	S0	**S20**	**S30**	**S40**	**SS30-2**	**SS30-5**	**SE30-2**	**SE30-5**
EPDM	100	100	100	100	100	100	100	100
Parafinic Oil	50	50	50	50	50	50	50	50
GPF-N660	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1
WB-215 [a]	2	2	2	2	2	2	2	2
CBS [b]	1	1	1	1	1	1	1	1
TMTD [c]	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
DPTT [d]	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Wood Sawdust	0	20	30	40	30	30	30	30
Silane Si69					0.6	1.5	-	-
ENR-50					-	-	0.6	1.5

Remark
[a] Struktol WB-215 is a process additive.
[b] *N*-Cyclohexyl-2-benzothiazolesulfenamide
[c] Tetramethylthiuram disulfide
[d] Dipentamethylene thiuram tetrasulfide

The effects of thermal ageing on the mechanical properties of the composites were investigated. The composite samples were aged in a hot air ageing oven with air circulating at 70 °C for 72 h. The test was conducted according to ASTM D573-00. The ozone testing chamber model OMS-LE (Suga, Japan) was used for static ozone testing performed according to JIS K6301-95. The conditions were 50 parts per hundred million (pphm) ozone at 40 °C under 20 % strain for 72 h. Photographs were taken using a digital microscope VHX-100K Keyence with magnification 10×.

Morphological Investigations

Dispersion of sawdust particles and interfacial wood sawdust-rubber adhesion were investigated using an SEM machine model JSM-5800LV- JEOL at 20 kV accelerating voltage. The composite fracture surfaces for examination were coated with gold. Before the fracture, the specimens were frozen in liquid nitrogen to impede the rubber deformation of the matrix and to get a well defined fibre-matrix interface. The poor dispersion of the composites presents holes and interfacial defects.

RESULTS AND DISCUSSION

Effect of Wood Sawdust Content

Curing Characteristic

Figure 1a shows the effect of wood sawdust loading on the scorch time and cure time for EPDM containing carbon black (GPF N-660) and various wood sawdust contents. Wood sawdust content had no effect on scorch time, but the cure time slightly increased with wood sawdust content. This could have been associated with an aggregation of wood sawdust particles as a result of hydrogen bonding, which retards crosslink formation in rubber according to Sombatsompop et al [5]. **Figure 1b** also indicates that the addition of wood sawdust increases the torque value of the EPDM compound. The increment in the torque with fibre content is due to the presence of more fibres which impart more restriction to the deformation of the rubber molecules and consequently increase the fibre-polymer composites stiffness [6].

