

Effect of Carbon Black Loading on Curing Characteristics and Mechanical Properties of Waste Tyre Dust/Carbon Black Hybrid Filler Filled Natural Rubber Compounds

H. Ismail, N. F. Omar, N. Othman

School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Penang, Malaysia

Received 22 March 2010; accepted 3 October 2010

DOI 10.1002/app.33511

Published online 28 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Curing characteristics, tensile properties, fatigue life, swelling behavior, and morphology of waste tire dust (WTD)/carbon black (CB) hybrid filler filled natural rubber (NR) compounds were studied. The WTD/CB hybrid filler filled NR compounds were compounded at 30 phr hybrid filler loading with increasing partial replacement of CB at 0, 10, 15, 20, and 30 phr. The curing characteristics such as scorch time, t_2 and cure time, t_{90} decreased and increased with increment of CB loading in hybrid filler (30 phr content), respectively. Whereas maximum torque (M_{HR}) and minimum torque (M_L) increased with increasing CB loading. The tensile properties such as tensile strength, elongation at break, and tensile modulus of WTD/CB hybrid filler

filled NR compounds showed steady increment as CB loading increased. The fatigue test showed that fatigue life increased with increment of CB loading. Rubber–filler interaction, Q_f/Q_s indicated that the NR compounds with the highest CB loading exhibited the highest rubber–filler interactions. Scanning electron microscopy (SEM) micrographs of tensile and fatigue fractured surfaces and rubber–filler interaction study supported the observed result on tensile properties and fatigue life. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1143–1150, 2011

Key words: curing characteristics; tensile properties; natural rubber; waste tire dust; carbon black

INTRODUCTION

Natural rubber is known for its outstanding performance in numerous properties. Although natural rubber (NR) has its outstanding properties, reinforcing fillers are necessarily added into NR in most cases to gain the appropriate properties for specific applications. A wide variety of particulate fillers are used in the rubber industry for various purposes, of which the most important are reinforcement, reduction in material costs, and improvements in processing.¹ Waste tires have become one of the major wastes in the entire world. A huge quantity of waste tires have been generated from the ever-increasing use of transportation vehicles such as motor cycles, cars, buses, and lorries throughout the world. The European Union, USA, and Japan alone account for around 6 million tons of scrap tires per year.²

USA itself generates ~ 242 million scrap tires per year, representing 1.2 wt % of all municipal solid waste. The US Environmental Protection Agency estimates that 2–3 billion scrap tires have already accumulated in illegal stockpiles or uncontrolled tire

dumps throughout the country, with millions more scattered in ravines, deserts, woods, and empty lots. The waste tire stream represents significant environmental, health, and esthetic problems. Therefore, one way to save the environment is by developing innovative solutions to solve this problem.³ One method is to reutilize the waste tires either for the community or industry. Waste tires are still beneficial to the industries in various applications. For example, activated carbon can be produced from waste tires.^{2,4} Besides, it is also used as additives for concrete modifying.^{3,5} The addition of rubber in concrete has resulted in the increase of toughness and ductility.^{3,5,6} Even though WTD itself has already contained carbon black (CB), the addition of CB is still a good solution as it is well known for its superior reinforcement properties. However in this work, the purpose of WTD addition was to study its reinforcing effect on mechanical properties NR compounds which involve tensile properties and fatigue life. In this work, WTD was chosen instead of shredded waste tire. It is because, WTD has higher surface area, higher inclination to get contact with NR and also able to disperse better within matrix. NR was compounded with the mixture of WTD and N330 CB hybrid in this work by using a two roll mills. Curing characteristics, swelling behavior, and morphological studies of WTD/

Correspondence to: H. Ismail (hanafi@eng.usm.my).

TABLE I
Formulation of WTD/CB Hybrid Filler Filled Natural Rubber Compounds

Ingredients/compound	WTD 30/CB 0	WTD 20/CB 10	WTD 15/CB 15	WTD 10/CB 20	WTD 0/CB 30
Natural rubber (SMR L)	100	100	100	100	100
Waste tyre dust (WTD)	30	20	15	10	0
Carbon black (N330)	0	10	15	20	30
Zinc oxide (ZnO)	5	5	5	5	5
Stearic acid	2	2	2	2	2
Sulphur (S)	2.5	2.5	2.5	2.5	2.5
<i>N</i> -cyclohexyl-2-benzothiazole sulfonamide (CBS)	0.6	0.6	0.6	0.6	0.6
2,2'-Methylene-bis (4-methyl-6- <i>tert</i> -butylphenol) (BKF)	2	2	2	2	2

CB hybrid filler filled NR compounds were also studied.

EXPERIMENTAL

Materials

Table I shows the formulation used for this study. Natural rubber (SMR L) was purchased from Kumpulan Guthrie Sdn Bhd, Seremban, Malaysia. The waste tyre dust (WTD) was obtained from Watas Holding (M) Sdn Bhd, Penang, Malaysia. An Endecotts sieve was used to obtain WTD particle size of 150–250 μm . Carbon black (N330) was purchased from Cabot (M) Sdn Bhd. Other compounding ingredients such as zinc oxide, stearic acid, sulfur, *N*-cyclohexyl-2-benzothiazole sulfonamide (CBS), and 2,2'-Methylene-bis (4-methyl-6-*tert*-butylphenol) (BKF) were all purchased from Bayer (M) Ltd.

