



Effects of Different Particle Sizes of Recycled Acrylonitrile-butadiene Rubber and its Blend Ratios on Mechanical and Morphological Properties and Curing Characteristics of SBR/NBRr Blends

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ABSTRACT

The effects of different particle sizes of recycled NBR (NBRr) on curing characteristics, mechanical, and morphological properties of styrene butadiene rubber/ recycled acrylonitrile butadiene rubber (SBR/NBRr) blends were examined. Three different size ranges of NBRr particles, i.e., 117 - 334 μm , 0.85 -15.0 mm, and 10 -19 cm were used in this study. The SBR/NBRr blends with blend ratios of 95/5, 85/15, 75/25, 65/35, and 50/50 were prepared using a two roll-mill at room temperature. The characterization results of the blends show that scorch time, t_2 , and cure time t_{90} of the SBR/NBRr blends decreased with increased NBRr content as well as decreasing sizes of NBRr particles due to the existence of cross-linked precursors and unreacted curative in the recycled rubber. Among all blend ratios, the SBR/NBRr blends with smallest size of NBRr particles exhibits lowest minimum torque (ML) compared with the bigger particle sizes of it in SBR/NBRr blends which resulted in more efficient processing. The maximum torque (MH) of all SBR/NBRr blends show the declining trend with increased NBRr content probably due to the poor interactions in SBR/NBRr blends. The SBR/NBRr blends with smallest size of NBRr particles show better mechanical properties (tensile, elongation-at-break, M100, and fatigue) compared with all other blend ratios of bigger sizes of NBRr particles. For physical properties, SBR/NBRr blends with smallest size of NBRr particles exhibited the highest hardness and cross-linking density at all blend ratios whereas resilience decreased, accordingly. As the particle size decreased, the contact surface area increased which provided more efficient interfacial bonds, leading to better properties. The scanning electron microscopy studies showed that the smallest size of NBRr particles in SBR/NBRr blends illustrated a better NBRr-SBR matrix interaction compared with the other NBRr particles in the related SBR/NBRr blends.

Key Words:

SBR;
recycled NBR (NBRr);
curing characteristics;
mechanical properties;
scanning electron microscopy.

INTRODUCTION

Development of science-based technologies and processes for rubber recycling, and the use of recycled rubbers in varied end-products, would significantly reduce worldwide energy consumption, provide renewable rubbers from scrap tyres and rubber wastes, and lead to less pollution of

the environment [1]. According to 2001 statistics of the Rubber Manufacturers Association, the total number of tyres scrapped annually in US is 281 million, and the approximate number of tyres in the stockpiles is 300 million [2]. Over 350 million pounds of rubber are scrapped annually from the

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production of non-tyre goods in the form of runners, trim, and pads [3]. Recycled rubber can be generalized to include any rubber waste that has been converted to an economically useful form, such as reclaimed rubber, ground rubber, or reprocessed synthetic rubber [4]. Numerous techniques have been applied in an attempt to solve the problem and to find more effective ways of waste rubber utilization. A simple process for reclaiming waste rubber is its conversion to powdered state by mechanical processes. The manufacturing of powdered rubber has obvious economic and social benefits, as it decreases the cost of product by blending fine powdered rubber with raw rubber [5]. Scrap latex rejects have become a focus of attention compared to reclaimed rubber as they are lightly cross-linked and have the high quality nature of rubber hydrocarbon [6]. Sombatsompop [7] has reported that the smaller filler size (200 μm) of polyurethane (PU) in vulcanizates SBR provides higher surface area that improves the surface area-to-volume-ratio and therefore better properties are obtained. The results showed the increasing of reclaimed filler in the blend has increased the elastic behaviour, probably due to the presence of carbon black left in the reclaim. Sreeja et al. [8] have reported that there is a significant drop in the tensile strength at lower levels of the addition of scrap rubber. According to Phadke et al. [9] an increase in the surface area as a result of size reduction and improvement in the interaction between cyroground rubber and natural rubber may lead to a higher efficient diffusion of sulphur and lower the concentration of sulphur in the rubber matrix phase. Ismail et al. [10] reported the effect of recycled rubber powder (RRP) incorporation on the properties of natural rubber (NR) compounds. The results showed that cure characteristics and mechanical properties do not show any significant adverse effect with RRP incorporation, even at 40% replacement of NR compounds.

