

The Effect of Dynamic Vulcanization on Properties of Rice Husk Powder Filled Polystyrene/Styrene Butadiene Rubber Blends

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ABSTRACT

The effect of dynamic cross-linking on processability, mechanical properties, water absorption, aging process and morphology of rice husk powder (RHP)/polystyrene (PS) / styrene butadiene rubber (SBR) blends were studied. The blends were prepared using a Brabender plasticoder at 170°C and rotor speed of 50 rpm. Dynamic vulcanization resulted in an increased in the tensile strength, impact strength and a decrease in percentage of elongation-at-break of RHP/PS/SBR composites. It was also found that dynamic cross-linking gives composites with better resistance to aging process and swelling in water through better dispersion of matrices and filler/matrix adhesion.

Key Words:

dynamic vulcanization;
rice husk powder; polystyrene;
styrene butadiene rubber;
thermoplastic elastomer composite.

INTRODUCTION

Blending of two polymers is a possible way to tailor their individual properties in a single material. Over the past two decades this method has undergone an extensive growth in production. One of them is known as TPE. Thermoplastic elastomers

(TPEs) are a combination of rubber and plastic. The material would perform processing characteristic of thermoplastics and technical properties of elastomers.

Polystyrene is characterized by poor impact behaviour because of its

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brittle material. The incorporation of elastomer particles offers a classical solution of these problems. The incorporation of fillers in TPEs produced a new class of material known as thermoplastic elastomer composites (TPEs composite). Fillers are incorporated mainly to improve service properties or to reduce material cost depending on the source of filler, type of filler, method of preparation and treatment.

Cross-linking or vulcanization is the process in which mainly polymer is converted from a plastic state to an elastic state or a hard rubber state. The process is brought about by linking of macromolecules at their reactive sites, thus forming a 3-dimensional network [1]. The best way to produce TPE's, which consists of cross-linked elastomer in melt processable plastic matrices, is by dynamic vulcanization. Dynamic vulcanization is a process of cross-linking the elastomer during its melt mixing with molten plastic [2]. It can improve properties such as mechanical properties [3], resistance to heat and resistance to attack by fluid [4]. It is quite obvious that the cross-link density of the dispersed rubber phase plays a key role in achieving higher strength [3-7].

In this work, the effect of dynamic vulcanization on processing, mechanical properties, water absorption, morphology, and influence of thermo-oxidative aging on tensile properties of rice husk powder (RHP) filled polystyrene (PS)/styrene butadiene rubber (SBR) blends is reported.

EXPERIMENTAL

Materials

Polystyrene used in this study was from Petrochemical (M) Sdn. Bhd., Johor, Malaysia (grade HH35) with a MFI value of 5.8 g/10 min at 200°C. Styrene butadiene rubber (Buna huls, 1502) and all rubber chemicals were obtained from Bayer (M) Ltd., Penang. The rice husk powders which have particle size in the range of 1.23-8.30 μm were obtained from Bernas Perdana Sdn. Bhd., Penang.

Compounding and Processing

The formulation used is shown in Table 1. The preparation of composite was carried out in a Brabender Plasticoder model PLE 331 at temperature of 170°C and rotor speed of 50 rpm for about 10 to 11 min.

Table 1. Formulation used in unvulcanized and dynamic vulcanized RHP filled PS/SBR blends.

Ingredient	Dynamic vulcanized system	Unvulcanized system
PS (php)	80	80
SBR (php)	20	20
RHP (php)	0, 15, 30, 45, 60	0, 15, 30, 45, 60
Curative system		
Zinc oxide (phr)	5	-
Stearic acid (phr)	2	-
CBS (phr)	2	-
TMTD (phr)	2.5	-
Sulphur (phr)	0.3	-

Note: (phr)-part per hundred rubber, (php)-part per hundred polymer.

Polystyrene was preheated for 2 min before rotor started and was melted in the mixer for 2 min. RHP was added to the molten PS and the mixing was continued for another 2 min. Then SBR was added as a last component and left for 4 min for further mixing. In dynamic vulcanized system, curative system is added after SBR loading and mixing continues for another 5 min. Mixing sequence is shown in Table 2. The torque development was recorded during mixing.

Mechanical Testing of the Composites

Tensile properties were tested with a Tensometric tensometer M 500 according to ASTM D 412 at 50

Table 2. Mixing sequences of components in preparation of the composites.

