

# Tea waste/carbon black hybrid filled natural rubber composites

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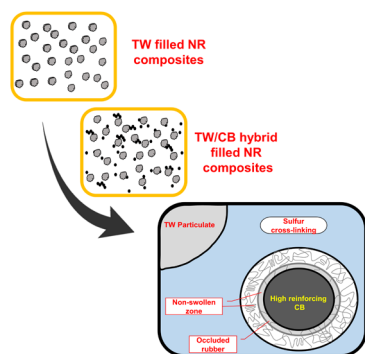
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## Article history

 Received 9 Mac 2020  
 Revised 22 April 2020  
 Accepted 09 July 2020  
 Published Online 24 December 2020

## Graphical abstract



## Abstract

This paper aimed to present the potential of tea waste (TW) as an alternative filler for natural rubber (NR). Considering the fact that TW is categorized as a non-reinforcing filler with big particle size, carbon black (CB) was then introduced as secondary filler for NR matrix. This is to improve the performance of the composite while maintaining the suitable amount of TW. TW was fixed at 30 parts per hundred rubber (phr) where the CB was varied from 10–30 phr. Incorporation of CB in the hybrid system can fasten the curing process of the composites, as the scorch and curing times increased with increasing the CB content. CB has greatly influenced the maximum torque, tensile strength, and tensile modulus due to its better rubber-filler interaction within the rubber matrix. However, the elongation at break of the composites dropped continuously with the addition of the CB. This is simply due to dilution effect of the composite which refers to the less amount of flexible phase. The enhanced performance of the composite in the presence of CB can be verified by the calculation of rubber-filler interaction ( $Q_f/Q_d$ ) values, indicating higher rubber-filler interaction when higher amount of CB was used. Apart from that, the images obtained from scanning electron microscope (SEM) also provided some evidence relating to the tensile properties observed. From the experimental results, hybridization of 30/20 phr/phr of TW and CB is highly suggested to gain the synergistic strength and processing safety.

**Keywords:** Natural Rubber, Tea Waste, Carbon Black, Composite

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## INTRODUCTION

Rubber formulation always involves many materials, each with distinct role to improve the final properties of the vulcanizate. One of the major materials used in designing the formulation is the filler. Filler is added into rubber compound to have a tremendous change in properties such as to give better processability, cheapen the manufacturing cost, and even modify the mechanical properties of the vulcanizates. There are many types of fillers available in the market. However, carbon black and precipitated silica are always the fillers of choice in industry. This is because these fillers enable to provide remarkable reinforcement to the rubber vulcanizates [1-3]. To some extent where the cost and other aspects are concerned, the addition of highly reinforcing fillers is not an option. In this regard, the use of non-reinforcing fillers, e.g., clay, calcium carbonate, and other alternative fillers from renewable resources and waste materials are highly recommended [4].

Nowadays, there has been a critical discussion about natural-based engineering products, and this has been spreading interest worldwide. This stems to the current issue concerning renewable resources. The context of sustainable development has been involved throughout the waste disposal strategy which is aimed to convert worthless materials into sustainable solution. In preparing rubber products, this term is also implemented. Many studies have focused and conducted on the use of natural fillers in the rubber compounds by both academicians and industrial researchers. One of the waste materials that is abundant is from lignocellulose materials. Studies on the utilization of this material in rubber matrix have been largely explored. As for example, Fiorote et al. [5] tried to modify the cellulose from empty fruit bunch to be used

as filler for NR, it was observed that the nanostructured particles of such material were successfully prepared and has greatly influenced on the mechanical properties of NR. Cellulose from kenaf fiber was also prepared by Roy and Potiyaraj [6], it was then compounded with NR to observe the mechanical and dynamic properties of the composites. It was clear that the prepared cellulose had a direct effect in enhancing the properties of the composites.