To the best of our knowledge, no work has been done dealing with recycled NBR waste. In Malaysia, the output of nitrile rubber gloves was found abundantly. Most of this material originates from medical, industrial as well as research activities. After a certain period of time these polymeric materials are not serviceable and mostly discarded. To solve this environmental issue, we have used a recycled NBR gloves

(waste) obtained from industrial floor in an effort to create a value added instead of being scrapped. Previously, we have studied the curing characteristics, mechanical, and morphological properties of styrene butadiene rubber/virgin acrylonitrile-butadiene rubber (SBR/vNBR) and styrene butadiene rubber/recycled acrylonitrile-butadiene rubber (SBR/NBRr) blends [11].

In the present work, we attempt to investigate the effect of different particle sizes of recycled NBR (NBRr) and blend ratios on curing characteristics and mechanical and morphological properties of styrene butadiene rubber/recycled acrylonitrile-butadiene rubber (SBR/NBRr) blends.

EXPERIMENTAL

Materials

Three sizes of NBRr particles, i.e., S1 (117-334 μm) < S2 (0.85-15.0 mm) < S3 (10-19 cm) were used in this study. S1 was obtained by a mechanical grinding using Crusher model RT34 (Chyun Industrial Co. Ltd.) to achieve a polydispersed rubber powder. S2 was obtained by passing the recycled gloves through a two-roll mixing mill for a fixed time (5 min). S3 was prepared directly from recycled gloves. The NBRr was sieved using an Endecotts sieve and particle size analysis was done by Mastersizer Instrument (Type E). The materials used in this study were styrene butadiene rubber (SBR), NBRr gloves, carbon black N330, *N*-cyclohexyl-2-benzothiazyl sulphenamide (CBS), zinc oxide, stearic acid, sulphur, and processing oil. Their characteristics are illustrated in Table 1.

Compounding, Cure Characteristics, and Vulcanization

SBR/NBRr blends were prepared with blends ratios of 95/5, 85/15, 75/25, 65/35, and 50/50, as shown in Table 2. The rubber was pre-blended and the mixing procedure was carried out according to ASTM D 3184-89 using a two-roll mill at room temperature. Cure characteristics were studied using a Monsanto Moving Die Rheometer (MDR 2000) according to ASTM D 2240-93. About 4 g samples of the respective compounds were used to test at vulcanization temperature (160°C).

Table 1. Materials characteristics.

Materials	Description	Source
Styrene butadiene rubber (SBR)	1502	Bayer (M) Ltd
NBRr glove size:	S1-117-334 μm S2-0.85-15.0 mm S3-direct sheeted form	Juara One Resources Sdn Bhd, Bukit Mertajam, Penang, Malaysia.
Carbon black	N330	Malayan Carbon (M) Ltd
N-Cyclohexyl-2-benzothiazyl sulphenamide (CBS), zinc oxide, stearic acid, sulphur, and processing oil		Anchor Chemical Co (M) Ltd

Mechanical Properties

The tensile testing (ASTM D 412-92), hardness (ASTM D 1415-88), fatigue Monsanto fatigue-to-failure test (FTFT) operating at 100 rev.min⁻¹ where the extension ratio was 1.6, resilience (ASTM D 1054-91) procedure was performed according to previous study [11] and cross-linked density was determined by applying the Flory-Rehner [12].

Scanning Electron Microscopy

The tensile fracture surfaces of respective compounds were investigated with a Zeiss SUPRA 35VP FESEM. The objective was to obtain some information concerning the bonding quality and to detect the presence of micro-defects if there were any.

RESULTS AND DISCUSSION

Cure Characteristics

Table 3 shows the effect of different particle sizes of NBRr and blend ratios on curing characteristics of SBR/NBRr blends. It can be seen that scorch time, t_2 and cure time t_{90} of all SBR/NBRr blends decrease as NBRr content increased. In our previous work [11], we have reported that the increment in NBRr content in SBR/NBRr blends reduces the t_2 and t_{90} due to the existence of cross-linked precursors and unreacted curative in the recycled rubber which the latter would accelerate the vulcanization process. The observation from FTIR spectrum in Figure 1 indicates the presence of unreacted accelerator in NBRr gloves.

