The Effects of Recycle Rubber Powder (RRP) Content and Various Vulcanization Systems on Curing Characteristics and Mechanical Properties of Natural Rubber/ RRP Blends

Hanafi Ismail[1(*)], Razif Nordin[1], and Ahmad Mohd Noor[2]

(1) School of Materials and Mineral Resources Engineering, University Sains Malaysia, 14300 Nibong Tebal, Seberang Perai Selatan, Penang, Malaysia

(2) School of Chemistry, University Sains Malaysia, 11800 Minden, Penang, Malaysia

A B S T R A C T

The effects of recycle rubber powder (RRP) content and conventional (CV), semi-efficient (semi-EV) and efficient vulcanization (EV) systems on curing characteristics and mechanical properties of natural rubber (NR)/recycle rubber powder (RRP) blends were examined. The minimum torque, maximum torque and torque difference are increased with increasing recycle rubber powder (RRP) content in NR/RRP blends, whereas, the scorch time and cure time show the opposite trend. NR/RRP Blends cured with the CV system showed the highest minimum torque, maximum torque and torque difference but longest cure time, t_{90}. Increasing RRP content in NR/RRP blends increases the tensile modulus and hardness but decreases the tensile strength, tear strength, resilience and elongation-at-break. Although the CV system exhibits the highest tensile modulus and hardness but NR/RRP blends cured with EV system show the highest tensile strength, tear strength, resilience and elongation-at-break followed by semi-EV and CV systems.

INTRODUCTION

Development of a process to reclaim scrap tyres and waste rubber is great interest for all countries, since accumulation of waste rubber has significant effect to environment. A normal disposal method of wastes rubber such as incineration or landfilled is not desirable approach as it caused several other environmental problems such as air or / and water pollution. Reclaiming waste rubber by mechanical [1,2] or chemical [3,4] methods is the ultimate approach to solve the problems created by waste rubber.

(∗)To whom correspondence should be addressed.
E-mail: ihanafi@usm.my

Transforming bulk waste rubber towards powdered state by mechanical process is the most preferable method of reclaiming waste rubber as it is more economical compared to chemical process. Several researchers have reported that powdered waste rubber can be used as a filler in mixtures with virgin rubber [5-8], thermoplastics [9-12], and as modifying concrete and asphalt [13-15]. Recently Ismail et al. [16,17] reported the effect of recycle rubber powder (RRP) incorporation (a waste product from mechanical process of rubber ball and artificial eggs) on the properties of natural rubber (NR) compounds. The results indicate that cure characteristics and mechanical properties do not show adversely significant effect with RRP incorporation, even at 40% replacement of NR compounds. This implied that RRP can be used as alternative cheap material (filler) or extender in rubber industry.

The purpose of this study is to investigate the curing characteristics and mechanical properties of NR/RRP blends. A systematic study on how the above properties will be affected by gradual replacement of NR compounds with a RRP cured using different sulphur vulcanization systems will be reported. The main objective of this work is to produce low cost rubber products, where the strength is not so much critical and an improvement in product stiffness is necessary.

EXPERIMENTAL

Ingredients and Formulation
Natural rubber (SMR L) was purchased from Kumpulan Guthrie Sdn. Bhd., Seremban, Malaysia. The recycle rubber waste (powder) [RRP] product from the sanding process (polishing) of rubber ball and artificial eggs with the particle size of RRP in the range of 250-500 μm was obtained from Watas Holding (M) Sdn. Bhd., Penang, Malaysia. Table 1 shows the formulation used in this study. Three different types of sulphur vulcanization systems were used to cure the natural rubber/recycle rubber powder blends. Other compounding ingredients were purchased from Anchor Chemical Co.

Cure Characteristics
Cure characteristics were studied using a Monsanto moving die rheometer (MDR 2000) according to

ASTM D 224. Samples of about 4 g of respective compound were tested at a vulcanization temperature (150 C). Sheets of 3 mm thickness were compression moulded at 150 C with 10 MPa force using a hot press according to respective cure time, t_{90}, determined with the MDR 2000.

Vulcanization Process
Sheets of 3 mm thickness were compression moulded at 150 C with the force of 10 MPa using a hot press according to respective cure time, t_{90}, determined with the MDR 2000.