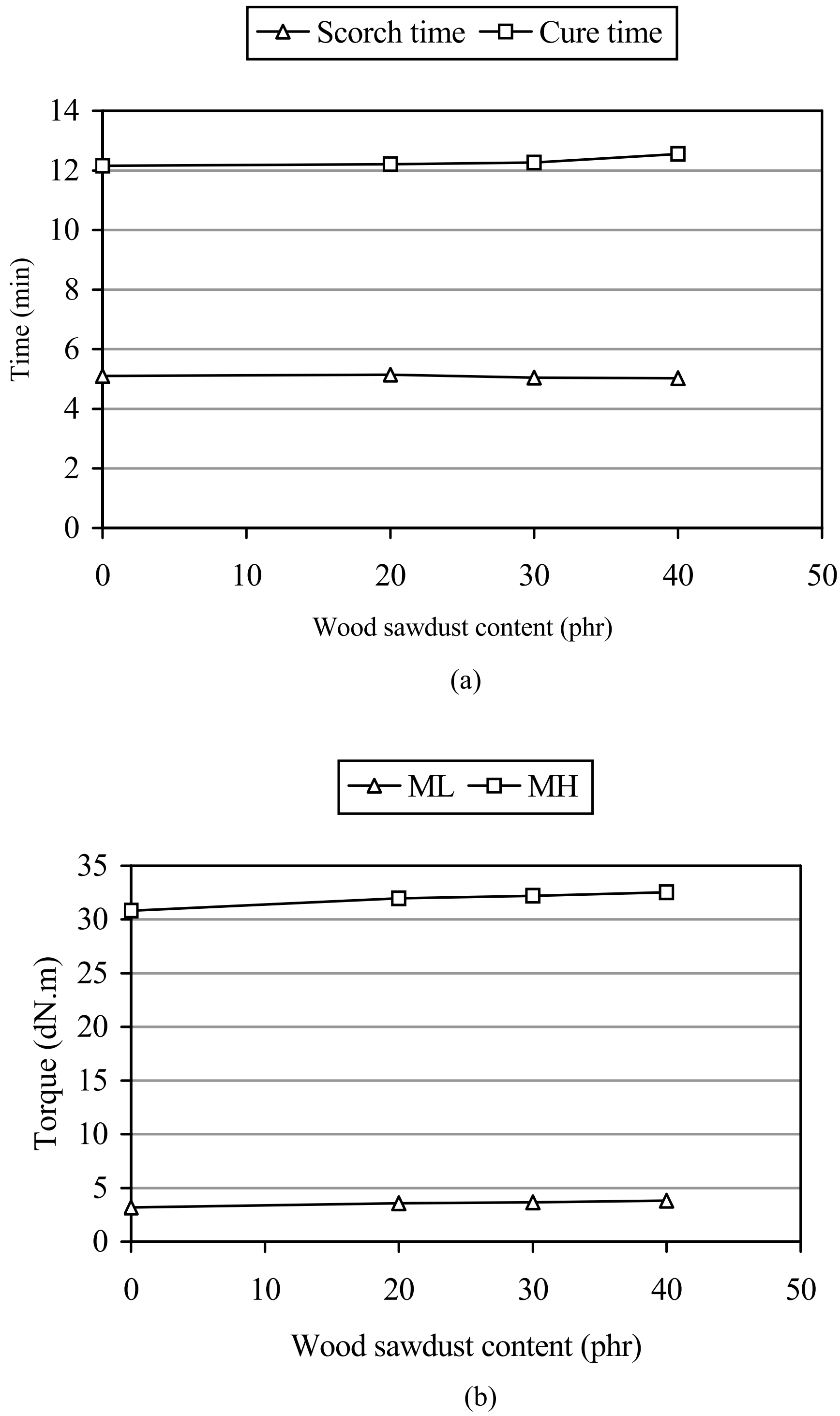
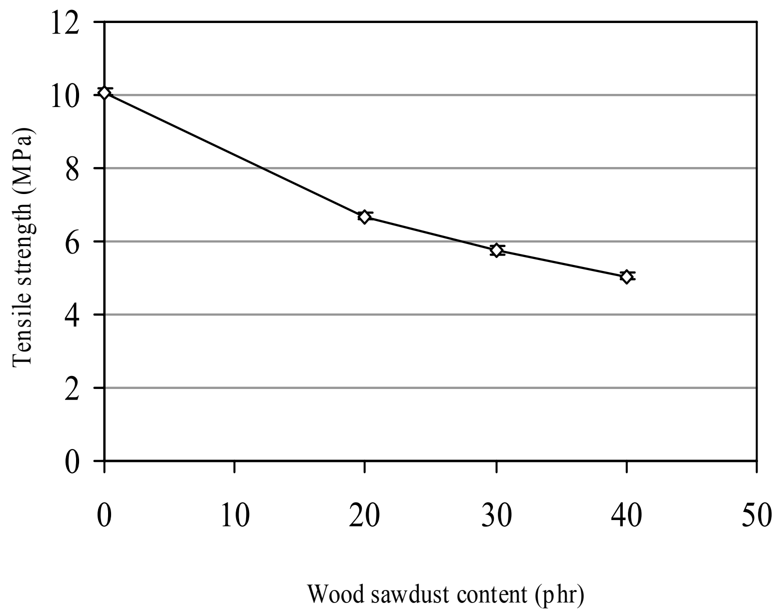


Figure 1 Effect of wood sawdust content on scorch time and cure time (a), minimum torque and maximum torque (b) of carbon black filled EPDM composites.

