

Comparative Study of Bentonite Filled Acrylonitrile Butadiene Rubber and Carbon Black Filled NBR Composites Properties

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ABSTRACT

This paper determines the potential of bentonite to replace the commonly used carbon black as filler in synthetic rubber composite product. Thus, the study made by comparing the results of curing, tensile thermal and morphological properties of bentonite and carbon black filled acrylonitrile butadiene rubber composites. The result of the tensile strength (TS), modulus at 100 % elongation (M100) and modulus at 300 % elongation (M300) for both bentonite (Bt) and carbon black (CB) filled NBR composites increased as the filler loading increased. The elongation at break (Eb) for Bt followed the same trend but not for NBR/CB composites. At similar filler loading, CB filled acrylonitrile butadiene rubber (NBR) composites demonstrated higher TS, M100, M300, and Eb compared to the Bt filled NBR composites. As the filler loading increased, the swelling percentage decreased for both types of fillers. However, at similar filler loading, the swelling percentage of CB filled NBR (NBR/CB) is lower than the Bt filled NBR (NBR/Bt). Scanning electron micrograph (SEM) of the tensile fractured surface of NBR/CB composites exhibits better filler dispersion and more tear lines compared to the NBR/Bt composites.

Keywords: Bentonite; NBR, carbon black; rubber composites.

INTRODUCTION

Rubber is one of the materials with high importance and impact in our life due to its amazing properties. These have been proven by the existence of it in most of the crucial engineering sectors such as automotive [1], the construction of the earthquake-resistance buildings [2] and aeroplanes [3, 4]. Generally, rubber is classified into two types; namely, natural rubber that is produced from the rubber tree and man-made synthetic rubber such as styrene butadiene rubber, acrylonitrile butadiene rubber, butadiene rubber etc. [7].

Filler in the rubber recipe is an important element to modify the properties and the performance of the rubber product [5]. One of the aspects used to categorize the filler is by its colour. For instance, carbon black is classified under the black filler, whereas clay is an example of a white filler. Carbon black is used extensively as a filler in this industry due to its leading performance. However, it has a harmful effect on the environment and hazardous to the health of the workers [9, 10]. Studies show that the incorporation of white filler has begun to match the capability of black filler. Also, the white filler is also capable of providing the colouring ability of the product which has made it more attractive. [8].

Clay type filler was one of the popular white filler used as study material in enhancing the rubber product and substitute the black filler [6, 8]. The list of common clay fillers is montmorillonite [11], bentonite [12], halloysite [14], kaolin, smectite, and palygorskite etc. [13]. Interesting characteristics possessed by clay such as the active site of it hydroxyl functional group, interlayer that is possible for the cations exchanges, ability to maintain chemical stability despite the difference in silicon-oxygen tetrahedral and alumina hydrated octahedral sheet, has opened to a huge possibility for discovery, research, and improvement [15].

METHODOLOGY

The synthetic rubber (acrylonitrile butadiene rubber, NBR) supplied by Zarm Scientific & Supplies (M) Sdn. Bhd. The other ingredients, i.e. stearic acid, zinc oxide, tetramethyl thiuram disulphide (TMTD), 2,2-Methylene bis (4-methyl-6-tert-butyl phenol) (BKF), N-Cyclohexyl-2-benzothiazole sulfenamide (CBS) and sulphur were distributed by Bayer (M) Ltd. The particle size of the bentonite was 5.31 μm , and the density was 2.654 g/cm^3 . Bentonite has a specific surface area of 0.975 m^2/g and supplied by Ipoh Ceramics (M) Sdn Bhd. The carbon black used was N330 type and was supplied by Malayan Carbon. Table 1 shows the formulation of NBR/Bt and NBR/CB composites used in this study. The formulation in Table 1 was compounded using two roll-mill model XK-160 at room temperature.

Table 1. Formulation of NBR/Bt and NBR/CB composites (part per hundred rubber).