Unvulcanized system		Dynamic vulcanized system	
Time (min)	Operation	Time (min)	Operation
0	Loading of PS	0	Loading of PS
2	Rotor started	2	Rotor started
4	Addition of RHP	4	Addition of RHP
6	Addition of SBR	6	Addition of SBR
10	Dump	7	Addition of curative
		11	Dump

mm/min cross-head speed. The moulded samples of 1 mm thick were cut into standard test pieces using a Wallace die cutter. The tensile strength, elongation-at-break and Young's modulus were reported. Izod impact strength was measured on a Zwick testing machine operating with a 7.5 J pendulum (ASTM D256). A minimum of five samples was tested in each series.

Aging Studies

Thermo-oxidative aging was conducted in an air-circulating oven operating at 70°C for 7 days periods. After being cooled down and conditioned at room temperature in the desiccators, the dimensions of each specimen were measured. The tensile properties of these samples as a function of aging were determined using the procedures mentioned above.

Water Absorption Test

Specimens, having 1 mm thickness, were used for studying the water absorption. The samples were immersed in distilled water and the percentage weight change was determined until the equilibrium value was reached. After immersion in distilled water, specimens were removed at different times, wiped with tissue paper to remove excess water and weighed with an analytical balance with 0.1 mg resolution. The percentage of weight gain was then calculated as follows:

$$W_t = \frac{W_1 - W_0}{W_0} \times 100\%$$

Where, W_t is the percentage of weight gain, W_0 is weight of the dry sample and W_1 is weight of wet sample.

Morphology Study

Examination of the tensile fracture surfaces was performed using a scanning electron microscope model Leica Cambridge S-360. All the surfaces were examined after first sputter coating with gold to avoid electrostatic charging and poor image resolution.

RESULTS AND DISCUSSION

Processability

Figure 1 shows the torque versus time at different filler loadings which represent the processability of dynami-

cally vulcanized RHP/PS/SBR composites. Generally, it can be seen that the torque increases sharply as PS granules, are charged into mixer chamber after preheating for 2 min. PS undergoes melting as the mixing time increases which results in a drop of torque. When the second component (RHP) was added to the molten PS (4th minutes), it shows sudden drop in torque due to the instant lubricant action from the fine RHP particles. The torque then steadily increases as the RHP is dispersed in PS matrix. Once the dispersion was completed, the mixture was homogenized and the torque started to decrease. SBR was added as a last component to RHP/PS mixture at the 6th minute. It can be seen that the torque increases due to the higher viscosity of SBR and this was contributed to the higher viscosity of the mixture. Then the torque again gradually decreases as a mixing time continues. At 7th minute of mixing process the curative was added. It can be seen that the sudden drop in torque occurs after the addition of curatives due to its lubricating effect. A similar observation was reported by Ismail et al. [4] in their study on dynamic vulcanization of rubber wood filled polypropylene/natural rubber blends. The torque then increases immediately as cross-linking takes place until a stable torque value is achieved. For unfilled samples the drop occurs earlier since the processing time excludes the mixing time of RHP. Figure 2 shows the stabilization torque at the end of mixing process (10 min) versus filler loading for uncured and dynamic cured composites. It can be seen that the torque values are higher in cured samples

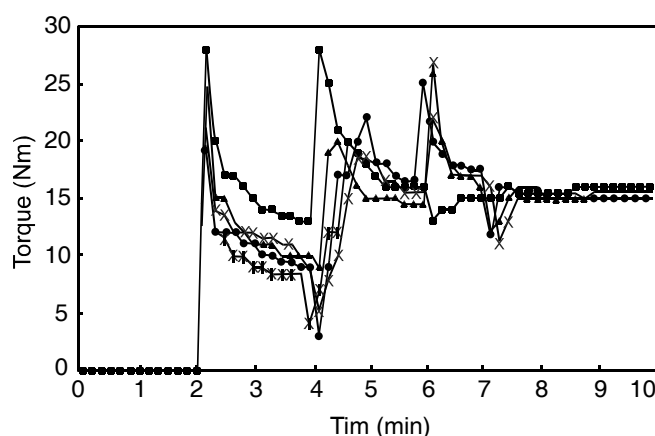


Figure 1. Brabender torque-time curves for dynamically cured RHP/PS/SBR composites with different filler loadings. (—■—) unfilled; (—▲—) 15 php; (—×—) 30 php; (—*—) 45 php; (—●—) 60 php.