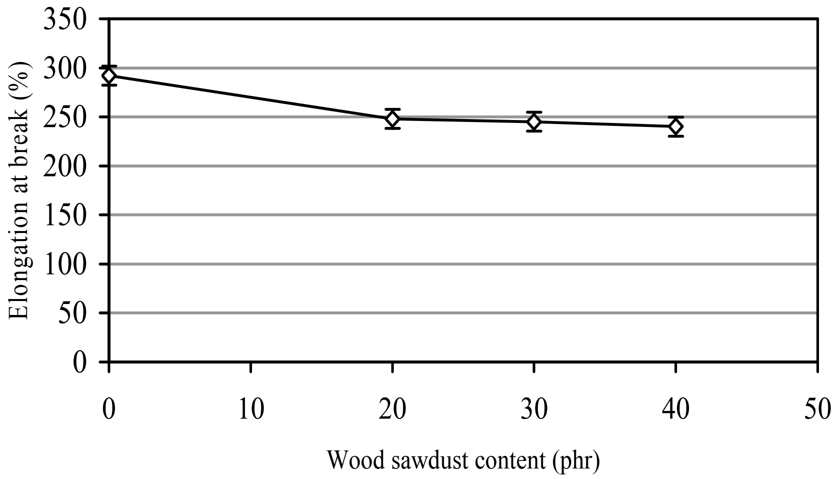
Mechanical Properties

Figures 2a and **2b** show the effect of wood sawdust loading on the tensile strength and elongation at break of the wood sawdust-EPDM composites. It can be seen that the tensile strength and elongation at break of the composites decrease with wood sawdust loading. The decrease in tensile strength and elongation at break of the composites by the addition of wood sawdust were attributed to the increase in interfacial defects between EPDM and wood sawdust phases due to the use of sawdust particles. The defect may be the result of poor dispersion or an agglomerate of the wood sawdust particles throughout the EPDM matrix due to incompatibility of the polar wood sawdust particles and the non-polar EPDM. Thus the strength of the composites decreases due to the inability of the filler to support stress transferred from the polymer matrix.

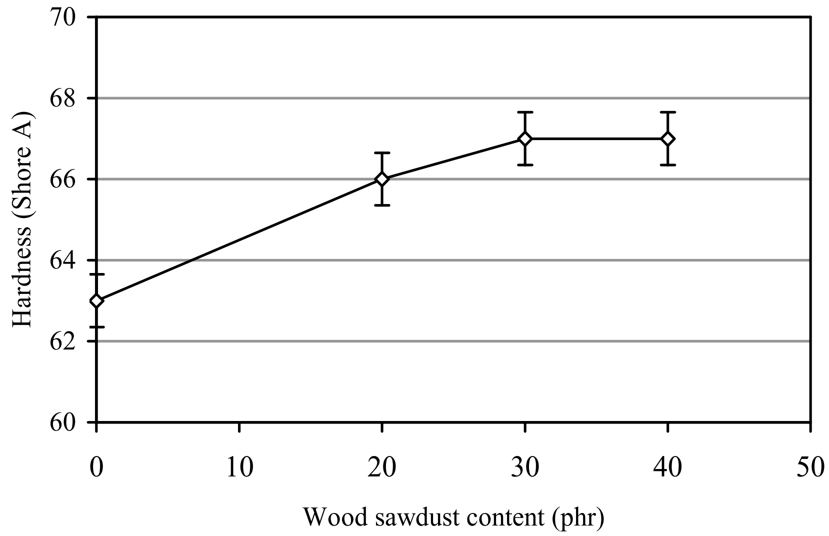
Figure 2c shows the effect of wood sawdust loading on the hardness of the composites. It can be seen that the hardness of the composites increases with wood sawdust loading. As more filler is incorporated into the rubber matrix, the elasticity and flexibility of the rubber chain is reduced, resulting in more rigid rubber composites [7].



(a)



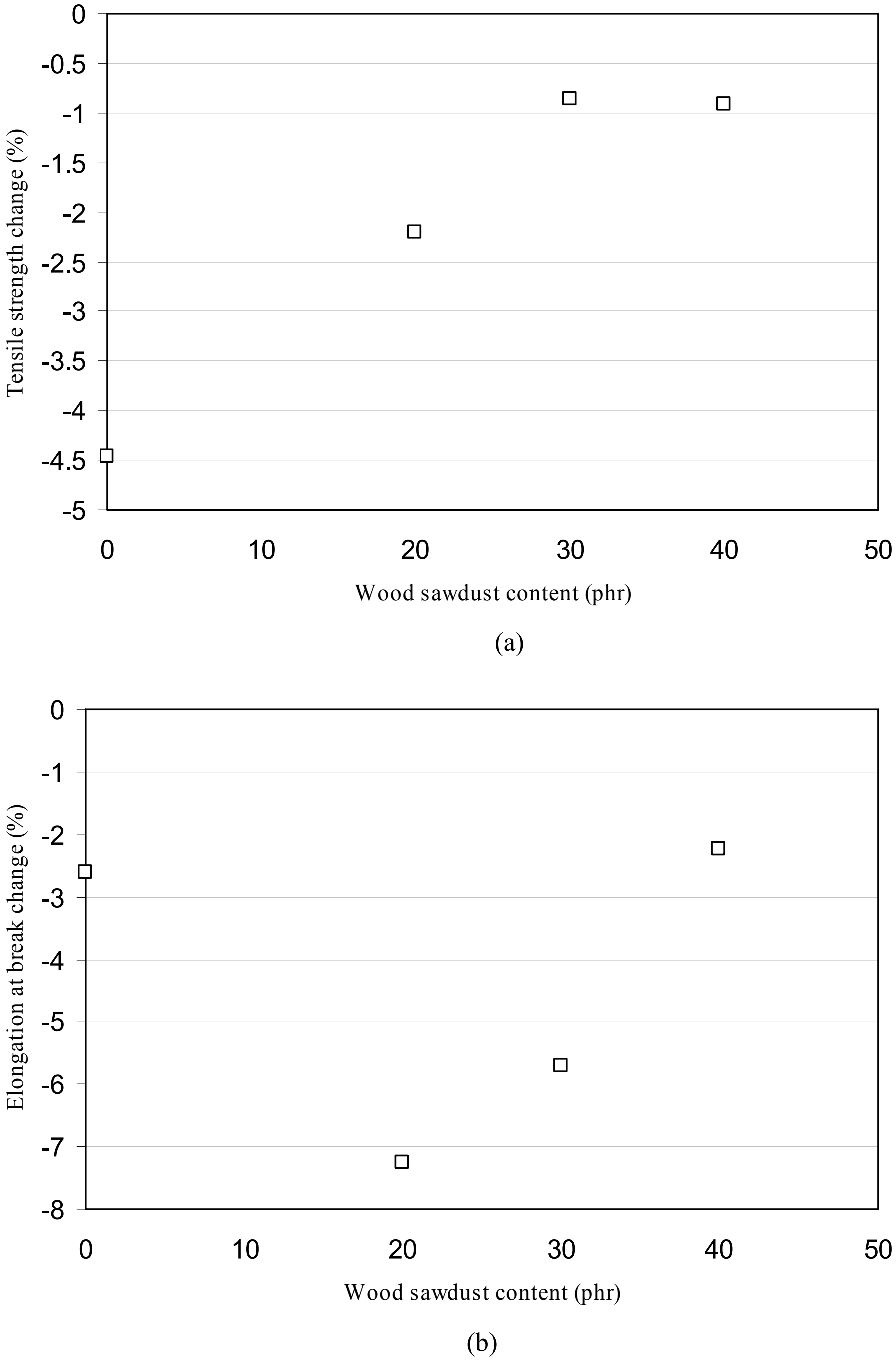
(b)