Cross-link Density Study
Cure test pieces of dimension $30 \times 5 \times 2$ mm were weighed using an electrical balance and each test piece was immersed in a glass vessel containing toluene (30 mL) at 25 C. The vessels were kept in the dark to prevent oxidation. The samples were then removed from glass vessels and excess toluene was removed by lens blotting paper. The samples were then placed in a closed vessel, to prevent toluene evaporation and the weights of the swollen samples were determined. The sample was then reimmersed in the toluene and the process was repeated until a constant swollen weight could be obtained. The sample was de-swollen in a vacuum at room temperature to a constant weight in order to find the volume fraction of toluene absorbed in the rubber. The cross-link density of samples was determined by using Flory-Rehner equation [18] (eqn 1). Physical cross-link density $(2M_c)^{-1}$ was related to volume fraction of the rubber in swollen gel by solvent at equilibrium (V_r).

$$-\ln(1-V_r) - V_r - XV_r^2 = 2\,P_{RN}\,V_0\,(2M_C)^{-1}\,V^{1/3} \qquad (1)$$

Where,
X: interaction constant characteristic between rubber sample and toluene (0.39);
P_{RN} : rubber network density = 0.932 at 35 C;
V_0: molar volume of the toluene = 108.05 at 35 C;
V_r: volume fraction of rubber in swollen filled sample is given by the following equation [19]:

$$V_r = (d - f_w)\,P_{RN}^{-1} / \{(d - f_w)\,P_{RN}^{-1} + A_s\,P_s\} \qquad (2)$$

where,

Table 1. Formulation for natural rubber/recycle rubber compounding.

Mix (phr)	A_a	B_a	C_a	D_b	E_b	F_b	G_c	H_c	I_c
Natural rubber (SMR L)	70	50	40	70	50	40	70	50	40
Recycle rubber powder (RRP)	30	50	60	30	50	60	30	50	60
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sulphur	2.5	2.5	2.5	1.5	1.5	1.5	0.6	0.6	0.6
N-Cyclohexyl-2-benzothiazole sulfenamide	0.6	0.6	0.6	2.0	2.0	2.0	4.0	4.0	4.0
2,2-Methylene-bis-(4-methyl-6-tert-butylphenol)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

(a) Cured with conventional vulcanization system (CV); (b) Cured with semi-efficient vulcanization system (semi-EV); (c) Cured with semi-efficient vulcanization system (semi-EV).

A_s : the amount of toluene absorbed.
P_s : density of the toluene.
d : desorbed weight of the sample.
f : volume fraction of the filler.
w : initial weight of sample.

Mechanical Properties

Dumb-bell shaped samples were cut from the moulded sheets according to ASTM D 3182. Tensile and tear tests were performed at a cross-head speed of 500 mm/min using a Monsanto Tensometer M500 according to ASTM D 412 and ASTM D 624(die B), respectively. Resilience was studied by using a Wallace Dunlop Tripsometer according to ASTM D 1054. Rebound resilience was calculated according to the following equation:

$$\text{Percentage resilience} = 100\,\{(1-\cos\theta_2)/(1-\cos\theta_1)\} \quad (3)$$

where,
θ_1 = initial angle (45), and
θ_2 = maximum rebound angle.
Hardness measurement of sample was done according

to ASTM D 1415 using a Wallace dead load, with hardness ranging from 30 to 85 IRHD (International Rubber Hardness Degree). The fracture surface of respective compounds was investigated with a Leica Cambridge S-360 scanning electron microscope. The objective is to obtain some information concerning the quality of bonding, and to detect the presence of micro-defect if any.

RESULTS AND DISCUSSION

Table 2 shows the curing characteristics of natural rubber (NR)/recycle rubber powder (RRP) blends using different sulphur vulcanization systems. It is clear that, the minimum torque, M_L of NR/RRP blends is increased with increasing content in all vulcanization systems. The increase of minimum torque is due to the presence of cross-linked rubber particle in RRP and the reduction of natural rubber content in NR/RRP blends. Consequently, the incorporation of RRP reduces the flow of NR/RRP blends, which resulted in an increase of minimum torque. It can be seen also that at a similar NR/RRP blend ratio, CV system exhibits the highest

Table 2. Cure characteristics of natural rubber/recycle rubber powder blends.