Ingredients	Loading (phr)				
NBR	100	100	100	100	100
Bt or CB	0	10	30	50	70
ZnO	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	0.25	0.25	0.25	0.25	0.25
Sulphur	1.5	1.5	1.5	1.5	1.5

Curing Characterisation

The curing characteristics of NBR/Bt and NBR/CB composites were determined using the Monsanto moving die rheometer (MDR 2000). The standard testing followed ASTM D 2240-93 at 150 °C. By analysing the rheograph, the curing time (t_{90}), scorch time (t_{s2}), minimum (M_L) and maximum torque (M_H) values were obtained.

Swelling Percentages

The swelling test followed the ASTM D 471-12a and ISO 1817-2005 standards. The cured sheets from the hot press were cut out into $30.0 \times 5.0 \times 2.0 \pm 0.1$ mm dimension. After that, the cut sheets were weighted by using electronic balance and labelled as initial weight (M_1). Then the cut sheets were immersed in liquid toluene. The weight of the samples was measured every 24 hours of immersion, and these processes were repeated for the next 24 hours until the mass of the cut sheets became constant. The

equilibrium mass values of cut sheets were labelled as (M2). The experiment was done at the room temperature. The swelling percentages of the rubber composites were calculated using Eq. (1).

$$\text{Swelling (\%)} = [(M2-M1) / M1] \times 100 \quad (1)$$

where; M1 is the initial mass of specimen (g), and M2 is the mass of specimen (g) after immersion.

Tensile Properties

The rubber composites were cured and pressed into 2 mm thickness. Then, the samples were cut to 5 pieces of dumb-bell shape according to the ASTM D 412 standard. After that, the samples were tested by using a universal tensile testing machine (UTM) brand model Instron 3366 under room temperature and the cross-head speed used was 500 mm/min.

Thermogravimetric Analysis (TGA)

The thermal analysis data were collected using a TGA machine model Perkin-Elmer Pyris 6. The experiment temperature was 25 to 600 °C under 50 ml of nitrogen flow. The heating rate used was ten °C per minutes.

Morphology Studies

The morphology of rubber composites was determined using a field emission scanning electron microscope, SEM (model Supra-35). The analysis was done on the tensile fractured surface of the rubber composites. The samples were coated with the thin layer of Palladium-Gold before running using the SEM machine. The coating procedure was made to prevent the electrostatic charging from interrupting the experiment.

RESULTS AND DISCUSSION

Curing Characteristics

The cure time (t_{90}), cure rate, scorch time (t_{s2}), minimum torque (M_L), maximum torque (M_H) and M_H-M_L were shown in Figures 1 to 6, respectively. The t_{90} of pristine NBR reduced as both the Bt and CB incorporated in NBR matrix. The incorporation of the filler into the matrix has increased the friction inside the composites thus generated the heat [22]. It also seems that CB has made the vulcanisation process became more active [23]. Thus, the cure rate for both types of filler increased, as shown in Figure 2. At similar filler loading, t_{90} of NBR/CB was shorter than NBR/Bt composites which indicate that CB increased the vulcanisation activities of the NBR composites faster than NBR/Bt composites. According to Hanafi and Anuar [25], the increasing of vulcanisation activities with the presence of CB was due to the formation of hydrogen sulphide and the S-N linkage ruptured after the sulfinamides plus heat were applied in the rubber.

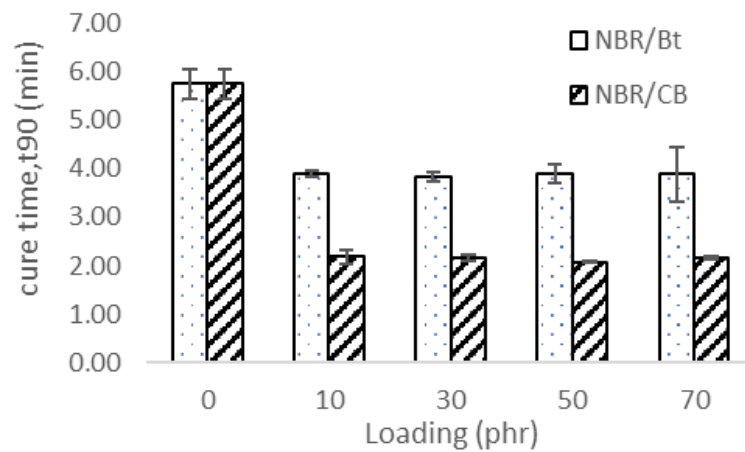


Figure 1. Cure time of NBR/Bt and NBR/CB composites.

