

The effect of carbon black (CB) loading on curing characteristics and mechanical properties of virgin acrylonitrile butadiene rubber (Nbrv)/recycled acrylonitrile butadiene rubber (Nbr) blends

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Abstract. Recently, the interest of polymer industry researchers have grown rapidly on the use of specific techniques which can reduce cost and utilize rubber waste into the processing form. The increasing of cognizance in environmental matters and the desire to sustain the resources had fortified the practice of recycling waste materials. In this work, the effect of carbon black loading on curing characteristics and mechanical properties of virgin acrylonitrile butadiene rubber/recycled acrylonitrile butadiene rubber (NBRv/NBRr) blends were studied. Cure time (t_{90}), scorch time (t_{s2}) and swelling percentage decreased but minimum torque (M_L) and maximum torque (M_H) increased with increasing carbon black (CB) loading in the blends. Increasing CB loading also increased tensile strength, tensile modulus (M_{100}), hardness and compression set but decreased elongation at break (E_b) of NBRv/NBRr blends.

1. Introduction

Currently, Malaysia is among the world biggest supplier and manufacturer of natural rubber and nitrile gloves. The properties of the NBR gloves are vary included an excellent resistance to punctures, tears and chemicals. Due to environment concerns, a lot of research to gives value to the recycled NBR gloves were done [1-3].

The NBR is well known to its excellent oil resistance, superior strength, abrasion, water and heat. Eventhough NBR did not shows any self-reinforcing effect which means no crystallinity but the vulcanizates with excellent mechanical properties can be achieved by using reinforcing filler in the rubber blend [4-6].

The reinforcement of rubber by rigid entities is one of the most important phenomena in material science where carbon black has been found to offer substantial improvement in the mechanical properties of rubber because of it has very good compatibility with rubbers [7, 8]. In this work, carbon black is used as the only reinforcing filler with different loading ranging from 30 up to 70 phr.

One of the most valuable technique to prepare materials with greater properties is blending method, where two or more types of materials will be blended. This method can gives added value of properties to the vulcinates which are lacking in the component of rubber. The best combination of the rubber compounding can be obtained through elastomer blends technique where it is widely used the rubber industry in order to improve physical properties, processability and reduce cost [9-11]. The



virgin acrylonitrile butadiene rubber (NBRv) and recycled acrylonitrile butadiene rubber (NBRr) were blended together with an intention to combine the best properties from each rubber component in order to improve the rubber blend properties.

In polymer compound area there are a lot studies had been conducted relate to recycled acrylonitrile butadiene rubber (NBRr) [5, 12]. However, no reports have been made so far on the use of carbon black (CB) filled recycled acrylonitrile butadiene rubber (NBRr) blend with virgin acrylonitrile butadiene matrix (NBRv). This study aimed to investigate the effect of carbon black loading on curing characteristics and mechanical properties of virgin acrylonitrile butadiene rubber/recycled acrylonitrile butadiene rubber (NBRv/NBRr) blends.

2. Materials and Methods

2.1 Materials

The recycled NBR glove was purchased from Juara One Resources (M) Sdn. Bhd., Bukit Mertajam, Penang, Malaysia. Some of ingredients of the NBRr glove obtained from manufacturer are listed as follows: stabilizer 25 % (0.5 phr), colorant 43 % (0.4 phr), accelerator 30 % (0.2 phr), heat sensitive agent 11 % (0.2 phr) and thickener 2 % (0.2 phr). NBR Nipol, DN3335 with ACN content of 33 % is a medium high nitrile rubber with Mooney viscosity [ML (1 + 4) at 100 °C] of 35 Mooney unit was used as a virgin NBR. Carbon black (N330) was supplied by Malayan Carbon (M) Ltd. The compounding ingredients such as stearic acid, zinc oxide (ZnO), 2,2-methylenebis-(4-methyl-6-tert-butylphenol) (BKF), N-cyclohexyl-2-benzothiazolesulfenamide (CBS), tetramethylthiuram disulfide (TMTD) and sulfur were supplied by Bayer (M) Ltd (Petaling Jaya, Malaysia).