Tea dust or tea waste (TW) is becoming a waste material especially in urban areas due to the increase in the consumption of tea globally. It was reported to reach about five million tons per year [5]. This has brought parallelly to the abundant TW. TW is considered as a solid biomass waste and generally disposes into an environment. It is not being used in any purpose unless discarded as wet garbage. From this point of view, TW can be advantageous waste, if they are used in the application of rubber materials because they are cheap, light in weight, and rich in polyphenols due to the tannin composed in tea leaves [7]. Although there are some attempts to utilize it in other industries such as textile industry, agricultural applications, and in a production of animal feed, the effectively usage of the TW is limited, and the utilization of TW remains largely unexplored. Besides, TW consists a high concentration of lignocellulose, this was evidently reported by Bernal et al. [8]. In this respect, TW has the potential to be used as filler for NR to replace lignocellulosic filler.

The composites based on TW and NR have been studied previously [9]. However, it was focused on the TW content on the mechanical properties of NR composites. The observed performance was not as good as expected where an alternative route to improve the properties of the composite is required. Recently, the use only one type of filler in the rubber formulation has been widely designed. In some cases, the

mechanical properties cannot usually be improved by an individual filler. This raises an idea to incorporate secondary fillers to the rubber compound. This approach has been demonstrated to provide great performance to the rubber vulcanizate. Therefore, synergistic advantages can be achieved by combining such fillers. Carbon black (CB) is again the filler of choice to be used as hybrid filler especially in the composite where non-reinforcing filler has been originally incorporated. The carbon black consists wide variety of grades depending on their size, surface area and structures [10-12]. The presence of CB in the rubber vulcanizate enormously improves the mechanical properties, morphology, and abrasion resistance.

To date, no research has been made in studying the use of TW in the rubber formulation. Apart from that, CB was also incorporated as a secondary filler in this system in a way to gain better properties. By varying the weight fraction of hybrid fillers, a new kind of value-added rubber composites with simultaneous improvement of swelling resistance and mechanical properties are developed. The results described here was part of a broader study aimed to develop a class of cost-effective rubber materials with good mechanical properties. It is an initial study to observe whether significant mechanical improvements can be obtained using readily and relatively cheap commercial filler. This study will bring us to the scientific understanding on how TW/CB hybrid fillers enable to have a great influence to the properties of the NR composites. The findings described in this present report will be insightful in manufacturing rubber articles based on TW/CB hybrid filled NR composites.

**EXPERIMENTAL**

**Materials**

All the compounding ingredients are listed in Table 1. These include SMR 20 grade NR which was processed by Mardec Malaysia Sdn. Bhd.; the tea waste (TW) powder supplied by Gold Leaf Marketing Sdn. Bhd.; and other ingredients such as zinc oxide, stearic acid, N-cyclohexyl-2-benzothiazole-sulfenamide (CBS), 2,2 methylene-bis-(4-methyl-6-tert-butylphenol) (Vulkanox BKF) and sulfur were purchased from Bayer (M) Ltd.

**Table 1** Formulation used for preparing the TW/CB hybrid filled NR composites.

Ingredients and Codes	Amount (phr)			
	F1	F2	F3	F4
NR	100	100	100	100
Tea Waste	30	30	30	30
Carbon black	0	10	20	30
Zinc Oxide	1.5	1.5	1.5	1.5
Stearic Acid	1.5	1.5	1.5	1.5
CBS	1.9	1.9	1.9	1.9
BKF	2.0	2.0	2.0	2.0
Sulfur	1.6	1.6	1.6	1.6

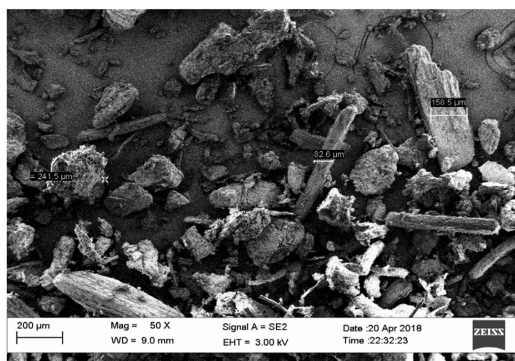
**Preparation of tea waste powder**

TW is unable to be used as received, the size was reduced by grinding it using a Pulverizing Machine assembled from Rong Tsong Precision Technology Co. Ltd., Taiwan. Then, the obtained powder was sieved with an Endicott’s sieve to get particle size below 100 μm. Finally, TW was washed and dried in a vacuum oven at 105°C for approximately 2 h to expel the moisture. The resultant TW was now ready to be used as filler for NR. The morphology of TW was also captured and is shown in Figure 1. It can be clearly seen that TW is in irregular shape, vary in both size and length. The particle size of TW is less than 200 μm as observed in the image.