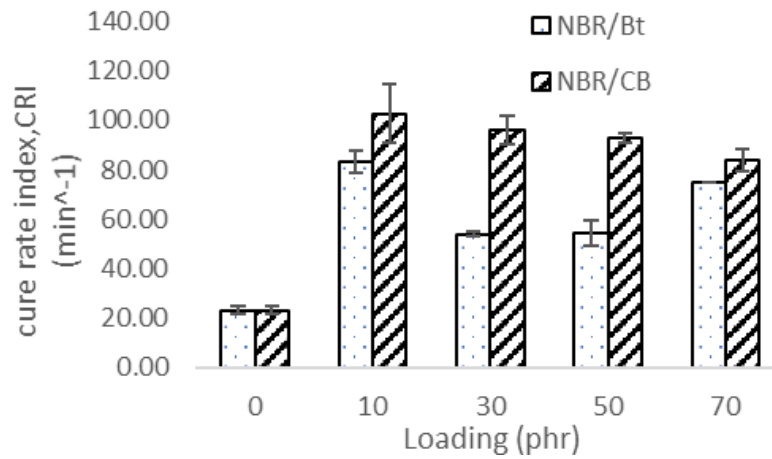


Figure 2. Cure rate index of of NBR/Bt and NBR/CB composites.

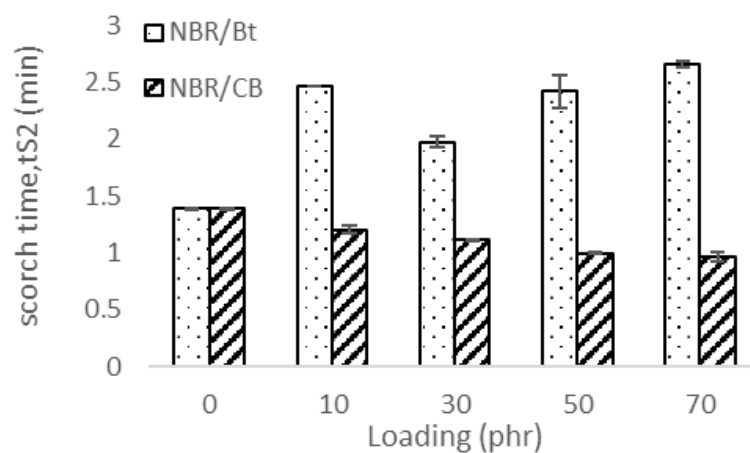


Figure 3. Scorch time of NBR/Bt and NBR/CB composites.

The t_{s2} of NBR/Bt was longer than NBR/CB composites which indicated that NBR/Bt has a better processing time. The minimum torque (M_L) in Figure 4 indicates that the chain entanglement of the rubber in the early stages of curing. The results show

that the incorporation of Bt and CB in the composites has increased the values of ML. In Figure 5, the maximum torque (M_H) of the NBR/Bt and CB increasing proportionally with the increasing of filler. This indicates that the incorporation of filler has restricted the mobility of the rubber chain which resulted in a stiffer rubber composite [27]. At similar filler loading, the value of ML and M_H of NBR/CB is higher than NBR/Bt composites. This could be due to the reactive element on the surface of CB adhere more to the rubber due to the smaller size of CB used. Smaller particle size provides higher surface contact area thus leads to the better adherence.