Preparation of rubber compound

Mixing was carried out using a conventional laboratory two roll mill size (160 \times 320 mm^2) according to ASTM designation D3184-80. Nip gap, mill roll speed ratio, time of mixing, and the sequence of addition of the ingredients were kept the same for all the composites. The sheeted rubber compound was conditioned at a temperature of 23°C \pm 2°C for 24 h in a closed container before cure assessment using a Monsanto moving die rheometer (MDR 2000). The respective scorch time, t_2 and cure time t_{90} were obtained from MDR 2000 at 150°C. The maximum torque was also determined from the rheograph. The rubber compounds were compression molded at 150°C according to their respective t_{90} , into two types of rectangular sheets; one with the size of 229 mm \times 76 mm \times 1.5 mm with beaded edges (fatigue test) and another one is flatter sheet with 2 mm thickness (tensile test).

Determination of tensile properties

Dumbbell specimens were cut out from compression-molded sheets. Tensile test was conducted following

ASTM D412 using a universal tensile testing machine Instron 3366 at room temperature (25°C \pm 2°C) and with crosshead speed of 500 mm min^{-1} . Tensile modulus at 100% (M100) and 300% elongation (M300), tensile strength and elongation at break (Eb) were recorded.

Determination of fatigue life

The vulcanized NR were cut into individual dumbbell samples using a BS type E dumbbell cutter. Fatigue test of the compounds were then carried out on a Monsanto Fatigue-to-Failure Tester (FTFT). Six specimens were used for each test. The samples were subjected to repeated cyclic strain at 100 rev min^{-1} and the extension ratio of 14. The number of cycles was recorded automatically. The fatigue life was calculated based on the Japanese Industrial Standard (JIS) average, which was determined from the four highest values recorded using the eq. (1):

$$\text{JIS average} = 0.5A + 0.3B + 0.1(C + D) \quad (1)$$

where *A* is the highest value followed by *B*, *C*, and *D*.

Measurement of rubber–filler interaction

Cured samples of dimension 30 mm \times 5 mm \times 2 mm were immersed in toluene in dark environment until equilibrium swelling was achieved, which normally took 48 h at 25°C. The samples were dried in the oven at 60°C until the constant weights were obtained. Lorenz and Park equation⁷ has been applied to study the rubber–filler interaction. According to eq. (2):

$$Q_f/Q_g = ae^{-z} + b \quad (2)$$

where *f* and *g* refer to filled and gum vulcanizates, respectively; *z* is the ratio by weight of the filler to the rubber hydrocarbon in the vulcanizates; and *a* and *b* are constants. The higher the Q_f/Q_g values, the lower the extent of interaction will be between the filler and the matrix. In this study, we

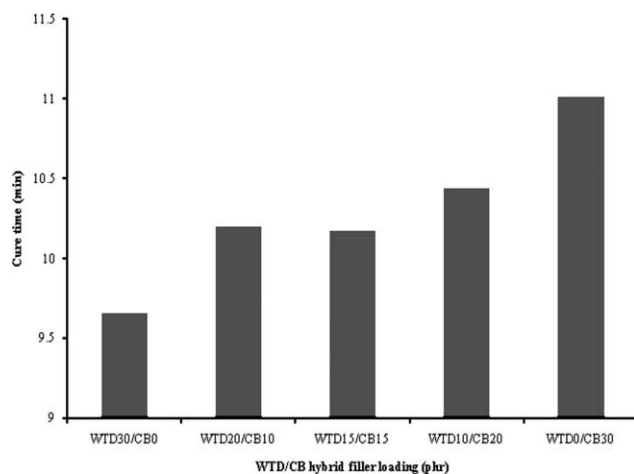


Figure 1 The effect of WTD/CB hybrid filler loading on the cure time (t_{90}) of natural rubber compounds.

determined the weight of toluene uptake per gram of rubber hydrocarbon (Q) as eq. (3):

$$Q = (W_s - W_d) / (W_i \times 100 / \text{Formula weight}) \quad (3)$$

where W_s is the swollen weight, W_d is the dried weight, and W_i is the original weight.

Morphological study

Scanning electron microscopy (SEM) model Zeiss SUPRA 35VP FESEM was used to characterize the WTD and fractured surface of WTD/CB hybrid filler filled

natural rubber compounds. All the surfaces were examined by SEM after first sputter coating with gold to avoid electrostatic charging and poor resolution.

Fourier transform infra red (FTIR) analysis

The chemical bonds in the WTD were analyzed using Perkin-Elmer Spectrum One FT-IR spectrometer. A sample of the WTD was prepared by milling it with KBr and compressed to a KBr disc for testing. The selected spectrum resolution and the scanning range were 4 cm^{-1} and $400\text{--}4000 \text{ cm}^{-1}$, respectively.