Table 2. Formulation of SBR/NBRr blends.

Compounds Ingredients	(phr)				
	R05	R15	R25	R35	R50
SBR	95	85	75	65	50
NBRr	5	15	25	35	50
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Sulphur	2	2	2	2	2
N-Cyclohexyl-2-benzothiazole Sulphenamide (CBS)	1	1	1	1	1
Processing oil	5	5	5	5	5
Carbon black (N330)	50	50	50	50	50

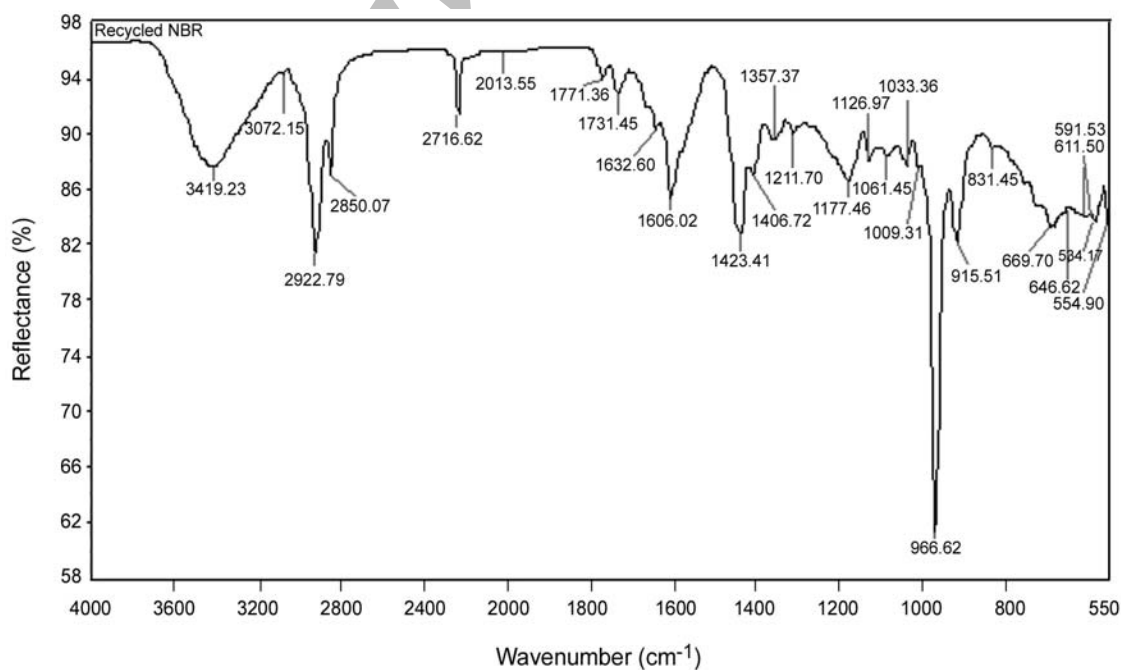
R05: 95/5; R15: 85/15; R25: 75/25; R35: 65/35; R50: 50/50.

Table 3. Effects of different particle sizes of NBRr and blend ratios on curing characteristics of SBR/NBRr blends.

Blend/Different particle sizes		Cure time (min)	Scorch time (min)	Minimum torque (dNm)	Maximum torque (dNm)
R05	S1	19.43	5.98	2.31	19.58
	S2	20.35	6.33	2.46	19.08
	S3	21.07	6.58	2.67	18.40
R15	S1	18.00	5.19	2.79	18.50
	S2	18.41	5.31	2.83	18.40
	S3	18.76	5.39	3.19	18.34
R25	S1	16.28	3.72	3.15	17.58
	S2	16.85	3.79	3.19	17.50
	S3	17.20	3.82	3.39	17.47
R35	S1	15.60	2.67	3.61	17.58
	S2	15.65	2.80	3.67	17.50
	S3	15.69	2.91	3.81	16.29
R50	S1	12.28	1.82	4.07	15.60
	S2	14.07	2.14	4.54	14.88
	S3	14.35	2.53	4.60	14.68