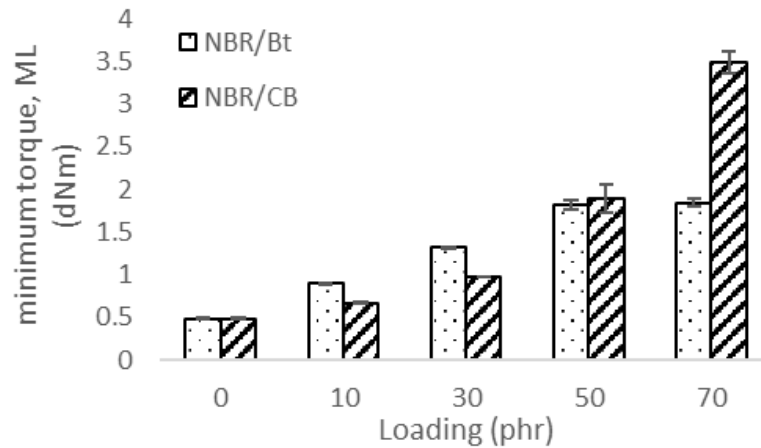


Figure 4. Minimum torque of NBR/Bt and NBR/CB composites.

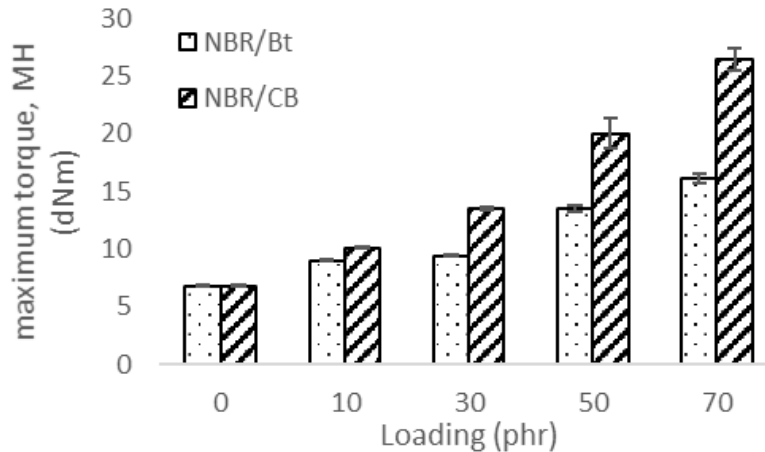


Figure 5. Maximum torque of NBR/Bt and NBR/CB composites.

Swelling Percentage

Swelling test was analysed by measuring the liquid uptake of the samples. The swelling percentage of NBR/Bt and NBR/CB composites against filler loading is shown in Table 2. The swelling composites were caused by absorption of toluene into the rubber composites. The percentage value shows that the liquid uptake was indirectly proportional to the increase of filler loading and it happens for both types of the composites. This caused by the activating effect by the increasing filler loading which made liquid absorption into the rubber reduced. The phenomenon was also reported by Salkhord and Sadeghi studies about incorporating the organoclay inside the NBR rubber

composites [17]. The comparison between NBR/Bt and NBR/CB composites at similar filler loading shows that NBR/CB composites have lower liquid uptake compared to NBR/Bt composites. This probably due to the surface contact area between the filler to the matrix of NBR/CB is higher than NBR/BT composites.

Table 2. Swelling percentage of NBR/Bt and NBR/CB composites against different type and filler loadings.

%	Bentonite filled NBR composites	Carbon black filled NBR composites
0	299.13	299.13
10	206.18	155.34
30	175.16	128.38
50	138.66	96.94
70	126.94	83.24

Tensile Properties

The TS, Eb, M10 and M300 of NBR/Bt and NBR/CB composites were shown in Figures 6 to 9, respectively. In can be seen that, the TS, Eb, M100, and M300 of NBR/CB is higher than NBR/Bt rubber composites. This probably due to the enhancement of the interface interaction [21] between CB and NBR compared to the NBR and Bt. Furthermore, the smaller particle size of CB has led to the high surface area contact between filler-rubber which also enhanced the filler matrix interaction and stiffness [24]. The values of M100 and M300 of NBR/CB composites were higher than NBR/Bt composites which indicated that the NBR/CB composites were stiffer than NBR/Bt composites.