RESULTS AND DISCUSSIONS

Curing characteristics

Figure 1 shows the effect of WTD/CB hybrid filler loading on cure time (t_{90}) of natural rubber compounds. It can be seen that WTD/CB hybrid filler filled NR compounds exhibit increasing trend with the increment of CB. This is due to the presence of crosslinked precursors and unreacted accelerator in the WTD. In Figure 2, there are several infrared (IR) spectra representing several bonds such as $N\text{--}H$, $C\text{--}N$, and $\text{--}CH_2$. These bonds are believed to be the bonds that exist in the unreacted accelerator within WTD. Nonhydrogen bonded of $N\text{--}H$ stretching symmetric vibration can be seen at 3422 cm^{-1} .⁸ Aliphatic $C\text{--}N$ stretching is indicated by adsorption band appeared at 1071 cm^{-1} while methylene asymmetric $C\text{--}H$ stretching is indicated by 2930 cm^{-1} .⁹

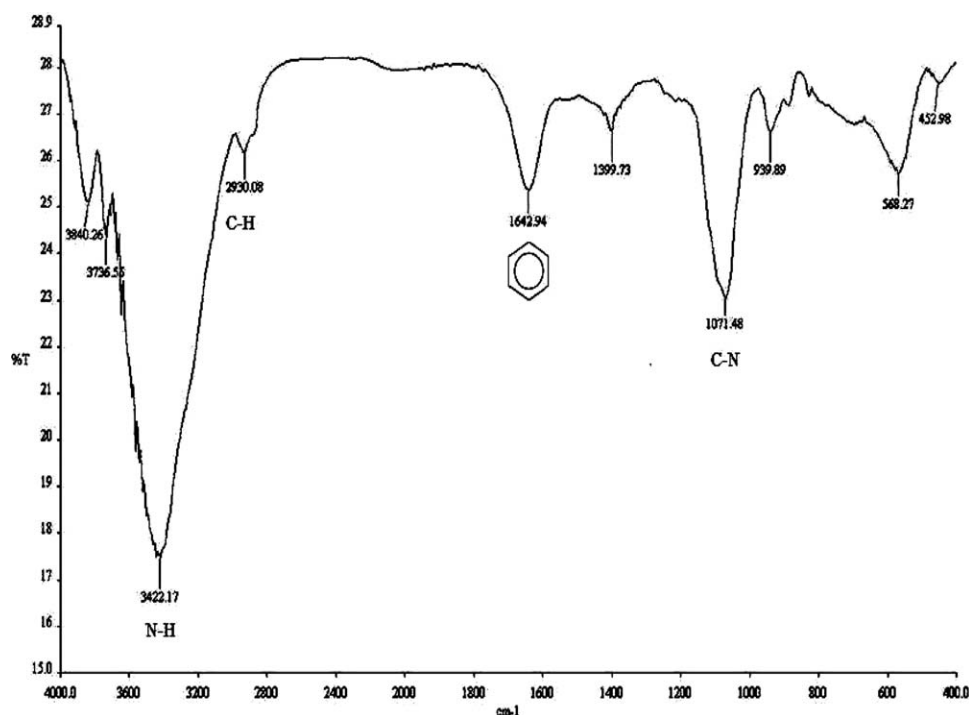


Figure 2 IR spectrum of a sample of WTD.

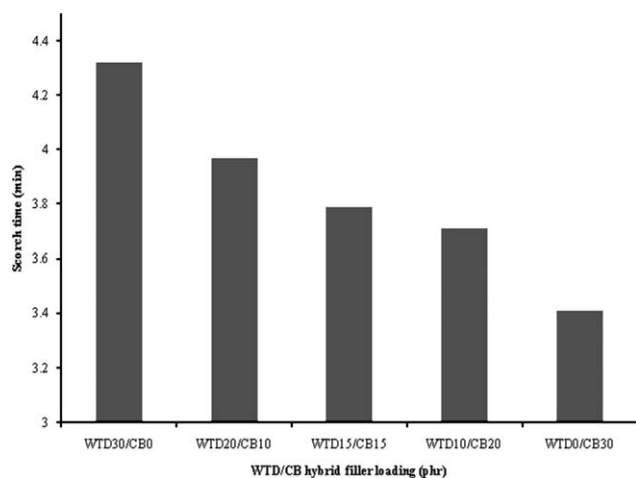


Figure 3 The effect of WTD/CB hybrid filler loading on the scorch time (t_2) of natural rubber compounds.

This indicates the presence of unreacted accelerator in WTD. The cure time difference between sample with 30 phr of WTD and sample with 30 phr of CB is only around 1.3, which is considered small in laboratory scale processing but in term of bigger scale processing this may be beneficial in term of time saving.