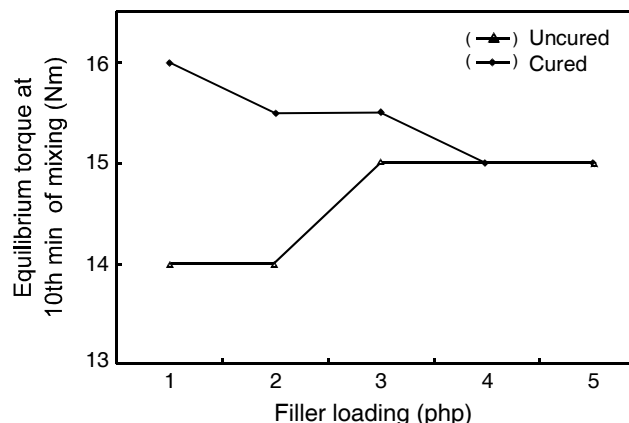


Figure 2. Equilibrium torque at 10th min for cured and uncured RHP/PS/SBR composites.

compared to uncured samples particularly below 45 php of filler. It should be noted that increasing in filler loading increases the viscosity of the composites thus higher torque values were registered as in uncured samples. On the other hand, curing increases the torque values because of the formation of cross-linked rubber particles which increases the viscosity thus giving higher resistance to brabender torque [3]. In dynamically cured RHP/PS/SBR composites the effect of cross-linked rubber particles is compensated by the effect of filler loading. With the increasing filler loading the effect of cross-linked rubber particles is almost negligible due to lesser amount of rubber in each composition thus giving less resistance to Brabender torque due to less cross-linked rubber particles. That is why the stabilization torque decreases as filler loading increases in cured composites and similar torque values were registered at higher filler loading (40-60 php), since the cured composites are dominant by the effect of filler loading than the cross-linked rubber particles. Siriwardena et al. [8] reported the similar observation in the system of EPDM/PP/WRHA composite. From this observation it clearly indicated that dynamic curing does not affect the processability of RHP/PS/SBR composites at higher RHP loading (40-60 php).

Mechanical Properties

Tensile Properties

Figures 3, 4 and 5 show the tensile properties as a function of filler loading for cured and uncured RHP/PS/SBR composites. The plot shows that cured samples have higher tensile strength and slightly lower elongation-at-break compared to uncured samples.

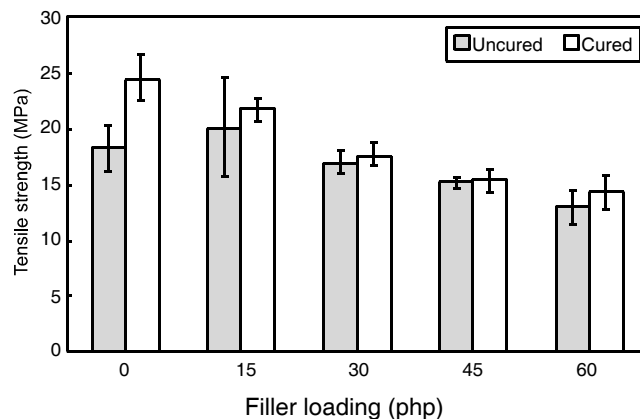


Figure 3. The effect of filler loading on the tensile strength of cured and uncured RHP/PS/SBR composites.

This indicates that higher applied stress is required to rupture the composites consisting of cross-linked rubber, thus increasing the tensile strength. Therefore, from this observation it can be concluded that the vulcanization processes of SBR are not affected by the existence of RHP as filler. The slightly lower elongation-at-break values for cured samples reveal that cross-linked rubber particles decreased the deformability of a rigid interface between filler and the matrix material thus maintaining the brittle fracture behaviour of the composites. Normally dynamic curing will transform the thermoplastic elastomer material (TPE) into a thermoplastic vulcanizate (TPV), which have the properties of vulcanized elastomer [8]. But, in this work the RHP/PS/SBR composites still maintain the brittle behaviour of plastic materials after curing since the composites are PS dominant system. As it can be seen

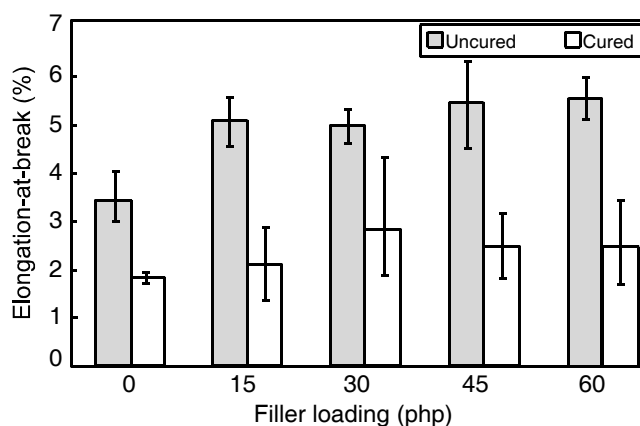


Figure 4. The effect of filler loading on the elongation-at-break of cured and uncured RHP/PS/SBR composites.