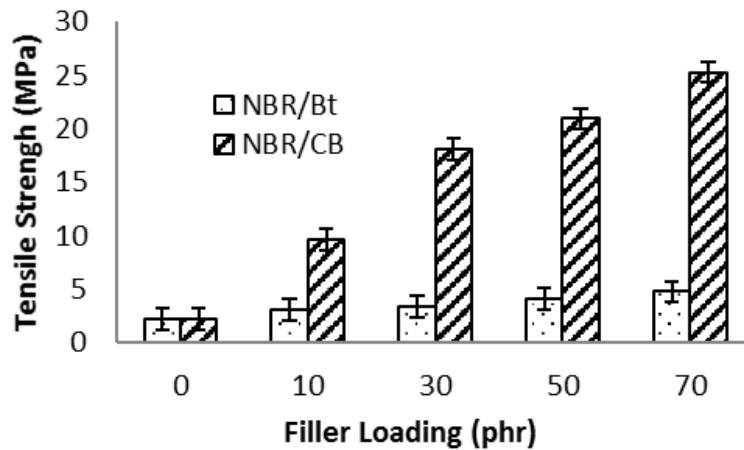


Figure 6. Tensile strength of bentonite and carbon black filled NBR composites.

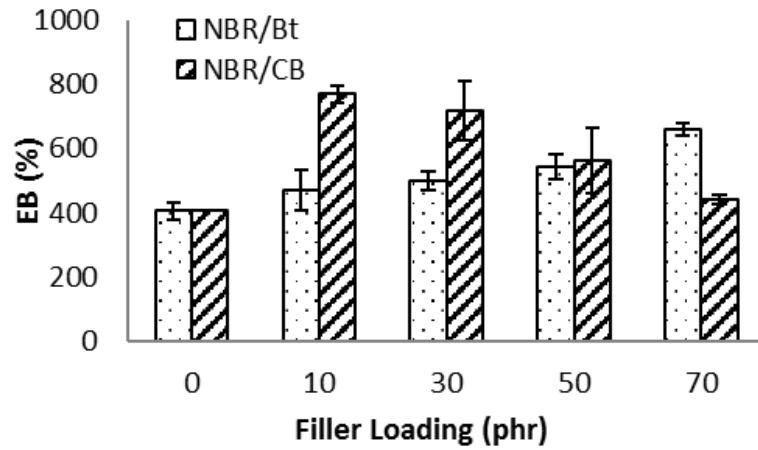


Figure 7. Elongation at break of bentonite and carbon black filled NBR composites.

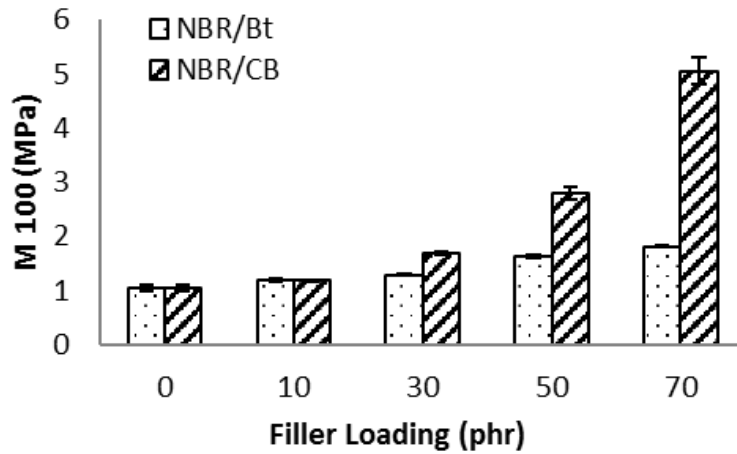


Figure 8. Modulus at 100 % (M100) of bentonite and carbon black filled NBR composites.

