Partial Replacement of Silica by White Rice Husk Ash in Natural Rubber Compounds: The Effects of Bonding Agents

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ABSTRACT

The effects of bonding agents on the partial replacement of silica by white rice husk ash (WRHA) in natural rubber compounds were studied. Results showed that the optimum weight ratio of WRHA/silica to obtain maximum enhancement of tensile and tear strengths was 20/30 (phr/phr). Increasing the WRHA in weight ratio of WRHA/silica decreases the cure time, t_{90}, scorch time, t_2, hardness and elongation at break but increases the resilience of the vulcanizates. For similar vulcanizates, the incorporation of bonding agents enhanced the tensile strength, tear strength, hardness, rubber-filler interaction and resilience, whereas, the elongation at break decreased. The incorporation of bonding agents also increases the t_{90} and t_2.

Key Words: silica, white rice husk ash, bonding agents, mechanical properties, rubber-filler interaction

INTRODUCTION

Bonding agents are used in rubber vulcanizates filled with non-reinforcing fillers, which by their nature show weak filler-rubber interaction. The incorporation of bonding agents was found to improve the interaction between the non-reinforcing fillers and rubbers. Kishore and Rajalingam [1] reported that the mechanical properties of rubber vulcanizates filled with non-reinforcing fillers increased with the incorporation of bonding agents. We also found [2–4] that the mechanical properties of oil palm fibre reinforced natural rubber composites improved with the incorporation of various bonding agents.

In our previous works [5, 6], the potential of white rice husk ash (WRHA) as a filler for natural rubber (SMR-L) compounds has been studied. The optimum loading of WRHA to obtain maximum mechanical properties was achieved at 10 phr after which there was deterioration in properties. In the case of epoxidized natural rubber (ENR 50), the maximum mechanical properties was observed to occur at 20 phr of filler loading. It was reported that WRHA has about 96% silica content with mean particle size of 5.4μm, surface area of 1.4 m^2/g and density of 2.2 g/m^3 [7, 8].

In this study the effects of bonding agents (resorcinol formaldehyde and hexamethylenetetramine) on the partial replacement of silica by WRHA in natural rubber compounds have been

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examined. The work was carried out to achieve the following objectives:

–The effect of bonding agents on curing characteristics.

–The effect of bonding agents on rubber-filler interaction.

–Scanning electron microscopy examination on tear fracture surface.

–The effect of bonding agents on mechanical properties.

EXPERIMENTAL

Materials

Natural rubber (SMR-L) was obtained from Rubber Research Institute of Malaysia (RRIM). White rice husk ash (WRHA) was supplied by Plastic Technology Centre, S.I.R.I.M., Malaysia. The physical properties of WRHA are given elsewhere [3, 4]. The precipitated silica (grade Vulcasil S) and other materials such as zinc oxide, sulphur, stearic acid, antioxidant and accelerators were purchased from Bayer (M) Ltd. Bonding agents, resorcinol formaldehyde (RF) was obtained from Lianco (M) Ltd., whereas, hexamethylenetetramine (hexa) was obtained from Fluka Chemical (M) Ltd. All materials were used as supplied and the semi-efficient sulphur vulcanization (semi-EV) system was employed.

Processing and the Mechanical Properties Evaluation

Formulations of the mixes are given in Table 1. The mixing was carried out as per ASTM D 3182–80 on a two-roll laboratory size mixing mill (160 mm×320 mm). Optimum cure time, t_{90}, was determined by Monsanto Rheometer R-100. Vulcanization was carried out at 150 °C on an electrically heated single daylight hydraulic press with a force of 10 MPa. The vulcanizates were tested for different mechanical properties according to respective ASTM standards. Tensile and tear properties were studied using an Instron Universal Testing Machine, model 1114 at a crosshead speed of 50 cm/min. For tensile properties, samples were punched out using die E from moulded sheets and were tested according to ASTM D412 method A. For tear strength measurements, standard test pieces (ASTM: D624 - Type C) were used.

Hardness measurements were made according to ASTM D2240 using Shore A durometer. Resilience test was done by using Wallace Tripsometer Dunlop according to BS 903: Part A8. The angle of rebound was measured and resilience was calculated using the equation below:

$$R = \frac{1-\cos(\text{angle of rebound}) \times 100}{1-\cos(\text{angle of fall})}$$

Table 1. Formulation to study the effect of bonding agents on the partial replacement of silica by WRHA in natural rubber compounds.