Figure 3 shows the effect of WTD/CB hybrid filler loading on the scorch time (t_2) of natural rubber compounds. This figure shows decreasing trend of scorch time with the increment of CB. The reason behind the decreasing trend is the curatives in WTD itself. Antioxidant that exists within WTD might be the reason of decreasing trend of scorch time as seen in Figure 3. Higher amount of antioxidant in rubber compound formulation can lengthen the scorch time or retard the vulcanization of the compound itself. The retardation phenomenon is attributed to the steric hindrance of bulky groups in the antioxidant i.e., 2,2'-methylene-bis (4-methyl-6-

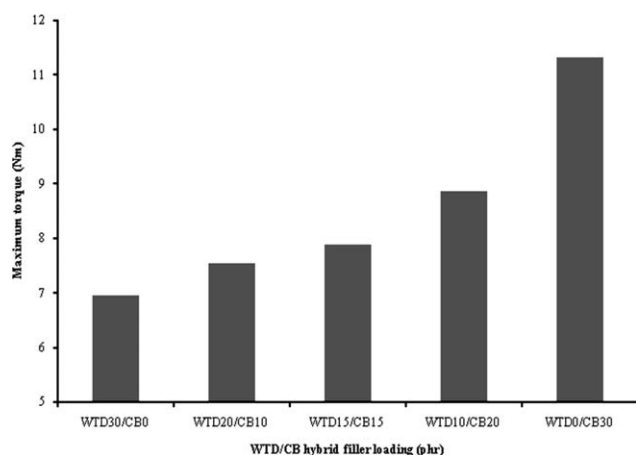


Figure 4 The effect of WTD/CB hybrid filler loading on maximum torque (M_{HR}) of natural rubber compounds.

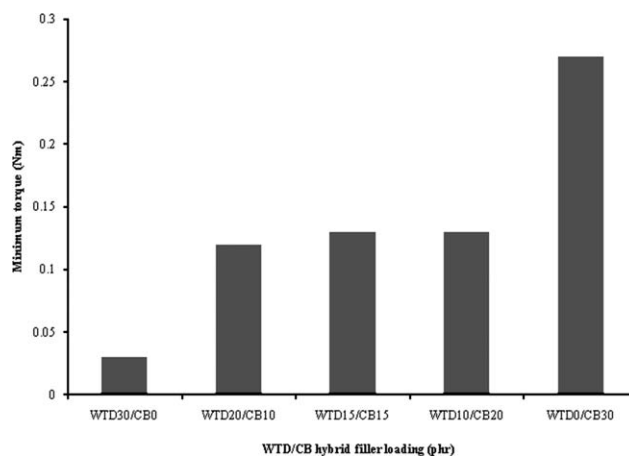


Figure 5 The effect of WTD/CB hybrid filler loading on minimum torque (M_L) of natural rubber compounds.

tert-butylphenol) (BKF). This steric effect would retard the formation of active sulfurating agents, a reaction intermediate necessary for vulcanization.¹⁰ The spectrum indicated at 1642 cm^{-1} is believed to represent Benzene groups' presence in BKF.⁹ Therefore, higher amount of antioxidant exist within WTD increased the scorch time of WTD/CB hybrid filler filled NR compounds. The similar observation was reported by Maridass and Gupta.¹¹ The trends observed in Figures 1 and 3 exhibit that incorporation of WTD give beneficial effect by decreasing cure time and increasing scorch time of WTD/CB hybrid filler filled NR compounds. This is beneficial in term of processing of rubber.

Figures 4 and 5 show the effect of WTD/CB hybrid filler loading on maximum torque (M_{HR}) and minimum torque (M_L) of natural rubber compounds, respectively. It can be seen that the minimum and maximum torques of WTD/CB hybrid filler filled NR compound increase with the increment of CB

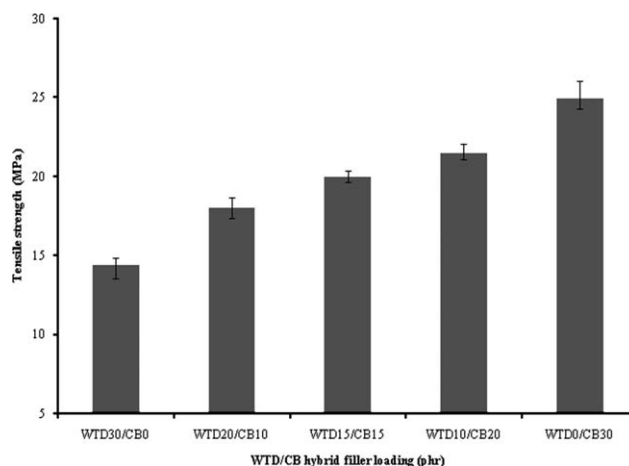


Figure 6 The effect of WTD/CB hybrid filler loading on tensile strength of natural rubber compounds.

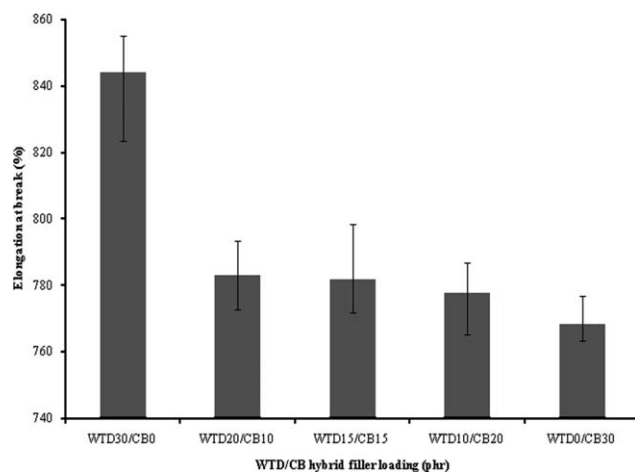


Figure 7 The effect of WTD/CB hybrid filler loading on elongation at break of natural rubber compounds.