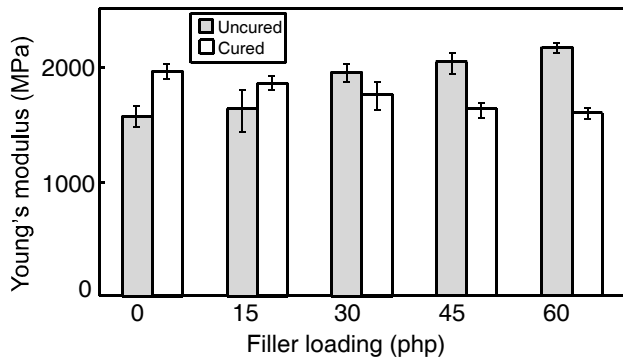


Figure 5. The effect of filler loading on the Young's modulus of cured and uncured RHP/PS/SBR composites.

in Figure 5, Young's modulus is higher for cured samples until 15 php filler loading. At higher filler loading (30-60 php) the Young's modulus is lower for cured samples compare to uncured samples. This may be due to the morphology of the composites itself [8], where at higher filler loading the morphology of the composites could be destabilized due to less wetting of RHP by matrix especially rubber chains since rubber have become extra rigid particles in the form of vulcanized elastomer particles in addition to RHP particles that exist in the PS matrix [7]. There may be no sufficient matrix to carry both filler particles and vulcanized rubber particles in the composites thus destabilizes the macrostructure of the composites.

Impact Strength

The Izod impact strength versus filler loading for cured and uncured RHP/PS/SBR composites are shown in Figure 6. From the plot it can be seen that the impact strength decreases sharply at 15 php of filler loading. After this

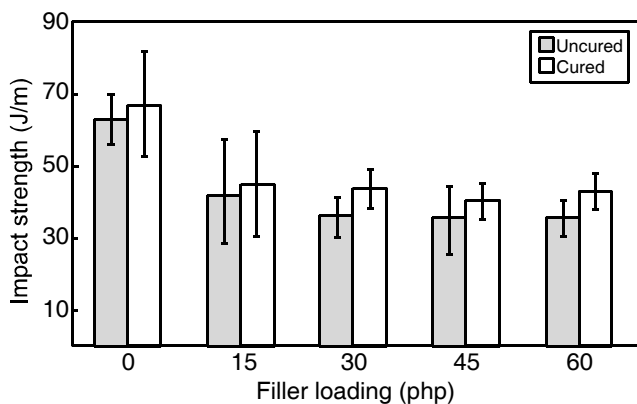


Figure 6. The effect of filler loading on the impact strength of cured and uncured RHP/PS/SBR composites.

loading the impact strength decreases slightly with increasing filler loading. Dynamic cross-linked samples show higher impact strength compared to uncured samples at each composition. Increase in filler loading will weaken the interfacial regions. The fillers cannot resist crack propagation as effectively as the polymer region and hence the impact strength is reduced [9,10]. Uncured samples having rubber droplets formed during blend preparation, coalesce during cooling which increases the irregularity size rubber domains that are larger than the critical size desired for impact toughening. This size enlargement and irregularity also reduce the stress concentration sites and the interfacial adhesion thus giving a low impact value [5]. Whereas, in the cured samples, rubber particles are cross-linked and their size is greatly reduced [5,7]. The discrete particles inhibit the probability of rubber cohesion during cooling thus improve the interfacial adhesion, which is more effective to resist the crack propagation when impact is applied to the samples compared to uncured samples

Water Absorption

Figure 7 shows the plots for percentage of water absorption versus time immersed in water for cured and uncured samples at different filler loadings. It can be seen that the percentage of water absorbed increases with increasing filler loading. This was due to the increase in polarity of the composites as filler loading increases. The cellulosic fillers are known as a hydrophilic material compared to polymer matrices