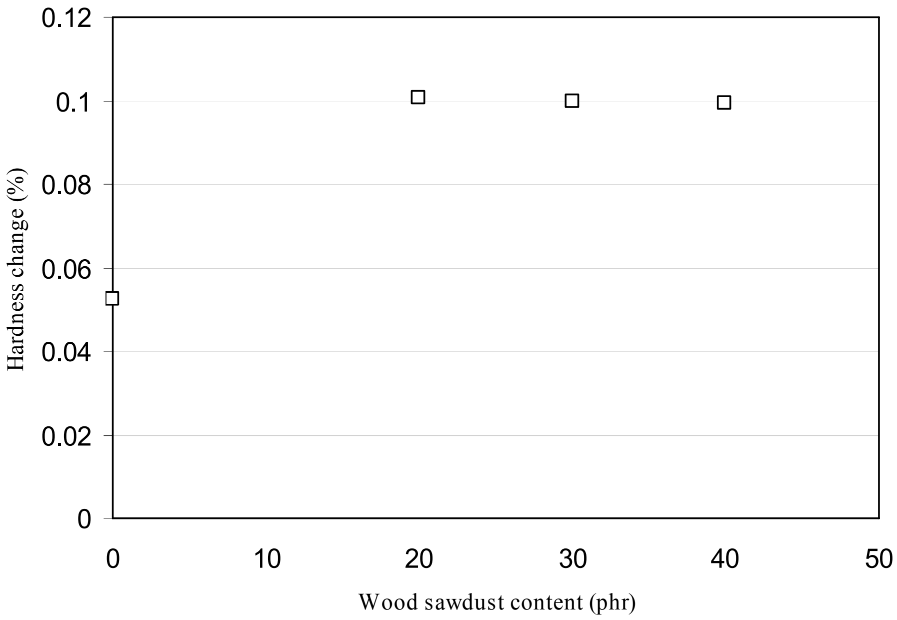


(c)

Figure 2 Tensile strength (a), elongation at break (b) and hardness (c) of carbon black filled EPDM composites with wood sawdust at various contents. Error bars indicate the standard deviation.

The percentage change after aging of tensile strength, elongation at break and hardness are shown in **Figures 3a - 3c** respectively. It can be seen that the reduction in tensile strength and elongation at break is observed for all aged samples, but the hardness slightly increases. This is simply attributed to the formation of additional crosslinks for the optimum cured samples. The increase in the crosslink density via postcuring reduces the mobility of the rubber chains. The influence of wood sawdust loading in EPDM composites on compression set is revealed in **Figure 4**. It tends to increase with increasing wood sawdust loading due to the high degree of compactness of the wood sawdust fibre networks.





(c)

Figure 3 Tensile strength change (a), elongation at break change (b) and hardness change (c) of carbon black filled EPDM composites.