amount. The increment of torque indicates that the processability of the compounds becomes more difficult. It is because of CB which is produced largely from oil, consists of irregular, branched aggregates of firmly fused nodular subunits. The dispersed carbon black agglomerates form a network themselves in the polymeric media. With increasing CB content, the network chains become shorter and the number of entanglements between two crosslinks decreases. Single molecules are likely to adsorb on several carbon black surface sites, so the bound rubber is essentially immobile. Reactive groups including acid groups, phenolic groups, quinonic groups, and lactone groups have all been identified on the carbon black surface and influence adsorption.¹² Therefore, the higher amount of CB, the more difficulties in processing. This proves that incorporation of WTD increases processability of rubber compounds which also indicates that less energy

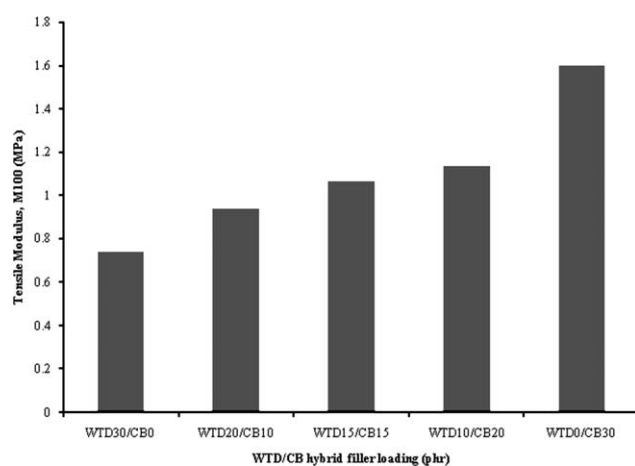


Figure 8 The effect of WTD/CB hybrid filler loading on stress at 100% elongation of natural rubber compounds.

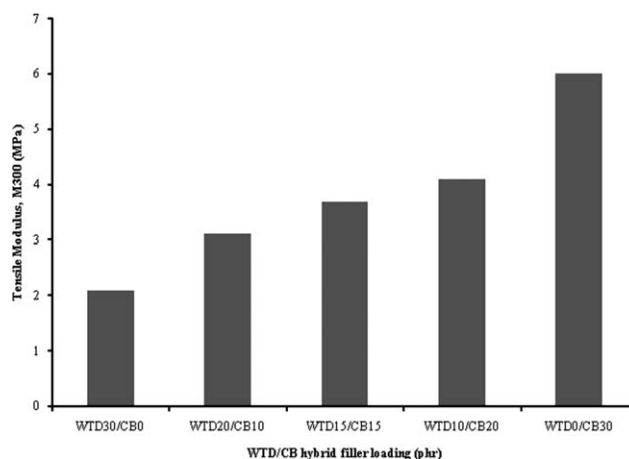


Figure 9 The effect of WTD/CB hybrid filler loading on stress at 300% elongation of natural rubber compounds.

needed for the compounds to be processed. This is also beneficial in term of rubber processing.

Tensile properties

Figure 6 shows the effect of WTD/CB hybrid filler loading on tensile strength of natural rubber compounds. This figure shows increasing trend of tensile strength with increment of CB loading. Natural rubber compound filled with 30 phr of WTD shows lowest value of tensile strength due to the lack of interfacial adhesion between WTD and natural rubber. WTD is a vulcanized rubber turned into dusts. Even when vulcanized rubber is processed into crumbs or dusts, the rubber molecules retain much of their physical properties. The strength of the crosslink bonds makes adhesion between WTD and natural rubber become difficult.¹³ Compared to WTD, CB adhered better with natural rubber and has reinforcing effect as because of its

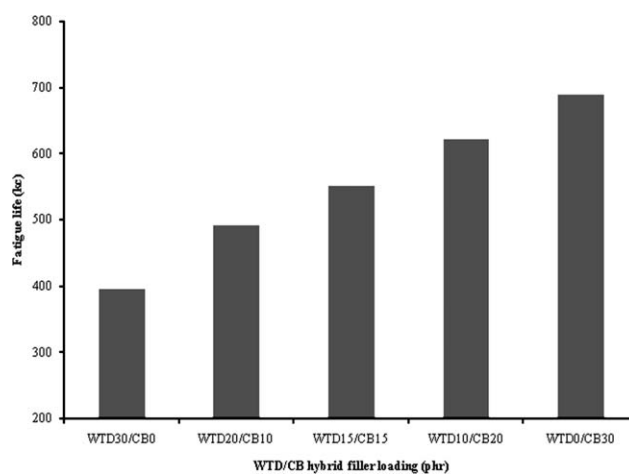


Figure 10 The effect of WTD/CB hybrid filler loading on fatigue life of natural rubber compounds.