Ingredients	Set 1 (phr)	Set 2 (phr)
Natural rubber	100	100
Zinc oxide	5.0	5.0
Stearic acid	3.0	3.0
Flectol H[a]	1.0	1.0
CBS[b]	2.0	2.0
Sulphur	2.5	2.5
WRHA[c]	0, 10, 20, 30, 40, 50	0, 10, 20, 30, 40, 50
Silica[c]	50, 40, 30, 20, 10, 0	50, 40, 30, 20, 10, 0
RF	–	5.0
Hexa	–	2.0

(a) Poly-1,2-dihydro-2,2,4-trimethylquinoline; (b) n-cyclohexylbenzthiazyl sulphenamide; (c) The total of WRHA and silica loadings are always 50 phr.

Scanning Electron Microscopy (SEM)

SEM studies of the tear failure surfaces were carried out on a scanning electron microscope, model Leica Cambridge S-360. All the surfaces were examined by SEM after first sputter coating with gold to avoid electrostatic charging and poor resolution.

Rubber-filler Interactions

Lorenz and Parks equation [7] has been applied to study rubber-filler interaction.

According to this equation:

$$\frac{Q_f}{Q_g} = ae^{-z} + b \quad (1)$$

where, Q is defined as grams of solvent per gram of hydrocarbon and is calculated by:

$$Q = \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Original weight} \times 100 / \text{Formula weight}} \quad (2)$$

The subscripts f and g in eqn (1) refer to filled and gum vulcanizates, respectively, and z is the ratio by weight of filler to rubber hydrocarbon in the vulcanizate, while a and b are constants. The higher the Q_f/Q_g values, the lower will be the extent of interaction between the filler and the matrix.

RESULTS AND DISCUSSION

The Effect of Bonding Agents on Curing Characteristics, t_{90} and t_2

Table 2 summarizes the curing characteristics, t_{90} and t_2 of partial replacement of silica by WRHA in natural rubber compounds with and without bonding agents. It can be seen from Table 2 that the t_{90} and t_2 decreased with increasing WRHA loading in WRHA/silica weight ratio.

According to Wagner [10], the most frequently used accelerator systems were severely deactivated when silicas were added to rubber compounds. As a result, both the optimum cure and the state of cure are reduced substantially. Table 2 shows that the t_2 and t_{90} become shorter as the silica loading in WRHA/silica weight ratio decreased. In our previous works [5, 6], we have reported that the WRHA which contains various metal oxides can increase the curing rate.

When the loading of WRHA in WRHA/silica weight ratio increases the metal oxides content in rubber mixes also increases and contributes to the increase in vulcanization rate, i.e. shorter t_2 and t_{90}. However, at a similar WRHA/silica weight ratio, the t_2 and t_{90} increase with the incorporation of bonding agents. According to Chakraborty et al. [11], the longer scorch time and cure time was due to the better bonding between the filler and rubber matrix when the various bonding agents were used.

The Effect of Bonding Agents on Rubber-filler Interaction

Figure 1 shows the effect of bonding agents in reducing the Q_f/Q_g value of the rubber vulcanizates. The lower value of Q_f/Q_g indicates the better rubber-filler interaction [9]. This means that the bonding agents increased the WRHA/silica and rubber matrix interaction.

It has been reported by many researchers [12–15] that the presence of tricomponent dry bonding

Table 2. The curing characteristics, t_{90} and t_2 of partial replacement of silica by WRHA in natural rubber compounds with and without bonding agents.

WRHA/silica (phr/phr)	0/50	10/40	20/30	30/20	40/10	50/0
Without bonding agents						
Cure time, t_{90} (min)	28.5	12.5	8.4	5.7	5.4	4.9
Scorch time, t_2 (min)	10.0	3.8	3.4	2.5	1.4	1.0
With bonding agents						
Cure time, t_{90} (min)	21.0	16.2	12.2	9.3	8.3	6.4
Scorch time, t_2 (min)	5.4	4.7	4.6	4.4	4.3	3.8

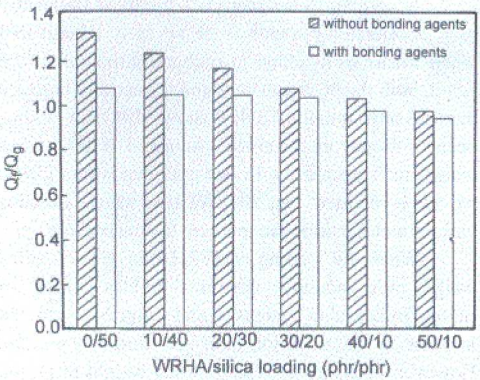

Figure 1. The effect of bonding agents on the partial replacement of silica by WRHA on Q_f/Q_g of natural rubber vulcanizates.

system (e.g., resorcinol-hexamethylenetetramine-silica) would be essential for the promotion of adhesion between the fibre and rubber matrix.