**Compounding and vulcanizing steps**

The compounding of NR, TW, CB, and other additives were performed on a laboratory-sized two-roll mill (160 × 320 mm2 model XK-160) at ambient temperature for approximately 20 min. The resulting compounds were then tested for their curing characteristics using a Monsanto Moving Die Rheometer (MDR 2000) according to ASTM D5289. The test was carried out at 150 °C and the outputs in

term of scorch time (ts2), curing time (tc90) and torques were recorded automatically. Subsequently, the compounds were placed on the stainless-steel mold and compressed at 150 °C with the pressure of 10 MPa based on the respective curing times.



**Fig. 1** SEM image of tea waste powder at magnification of 50×.

**Measurement of tensile properties**

The rubber vulcanizates was first cut into dumbbell shape by using Wallace die cutter before undergoing the tensile testing. The tensile test was carried out by using Instron machine model 3366 according to ASTM D412 with a crosshead speed of 500 mm/min. The data obtained from this test were the tensile strength, elongation at break and the modulus at specific strain or so-called tensile modulus.

**Swelling uptake, rubber-filler interaction, and diffusion studies**

A vulcanized rubber was cut into rectangular shape of 30 mm x 5 mm x 2 mm for every formulation. The sample was then soaked in toluene and left swollen till equilibrium which usually took 72 h at room temperature. Afterwards, the sample was removed and wiped rapidly before being weighed. The sample was then dried and weighed again. All the recorded data was used to calculate the following parameters:

$$Swelling\% = \frac{M_{\infty} - M_o}{M_o} \times 100 \tag{1}$$

where  $M_{\infty}$  is the mass of specimen (g) after immersion in toluene and  $M_o$  is the initial mass of specimen (g)

Calculation of rubber-filler interaction was based on the Lorenz and Park’s equations which is seen below [13, 14].

$$\frac{Q_f}{Q_g} = ae^{-z} + b \tag{2}$$

where the subscripts f and g are respectively referred to the filled and gum vulcanizates. Z is the ratio by weight of filler to rubber hydrocarbon in the vulcanizates, a and b are constant. As the results, if  $Q_f/Q_g$  has the higher value, it means that the extent of interaction between filler and matrix is lower. While Q, the weight of toluene uptake per gram of rubber hydrocarbon was calculated by using the equation 3.

$$Q = \frac{Swollen\ weight - Dried\ weight}{Original\ weight \times \frac{100}{Formula\ weight}} \tag{3}$$

The data obtained from swelling study was implemented to further determine for diffusion studies. The mass recorded previously was inserted into equation 4 to calculate the swelling coefficient ( $\beta$ ) as follows;

$$\beta = \frac{M_{\infty} - M_o}{M_o} \times \rho_s^{-1} \tag{4}$$

where  $\rho_s$  is the density of the toluene.

As for the diffusion coefficient ( $D$ ) it can be calculated using equation 5 through the second Fickian law:

$$D = \pi \left( \frac{h\theta}{4Q_\infty} \right)^2 \quad (5)$$

where  $h$  is the thickness of the sample before swelling,  $\theta$  is the slope of the linear sorption curve, and  $Q_\infty$  is the equilibrium solvent uptake.