2.2 Preparation of blends

The NBRv/NBRr blends were prepared at fixed recycled NBR content which is 15 phr with different carbon black loading ratio. Table 1 shows rubber blend formulations. In compliance with ASTM method D3184-80, a laboratory-sized two roll mills (160mm x 320 mm) was used to prepare rubber blends with five diverse compositions as shown in table 1. Monsanto Moving Die Rheometer (MDR 2000) was used in order to study the curing characteristics of the rubber blends. Approximately 4g of each compounds was tested where the vulcanization temperature was set at 160 °C and the informations obtained from the test were cure time (t_{90}), scorch time (t_{s2}), maximum torque (M_H) and minimum torque (M_L). At 160°C, the rubber compounds were compressed by using a hot press conferring to each rubber blend cure time, t_{90} .

2.3 Characterization and Testing of blends

Conferring to ASTM D3182, the molded sheets were cut into five samples dumb-bell shaped for each compound. Universal tester tensile machine (Instron 3366) were used to perform tensile test at a cross-head speed of 500 mm/min conferring to ASTM D412-06ae2. Wallace dead load was used to measure the hardness of the samples ranging from 30 to 84 IRHD (International Rubber Hardness Degree) and the hardness test was done according to ASTM D2240-05 (2010).

By conferring to ASTM D471, the swelling test in motor oil was conducted in order to measure the crosslink density of the samples. From the molded sheets, the test pieces with dimensions of 30 mm × 5 mm × 2 mm were prepared. The initial weight of the test samples was recorded before the test. Prior to equilibrium, it takes 48 h at room temperature (25°C) after the test pieces immersed and conditioned in motor oil. The samples were weighed again prior to the conditioned period. The motor oil was removed from the sample surfaces prior to removing the samples from the liquid, and the weight was determined. The swelling percentage (Q) is calculated as follows:

$$Q = \left(\frac{w_s - w_{ds}}{w_{ds}} \right) * 100 \quad (1)$$

where w_s is the weight of the swollen specimen and w_{ds} is the weight of the initial specimen.

Conferring to compression set test ASTM D395, the samples undergo vulcanization by compression molding method where the standard of the test specimens is cylindrical shape of 25 ± 0.1 mm diameter and 12 ± 0.5 mm thickness. The compression device has spacers on each side in order to allow sufficient clearance of bulging when the rubber were compressed and the test samples was placed between the plates of the device. In order for the plates to drawn together uniformly until in contact with the spacers, the bolts were tightened. The percentage of the compression laboring was 25% of the original thickness. For 22 h at 70 °C in oven, the assembled compression device was placed. As for heating period the completed assembly were remain in dry air circulated oven, the device had taken out from the oven and the test specimen removed immediately and allowed to cool for 30 min, using an electronic digital caliber (0.01 mm) accuracy the final thickness was measured prior to rest time. The compression set can be expressed as:

$$C\% = \frac{t_0 - t_1}{t_0 - t_s} * 100 \quad (2)$$

Where t_0 = the original thickness of the sample; t_1 = the thickness of the sample after removed from the clamp; and t_s = thickness of the spacer bar used.

Table 1. Formulation of NBRv/NBRr blends with different CB loading

Ingredients	Blends (phr ^a)				
NBRv	85	85	85	85	85
NBRr	15	15	15	15	15
Sulfur	1.5	1.5	1.5	1.5	1.5
Zinc Oxide	4.5	4.5	4.5	4.5	4.5
Stearic Acid	2	2	2	2	2
BKF	1	1	1	1	1
CBS	1	1	1	1	1
TMTD	1	1	1	1	1
CB (N330)	30	40	50	60	70

^a per hundred resin

3. Results and Discussion

3.1 Curing characteristics

The scorch time (t_{s2}), optimum cure time (t_{90}), minimum torque (M_L) and maximum torque (M_H) of NBRv/NBRr blends were studied. Scorch time was known as induction time and it is the time at which crosslink starts to form in the blends. From Figure 1 and 2, the scorch time and cure time decreased with increasing carbon black content. This can be explained by the cross-link and relics additives in the recycled rubber and the presence of curative agent such as sulfur in recycled NBRr that had crosslinked with carbon black.