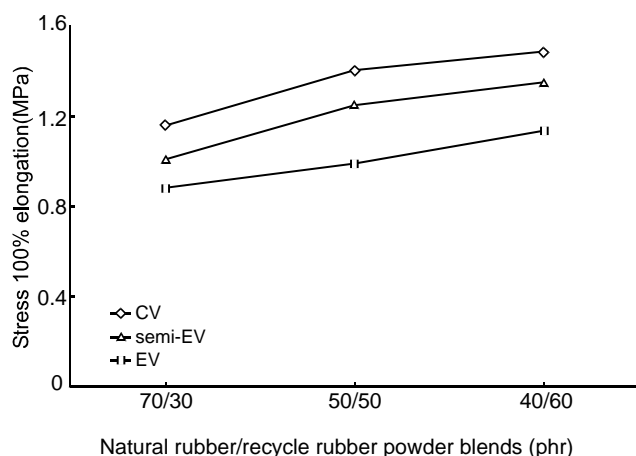| Mix (phr)	A_a	B_a	C_a	D_b	E_b	F_b	G_c	H_c	I_c
Minimum torque (dNm)	0.19	0.27	0.38	0.18	0.25	0.32	0.15	0.23	0.27
Maximum torque (dNm)	9.38	13.04	14.88	8.76	12.40	13.98	8.03	11.23	12.80
Difference torque (dNm)	9.64	12.77	14.50	8.58	12.15	13.66	7.88	11.00	12.53
Cure time (min)	8.11	6.91	6.28	5.46	4.50	4.19	7.79	6.49	6.06

Figure 1. M100 (stress at 100% elongation) versus NR/RRP blends cured with different sulphur vulcanization systems.

minimum torque followed by semi-EV and EV systems.

It is believed that the high sulphur-to-accelerator ratio in CV systems provided high concentration of polysulphide linkages in NR/RRP blends, which influenced the minimum torque of the blends. The other reasons can be due to the migration of sulphur from natural rubber matrix to recycle rubber powder and unreacted curative contained in RRP. Meanwhile, for semi-EV and EV systems, polysulphide linkages were less due to lower concentration of sulphur-to-accelerator ratio, compared to CV system and thus migration of sulphur for semi-EV and EV was less.

The similar trends are observed for maximum torque, M_H and torque difference, M_H-M_L. The torque
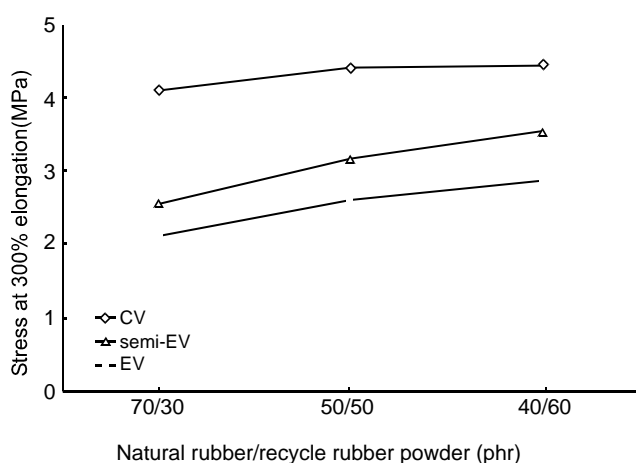
Figure 2. M300 (stress at 300% elongation) versus NR/RRP blends cured with different sulphur vulcanization systems.
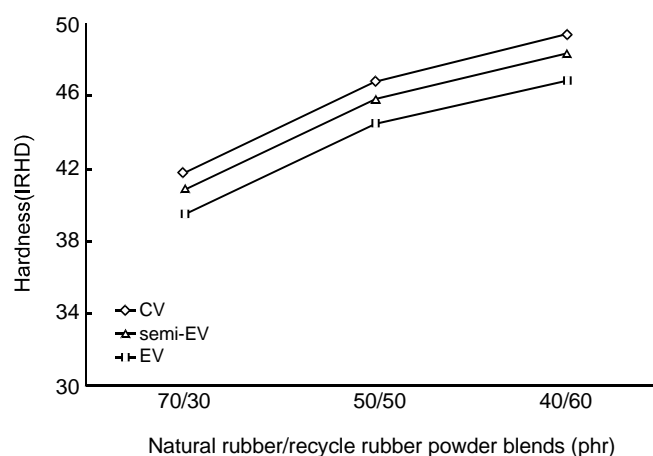

Figure 3. The effects of different RRP content and sulphur vulcanization systems on hardness of NR/RRP blends.

difference is an indication of extent of cross-link [20]. It can be seen that the torque difference increases with increasing RRP content in NR/RRP blends. This is a result of combined effect of the new cross-link being formed and those originally present in RRP. The similar observations were reported by Phadke et al. [5,21]. Again, at a similar NR/RRP blend ratio the torque difference in CV system is higher than semi-EV and EV systems.