Sorption coefficient ( $S$ ) and permeability coefficient ( $P$ ) were also calculated to describe the initial penetration solvent into the rubber matrix and the amount of the solvent permeates through a uniform area of the sample per minute, respectively.  $S$  and  $P$  can be calculated using equations 6 and 7:

$$S = \frac{M_\infty}{M_o} \quad (6)$$

$$P = DS \quad (7)$$

### Scanning electron microscopy

The morphological properties for the sample of tensile fractured surface and TW was studied by using Scanning Electron Microscopy (SEM). The sample from the broken tensile testing were collected and cut. The vulcanizates rubber sample and the TW then undergo sputter-coated process with a thin layer of gold to avoid electrostatic changing and poor image resolution.

### Fourier Transform Infrared Spectroscopy (FTIR)

The functionalities of TW were detected by using Fourier transform infrared spectroscopy (FTIR; Perkin Elmer System 2000). The FTIR spectrum was obtained in the wavenumber range of 550 to 4000  $\text{cm}^{-1}$ . The TW was ground with potassium bromide (KBr) for the formation of pellet that has been used to obtain the infrared spectrum.

## RESULTS AND DISCUSSION

### FTIR analysis

The results of FTIR spectrum of TW is shown in Figure 2. There are some interesting absorbance peaks observed especially at wavenumbers of 3298, 2993, 1620 and 1032  $\text{cm}^{-1}$ . An obvious and broad peak at a wavenumber of 3298  $\text{cm}^{-1}$  corresponds to O-H stretching due to the presence of alcohols and phenols composed in TW. The peaks at 2993 (medium) and 1032  $\text{cm}^{-1}$  (strong) respectively which indicate the existence of carboxylic acid in TW. Another interesting peak is at 619  $\text{cm}^{-1}$  which is responsible to the amine group in the form of N-H bond available in TW. The peaks observed are very good agreement to the previous work reported by Uddin et al. [8] and Tian et al. [15].

### Curing characteristics

Table 2 lists the curing characteristics of the TW/CB hybrid filled NR composites. It was observed that the maximum torque ( $M_H$ ) increased with increasing the CB contents.  $M_H$  defines as an elastic modulus of the fully cured rubber. The enhanced torque values confirm that the processing of NR compounds characterized by higher amount of CB becomes harder, decreasing the movement of rubber chain and the flexibility of chain thus allowing the increasing of the  $M_H$  value. Scorch time ( $ts_2$ ) and curing time ( $tc_{90}$ ) showed a decreasing trend over the CB contents.  $ts_2$  is a time where the crosslinks begin whereas the  $tc_{90}$  is a time that required for the compound to reach 90% of the total cure during curing characteristics test. Delayed  $ts_2$  and  $tc_{90}$  of the NR composite with solely TW was clearly responsible to its affinity to adsorb accelerator. TW consists of highly hydroxyl content as shown in FTIR spectrum (see Figure 2). This functionality has high affinity to interact with accelerator which leading to longer vulcanizing process. However, shorter  $ts_2$  and  $tc_{90}$  observed when addition CB was also due

to the nature of CB. According to Baccaro et al. [16], shorter time needed for vulcanization especially at higher content of CB is clearly due characteristics of CB itself. CB has very large surface area where the rubber and additives enable to interact effectively, leading to a high possibility to initiate crosslinks. This has brought to a decrease in the vulcanization time. Ismail et al. [17] also explained that CB is able to trigger the process of vulcanizing by the formation of hydrogen sulphide between the rupture of S-N bond and sulfenamides (accelerator) during heating, this consequently quicken the process of vulcanization. Another possible explanation might be due to the thermal conductivity of CB, CB is considered thermally conductive filler where TW is not. The thermal conductivity of CB which is about 0.00067  $\text{cal/cm}\cdot\text{sec}\cdot^\circ\text{C}$  [18]. This makes the heat transfer more efficient to the rubber chain and takes shorter time to complete the vulcanization process.

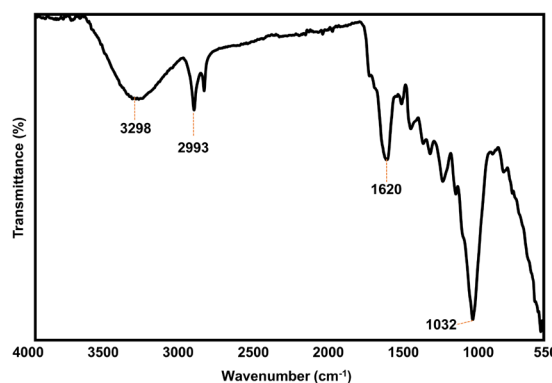


Fig. 2 FTIR spectrum of tea waste powder.