The effect of the different loading of carbon black that filled NBRv/NBRr blend on minimum torque (M_L) and maximum torque (M_H) is shown in Figure 3 and Figure 4. It has shown that the maximum torque (M_H) and minimum torque (M_L) of NBRv/NBRr blends increase with increasing carbon black loading. This observation was probably due to the cross-linked of NBRv/NBRr rubber blend with carbon black and other additives [13] that caused the flow resistance in the rubber blend increases.

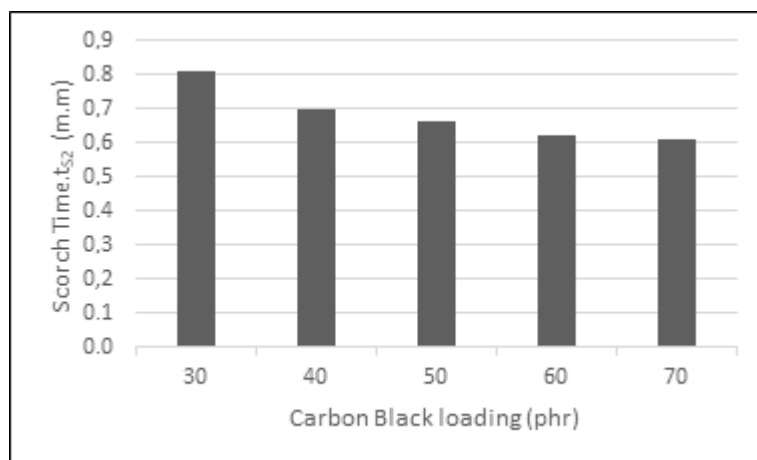


Figure 1. The effect of carbon black loading on the scorch time of carbon black filled NBRv/NBRr blends

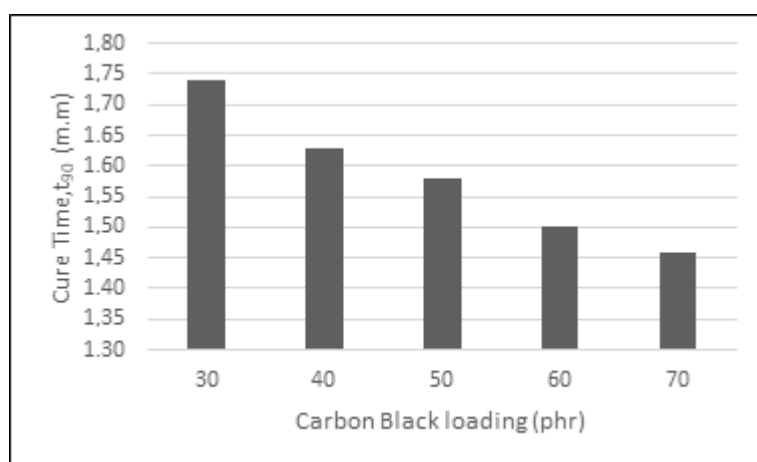


Figure 2. The effect of carbon black loading on the cure time of carbon black filled NBRv/NBRr blends

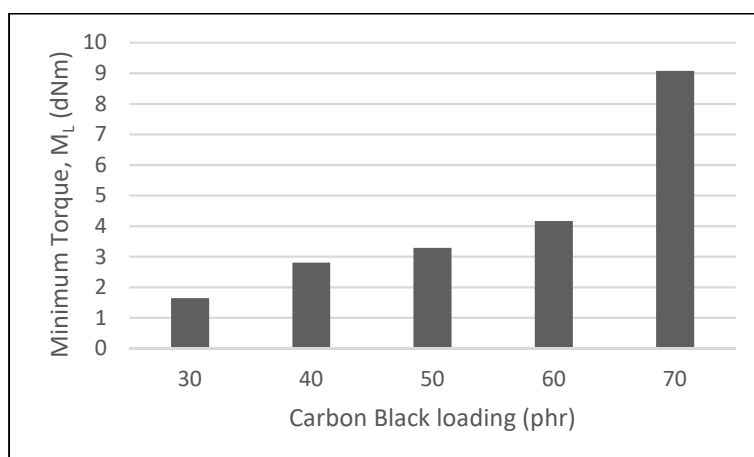


Figure 3. The effect of carbon black loading on the minimum torque of carbon black filled NBRv/NBRr blends