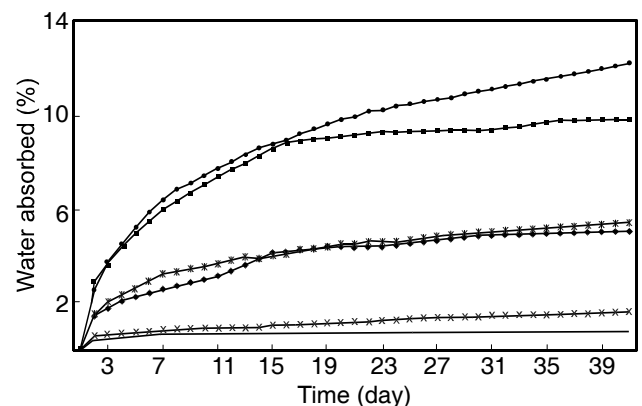


Figure 7. Absorption of water at ambient temperature in cured and uncured RHP/PS/SBR composites.

(-x-) uncured-0; (-*) uncured-15; (-●) uncured-45; (-○) cured-0; (-◆) cured-15; (-■) cured-45.

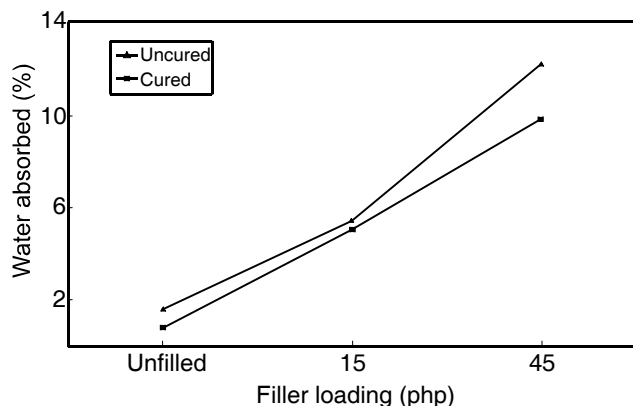


Figure 8. Equilibrium swelling at 40 days immersion in water for cured and uncured RHP/PS/SBR composites.

which are hydrophobic in nature [11]. The plots also show that cured samples reach saturated point earlier than uncured samples and the equilibrium state (Figure 8) in cured samples is lower compared to uncured samples. This was due to the compact structure (stiffer) in cured samples (Figures 9 and 10) compared to uncured samples (Figures 11 and 12) as shown in SEM micrographs. As mentioned in morphology study, dynamic cross-linking improved filler/matrix adhesion and matrix distribution which reduce void and gap between the filler and matrix (Figures 9 and 10), thus reduced the penetration of water molecules into cured samples. H. Ismail et al. [5] found that, as cross-linking density increases within the NR phases, the blend becomes stiffer and less penetrable by the water molecules.

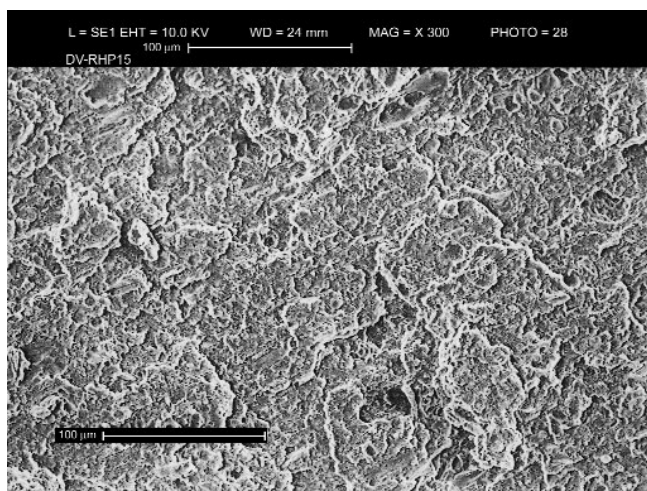


Figure 9. Scanning electron micrograph of tensile fracture surface of cured RHP/PS/SBR composite (15 php of RHP) at magnification of 300X.

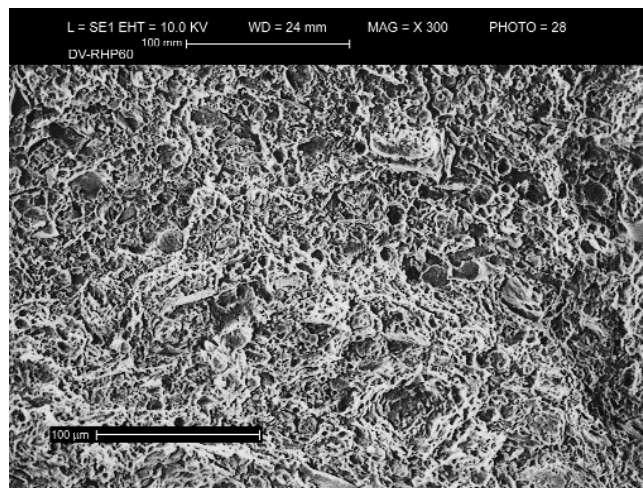


Figure 10. Scanning electron micrograph of tensile fracture surface of cured RHP/PS/SBR composite (60 php of RHP) at magnification of 300X.

