The Effects of Different Particle Sizes of Recycled Acrylonitrile Butadiene Rubber and its Blend Ratios on Mechanical and Morphological Properties of vNBR/rNBR Blends

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One of the biggest dangers to our environment today is the increasing number of unused synthetic rubber in the environment and these pose a big threat to nature, if it is not disposed properly. Typically, synthetic rubber is developed for specific applications, and is specifically for those applications due to the process used to make them, and the resulting properties. Dumping these synthetic rubber in dumpsites could contaminate nearby water sources. Heating these synthetic rubber with normal heat will generate harmful chemical substances, like carbon and lead, which are really dangerous for humans. Dealing with rubber properly is not only advantageous to nature, but also to humans. Recycling represents a best alternative to the disposal of post-consumer rubber in common landfills if it is possible to obtain new materials with good final properties compatible with practical application. In this study, characterization and properties of virgin acrylonitrile butadiene rubber/recycle acrylonitrile butadiene rubber (vNBR/rNBR) were examined. Three different size ranges of rNBR particles, i.e., 150 - 350 μm, 2.0 -15.0 mm, and 5 -10 cm were used in this study. The vNBR/rNBR blends with blend ratios of 95/5, 85/15, 75/25, 65/35, and 50/50 phr (part per hundred rubber) were prepared using a two roll-mill at room temperature. The vNBR/rNBR blends with smallest size of rNBR particles show better tensile properties (tensile, elongation-at-break and M100) compared with all other blend ratios. For physical properties, vNBR/rNBR blends with smallest size of rNBR particles exhibited the highest hardness and cross-linking density at all blend ratios whereas resilience decreased, accordingly. The cross-linking density of vNBR/rNBR blends also show an increasing trend with increasing rNBR content. A morphological study of tensile fracture surface of the blends was also carried out. The scanning electron microscopy study indicates that rNBR exhibited a weak rNBR-vNBR matrix interaction particularly when more than 25 phr of rNBR was used, thus decreasing the mechanical properties of vNBR/rNBR blends.

Keywords: vNBR, rNBR, Curing characteristic, Mechanical properties, Morphological properties

The abundance of waste rubber created huge environmental problems, because all waste rubber is non-degradable material. The conventional method of disposing of waste rubber, such as discarding in a landfill and burning was not suitable as it causes severe environment pollutions and uneconomical [1]. The recycling of waste rubbers is an important process, both from the point of view of utilization of resources and prevention of environmental pollutions [2]. The utilization of waste material also is an important factor in the expansions of the raw material basis of industry, the reduction of demand of primary materials and economization of financial resources [3].

An approach to reutilization of waste rubber can be done by mechanical [4, 5] and chemical processes [6, 7]. 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 an recycled acrylonitrile butadiene rubber (rNBR) gloves (waste) obtained from medical industry (Top Glove Sdn. Bhd.) in effort to create a value added rubber materials based on blend of rNBR glove with virgin acrylonitrile butadiene rubber (vNBR) [8-14].

rNBR gloves are a type of disposable glove made of synthetic rubber. They contain no latex proteins and offer excellent resistance to wear and tears. rNBR gloves are more puncture resistant than many other types of rubber gloves and can be used to offer superior resistance to many types of chemicals. Unlike other disposable gloves, rNBR gloves have low resistance to friction and are very easy to slide on. As with some other types of disposable gloves, however, powder such as cornstarch may be added in order to make putting on the gloves as easy as possible. These gloves are popular for their high degree of flexibility and superior solvent resistance. They are resistant to many oils and some acids, making rNBR gloves a good choice for many manufacturing environments.

Many researchers tend to reutilization of waste rubber by mechanical process, as it is more cost effective

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Materials	Description	Source
Virgin acrylonitrile butadiene rubber (vNBR)	-	JSR Corporation Sdn. Bhd.
Recycled acrylonitrile butadiene rubber (rNBR)	Size = S1: 150 - 350 μm Size = S2: 2.0 -15.0 mm Size = S3: 5 -10 cm	Top Glove Sdn. Bhd.
N-cyclohexyl-2-benzothiazyl sulfenamide (CBS), zinc oxide, stearic acid, sulphur, antioxidant and processing oil	-	Anchor Chemical Co (M) Ltd