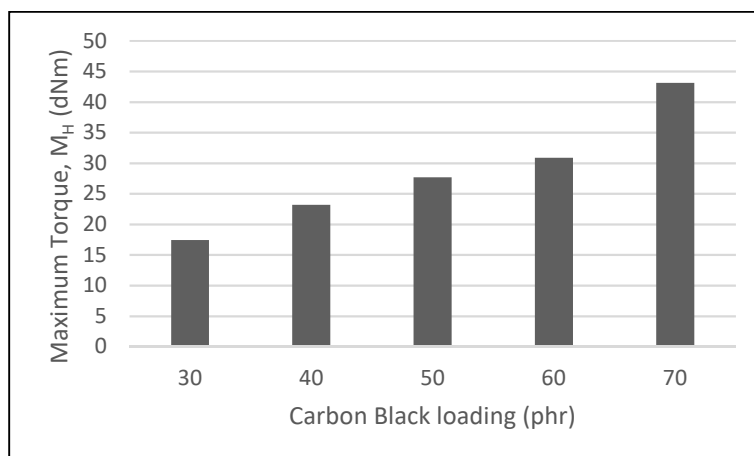


Figure 4. The effect of carbon black loading on the maximum torque of carbon black filled NBRv/NBRr blends

3.2 Mechanical properties

The addition of fillers to polymeric materials leads to improvement in the mechanical properties of the polymer matrix. The reinforcement effect is directly related to the properties of the interphase and depends on the nature of the specific interactions between polymer and reinforcing fillers [14].

The effect of blend ratio on the tensile strength of the carbon black filled NBRv/NBRr blends is shown in Figure 5. It can be seen that with increasing carbon black loading the tensile strength of the rubber blends increases. The reinforcement of carbon black with the NBRv/NBRr blends has caused the increasing of tensile strength. When more carbon black were added into the blends, it increases the crosslinking density of the blends thus increases the tensile strength of the NBRv/NBRr blends [15].

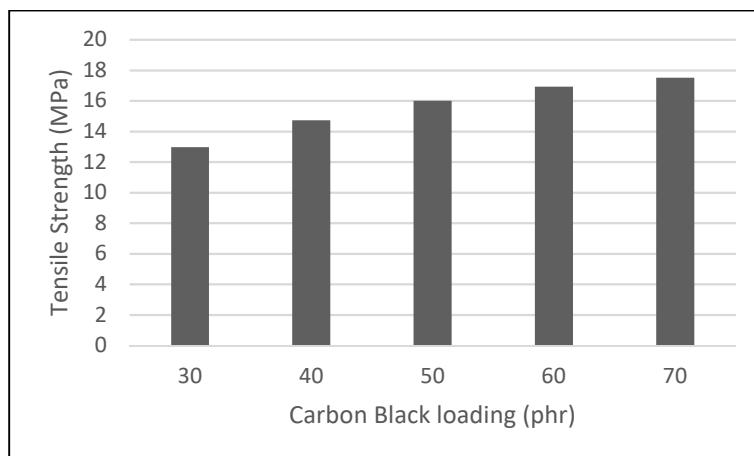


Figure 5. The effect of carbon black loading on the tensile strength of carbon black filled NBRv/NBRr blends