It can be seen from Table 2 that the cure time, t_{90} decreases with increasing RRP content in NR/RRP blends for all vulcanization systems. Various researchers [22-24] who studied the cure characteristics of the rubber compounds containing vulcanized rubber powder reported that sulphur migrates from matrix into the rubber powder. Rigbi [23] also found that the unreacted accelerator complex migrates from the rubber powder into the matrix. Consequently, with increase in RRP content, the accelerator concentration in the blend increases and this accounts for decreases in t_{90}. However, at a similar NR/RRP blend ratio, CV system exhibits longest cure time followed by EV and semi-EV systems. This result shows that the sulphur-to-accelerator ratio plays an important role in the curing process for NR/RRP blends.

The effects of RRP content on tensile modulus, M100 and M300 (stress-at-100% elongation and stress-at-300% elongation) and hardness of NR/RRP blends cured with different vulcanization systems are shown in Figures 1-3. It can be seen that, tensile modulus (M100 and M300) and hardness increase with increas-
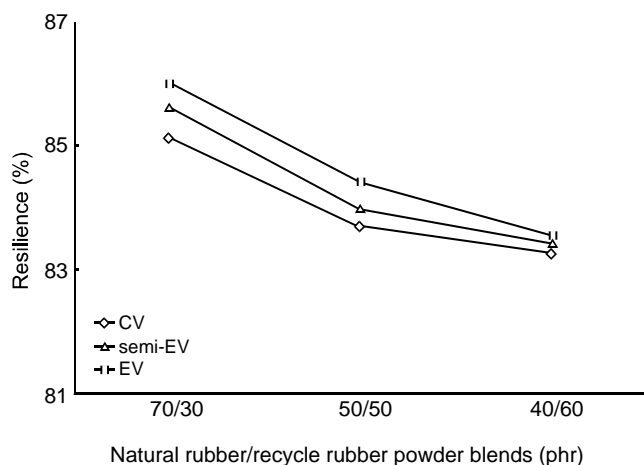
Figure 4. The effects of different RRP content and sulphur vulcanization systems on resilience of NR/RRP blends.

Figure 6. Cross-link density versus NR/RRP blends cured with different sulphur vulcanization systems.

ing RRP content in NR/RRP blends. As it was discussed before, the increase in both properties with increasing RRP content was due to increase in cross-link density in NR/RRP blends. As the content of RRP in the NR/RRP blends increases, it makes the blends stiffer, and so there would be an increase in hardness and modulus, and at the same time there is a decrease in resilience (Figure 4) and elongation-at-break (Figure 5). However, at a similar NR/RRP blend ratio, M100, M300 and hardness of CV system is higher than semi-EV and EV systems. As shown in Table 2, the torque difference, M_H-M_L of CV system is the highest followed by semi-EV and EV systems. Figure 6 shows the cross-link density values of NR/RRP blends cured with different vulcanization systems. It can be seen
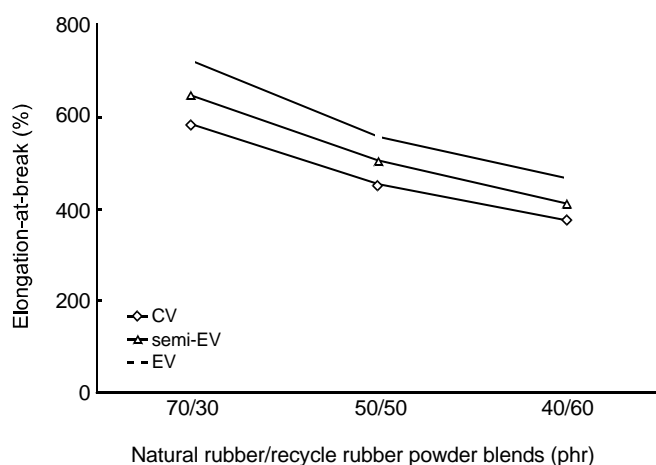
that, the cross-link density of all NR/RRP blends increases with increasing RRP content in the blends. Also at a similar NR/RRP blend ratio, cross-link density for CV system is highest followed by semi-EV and EV systems.