Scanning Electron Microscopy

Micrograph in Figure 2 shows the tear fracture surface of 10 phr of WRHA and 40 phr of silica filled natural rubber compounds without bonding agents. The micrograph of similar compound, but with the addition of bonding agents, is shown in Figure 3. Compared to Figure 2, it can be seen that the tear failure surface in Figure 3 is more brittle and rough with many tear lines. The rougher surface structure indicates that failure occurred with higher tear strength. This observation supports our previous result that the incorporation of bonding agents improved the rubber-filler interaction.

The Effect of Bonding Agents on Mechanical Properties

It can be seen from Figures 4 and 5 that the vulcanizate containing 30 phr of silica exhibits the highest tensile and tear strengths. Silica is a good reinforcing filler and has a high specific surface energy [16]. Silica-silica interaction is stronger than silica-rubber interaction. The tendency of silica to form agglomerates is high especially at a high concentration [17]. The agglomeration of silica reduces the interaction with rubber matrix and becomes the weak point in the vulcanizates. The tensile and tear strengths of the

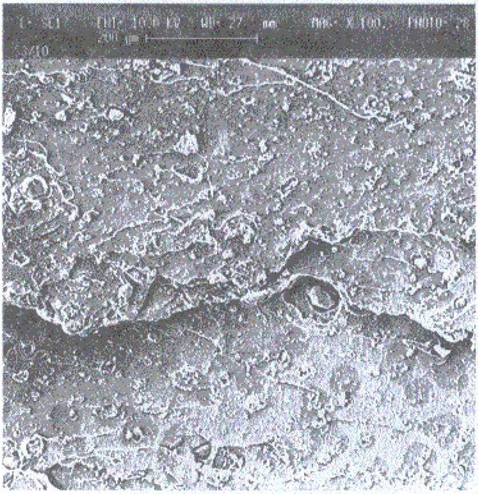

Figure 2. SEM Micrograph of tear failure surface of 10/40, WRHA/silica (phr/phr) filled SMR-L vulcanizate at magnification of 100X (without bonding agents).

Figure 3. SEM Micrograph of tear failure surface of 10/40, WRHA/silica (phr/phr) filled SMR-L vulcanizate at magnification of 100X (with bonding agents).

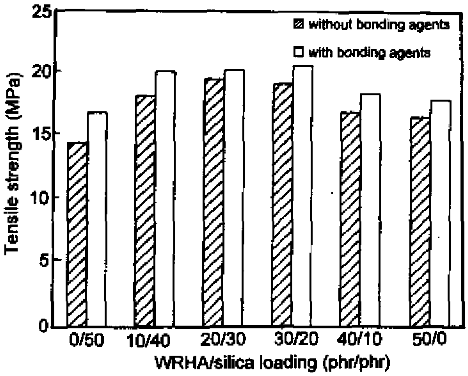

Figure 4. The effect of bonding agents on the partial replacement of silica by WRHA on tensile strength of natural rubber vulcanizates.

vulcanizates were reduced when the silica loading exceeded 30 phr.

For WRHA, the maximum tensile and tear strengths of the vulcanizates (containing both WRHA and silica) occurred at WRHA loading of 20 phr (20/30, WRHA/silica (phr/phr)). Compared to vulcanizates filled with WRHA only, the optimum loading of WRHA was 10 phr [5, 6]. This means that both the silica and WRHA could be used in this system to reinforce the natural rubber vulcanizates. The latter could be used at higher concentration to give better tensile and tear strengths. At similar WRHA/silica weight ratio, the incorporation of bonding agents improved the tensile and tear strengths.

Results from rubber-filler and SEM studies show that rubber-filler interaction is stronger with the addition of bonding agents. The stronger rubber-filler interaction would increase the effectiveness of the stresses transferred from the rubber matrix to filler particles dispersed in vulcanizate's rubber matrix and consequently enhances the tensile and tear strengths.

The effect of partial replacement of silica by WRHA on elongation at break, E_b, is shown in Figure 6. It can be seen that E_b decreases with increasing WRHA loading in the weight fraction of WRHA/silica filled vulcanizates. We have reported [5, 6] that E_b decreases with increasing WRHA in the rubber vulcanizates. However, the increment in the elongation at break with increasing silica loading was reported by Tultz et al. [18] and Bachmann et al. [19]. When the loading of WRHA in weight fraction of WRHA/silica increases, the effect of WRHA on E_b is more dominant than silica and this causes the E_b of the vulcanizates to decrease.