Table 1
CHARACTERISTICS OF MATERIALS

Ingredients (phr)	Blend Ratios					
	C	RO5	R15	R25	R35	R50
vNBR	100	95	85	75	65	50
rNBR	0	5	15	25	35	50
Zinc Oxide	5	5	5	5	5	5
Stearic Acids	2	2	2	2	2	2
Sulphur	2	2	2	2	2	2
N-cyclohexyl-2-benzothiazole sulfenamide (CBS)	1	1	1	1	1	1
Antioxidant	1	1	1	1	1	1
Processing Oil	5	5	5	5	5	5

Table 2
FORMULATION FOR vNBR/rNBR BLENDS

compared to chemical process [15-17]. The incorporation of recycle nitrile glove (rNBR) with virgin acrylonitrile butadiene rubber (vNBR) can be a new alternative to the rubber based product. To the best of our knowledge, no attempts have been made so far to investigate the characterization and properties of virgin acrylonitrile butadiene rubber (vNBR)/recycled acrylonitrile butadiene rubber (rNBR) blends.

The purpose of this paper is to study the effects of different particle sizes of recycled acrylonitrile butadiene rubber and its blend ratios on mechanical and morphological properties of vNBR/rNBR blends. Three different sizes of NBRr particles, 150 - 350 μm, 2.0 -15.0 mm, and 5 -10 cm were used in this study. vNBR/rNBR were prepared with five different composition ratio which are 95/5, 85/15, 75/25, 65/35, and 50/50. The properties such as mechanical properties and morphological properties of vNBR/rNBR blends were reported.

Experiemntal part

Materials and methods

vNBR was purchased from JSR Corporation Sdn. Bhd.. The rNBR glove was supplied by Top Glove Sdn Bhd, Malaysia. Other compounding ingredients, such as N-cyclohexyl-2-benzothiazyl sulfenamide (CBS), zinc oxide, stearic acid, sulphur and processing oil were all purchased from Anchor Chemical Co (M) Ltd.

Compounding and Sample Preparation

The vNBR/rNBR blends were formulated with blends ratio of 95/5, 85/15, 75/25, 65/35, and 50/50 as given in table 2. The rubber was pre-blended and the mixing procedure was carried out in accordance with ASTM D 3184-89 [18] using a two-roll mill (Model: X(S)K – 160X320) at room temperature. Cure characteristics were studied using a Rheometer Model HT-M2000 according to ASTM D 2240-93. Samples of about 4 g of the respective compounds were used to test at vulcanization temperature (160 °C). The rubber compounds then were compression molded at 160°C with a force of 10MPa using a hot press according to respective cure times, t_{90}.

Measurement of Mechanical Properties

Dumb-bell shaped samples were cut from the molded sheets, and the tensile testing procedure was done according to ASTM D 412-93. The tensile test was performed at a crosshead speed of 500mm/min using a Monsanto Tensometer M500. The hardness measurement of sample was done according to ASTM D 1415-88 using a Wallace dead load, with the hardness ranging from 30 to 85 IRHD (International Rubber Hardness Degree). Resilience was studied using a Wallace Dunlop Tripsometer according to ASTM D 1054-91. Rebound resilience was calculated according to the following equation:

$$\text{Percentage resilience} = [(1 - \theta\cos_2)] / [(1 - \theta\cos_1)] \times 100\% \quad (1)$$

where θ1 is the initial angle (45°) and θ2 is the maximum rebound angle.

Cross-link Density Study

Cure test pieces of dimension 30 x 5 x 2 mm were weighed using an electrical balance and each test piece was immersed in a glass vessel containing toluene (30mL) at 25°C. The vessel was kept in the dark to prevent oxidation. The samples from the glass vessels and the excess toluene were removed by lens blotting paper. The samples were then kept in a closed vessel to prevent toluene evaporation and the weights of the swollen samples were determined. The sample was then re-immersed 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 swelling data were utilized to calculate the molecular weight between two cross-links (Mc) by applying the Flory-Rehner equation [19]:

$$M_c = \frac{-\rho_p V_s V_r^{1/3}}{\ln(1 - V_r) + V_r + \chi V_r^2} \quad (2)$$

$$V_r = 1 / (1 + Q_m) \quad (3)$$

Where ρ is the density of the rubbers, Vs is the molar volume of the solvent (toluene), Vr is the volume fraction of the swollen rubber, χ is the interaction parameter of the rubber, and Qm is the weight swollen ratio of the vNBR/rNBR blends in toluene. The degree of cross-linking density (v) is given by

$$V = 1 / (2\ Mc) \quad (4)$$

The following constant values were used to determine the degree of cross-linking density of vNBR/rNBR:

ρ (NBR) 1.17g/cm^3; χ (NBR) 0.390; Vs (toluene) 106.35 cm^3/mol (5)

Morphology analysis

Testing on morphology of tensile fracture surface of the sample was done by using scanning electron microscope

Different Blends and rNBR sizes		Tensile Strength (MPa)	Elongation at break (%)	M100 (MPa)
100/0	CONTROL	1.73	257.00	0.97
95/5	S1	2.39	303.5	1.15
	S2	2.23	289.70	1.11
	S3	2.08	278.30	1.02
85/15	S1	2.80	317.10	1.24
	S2	2.48	300.00	1.19
	S3	2.32	287.50	1.13
75/25	S1	3.18	333.30	1.32
	S2	2.90	318.40	1.25
	S3	2.70	306.70	1.18
65/35	S1	3.06	296.70	1.42
	S2	2.85	278.30	1.37
	S3	2.66	263.00	1.34
50/50	S1	2.79	278.3	1.54
	S2	2.62	264.00	1.46
	S3	2.54	246.70	1.42

Table 3
EFFECTS OF DIFFERENT rNBR AND ITS BLEND RATIOS ON TENSILE PROPERTIES OF vNBR/rNBR BLENDS

Different Blends and rNBR sizes		Hardness (Shore A)	Cross-link Density (x10^{-4}mol/cm^3)	Resilience (%)
100/0	CONTROL	50.20	1.69	64.96
95/5	S1	52.40	1.78	66.72
	S2	51.50	1.76	66.97
	S3	51.20	1.74	68.14
85/15	S1	54.20	1.89	65.14
	S2	53.20	1.87	66.33
	S3	52.20	1.84	66.61
75/25	S1	55.40	1.97	63.71
	S2	54.40	1.93	65.17
	S3	53.10	1.87	65.73
65/35	S1	57.10	2.14	62.64
	S2	56.10	2.12	63.81
	S3	54.40	2.02	64.61
50/50	S1	58.80	2.29	61.92
	S2	57.60	2.27	62.16
	S3	56.40	2.21	62.77

Table 4
EFFECTS OF DIFFERENT rNBR AND ITS BLEND RATIOS ON PHYSICAL PROPERTIES OF vNBR/rNBR BLENDS

(SEM) model JEOL JFC6460LA. The fracture surface for dumbbell sample is cut. Then, the cut sample is placed on provided aluminum plate. In order to be observed with a SEM, sample needs first to be made conductive for current. This was done by coating it with an extremely thin layer (1.5 – 3.0 nm) of gold or gold-palladium inside "sputter coater" machine. It is also to avoid electrostatic charging and poor image resolution.

Results and discussions

Mechanical Properties

Table 3 and 4 show the effects of different sizes of rNBR and blend ratios on tensile properties of vNBR/rNBR blends and the effects of different sizes of rNBR and its blend ratios on physical properties of vNBR/rNBR blends, respectively. It can be seen that, the tensile strength (TS) and elongation at break (Eb) of all vNBR/rNBR blends increased up to 25 phr (optimum), thereafter decreased with further loading of rNBR. The reduction of TS and Eb was resulted in weak rubber-rubber interaction due to the formation of rNBR aggloremation [20]. However, at a similar blend ratio, vNBR/rNBR (S1) blends exhibit higher TS and Eb followed by vNBR/rNBR (S2) and vNBR/rNBR (S3) blends. It is believed that smaller size and uniform dispersion of NBRr have contributed to an efficient stress transfer in the vNBR/NBRr blends and are responsible for better TS [12, 21]. As the particle size decreases, the contact surface area increases, by which it provides more efficient interfacial bonds to achieve better properties.

As the rNBR loading increases, the M100 and hardness also increase at all over the blends. The incorporation of rNBR into the vNBR matrix increased the stiffness of the blends because M100 represents stiffness of the material [22]. The flexibility and elasticity of the rubber chain was less when more rNBR were incorporated into vNBR, which also resulted in more rigid rubber blends and increase in hardness [23]. At a similar blend ratio, vNBR/rNBR (S1) blends showed highest M100 and hardness followed by vNBR/rNBR (S2) and vNBR/rNBR (S3) blends. This again was due to the largest surface area of the smallest size of rNBR which resulted in better interaction with vNBR matrix.