The accelerator that was used by the company was *N*-cyclohexyl-2-benzothiazyl sulphenamide (CBS). This accelerator was represented by functional

groups of N-H, Ar-H, CH₂ and C-S. Non-hydrogen bonded of N-H stretching symmetric vibration can be seen at 3419 cm⁻¹ and N-H bending vibrations at

**Figure 1.** IR spectrum of a sample of NBRr glove.

1632 and 1606 cm^{-1} . While absorption band appeared at 3072 cm^{-1} indicates Ar-H of benzene. Absorption bands at 2922 and 2850 cm^{-1} representing CH_2 of cyclohexane of CBS structure. The stretching vibration bands of C-S were weak at 669 and 554 cm^{-1} . This indicates the presence of unreacted accelerator in the NBRr gloves.

The deterioration in properties can be attributed to the role of carbon black which activates the vulcanizing process through the promotion of hydrogen sulphide formation and the rupture of S-N linkage when heated with sulphanamides in rubber either in the presence or absence of the other compounding ingredients [13]. However, at a similar blend ratio, NBRr(S1) exhibited the shortest t_2 and t_{90} values. This observation might be due to the presence of more cross-linked precursors and unreacted curative in the smallest size of NBRr particles.

The ML of SBR/NBRr blends increased with increasing NBRr content, probably due to the presence of cross-linked NBRr rubber and other additive in SBR/NBRr blends. This indicates that the processability of the SBR/NBRr blends becomes more diffi-

cult. However, at a similar blend ratio, the SBR/NBRr (S1) blends exhibit the lowest ML. This indicates that they could be processed more easily.

The MH of SBR/NBRr blends shows the opposite trend with increasing of NBRr content. This was due to the poor interaction of SBR/NBRr blends as shown later in morphological studies. However, at a similar blend ratio, the SBR/NBRr(S1) blends showed highest MH value due to their largest surface area and better interaction with SBR.

Mechanical Properties

Table 4 shows the effect of different sizes of NBRr particles and blend ratios on mechanical properties of SBR/NBRr blends. It can be seen that the tensile strength of all SBR/NBRr blends declined gradually with increasing NBRr content and also with the decrease of NBRr size at all blend ratios. This observation was probably due to the incompatibility of SBR/NBRr blends [14,15]. It is well known that physico-mechanical properties of SBR and NBR will drop due to the fact that NBR has greater polarity than SBR [16]. Okieimen et al. [17] reported that the

Table 4. Effects of different particle sizes of NBRr and blend ratios on mechanical properties of SBR/NBRr blends.

Blend/Different particle sizes		Tensile strength (MPa)	Elongation-at-break (%)	M100 (MPa)	Fatigue life (kc)
R05	S1	23.47	520.33	2.81	220.0
	S2	22.60	510.44	2.79	217.1
	S3	22.10	505.00	2.67	216.3
R15	S1	21.00	502.67	3.22	205.7
	S2	20.79	485.00	3.09	202.8
	S3	20.37	470.00	2.94	201.0
R25	S1	17.53	452.93	3.38	84.1
	S2	17.34	444.67	3.23	64.3
	S3	16.26	415.00	3.09	45.5
R35	S1	16.36	414.00	3.80	52.6
	S2	15.95	401.00	3.61	36.3
	S3	15.70	388.00	3.50	25.9
R50	S1	10.55	356.20	4.23	19.0
	S2	10.20	262.87	4.15	8.20
	S3	10.00	252.33	3.94	6.30

Table 5. Effects of different particle sizes of NBRr and blend ratios on physical properties of SBR/NBRr blends.

Blend/Different particle sizes		Hardness (Shore A)	Cross-link density ($\times 10^{-8}$ mol/cm ³)	Resilience (%)
R05	S1	70.22	5.63	42.13
	S2	70.00	5.49	44.69
	S3	69.83	5.37	48.14
R15	S1	71.22	6.23	38.58
	S2	70.87	6.03	39.40
	S3	70.42	5.89	41.96
R25	S1	72.55	6.59	35.64
	S2	72.23	6.53	36.84
	S3	72.00	6.10	38.85
R35	S1	74.66	7.70	34.45
	S2	73.97	7.42	35.95
	S3	73.67	7.18	37.85
R50	S1	75.84	10.00	32.95
	S2	75.33	9.90	34.04
	S3	75.11	9.77	35.06