Table 2 Curing characteristics of TW/CB hybrid filled NR composites.

Codes	$M_H$ (dNm)	$ts_2$ (min)	$tc_{90}$ (min)
F1	5.58	2.44	3.50
F2	6.17	2.16	3.42
F3	7.17	2.15	3.32
F4	8.87	1.56	3.21

### Tensile properties

Tensile properties of TW/CB hybrid filled NR composites were also observed in this experiment and are listed in Table 2. Tensile strength is measured by maximum stress for material to withstand while being pulled or stretch before breaking. The tensile strength of the TW/CB hybrid filled NR composites increased as the CB loading increased. This could be due to the compatibility or good adhesion between CB and matrix of rubber. The smaller particles and higher structure of CB are responsible to improve the rubber-filler interaction. Thus, stress was able to be transferred by the rubber matrix. TW is considered as hydrophilic filler, it was reported earlier by Xie et al. [19] that using the hydrophilic filler in non-polar rubber can lead to the agglomeration of filler and later distribute unevenly throughout the matrix. Besides, insufficient wetting of TW throughout the matrix has also led to a weak interfacial adhesion, this later provides less efficiency of the stress to be transferred from the matrix to filler.

Table 3 Tensile properties of TW/CB hybrid filled NR composites.

Codes	Tensile strength (MPa)	Elongation at break (%)	M100 (MPa)	M300 (MPa)
F1	7.26 ± 0.51	655.0 ± 4.15	0.99 ± 0.01	2.03 ± 0.04
F2	8.62 ± 0.35	382.2 ± 5.13	1.51 ± 0.02	3.21 ± 0.01
F3	8.78 ± 0.26	435.6 ± 9.21	1.67 ± 0.01	3.95 ± 0.02
F4	9.86 ± 0.22	461.1 ± 4.26	2.20 ± 0.03	5.62 ± 0.05

Reverse finding was observed for the elongation at break of the composites. This could be due to the incorporation of unstrained particle of CB that leads to restrict the mobility of rubber chains. The

addition of filler may reduce the elasticity of the composites; higher CB loading has caused a stiffer NR composite. As for the tensile modulus, the stresses at 100% and 300% strains significantly increased with the addition of CB. When more CB gets into the NR matrix, the composites become stiffer, the macromolecular chains of the rubber has the difficulty to move because of the restriction to the deformation hence increased the tensile modulus.

### Swelling uptake, diffusion studies and their rubber-filler interaction

The swelling uptake of TW/CB hybrid filled NR composites is plotted in Figure 3. The swelling study was determined by immersing the sample in the toluene until equilibrium. The data obtained from the swelling results were used to calculate swelling uptake, rubber-filler interaction and diffusion behaviors. The swelling percentages decreased with increasing CB loading. The highest swelling percentage is at 0 phr CB where the value is about 323.151%. Then it was decreased with increasing CB loading at 281.44%, 256.11% and 221.53%. for 10–30 phr of CB, respectively. The presence of CB has brought to a strong interfacial interaction. As a consequence, less penetration of toluene is observed upon inclusion of CB.

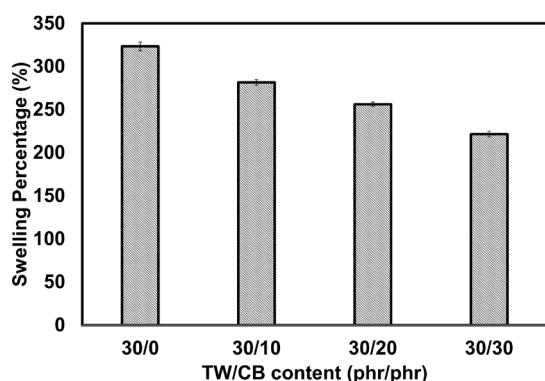


Fig. 3. Swelling percentage of TW/CB hybrid filled NR composites.