The crosslink density increased with increasing rNBR content in the vNBR/rNBR blends. Generally, rNBR and vNBR are both polar rubbers. With the addition of rNBR in vNBR/rNBR blends, compatibility between these rubbers might occur due to the interaction between vNBR and rNBR which increased the crosslinking rate. At similar blends ratio, vNBR/rNBR (S1) blends exhibit higher cross-link density followed by vNBR/rNBR (S2) and vNBR/rNBR (S3) blends. As discussed before, as the rNBR size decreases, the contact surface area increases, by which it provides more efficient interfacial bonding and therefore it leads to a better cross-link density.

The resilience of vNBR/rNBR blends significantly dropped with increasing rNBR content. vNBR/rNBR blends become more rigid as more rNBR were added into the vNBR 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 accordngly [24]. However, at a similar blend ratio, vNBR/rNBR (S1) blends exhibit the lowest value of resilience.

Morphological properties

Figure 1 shows the effect of different particle sizes and blend ratios at (a) control; (b) S1-R05; (c) S1-R25; (d) S2-R05; (e) S2-R25; (f) S3-R05; (g) S3-R25 of rNBR on SEM tensile fracture surfaces of vNBR/rNBR blends, respectively.

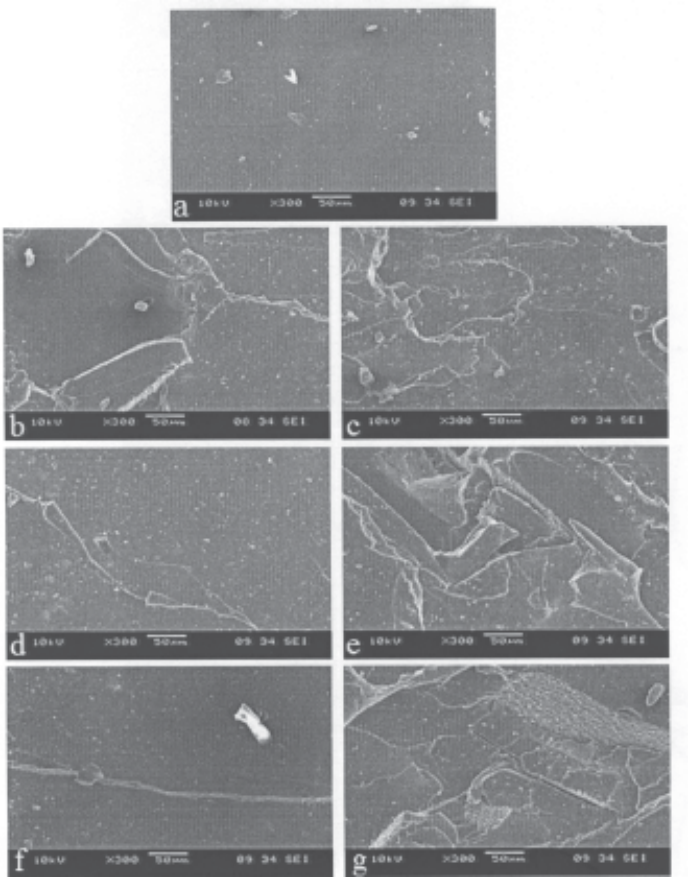

Fig. 1. The effect of different particle sizes and blend ratios at (a) control; (b) S1-R05; (c) S1-R25; (d) S2-R05; (e) S2-R25; (f) S3-R05; (g) S3-R25 of rNBR on SEM tensile fracture surfaces of vNBR/rNBR blends

It can be seen that at any blend ratio, the rNBR (S1) was well dispersed in vNBR matrix and the tensile fracture surfaces exhibit many tear lines with minimum pull-out of rNBR from vNBR matrix. However, with the larger sizes of rNBR particles such as S2 and S3 [12] the vNBR-rNBR interactions are weaker.

Conclusions

The following summaries can be drawn from this study:

1) The TS and Eb increased particularly up to 25 phr of rNBR content, thereafter decreased with further loading of rNBR. At a similar blend ratio, vNBR/rNBR (S1) blends exhibited higher TS and Eb values.

2) The M100, hardness, and cross-linking density increased with increasing rNBR content in vNBR/rNBR blends except for resilience. However, at similar blend ratio, vNBR/rNBR (S1) blends the lowest M100, hardness, cross-linking density and resilience values.

3) The scanning electron microscopy (SEM) studies on the tensile fracture surface showed that, as the rNBR particles size decreases (S3 > S2 > S1) a better vNBR-rNBR matrix interaction.

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