Morphology

Examination of the fractured surfaces of the composites by SEM shows the difference of two systems (cured and uncured). The cured samples (Figures 9 and 10) have smooth surfaces compared to the uncured samples (Figures 11 and 12), which have rough surfaces. These indicated that the cured samples have better dispersion of matrices compared to uncured samples. It can also be seen that in cured samples the fillers are embedded in the PS/SBR matrices and less filler pull-out (Figure 10). However, in uncured samples, most of the filler protrude and more filler bundles pull-out from PS/SBR matrices can be seen (Figure 12). This indicated that the filler/matrix adhesion has been

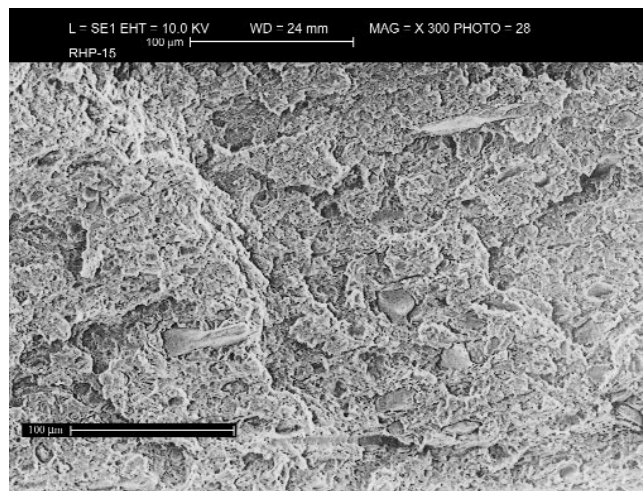


Figure 11. Scanning electron micrograph of tensile fracture surface of uncured RHP/PS/SBR composite (15 php of RHP) at magnification of 300X.

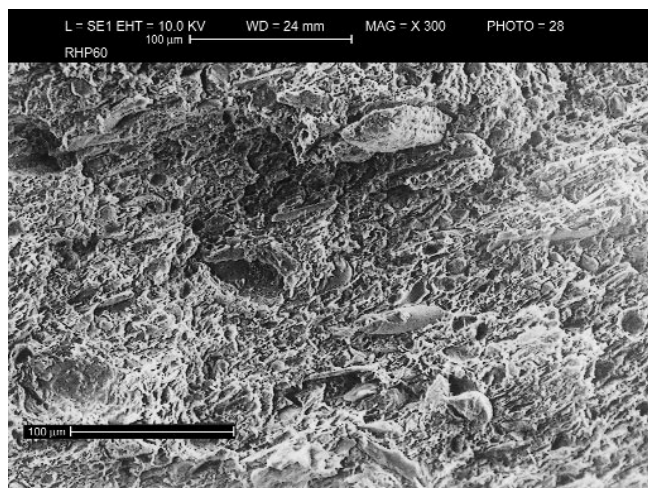


Figure 12. Scanning electron micrograph of tensile fracture surface of uncured RHP/PS/SBR composite (60 php of RHP) at magnification of 300X.

improved by cross-linking, the rubber phase and so it supported the tensile properties result of dynamically cured RHP/PS/SBR composites as illustrated in Figure 3.

Effect of Thermo-Oxidative Aging

Tensile Properties

Figures 13, 14 and 15 show the influence of thermo-oxidative aging on the tensile properties of dynamically cured RHP/PS/SBR composites as a function of filler loading. It can be seen that tensile strength decreased and Young's modulus increased after thermo-oxidative aging, whereas, the value of elongation-at-break shows no significant difference before and after aging which indicated that the composite still maintain the brittle behaviour of composites material. A slight reduction in tensile properties after aging could be explained by the degradation of matrices in the com-