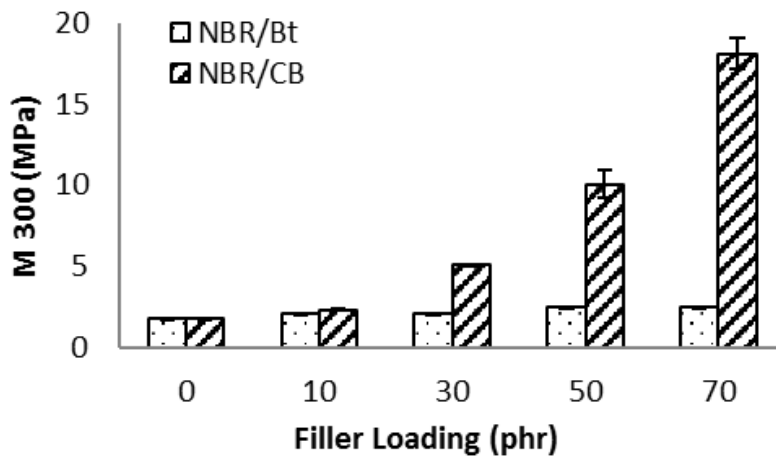


Figure 9. Modulus at 300 % (M300) of bentonite and carbon black filled NBR composites

Thermal Properties

The TGA curves of NBR/Bt and NBR/CB composites are shown in Figure 10, and the data from thermal degradation curves of NBR/Bt and NBR/CB composites are summarized in Table 3. The temperature at 10% and 50% of weight loss were marked as T10 and T50, respectively and the temperature at a higher rate of weight loss marked as T at Max Peak. The leftover residue of the rubber composites referred as char percentage. At similar filler loading, it seems that the NBR/CB composites required higher degradation temperature compared to NBR/Bt composites. This was observed at T10, T50, and T at max peak for both composites. As the filler increased, the T10, T50 and char percentage increased. Thus, both conditions show that the performance of thermal resistance or thermal stability of the rubber composites has been increased [20]. In other words, the addition of Bt and CB into the NBR rubber has made the rubber composites required more heat for thermal degradation compared to the pristine NBR.

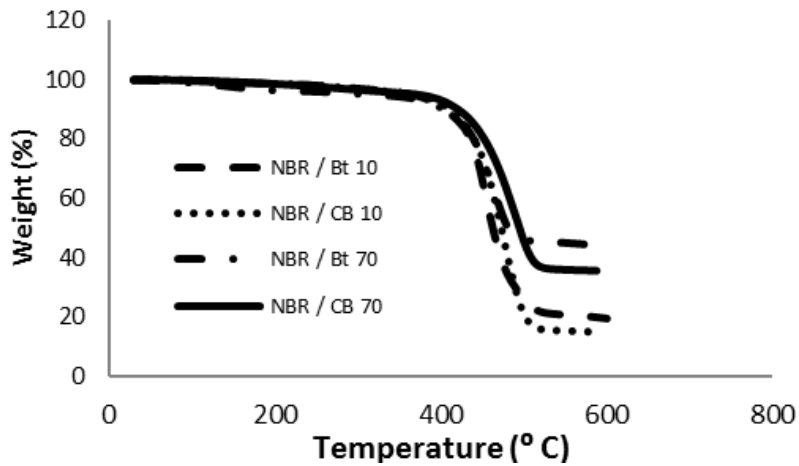


Figure 10. TGA curves of NBR/Bt and NBR/CB composites.

Table 3. The data collected from TGA curves of bentonite and carbon black filled NBR composites.