The effects of carbon black filled NBRv/NBRr rubber blends on elongation at break (E_b), M100 (stress at 100 % elongation), hardness and swelling percentage are shown in Figure 6-9. The results indicated that elongation at break decreasing with increasing content of carbon black while M100 and hardness were decreasing. The trend shows that M100 slightly increase with increasing carbon black content. While the increment in crosslink density of the rubber blend caused the increased in modulus and hardness. When more carbon black were incorporated into the NBRv/NBRr blend, the flexibility

and elasticity of the rubber chain reduced which caused an increase in hardness and more rigid rubber vulcanizates. The maximum swelling percentage decreases (Figure 6) with increasing of carbon black content. The decreasing in swelling percentage might due to lessen penetration of motor oil into NBRv/NBRr blend. In practice, the density of crosslinking in rubber compound increases drastically with increasing CB content, resulting a rise of network elasticity contributions. These crosslinks restrict extensibility of the rubber chains induced by swelling and make it more difficult for motor oil to diffuse into the gaps between rubber molecules thus decrease the swelling percentage [16-18].

Figure 7 shows the decreasing of elongation at break of the NBRv/NBRr blends with increasing carbon black content. The decreasing trend was due to the presence of the carbon black in the compound which restrict the mobility of NBRv/NBRr blend that cause the sample to fail at lower elongation.

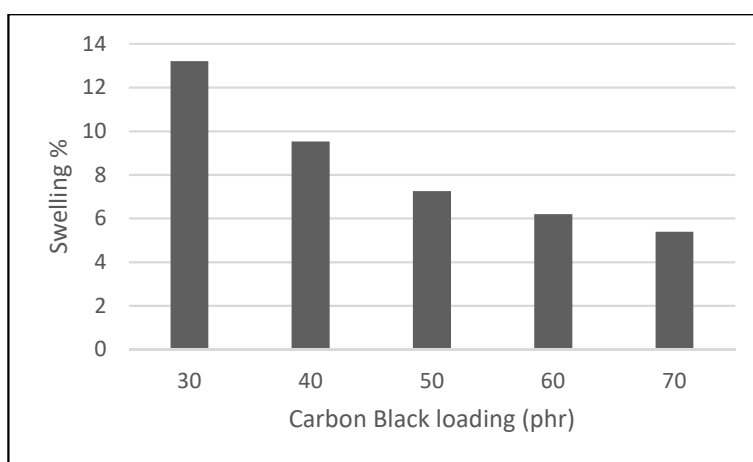


Figure 6. The effect of carbon black loading on the maximum swelling percentage of carbon black filled NBRv/NBRr blends

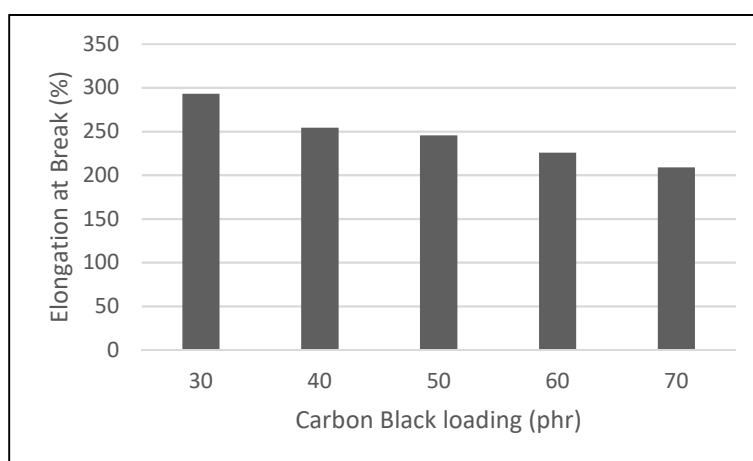


Figure 7. The effect of carbon black loading on the elongation at break of carbon black filled NBRv/NBRr blends

Figure 10 shows the variation of the percentage of compression set (C%) against NBRv/NBRr blend ratio. With increasing the carbon black loading, the compression set of NBRv/NBRr compounds increases. As carbon black loading increases, the mobility of the rubber chains decreased due to the increasing of the crosslink density in NBRv/NBRr blend, subsequently, induce stiffness in the filled compounds [19].