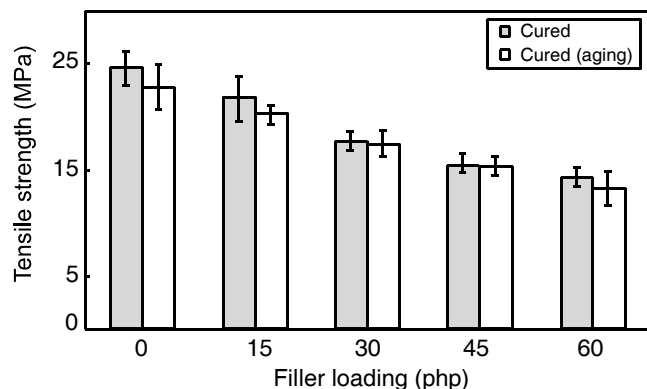


Figure 13. The effect of thermo-oxidative aging (at 70°C for 7 days) on tensile strength of cured RHP/PS/SBR composites.

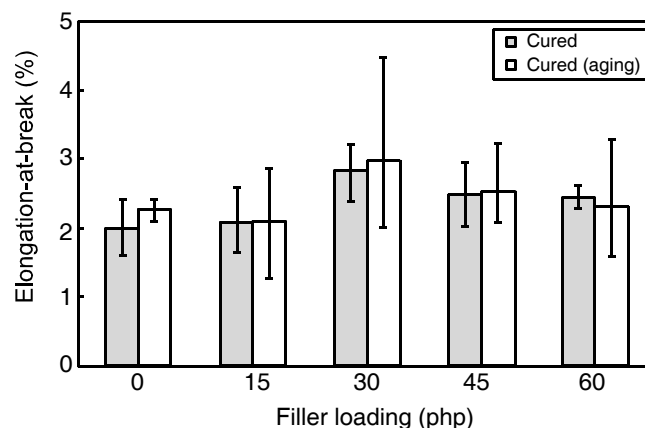


Figure 14. The effect of thermo-oxidative aging (at 70°C for 7 days) on elongation-at-break of cured RHP/PS/SBR composites.

posites during aging process. At any filler loading, the Young's modulus of aged samples is slightly higher than the unaged samples. This increment may be due to the increasing stiffness that occurred in matrices and RHP after prolonged aging.

The comparison of tensile strength between the aged RHP/PS/SBR composites and the aged dynamically cured RHP/PS/SBR composites is shown in Figure 16. It shows that the tensile strength for aged cured composites is higher than the aged uncured composites. At lower filler loading (0-15 php) the difference in tensile strength is greater than at higher filler loading (30-60 php). This was due to the amount of the rubber phase in each composition. Increase in filler loading will decrease the amount of rubber used in each composition. More rubber phase will produce more cross-linked rubber particles, which enhance the resistance to aging process thus reducing its effect on the

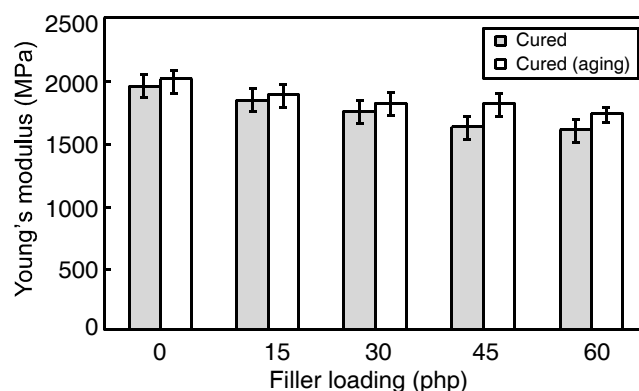


Figure 15. The effect of thermo-oxidative aging (at 70°C for 7 days) on Young's modulus of cured RHP/PS/SBR composites.

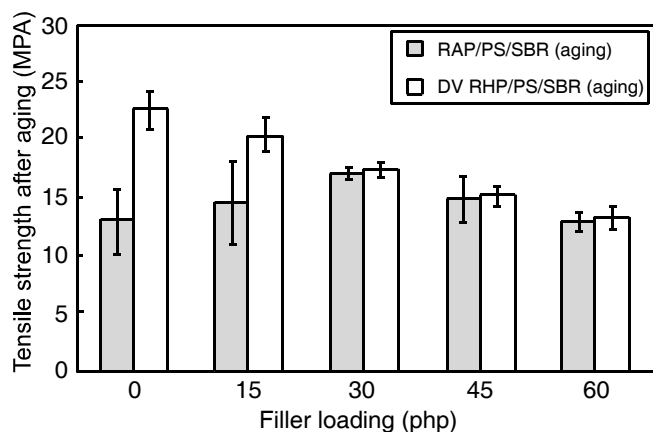


Figure 16. The effect of thermo-oxidative aging (at 70°C for 7 days) on tensile strength of uncured and dynamic cured RHP/PS/SBR composites.

tensile strength of cured composites. This observation confirmed that cross-linked rubber particle, has influence on the resistance to aging process (heat) [2, 4, and 6].