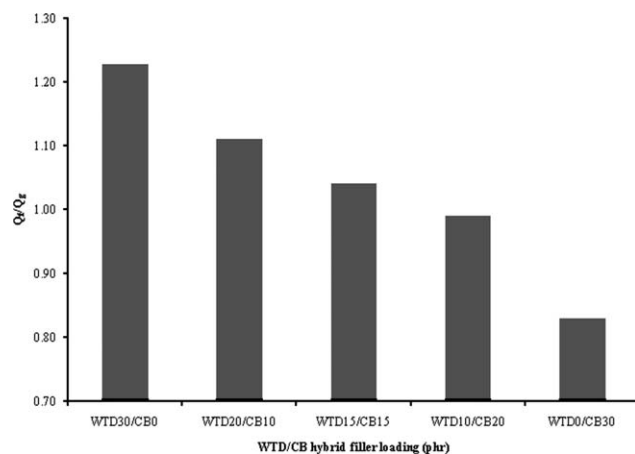


Figure 11 The effect of the WTB/CB hybrid filler loading on the rubber–filler interaction of natural rubber compounds.

porous surface.¹⁴ Matrix or rubber fulfill the pores on CB's surface and create strong adhesion between rubber and CB which thus contributing to increasing value of tensile strength.

Figure 7 shows the effect of WTD/CB hybrid filler loading on elongation at break of natural rubber compounds. Elongation at break of natural rubber compound exhibits significant decrease with addition of CB. It can be seen that the compound with 30 phr of CB loading without addition of WTD shows the lowest elongation at break value. Again this was due to reinforcement effect of CB due to its porous surface. Therefore when rubber matrix fulfilled the pores on CB surface, it will hinder the deformation or elongation of the compounds. A similar observation was reported by Maridass et al.¹¹ and Ismail et al.¹⁵ for NR-waste rubber powder compounds. The significant increase of elongation at break with increment of WTD exhibits the advantage of WTD in term of toughness which also indicates that incorporation of WTD will lead to higher elongation of rubber compounds.

Figures 8 and 9 show the effect of WTD/CB hybrid filler loading on stress at 100% elongation (M100) and stress at 300% elongation (M300) of natural rubber compounds. M100 and M300 increase with the increment of CB loading. This is expected

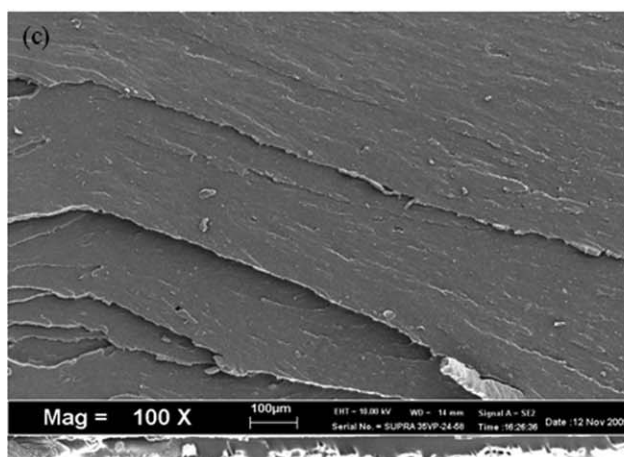
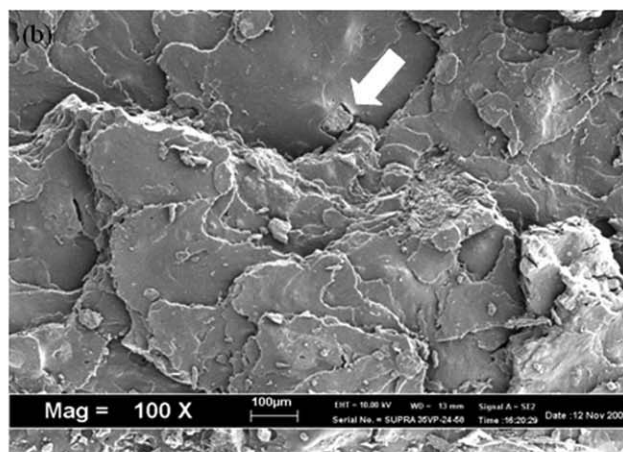
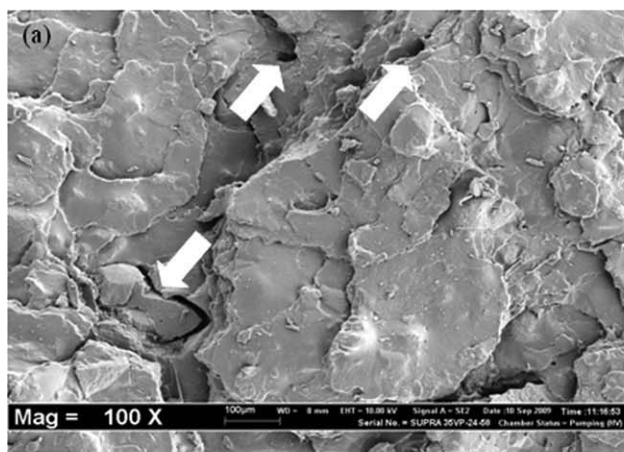


Figure 12 SEM micrograph of tensile fractured surface of WTD/CB hybrid filler filled natural rubber compounds: (a) 30 WTD/0 CB, (b) 20 WTD/10 CB, (c) 0 WTD/30 CB (magnification $\times 100$).