tensile strength of uncompatibilized SBR/NBR blend showed an irregular relationship with NBR content in the blend which points to incompatibility of that blend, as well. However, at a similar blend ratio, SBR/NBRr(S1) blends exhibit higher tensile strength followed by SBR/NBRr(S2) and SBR/NBRr(S3) blends. It is believed that smaller and uniform dispersion of NBRr have contributed to an efficient stress transfer in the SBR/NBRr blends and are responsible for a better tensile strength [11,18]. As the particle size decreases, the contact surface area increases, by which it provides more efficient interfacial bonds to achieve better properties. The deterioration of tensile strength at higher NBRr content was due to a weak interaction between NBRr and SBR matrix due to the increased agglomeration of NBRr [19].

The results indicate that fatigue life of SBR/NBRr blends significantly decreased with increasing NBRr content. Ishak et al. [20] reported that with higher filler loading, the filler particles and aggregates are not dispersed and wetted efficiently by the rubber matrix and stress concentration factor can cause

fatigue failure [21]. However, at a similar blend ratio, SBR/NBRr(S1) blends show highest value of fatigue life followed by SBR/NBRr(S2) and SBR/NBRr(S3) blends. As discussed before, this was due to a smaller size and better dispersion of the NBRr(S1) particles in SBR/NBRr blends which gives more efficient interfacial bonding and therefore it leads to a better fatigue life.

As NBRr content increases, the M100 (Table 4) and hardness (Table 5) also increase, correspondingly. This was due to the incorporation of NBRr in the SBR/NBRr blends that enhanced the cross-linking density properties of SBR/NBRr blends. When more NBRr was blended with SBR matrix, a more rigid SBR/NBRr blends was obtained which led to higher values of M100 and hardness. At a similar blend ratio, SBR/NBRr(S1) blends showed highest M100 and hardness followed by SBR/NBRr(S2) and SBR/NBRr(S3) blends. This again might be due to the largest surface area of the smallest size of NBRr particles which resulted in better interaction with SBR at any blend ratio.

The increment in cross-linking density shown in

Table 5 has contributed to the decrease in E_b values (Table 4). At a similar blend ratio, SBR/NBRr(S1) blends showed highest E_b values. This may be due to better interaction with SBR as a result of better dispersion of NBRr(S1) in SBR/NBRr blends, thus being able to elongate at higher strains.

The resilience of SBR/NBRr blends (Table 5) dropped with increasing NBRr content. SBR/NBRr blends become more rigid as more NBRr were added into the SBR matrix and consequently decreased the resilience. NBR is known as a copolymer of acrylonitrile and butadiene which is also a polar rubber.

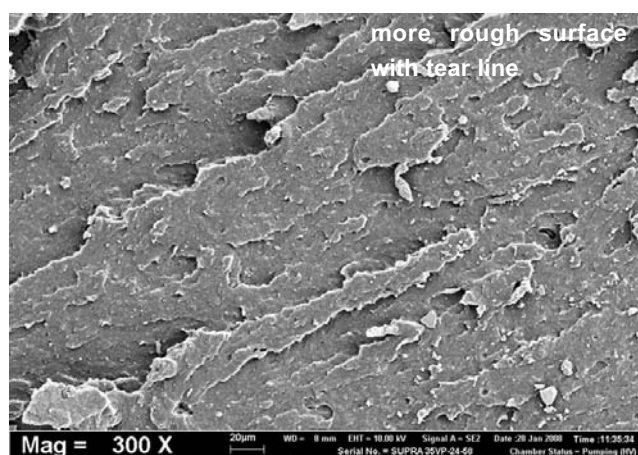
As the acrylonitrile content is increased the rebound resilience is decreased accordingly [22]. However, at a similar blend ratio, SBR/NBRr(S1)

blends exhibit the lowest value of resilience.