Low solvent penetration in the case of the composites containing CB is due to their higher crosslink density. As been explained in the preceding session [16] that CB can help trigger the vulcanization process by forming certain interaction with rubber molecules. Besides, this mechanism correlates to the occurrence of electron acceptor sites on the cluster surfaces of CB where the rubber radicals formed during masticating the rubber. Therefore, swelling was comparatively less as for the composites containing the CB.

The results obtained from the swelling data were also implemented and explained in term of the swelling coefficient, diffusion coefficient, sorption coefficient, and permeability coefficient. These parameters provide useful information on the efficiency of solvent to penetrate rubber molecules. As can be seen in Figures 4 and 5, it is clear that these values decreased significantly over the incorporation of CB in the hybrid systems. This is because CB is capable of restricting the penetration of solvent throughout the rubber molecules. The reduction of these values can be explained regarding to the physical and chemical crosslink observed in the presence of CB.

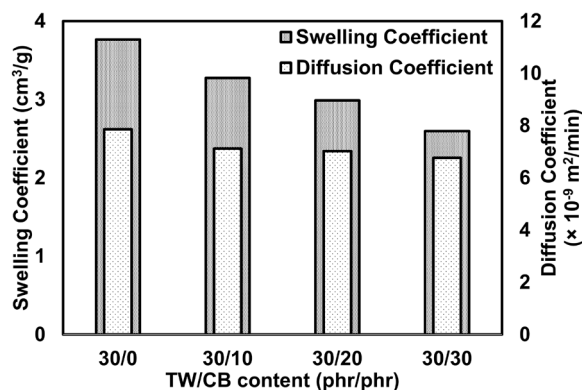


Fig. 4. Swelling and diffusion coefficients of TW/CB hybrid filled NR composites.

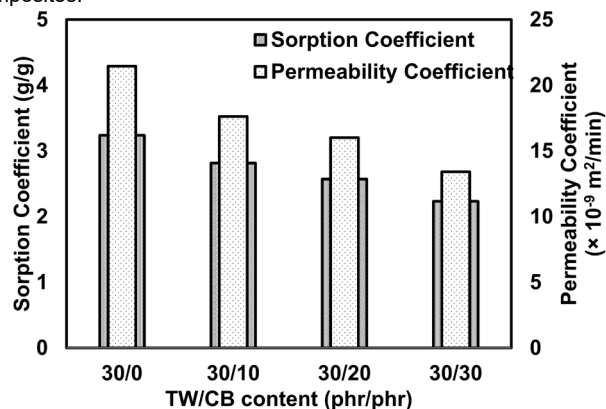


Fig. 5. Sorption and permeability coefficients of TW/CB hybrid filled NR composites.

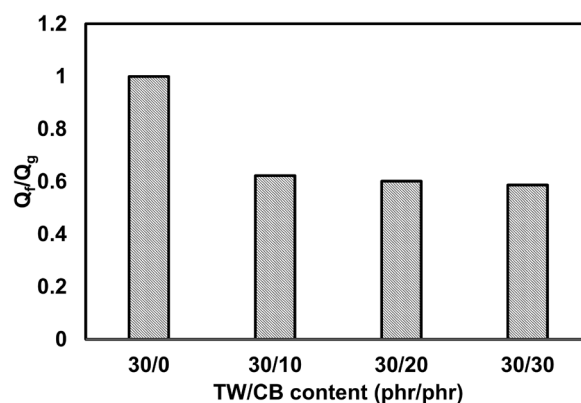
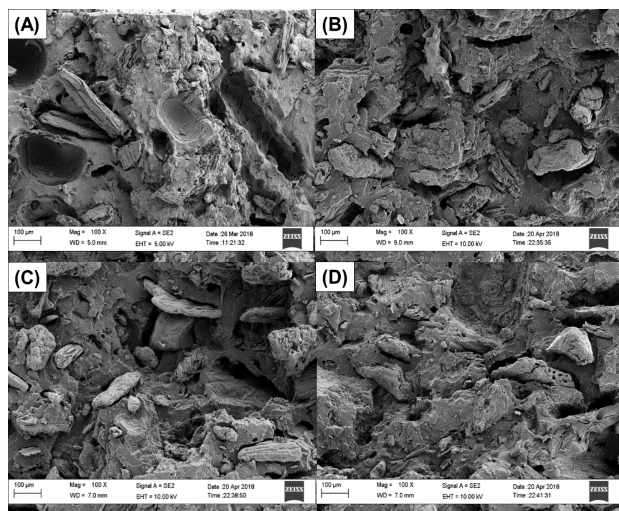