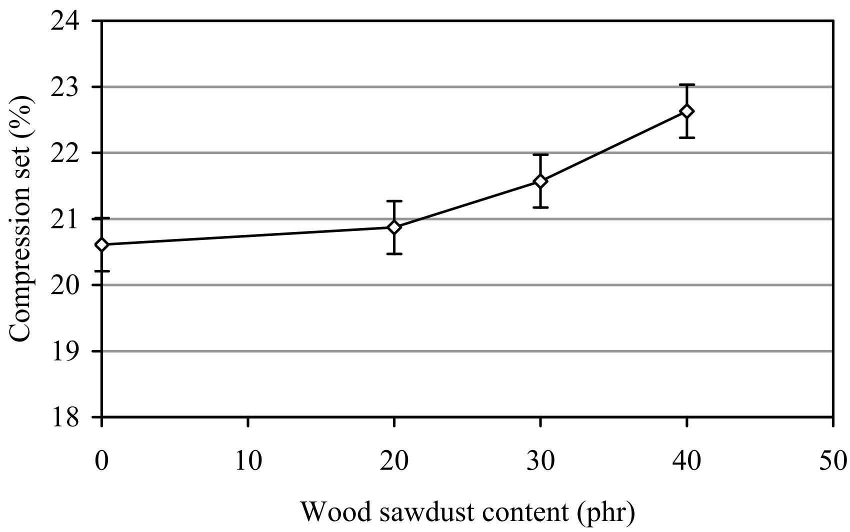


Figure 4 Compression set of carbon black filled EPDM composites with wood sawdust at various contents. Error bars indicate the standard deviation.

Figure 5 shows the effect of wood sawdust loading on the ozone cracking resistance of the EPDM composites after exposing the samples in ozonised air for periods of 72 h. In all samples, no cracks were observed, this is due to the fact that the highly ozone resistant EPDM which has a saturated backbone structure forms a protective layer during the processing of EPDM composites for under the hood applications.

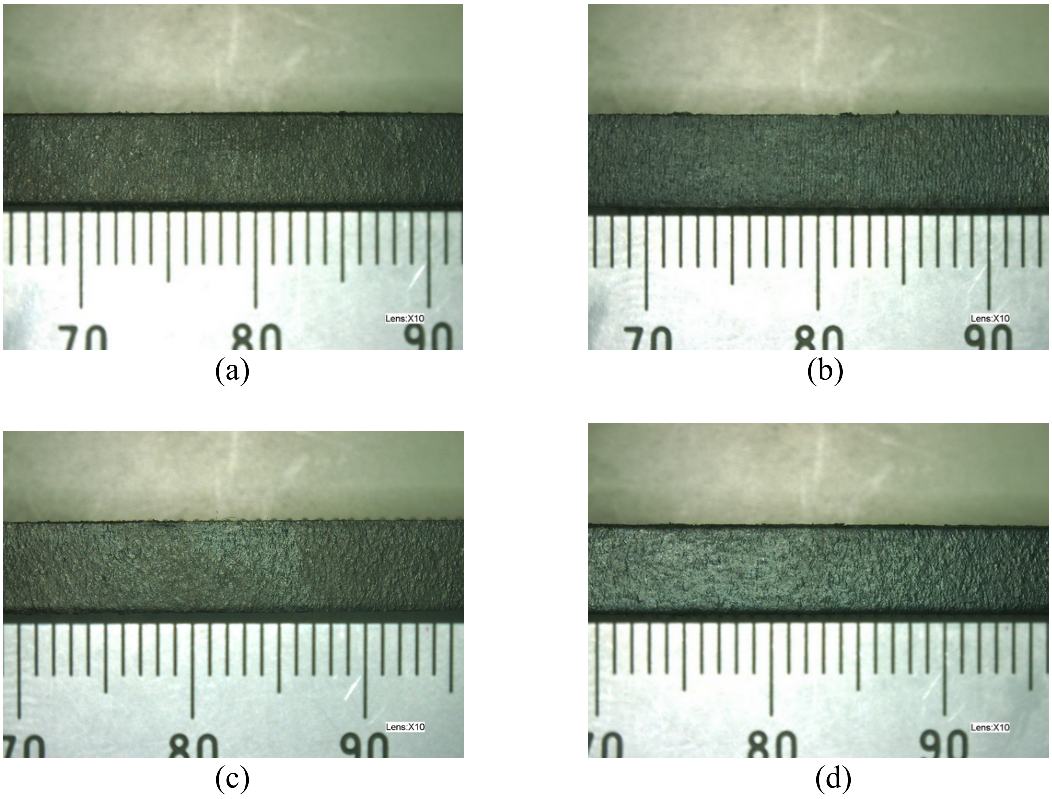
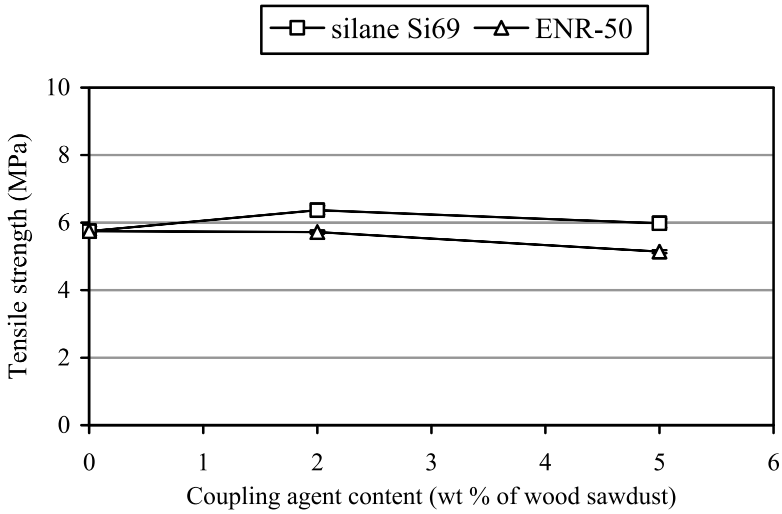