It can be seen also in Figure 6 that the

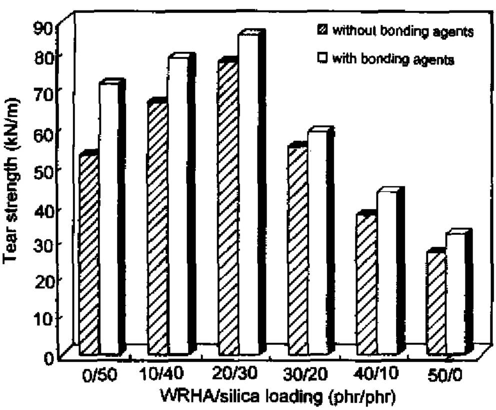

Figure 5. The effect of bonding agents on the partial replacement of silica by WRHA on tear strength of natural rubber vulcanizates.

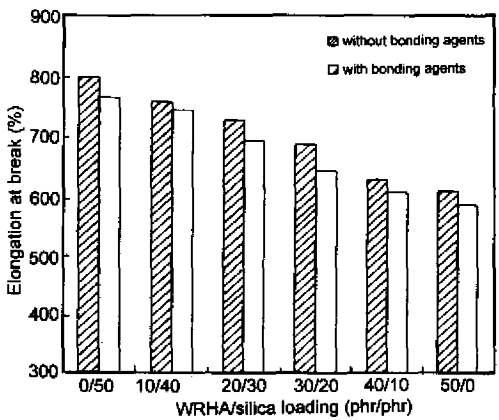

Figure 6. The effect of bonding agents on the partial replacement of silica by WRHA on E_b of natural rubber vulcanizates.

Table 3. The effect of bonding agents on M100.

WRHA/silica (phr/phr)	0/50	10/40	20/30	30/20	40/10	50/0
Without bonding agents						
M100 (mpa)	1.046	1.215	1.367	1.451	1.463	1.482
With bonding agents						
M100 (mpa)	1.912	1.992	1.941	1.830	1.765	1.752

vulcanizates with bonding agents have lower E_b. As previously discussed, the bonding agents improved the rubber-filler interaction. This better rubber-filler interaction was due to the specific bond formed between the filler and rubber matrix which resulted in higher cross-link density of the vulcanizates. The increment in cross-link density can be seen from M100 (modulus at 100% extension) data in Table 3.

According to Hoffman [20], the value of extension modulus is proportional to cross-link density. Table 3 shows that the addition of bonding agents increases the M100. Hoffman also reported that the elongation at break is inversely proportional to the degree of cross-linking. Higher cross-link density resulted in vulcanizates to become stiffer and consequently the elongation at break decreases with the addition of bonding agents.

The addition of particulate filler reduces the resilience of the rubber vulcanizates. The reduction is more significant if the filler used is reinforcing fillers such as carbon black and silica [20]. We have reported that the effect of WRHA loading on resilience is not significant [5, 6]. So for vulcanizates filled with both WRHA and silica, the resilience is more affected by silica. This explains why the resilience decreases as the silica loading in the weight fraction of WRHA/silica increases (see Figure 7).

Figure 7 also shows clearly that the addition of bonding agents increases the resilience property. This increment is due to the better rubber-filler interaction as a result of bonding agents addition.

According to Hoffman [20], the better rubber-

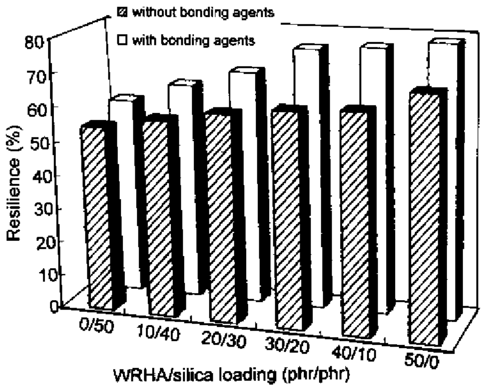

Figure 7. The effect of bonding agents on the partial replacement of silica by WRHA on resilience of natural rubber vulcanizates.