CONCLUSION

The following conclusions can be drawn from this study:

- At higher filler loading, dynamically cured RHP/PS/SBR composites show better processability than uncured composites.
- Dynamic vulcanization process has increased the tensile strength and Izod impact strength but it has reduced the percentage of elongation-at-break of RHP/PS/SBR composites
- Dynamic vulcanization of ternary system (RHP/PS/SBR) shows that RHP has no adverse effect on the vulcanization process of SBR.
- The existence of cross-linked rubber particles in RHP/PS/SBR composites has given a better resistance toward aging process and swelling in water.
- Based on SEM micrograph, dynamic vulcanization process has produced better results.
- Dispersion of matrices and better filler/matrix adhesion in RHP/PS/SBR composites.

REFERENCES

1. Hofmann W., Vulcanization and vulcanizing agent,

Maclaren, London, New York, 225 (1967).

2. Coran A.Y., Thermoplastic rubber-plastic blends, in: *Handbook of Elastomers*, Bhowmick A.K. and Stephens H.L., Eds., Marcel & Dekker, New York, 249 (1988).
3. Mehrabzadeh M. and Delfan N., Thermoplastic elastomers of butadiene-acrylonitrile copolymer and polyamide. VI. Dynamic crosslinking by different systems, *J. Appl. Polym. Sci.*, **77**, 2057-2066 (2000).
4. Ismail H., Salmah A., and Nasir M., Dynamic vulcanization of rubber-wood-filled polypropylene/natural rubber blends, *Polym. Test.*, **20**, 819-823 (2001).
5. Jain A.K., Nagpal A.K., Singhal R., and Gupta N.K., Effect of dynamic crosslinking on impact strength and other mechanical properties of polypropylene/ethylene propylene diene rubber blends, *J. Appl. Polym. Sci.*, **78**, 2089-2103 (2000).
6. Mousa A., Ishiaku U.S., Ismail H. and Mohd Z.A., Mechanical properties and thermo-oxidative ageing of dynamically vulcanized PVC/ENR thermoplastic elastomer, *Int. Rubb. Conf.*, 1997 (IRC 97), Kuala Lumpur, Malaysia, 756-764 (1997).
7. Katbab A.A., Nazockdast H., Bazgir S., Carbon black-reinforced dynamically cured EPDM/PP thermoplastic elastomers.I. Morphology, rheology and dynamic mechanical properties, *J. Appl. Polym. Sci.*, **75**, 1127-1137 (2000).
8. Siriwardena S., Ismail H., Shako U.S., and Perera M.C.S., Mechanical and morphological properties of white rice husk ash filled polypropylene.ethylene-propylene-diene terpolymer thermoplastic elastomer composites, *J. Appl. Polym. Sci.*, **85**, 438-453 (2002).
9. Rader C.P., Thermoplastic elastomers, in: *Handbook of Thermoplastic Elastomers*, Walker B.M., Ed., Van Nostrand Reinhold, New York, 51 (1988).
10. Coran A.Y. and Patel R., Rubber-thermoplastic compositions. Part 1. EPDM-polypropylene thermoplastic vulcanizates, *Rubber Chem. Tech.*, **53**, 141-150 (1979).
11. Rozman H.D., Tay G.S., Kumar R.N., Abubakar A., Ismail H., and Z.A. Mohd., Ishak, Polypropylene hybrid composites: A preliminary study on the use of glass and coconut fibre as reinforcements in polypropylene composites, *Polym. Plast. Technol. Eng.*, **38**, 997-1011 (1999).
12. Ahmad Fuad M.Y., Mohd Ishak Z.A., and Mohd Omar A.K., Rice husk ash as filler in polypropylene: Effect of wax and silane coupling agents, *Plast. Rubb. Comp. Process Appl.*, **21**, 225-235 (1994).
13. Mishra S. and Naik J. B., Studies on swelling behaviour

of wood-polymer composites based on agro-waste and HDPE in steam and water at ambient temperature, *Polym. Plast. Technol. Eng.*, **38**, 1051-1058 (1999).