	T10 (°C)		T50 (°C)		T at max peak (°C)		Char percentage (%)	
	NBR/Bt	NBR/CB	NBR/Bt	NBR/CB	NBR/Bt	NBR/CB	NBR/Bt	NBR/CB
0	415.51	415.51	458.22	458.22	86.42	86.42	13.58	13.58
10	404.82	410.44	462.39	472.45	452.30	475.91	15.53	15.89
30	400.72	420.57	465.42	486.33	461.79	482.56	26.15	28.36
50	403.93	420.57	473.29	494.46	473.88	494.35	35.22	35.65
70	402.53	461.61	480.99	488.98	464.65	486.63	42.86	46.16

Morphology

Figure 11 shows the SEM micrograph of bentonite particle at 4000× magnification. The pores could be observed on the bentonite filler surface. This made the NBR matrix easy to penetrate through it and have a good rubber-filler interaction [18]. Figure 12 shows the tensile fractured surface of NBR/Bt composites at (a) pristine NBR (b) 10 phr of NBR/Bt composites (c) 10 phr of NBR/CB composites (d) 50 phr of NBR/Bt composites and (e) 50 phr of NBR/CB composites at 300× magnification.

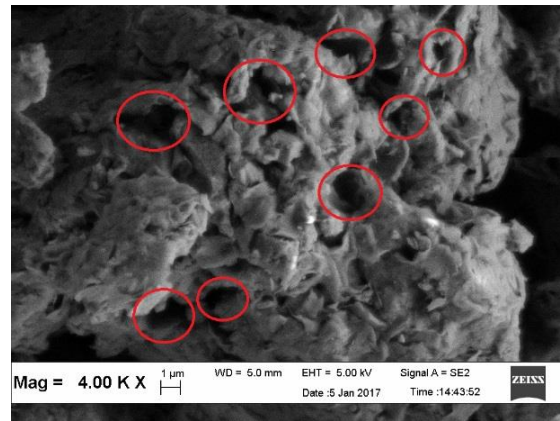
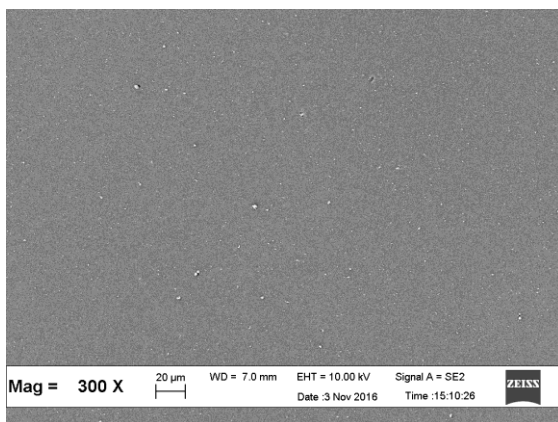
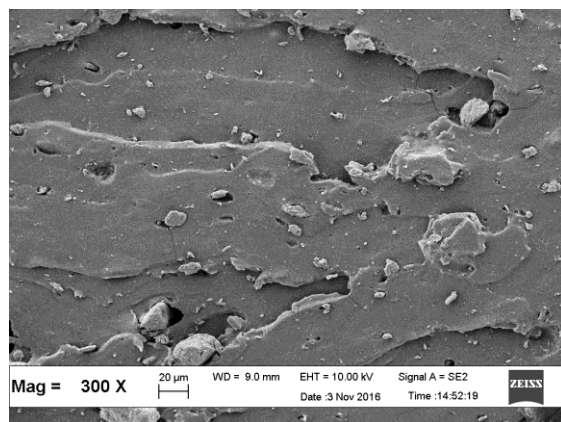


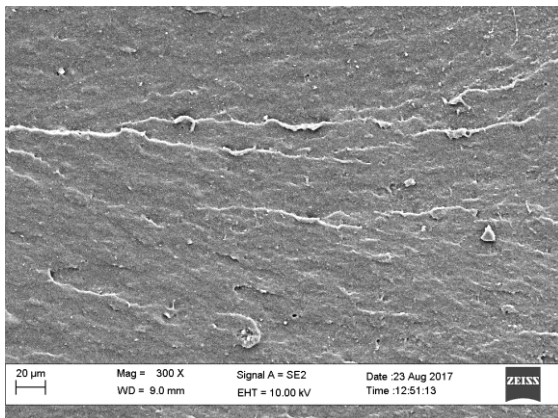
Figure 11. SEM micrograph of bentonite particle at 4000× magnification.