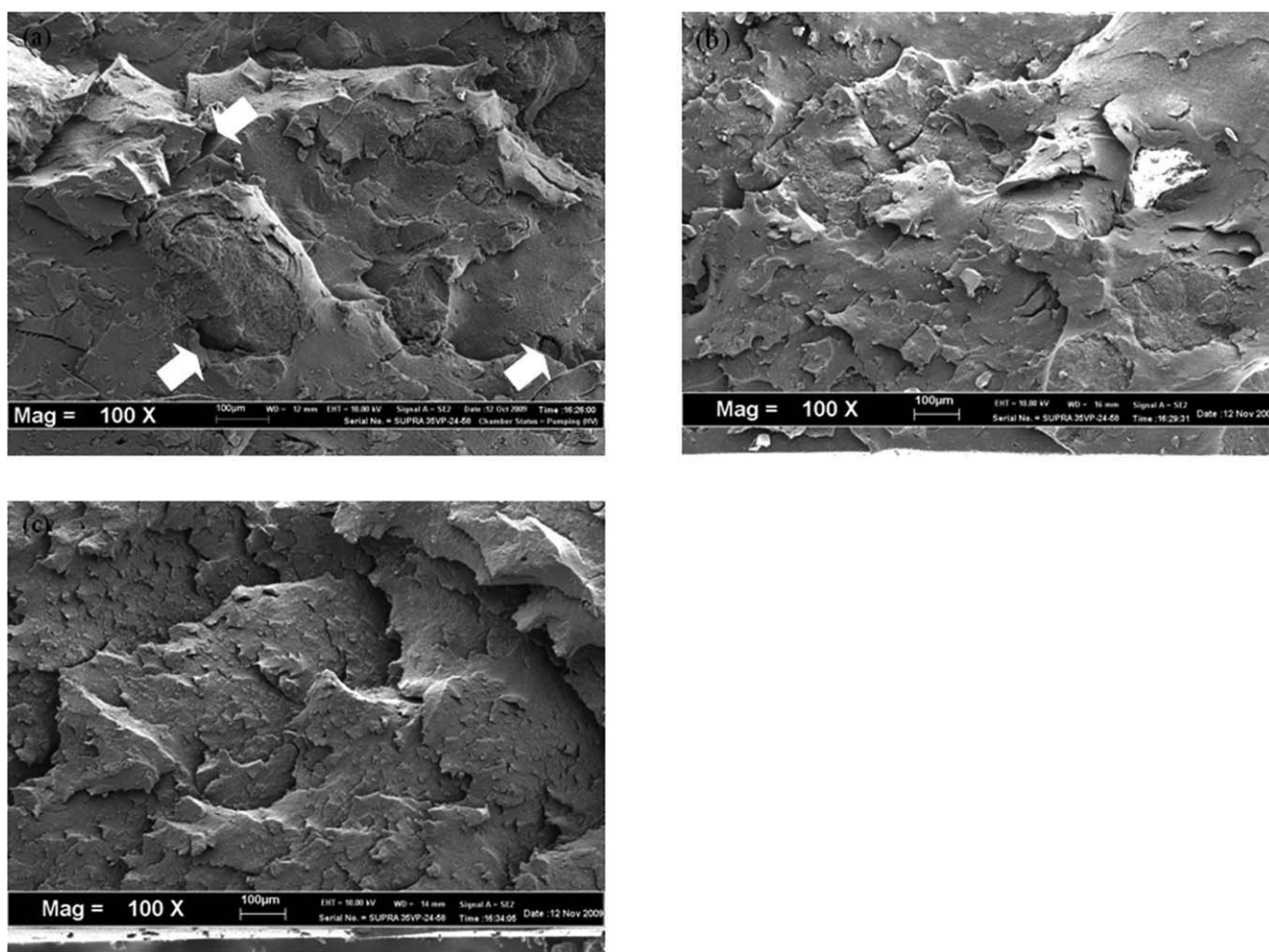


Figure 13 SEM micrograph of fatigue fractured surface of WTD/CB hybrid filler filled natural rubber compounds: (a) 30 WTD/0 CB, (b) 20 WTD/10 CB, (c) 0 WTD/30 CB (magnification $\times 100$).

as CB has higher stiffness than WTD. Moreover, CB also tends to form agglomeration as the amount increases as explained in maximum and minimum torque session. Hence higher strength will be needed to deform compounds filled with CB which resulting in higher tensile modulus. Therefore, the higher the amount of CB loading the higher the tensile modulus will be.

Fatigue life

Figure 10 shows the effect of WTD/CB hybrid filler loading on fatigue life of natural rubber compounds. This figure exhibits increasing trend of fatigue life with increment of CB loading. This increasing trend was due to reinforcement effect of CB. As previously explained, CB has porous surface which was fulfilled by rubber matrix. The pores fulfilling by rubber matrix will “lock” or hinder any deformation happen within rubber compound. This may result to the increase of fatigue life with the increment of CB loading.