Figure 5 Optical photomicrographs of ozone exposed (72 h) EPDM composites (a) S0 (b) S20 (c) S30 and (d) S40.

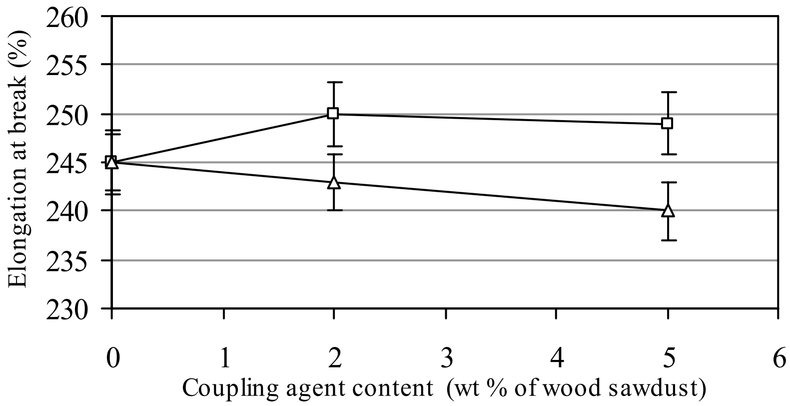
Effect of Coupling Agents on Mechanical Properties

In order to improve the mechanical properties of the wood sawdust/EPDM composites, silane Si69 and ENR-50 were introduced. In this work, the reason for selecting these contents of wood sawdust was the economic benefit of replacing the rubber volume. The silane concentration used was 2.0 wt % and 5.0 wt % of sawdust. They were selected for investigating the effect of concentration of the coupling agents on the composites properties.

Figures 6a - 6b show the tensile strength and elongation at break of composites added with silane Si69 and ENR-50. It can be seen that the tensile strength slightly increased to a maximum value around the silane Si69 concentration 2 wt % of wood sawdust. After that, the tensile strength tended to decrease with a further increase of the coupling agent content. In contrast, the tensile strength and elongation at break decreased with increasing ENR-50 content because ENR-50 was not able to improve the interfacial tension between the wood sawdust and EPDM due to the incompatibility of ENR and EPDM. **Figure 6c** shows the hardness of composites, it can be seen that the hardness increased with increasing coupling agent up to 2 wt % of wood sawdust. The silane coupling agent is believed to improve the surface functionality of wood sawdust to bond chemically to the rubber matrix. The fibre surface can be transformed to be hydrophobic with the ability to bind active groups of the polymer. Chemical bonds are formed between the hydroxyl groups of the fibres and silanyl groups of coupling agents. Consequently, rubber chemisorptions on the surface of fibres increase and the rubber exhibits increased hardness and strength [8].