Fig. 6.  $Q_f/Q_g$  values of TW/CB hybrid filled NR composites.

As demonstrated, CB plays an important role in enhancement of curing, swelling, and mechanical properties of the composites. The obtained results based on the tensile properties were again verified by determining the rubber-filler interaction parameter through Lorenz and Park's equations [13, 20-22]. This is shown in Figure 6. The value of  $Q_f/Q_g$  slightly decreased with increasing the CB contents. As widely known that the lower value of  $Q_f/Q_g$  indicates higher extent of interaction between rubber and filler. CB consists of high surface activity and, consequently, high affinity to elastomer. The NR composites that contain higher loading of CB hence have the stronger interaction between rubber and filler. Through this result, it is in a good agreement with the tensile strength observed in the previous study.

### Morphological characteristics of the composites

Figures 7A–7D show the SEM images obtained from the tensile fractured surfaces of TW/CB hybrid filled NR composites. Considering the composite at 0 phr of CB (see Figure 7A), the image shows a lot of TW pullouts from the matrix of rubber and some cavities are noticed. This is because of the poor adhesion between irregular shaped of TW particles and the matrix of rubber that cause the TW to be pulled out from the rubber easily when stress is applied hence leaving the gaping holes. This correlates to the lower tensile strength observed according to the previous results. When the CB was incorporated (see Figures 7B–7D), the morphology was more towards rougher surfaces. Increasing the CB content has given the surface with more roughness and tortuous path along the image. This obvious behavior is a good indication that the existence of failure is towards a more difficult manner which then resulting to give a high tensile strength. Such explanation is also in good agreement to the work reported elsewhere [23, 24], who observed the same morphology upon the replacement of alternative fillers by carbon black and hence resulting to enhance the mechanical properties of the composites.



**Fig. 7.** SEM images at the magnification of 100× of TW/CB hybrid filled NR composites i.e., 30/0 phr/phr (A), 30/10 phr/phr (B), 30/20 phr/phr (C) and 30/30 phr/phr (D) of TW/CB hybrid fillers.

**CONCLUSION**

This work aimed to study the potential use of TW as an alternative filler for NR. Because of the bigger particle size (>250 μm as shown by SEM) of TW which is considered to be in a class of non-reinforcing filler. CB was therefore hybridized to improve the tensile properties of the composites. Increasing the amount of CB in the hybrid system can fasten the curing process of the composites, as the  $t_{s2}$  and  $t_{c90}$  increased with increasing the CB content. Adding the CB has increased the  $M_H$ , tensile strength and tensile modulus due to its better rubber-filler interaction within the rubber matrix. However, the elongation at break of the composites drop continuously with the addition of the CB. This is simply due to several factors, i.e., the higher surface area of CB and its corresponding compatibility within the NR matrix as well as the better distribution of CB throughout the matrix. Such findings can be verified by the  $Q_f/Q_g$  values, indicating higher rubber-filler interaction when higher amount of CB was used. Apart from that, SEM images also provided some evidence relating to the tensile properties observed. In summary, TW can be a potential filler for NR matrix with the assistance of CB as hybrid filler. Considering the overall properties, the TW/CB at the loadings of 30/20 (phr/phr) is highly suggested. Such hybrid system is also suitable in applications where the strength and processing safety is concerned.

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