The effects of RRP content on tensile strength and tear strength of NR/RRP blends cured with different vulcanization systems are shown in Figures 7 and 8. It can be seen that, both properties decrease with increasing RRP content in NR/RRP blends. The weak interaction and bonding between the rubber powder particles and natural rubber matrix is responsible for the deterioration in both properties. As the RRP content increases, agglomeration and hence particle-particle interaction of the RRP also increases. The similar observations

Figure 5. The effects of different RRP content and sulphur vulcanization systems on elongation-at-break of NR/RRP blends.

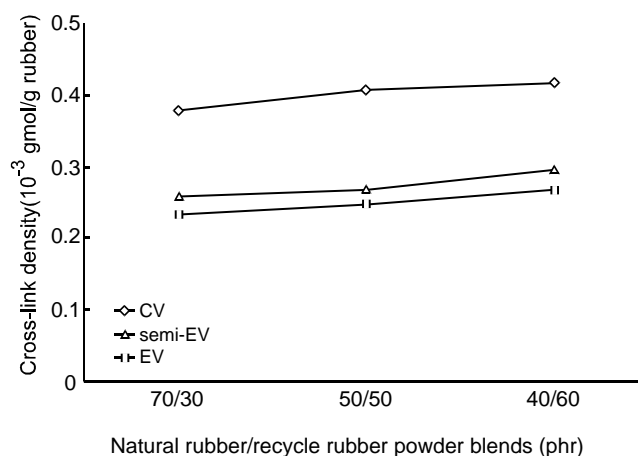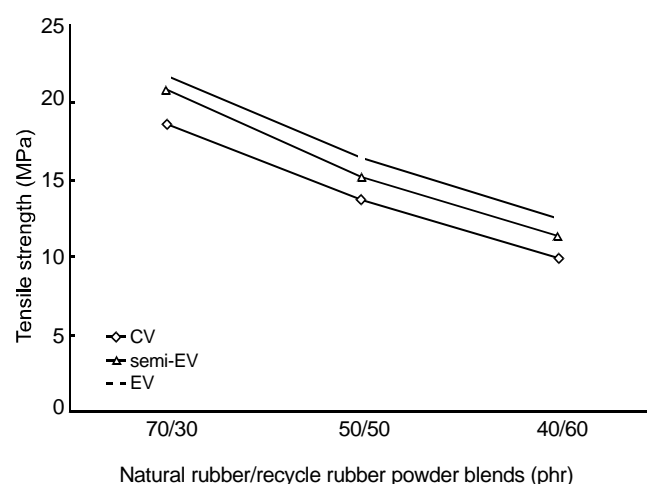**Figure 7.** The effects of different RRP content and sulphur vulcanization systems on tensile strength of NR/RRP blends.
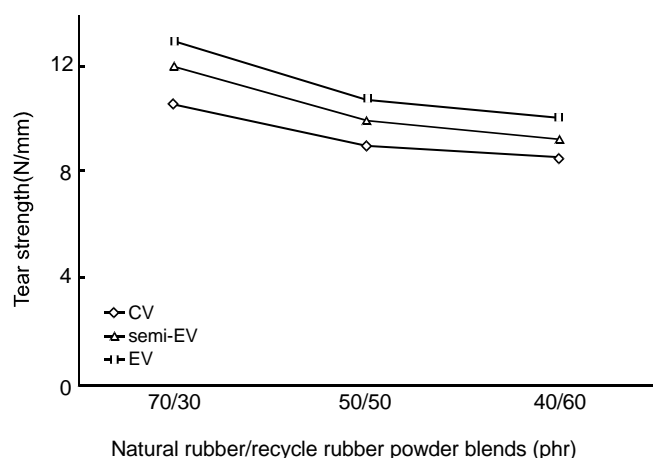
Figure 8. The effects of different RRP content and sulphur vulcanization systems on tear strength of NR/RRP blends.

were reported in our previous works [16,17]. However, at a similar NR/RRP ratio, tensile strength and tear strength of NR/RRP blends, cured with EV system, exhibit highest values followed by semi-EV and CV systems.

According to Morrison and Porter [25], an increase in degree of cross-linking may be one of the factors contributing to the enhancement in tensile and tear strengths. Actually an increase in cross-link density resulted in the higher tear and tensile strength initially, followed by a decrease. Gee [26] and Flory et al. [27] suggested that the tensile strength decreases at high degree of cross-linking owing to the breaking point being reached before the extension is high enough for crystallization to occur in the bulk rubber.