(a)



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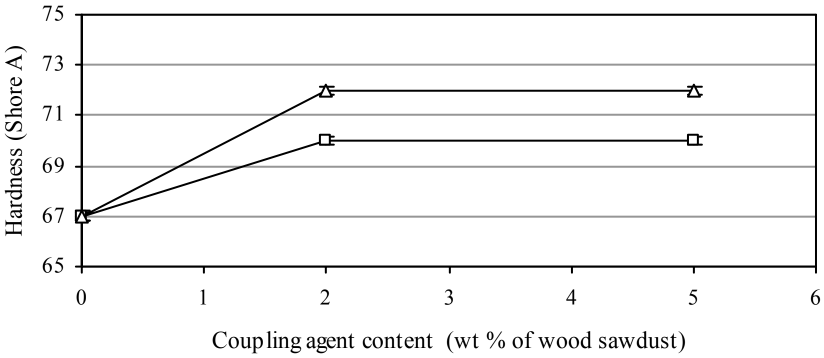
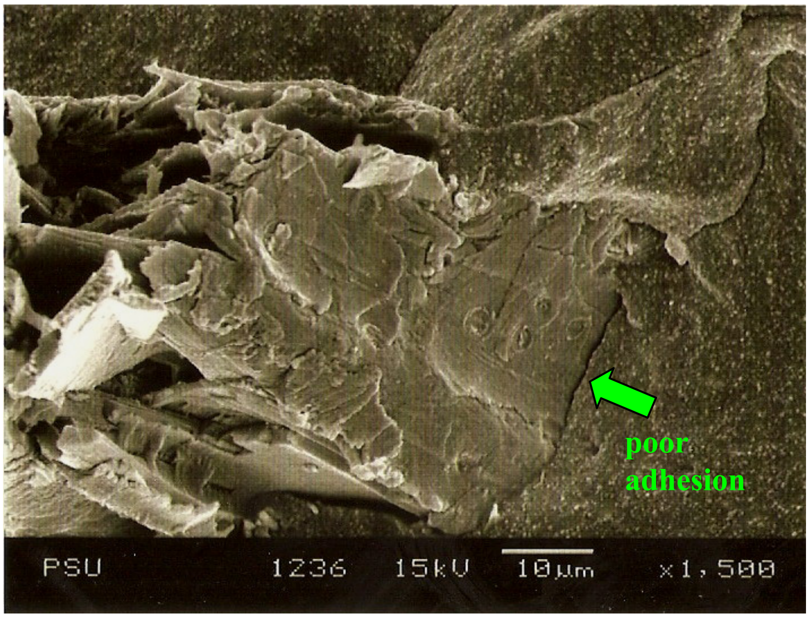


(c)

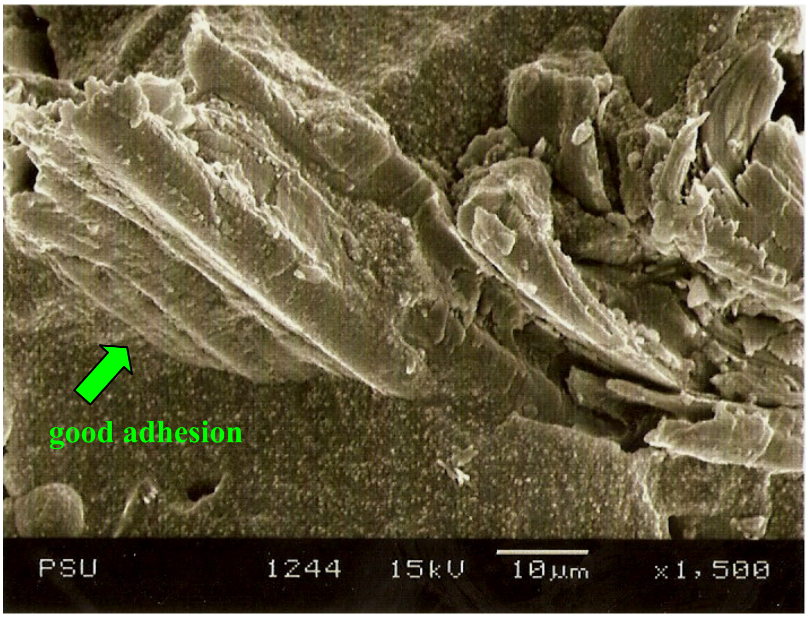
Figure 6 Effect of coupling agent type on tensile strength (a), elongation at break (b) and hardness (c) of EPDM composites with different contents of coupling agent. Error bars indicate the standard deviation.