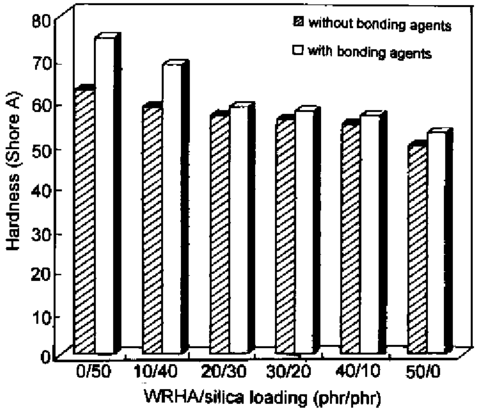

Figure 8. The effect of bonding agents on the partial replacement of silica by WRHA on hardness of natural rubber vulcanizates.

filler interaction would improve the perfectness of the cross-link network in the vulcanizates. A perfect cross-link network would reduce the energy lost through hysteresis and consequently increase the resilience property.

Figure 8 shows the hardness of the vulcanizates increases with increasing silica loading in the weight fraction of WRHA/silica. The more reinforcing filler would result in harder vulcanizates [21]. Nasir and Low [22] reported that silica is a more reinforcing filler than WRHA. As the silica loading in the weight fraction of WRHA/silica increases the hardness of the vulcanizates also increases. Figure 8 also shows that the incorporation of bonding agents increases the hardness of the vulcanizates. As explained before, this is due to the higher cross-link density.

CONCLUSION

–The increase of WRHA in weight ratio of WRHA/silica (phr/phr) decreases the cure time, t_{90}, and scorch time, t_2, of the vulcanizates. However, at a similar WRHA/silica weight ratio, the t_{90} and t_2 increase with the incorporation of bonding agents.
–The rubber-filler interaction studies and scanning electron microscopy examination indicate that the incorporation of bonding agents improved the rubber-filler interaction.
–The incorporation of bonding agents enhanced the mechanical properties of the vulcanizates i.e., tensile strength, tensile modulus (M100), tear strength, hardness and resilience.

REFERENCES

1. Kishore K. and Rajalingam P., *J. Appl. Polym. Sci.*, **37**, 2845, 1989.
2. Hanafi Ismail, Rosnah N., and Rozman H.D., *Eur. Polym. J.*, **33**, 123, 1997.
3. Hanafi Ismail, Rosnah N., and Rozman H.D., *Polymer*, **38**, 4059, 1997.
4. Hanafi Ismail, Rosnah N., and Ishiaku U.S., *Polym. Int.*, **43**, 223, 1997.
5. Hanafi Ismail and Nasaruddin M.W., *Polym. Int.*, in press.
6. Hanafi Ismail and Chung F.L., *Polym. Plast. Technol. Eng*, in press.
7. Hanafi Ismail, Ishiaku U.S., Arinab A.R. and Mohd Ishak Z.A., *Int. J. Polym. Mater.*, **36**, 39, 1997.
8. Hanafi Ismail, Ishiaku U.S., Azhar A.A. and Mohd Ishak Z.A., *J. Elast. and Plast.*, **29**, 270, 1997.
9. Lorenz O. and Parks C.R., *J. Polym. Sci.*, **50**, 299, 1961.
10. Wagner M.P., *Rubber Technology*, Ed. Morton, M., Van Nostrand Reinhold, New York, p. 95, 1987.
11. Chakraborty S.K., Setua D.K., and De S.K., *Rubb. Chem. Technol.*, **55**, 1286, 1982.
12. Murty V.M. and De S.K., *Rubb. Chem. Technol.*, **55**, 287, 1982.
13. Creasey J.R. and Wagner M.P., *Rubber Age.*, **100**, 72, 1968.
14. Hewitt N.L., *Rubber Age*, **104**, 59, 1972.
15. Morita E., *Rubb. Chem. Technol.*, **53**, 795, 1980.
16. Fetterman M.Q., *Rubber World*, **194**, 38, 1986.
17. Wolff S., Gorl U., Wang M.J., and Wolff W., *Europ. Rubber J.*, **171**, 16, 1993.
18. Tultz J.P., Bice J.A.E., Okel T.A., and Patkar S.D., *Int. Rubber Conference*, Kuala Lumpur, Malaysia, Oct. 6–9, PR 417, 1997.
19. Bachmann J.H., Sellers J.W., Wagner M.P. and Wolff R.F., *Rubb. Chem. Technol.*, **32**, 1286, 1959.
20. Hoffmann, *Vulcanization and Vulcanizing Agents*, Maclaren and Sons Ltd., London, pp 6, **16**, 73, 1967.
21. Jacques J.E., *Rubber Technol. and Manuf.*, Ed. Blow, C.M., Butterworth and London, 321, 1971.
22. Nasir M. and Low M.H., Proc. *Int. Rubber Technol. Conference*, Penang, Malaysia, Oct. 17–19, 370, 1988.