Rubber–filler interaction

Figure 11 shows the effect of WTB/CB hybrid filler loading on rubber–filler interaction, Q_f/Q_g of WTB/CB hybrid filler filled natural rubber compounds. Q_f/Q_g of WTD/CB hybrid filler filled natural rubber compounds decreased with increment of CB. This was due to good interaction between natural rubber and CB compared to natural rubber to WTD. The good interaction hindered toluene from penetrating through the natural rubber compound.

Morphological study

Figure 12 shows the SEM micrograph of tensile fractured surface of WTD/CB hybrid filler filled natural rubber compounds. Figure 12(a–c) shows the tensile fractured surface for WTD/CB hybrid filler filled natural rubber compounds with 0, 10, and 30 phr of CB, respectively. For natural rubber compound filled with 30 phr of WTD, the fractured surface is rough and coarse and detachment of WTD can be seen (shown by arrow). As for WTD/CB hybrid filler

filled NR compound with 10 phr partial replacement of CB [Fig. 12(b)], the fractured surface is rougher than NR compound filled with 30 phr WTD [Fig. 12(a)]. This is evident from increasing value of tensile modulus with increasing partial replacement of CB for WTD/CB hybrid filler compared to NR compounds filled with 30 phr of WTD which signifies higher stress to propagate the cracks. In this figure, WTD is seen embedded within rubber matrix (shown by arrow). In Figure 12(c), the tensile fractured surface of natural rubber compound filled with 30 phr of CB exhibits many tear lines which in fact indicates high value of tensile strength. This is proven by the highest tensile strength value of NR compound filled with 30 phr of CB.

Figure 13 shows the SEM micrograph of fatigue fractured surface of WTD/CB hybrid filler filled natural rubber compounds. Figure 13(a–c) shows the fatigue fractured surface for WTD/CB hybrid filler filled natural rubber compounds with 0, 10, and 30 phr of CB respectively. From Figure 13(a), it can be seen that WTD particle was less wetted by rubber matrix (shown by arrow). This exhibits weak interaction between WTD and natural rubber matrix. On the other hand, after 10 and 30 phr partial replacement of CB more tear lines started to be seen which proven higher value of fatigue life [Fig. 13(b–c)]. Figure 13(c) also shows that CB was dispersed and wetted by rubber matrix which indicated the good interaction between CB and NR as compared to WTD and NR. The better filler dispersion and wettability improvement of the filler by the matrix reduce the formation of stress concentration points and consequently increase the fatigue life of the composites.¹⁶ The good interaction between CB and natural rubber has resulted to highest value of fatigue life of WTD/CB hybrid filler filled natural rubber compounds.

CONCLUSIONS

From this study, the following conclusions can be drawn:

1. The incorporation of CB for WTD/CB hybrid filler filled NR increased the cure time, t_{90} and

decreased the scorch time, t_2 . For maximum torque (M_{HR}) and minimum torque (M_L), the values increased with increasing partial replacement of CB.

2. The tensile properties i.e., tensile strength and tensile modulus, increased with increasing partial replacement of CB loading except for elongation at break.
3. Results from measurement of rubber–filler interaction showed that the WTD/CB hybrid filler filled natural rubber compounds with highest CB loading exhibited the highest rubber–filler interactions.
4. SEM study indicated that the better WTD/CB hybrid filler dispersion and wettability by the natural rubber matrix increased the tensile strength and fatigue life of NR compounds.

References

1. Rattanasom, N.; Saowapark, T. *Polym Test* 2007, 26, 369.
2. Zhu, J.; Shi, B.; Zhu, J.; Chen, L.; Zhu, J.; Liu, D. *Waste Manage Res* 2009, 27, 553.
3. Tuncan, M.; Tuncan, A.; Cetin, A. *Waste Manage Res* 2003, 21, 83.
4. Leung, S. Y.; Cheung, W. H.; McKay, G. *Int J Environ Waste Manage* 2009, 3, 286.
5. Li, G.; Stubblefield, M. A.; Garrick, G.; Eggers, J.; Abadie, C.; Huang, B. *Cement Concrete Res* 2004, 34, 2283.
6. Papakonstantinou, C. G.; Tobolski, M. J. *Cement Concrete Res* 2006, 36, 1686.
7. Lorenz, O.; Park, C. R. *J Polym Sci* 1961, 50, 299.
8. Zulkepli, N. N.; Ismail, H.; Rashid, A. *Iran Polym J* 2009, 18, 139.
9. Stuart, B. H. *Infrared Spectroscopy: Fundamentals and Applications*; Wiley: West Sussex, 2004.
10. Poh, B. T.; Te, C. S. *J Appl Polym Sci* 2000, 77, 3234.
11. Maridass, B.; Gupta, B. R. *J Elastomers Plast* 2006, 38, 211.
12. Koenig, J. L. *Acc Chem Res* 1999, 32, 1.
13. Tang, Y. US Patent US 6,590,042 B1, 2003.
14. Ismail, H. *Pengisi Dan Penguatan Getah*; Penerbit Universiti Sains: Malaysia, Penang, 2000.
15. Ismail, H.; Nordin, R.; Noor, A. M. *Polym Test* 2002, 21, 565.
16. Ismail, H.; Haw, F. S. *J Appl Polym Sci* 2008, 110, 2867.