Morphology

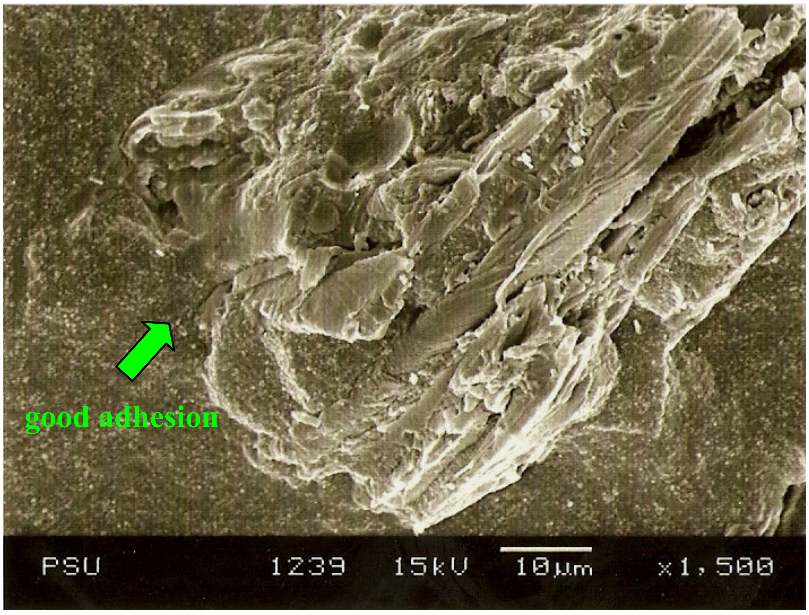
Figure 7a shows the tensile fracture surface of the wood sawdust fibres filled EPDM composites at 30 phr wood sawdust loading. It can be seen that there are many holes remaining after the fibres are pulled out from the rubber matrix and unwetted fibres on the surface particularly. However, for similar composites with silane Si69 present (**Figure 7b**), a better adhesion between the wood sawdust fibres and rubber matrix can be seen. Compared with previous coupling agents, the ENR-50 (**Figure 7c**) shows a good adhesion between the wood sawdust fibres and the rubber matrix. However it was not able to improve the mechanical properties of composites due to incompatibility of EPDM with ENR-50.


poor adhesion
PSU 1236 15kV 10µm x1,500

(a)


good adhesion
PSU 1244 15kV 10µm x1,500

(b)



(c)

Figure 7 SEM of carbon black filled EPDM composites with 30 phr wood sawdust without coupling agent (a) with 2 wt % silane Si69 (b) and with 2 wt % ENR-50 (c).

CONCLUSIONS

The cure time, minimum torque and maximum torque increased with increasing wood sawdust loading but the loading had no effect on the scorch time. The mechanical properties i.e. tensile strength, elongation at break and thermal ageing properties decreased with increasing wood sawdust loading. However, the hardness and compression set showed an opposite trend. The presence of the silane coupling agent, Si69 at concentration 2 % wt of wood sawdust improved the adhesion between the fibres and rubber matrix and consequently enhanced the mechanical properties of the composites. In contrast, ENR-50 was not able to improve the mechanical properties due to the incompatibility of EPDM with ENR-50.

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บทคัดย่อ

ประชิด สระโมพี และ ศรันยู บุญลอย

ลักษณะการวัลคาไนซ์และสมบัติเชิงกลของยางอีพีดีเอ็มกับเขม่าดำผสมขี้เลื่อยไม้

งานวิจัยนี้ได้เตรียมคอมโพสิทยางอีพีดีเอ็มโดยผสมขี้เลื่อยไม้และเขม่าดำบนเครื่องผสมสองลูกกลิ้ง จากนั้นศึกษาอิทธิพลของปริมาณของขี้เลื่อยไม้ต่อลักษณะการวัลคาไนซ์และสมบัติเชิงกลของคอมโพสิทยางอีพีดีเอ็ม ที่ขนาดขี้เลื่อยไม้เท่ากันพบว่า ปริมาณขี้เลื่อยไม้ไม่มีผลต่อระยะเวลาที่ยางจะเกิดการคงรูป โดยระยะเวลาการสุกตัวของยาง ค่าแรงบิดต่ำสุดและค่าแรงบิดสูงสุดจะเพิ่มขึ้นตามปริมาณขี้เลื่อยไม้ การเพิ่มปริมาณขี้เลื่อยไม้ทำให้ค่าความแข็งเพิ่มขึ้นแต่ความต้านทานต่อแรงดึงและความสามารถยืดขาดลดลง สมบัติด้านความต้านทานต่อความร้อนและความต้านทานต่อโอโซนลดลงเล็กน้อย นอกจากนี้ยังศึกษาชนิดและความเข้มข้นของสารเชื่อมโยงต่อสมบัติเชิงกลของคอมโพสิทยางอีพีดีเอ็ม โดยเปรียบเทียบสารเชื่อมโยงไซเลน Si69 และยางอิพอกไซด์เข้มข้น 50 เปอร์เซ็นต์โดยโมล พบว่า การใช้สารเชื่อมโยงไซเลน Si69 ที่ความเข้มข้น 2.0 เปอร์เซ็นต์โดยน้ำหนักของขี้เลื่อยไม้สามารถปรับปรุงสมบัติเชิงกลของคอมโพสิทยางอีพีดีเอ็มได้ แต่การใช้ยางอิพอกไซด์ไม่ช่วยเพิ่มการยึดติดระหว่างผิวของไม้กับยางอีพีดีเอ็ม

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