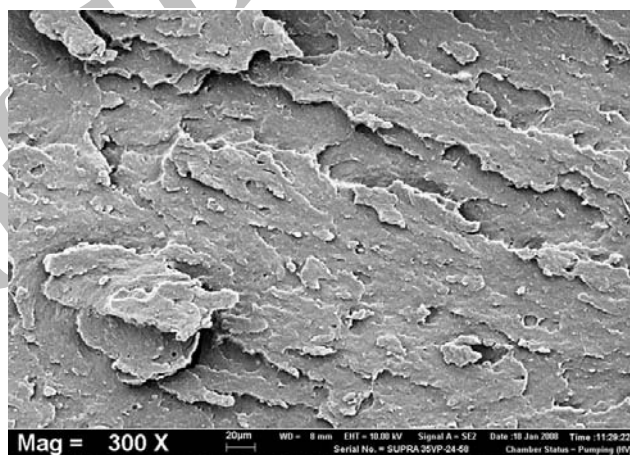
Morphological Properties

Figures 2-4 show the effect of different particle sizes of NBRr on SEM tensile fracture surfaces of SBR/NBRr blends at 95/5, 85/15, and 50/50 blend ratios, respectively. It can be seen that at any blend ratio, the NBRr (S1) was well dispersed in SBR matrix and the tensile fracture surfaces exhibit many tear lines with minimum pull-out of NBRr from SBR matrix (Figures 2a, 3a, and 4a).

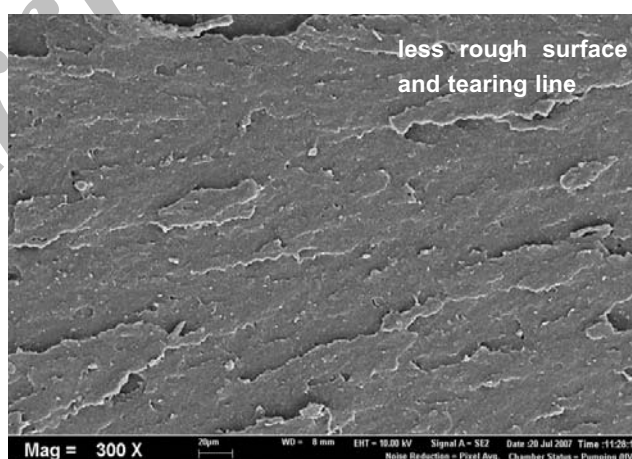
However, with the larger sizes of NBRr particles, i.e., S2 and S3 [11] the NBRr-SBR interactions are weaker, especially at 85/15 and 50/50 blend ratios of SBR/NBRr blends.



(a)

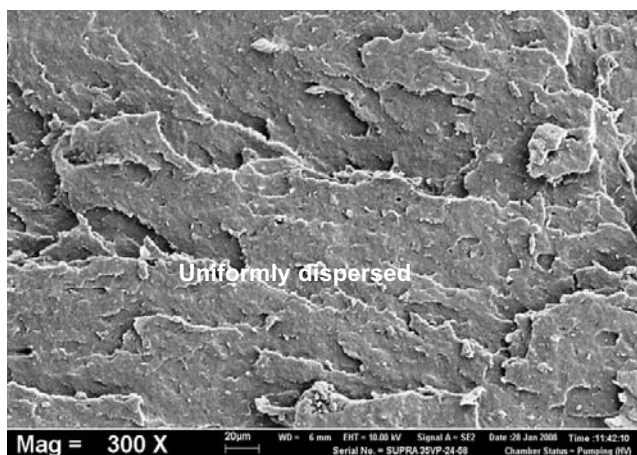


(b)

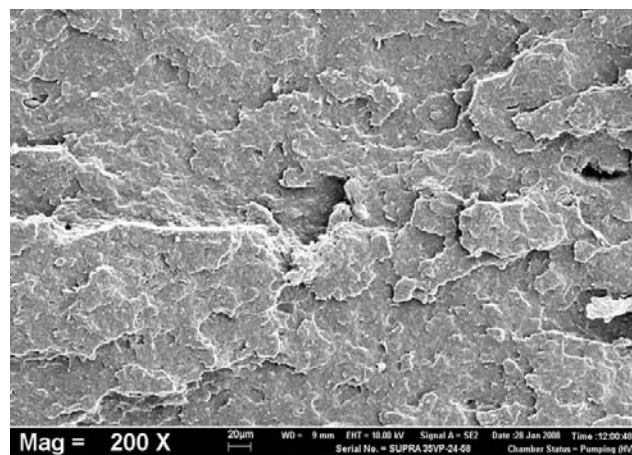


(c)

Figure 2. Effects of NBRr particle size: (a) S1, (b) S2, and (c) S3 on SEM tensile fracture surfaces of SBR/NBRr blends at 95/5 blend ratio.