From Figure 6 and Table 2, it is clear that the cross-link density in CV systems is highest compared to semi-EV and EV systems.

Figures 9 (a, b and c) and 10 (a, b and c) show the tensile fracture surfaces of NR/RRP blends cured with different vulcanization systems at 40/60 (wt/wt) and 70/30 (wt/wt), respectively. Compared to tensile fracture surfaces of CV system in Figures 9a (40/60) and 10a (70/30), tensile fracture surfaces of semi-EV [Figure 9b (40/60) and Figure 10b (70/30)] and EV systems [Figures 9c (40/60) and Figure 10c (70/30)] exhibit more rough surfaces with many matrix tearing. This type of failure surface indicates that a higher strength is needed to cause a catastrophic failure. As shown in Figures 7 and 8, at a similar NR/RRP blend ratio, EV system exhibits highest tensile and tear strengths followed by semi-EV and CV systems.
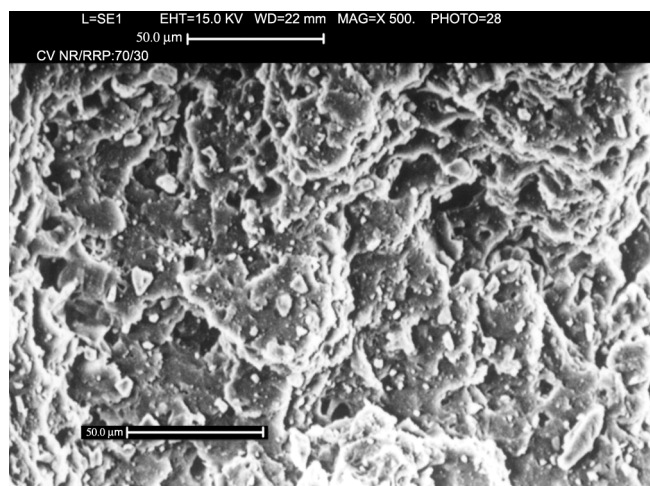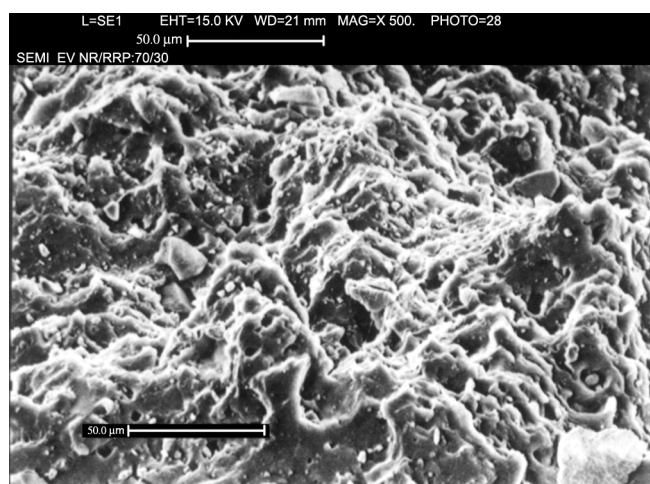
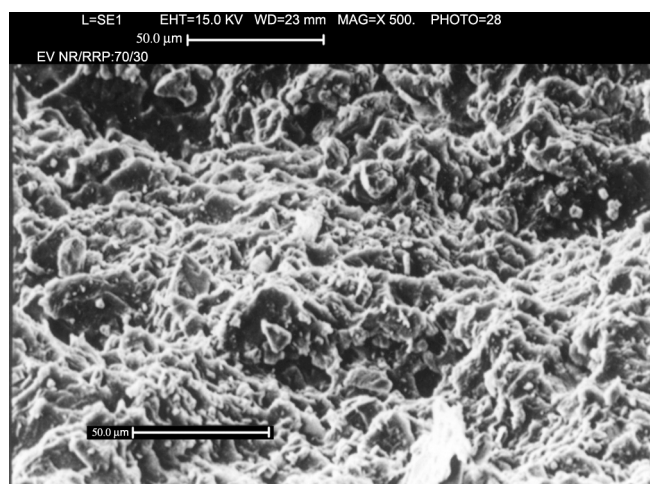