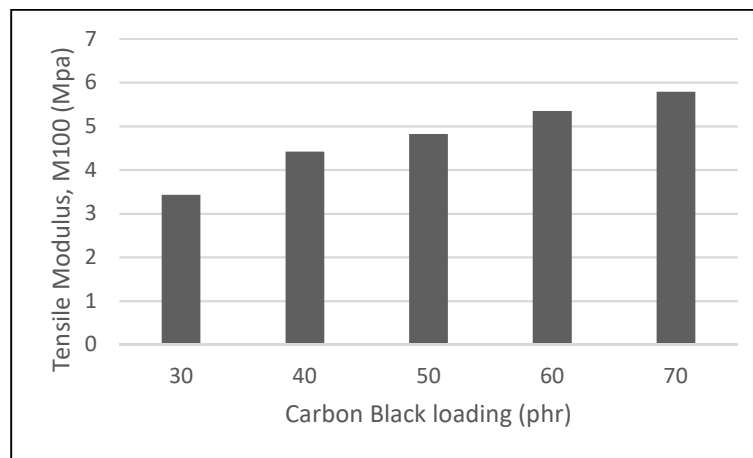


Figure 8. The effect of carbon black loading on the M100 of carbon black filled NBRv/NBRr blends

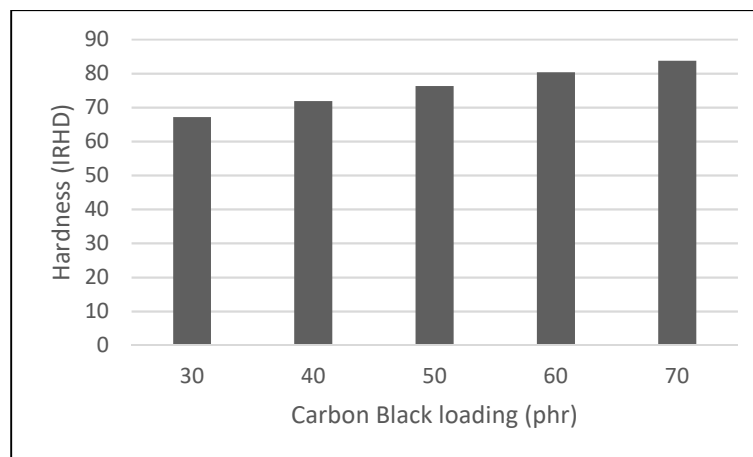


Figure 9: The effect of carbon black loading on the hardness of carbon black filled NBRv/NBRr blends.

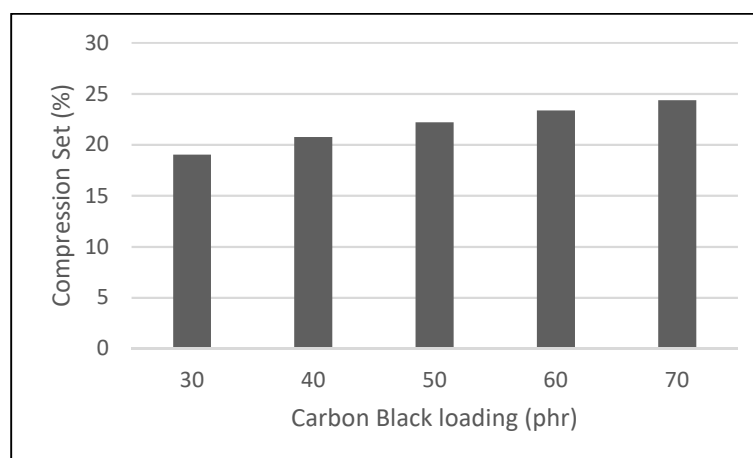


Figure 10. The effect of carbon black loading on the compression set of carbon black filled NBRv/NBRr blends

4. Conclusions

The following conclusions were derived from the experimental results:

1. The scorch time, cure time and swelling percentage decreased with increasing carbon black loading in the NBRv/NBRr blends.
2. The ML and MH increased with increasing carbon black loading in the NBRv/NBRr blends.
3. The elongation at break decreased meanwhile tensile strength, M100 and hardness increased with increasing carbon black loading content.
4. The compression set of the NBRv/NBRr blends increased as carbon black loading content increasing. The higher compression set value is due to higher crosslinking density of the NBRv/NBRr blends.

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