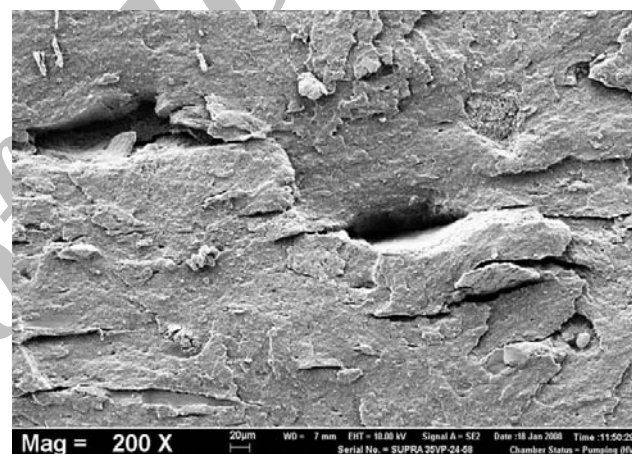
(a)



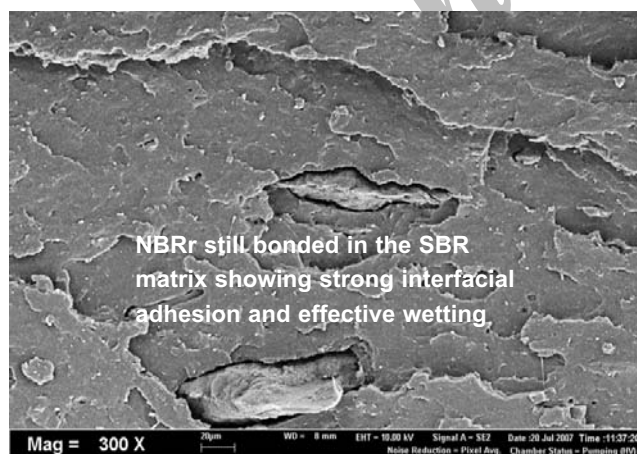
(a)



(b)



(b)



(c)



(c)

Figure 3. Effects of NBRr particle size: (a) S1, (b) S2, and (c) S3 on SEM tensile fracture surfaces of SBR/NBRr blends at 85/15 blend ratio.

Figure 4. Effects of NBRr particle size: (a) S1, (b) S2, and (c) S3 on SEM tensile fracture surfaces of SBR/NBRr blends at 50/50 blend ratio.

CONCLUSION

The following conclusions can be drawn from this study:

- Scorch time, t_2 , and cure time, t_{90} , of SBR/NBRr blends decreased with increasing NBRr content. At a similar blend ratio, SBR/NBRr(S1) blend exhibits longest t_2 and shortest time of t_{90} values.

- Minimum torque (ML) of SBR/NBRr blends significantly increased with increasing NBRr content. SBR/NBRr(S1) blends exhibited lowest ML as compared with SBR/NBRr(S2) and SBR/NBRr(S3) blends at all blend ratios. Maximum torque (MH) of SBR/NBRr blends exhibited opposite trend with increasing NBRr content. SBR/NBRr(S1) blends exhibited the highest MH as compared with SBR/NBRr(S2) and SBR/NBRr(S3) blends at all blend ratios.

- The tensile strength, elongation-at-break (E_b) and resilience decreased with increasing NBRr content in SBR/NBRr blends. At a similar blend ratio, SBR/NBRr(S1) blends exhibited higher tensile strength and E_b values but lower for resilience at the same time. M100, hardness, and cross-linking density increased with increasing NBRr content and decreasing of NBRr particles size ($S1 < S2 < S3$).

- Fatigue life of SBR/NBRr blends significantly decreased with increasing NBRr content. At a similar blend ratio, SBR/NBRr(S1) blends show the highest fatigue life.

- The scanning electron microscopy (SEM) studies on the tensile fracture surface showed that, as the NBRr particles size decreases ($S3 > S2 > S1$) a better NBRr-SBR matrix interaction takes place.

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