(a) CV
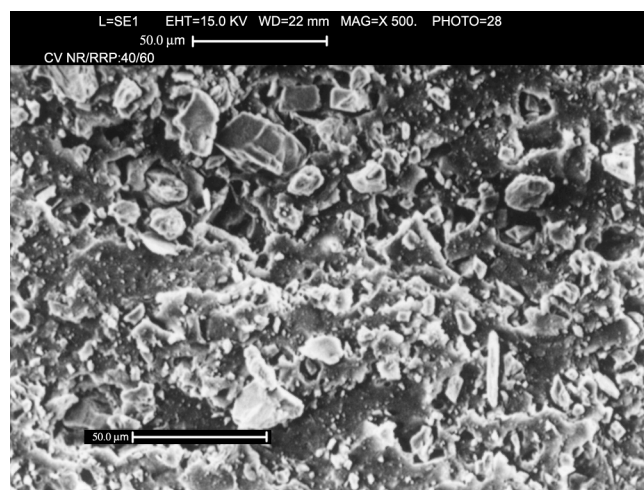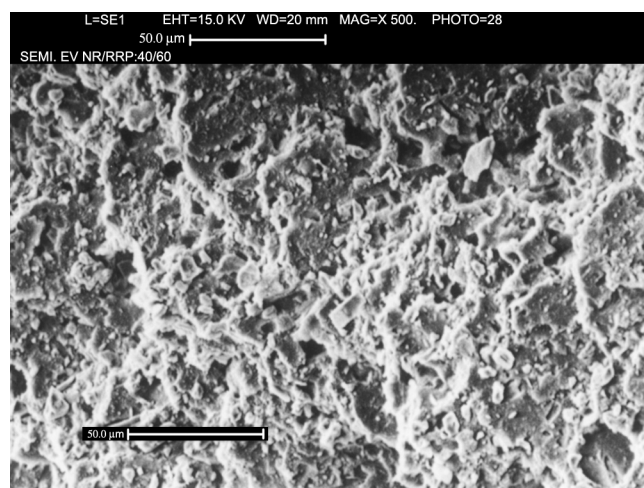
(b) Semi-EV
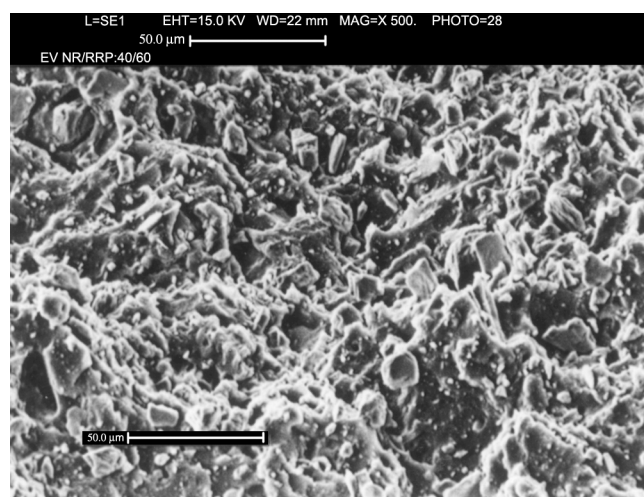
(c) EV

Figure 9. Tensile fracture surfaces of NR/RRP blends [40/60 (wt/wt)] cured with different vulcanization systems viz (a) CV; (b) semi-EV; and (c) EV.

(a) CV

(b) Semi-EV

(c) EV

Figure 10. Tensile fracture surfaces of NR/RRP blends [70/30 (wt/wt)] cured with different vulcanization systems viz (a) CV; (b) semi-EV; and (c) EV.

CONCLUSION

The following conclusions about the effects of vulcanization systems and RRP content in NR/RRP blends can be drawn:

- The minimum torque, maximum torque and torque difference are increased with increasing RRP content in the NR/RRP blends. At a similar NR/RRP blend ratio, CV system shows highest properties followed by semi-EV and EV systems.

- The cure time is decreased with increasing RRP content in the NR/RRP blends. At a similar NR/RRP blend ratio, CV system exhibits longest t_{90} followed by EV and semi-EV systems.

- Tensile modulus and hardness increase with increasing RRP content in NR/RRP blends but tensile strength, tear strength, resilience and elongation-at-break show opposite trend. At a similar NR/RRP blend ratio, CV system shows the highest tensile modulus and hardness followed by semi-EV and EV systems. However, EV system shows the highest tensile strength, tear strength, elongation-at-break and resilience followed by semi-EV and CV systems.

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