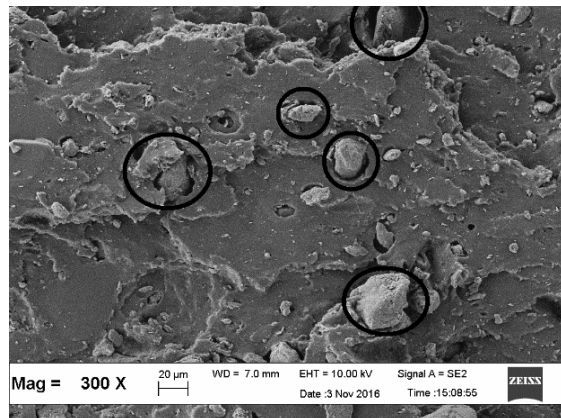
(a)



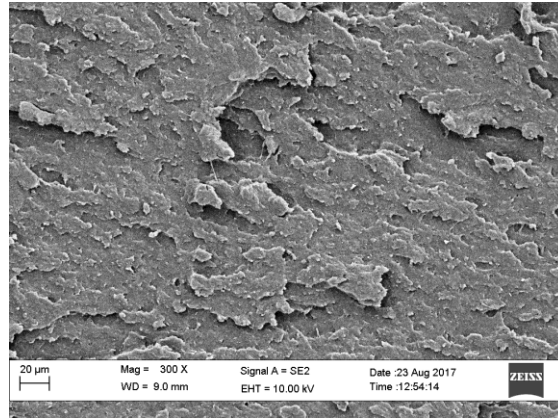
(b)



(c)



(d)



(e)

Figure 12. SEM micrograph of tensile fractured surface of (a) pristine NBR (b) 10 phr of NBR/Bt composite (c) 10 phr of NBR/CB composite (d) 50 phr of NBR/Bt composite and (e) 50 phr of NBR/CB composite at 300× magnification.

As the filler loading increased, the tear lines were also increased as observed in both NBR/Bt and NBR/CB composites. This shows that the more tear lines on the tensile fracture surfaces were resulted from good tensile properties of the rubber composites [19]. However, on the surface of the NBR/Bt composites, the filler agglomeration and filler detachment could be observed in Figures 12(b) and 12(d). This could be the reason for the lower tensile properties shown by the NBR/Bt composites compared to NBR/CB composites. On the other hand, at higher filler loading, a few filler detachments could be found on the tensile fractured surface of NBR/Bt composites as compared to NBR/CB composites surface, which also causes the lower tensile strength of NBR/Bt composites. These results supported by the research made by Vijay [26], where the agglomeration of fillers and the cavity of detachment at the tensile surface fracture of rubber composites, leading to the lower tensile properties of the composites.

CONCLUSION

The results show that the TS, M100, and M300 for both NBR/Bt and NBR/CB composites proportionally increased with increasing of filler. The Eb for NBR/Bt composites followed the same trend but not for NBR/CB composites. At the same filler loading, NBR/CB composites show higher tensile properties (TS, M100, M300, and Eb) compared to NBR/Bt composites.

- i. Swelling percentage for both types of fillers decreased. At similar loading, the swelling percentage of NBR/CB composites is lower than NBR/Bt composites.
- ii. Thermal degradation properties (T10, T50, and T at Max Peak points) of NBR/CB composites show better results than NBR/Bt composites. In other words, temperature required for thermal degradation for the NBR/CB composites.
- iii. Scanning electron micrograph (SEM) of the tensile fractured surfaces of NBR/CB composites exhibits a better filler dispersion and less filler detachment compared to NBR/Bt composites

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