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COMPARATIVE STUDIES ON CURE CHARACTERISTICS AND MECHANICAL PROPERTIES OF OIL PALM BIOMASS FILLED NATURAL RUBBER COMPOSITES

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ABSTRACT

Oil palm is categorised as the most important agricultural crop in Malaysia occupying about 70% of the agricultural land. The palm oil industry is one of the biggest contributors to Malaysia's Gross National Income (GNI). However, the rapid development of the palm oil industry causes high production of palm oil waste which is a worrying environmental issue these days. As the need to promote sustainable, renewable and clean energy keeps rising, researchers have taken a keen interest in utilising palm oil waste as a source of biomass. Palm oil waste such as palm kernel shell (PKS) is a great source of valuable biomass and readily available in large amounts which can then be transformed into biochar and activated carbon via pyrolysis and activation processes, respectively. By producing palm kernel shell biochar (PKSB) and activated palm kernel shell (APKS) derived from palm oil waste, they can potentially be used as potential bio-fillers in rubber composites. The research aimed to study the effect of different loading of PKSB and APKS in natural rubber (NR) composite since they have higher carbon content, porosity and surface area compared to other biomass fillers. The surface morphology analysis by scanning electron microscopy, cure characteristics, swelling measurements, and mechanical properties was analysed. APKS was observed to have well-developed pores that could provide a high surface area of contact resulting in improved mechanical interlocking between filler and rubber matrix. Comparisons were made between PKSB, APKS and other bio-fillers such as coconut fibre (CF), bamboo charcoal (BC) and untreated kenaf (UK). The cure characteristics for PKSB showed a high range of maximum torque (M_H) values (11-23 dN.m), better in ts_2 (1 min) and t_{90} (2-3 min), whereas the M_H values for APKS were slightly lower and longer in t_{90} which were 14-15 dN.m and 2-4 min, respectively. PKSB also showed a better swelling percentage (226%-329%) which would indicate high crosslink density compared to APKS (305%-336%). Moreover, APKS showed better tensile strength (8-18 MPa) and elongation at break (519%-669%) as the filler loading increased in comparison with PKSB which recorded a tensile strength of 5-14 MPa and elongation at break of 385%-561%. Based on the results, it can be concluded that the optimum value of APKS filler loading ratio in NR composite is 40 phr as 40 phr of APKS filled NR composite had the highest mechanical properties compared to the other filler loading ratios. Both PKSB and APKS have great potential to be used and commercialised as semi-reinforcing fillers in the rubber industry. This way, PSKB and APKS are able to provide a sustainable alternative to existing petroleum-based fillers and could help to reduce the abundance of palm oil waste while producing high-performance rubber-based products.

Keywords: activated carbon, biochar, cure characteristic, mechanical properties, palm kernel shell.

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INTRODUCTION

Palm oil production has increased rapidly over the past 50 years (Basiron, 2007). According to the Malaysian Palm Oil Council (MPOC), Malaysia is among the world's largest palm oil producers, generating approximately 19.14 million tonnes and exporting 17.37 million tonnes of palm oil, respectively in 2020. However, these figures were lower than in 2019 due to the COVID-19 pandemic and the government's movement control order (MCO) (Parveez *et al*., 2020). Massive palm oil production generates large amounts of oil palm waste, causing disposal issues, pollution and global warming effects if not handled properly (Abbas *et al*., 2019). Oil palm trunks (OPT), oil palm fronds (OPF), empty fruit bunches (EFB), mesocarp fibres (MF), palm kernel shell (PKS) and palm oil mill effluent (POME) are the waste biomasses that are produced from the palm oil industry. However, these palm oil biomasses can be converted into useful applications such as potential fillers in polymer composites to curb these environmental problems. Among these palm oil biomass, PKS can be transformed into biochar and activated carbon as fillers due to its physico-chemical properties in terms of porous surface, high mechanical strength, insolubility in water, and various functional groups (Anisuzzaman *et al*., 2021).

Fillers are compounding ingredients used in rubber compounding to reinforce or reduce the cost of polymeric material (Abidin *et al*., 2020; Egwaikhide *et al*., 2007; Mamauod *et al*., 2018). Carbon black (CB) and silica are the most widely used conventional fillers in the rubber industry because of their ability to improve particular mechanical qualities and their high availability (Moonchai *et al*., 2012). Biomass resources such as bamboo, kenaf, cellulose, starch, coconut fibre, rice husk and palm kernel shell are frequently employed in rubber composites as alternative bio-fillers (Arayapranee *et al*., 2005; Egwaikhide *et al*., 2007; Ismail *et al*., 2010; Onyeagoro, 2012). Alternative bio-fillers from these biomasses have numerous advantages over conventional fillers as they are inexpensive, possess low density, are easily biodegradable and have a low environmental impact (Daud *et al*., 2017; Hidayu and Muda, 2016; Onoja *et al*., 2019). Many researchers have investigated the use of PKS as fillers in rubber compounds due to their biomaterial compatibility with interesting properties such as porosity, water content, lignocellulosic properties, solid density and carbon content (Baffour-Awuah *et al*., 2021). However, there are some weaknesses in PKS such as having low or blocked porous structure due to the presence of contaminants and a low percentage of carbon content that could limit its performance as a bio-filler for rubber composites.

Thus, the carbonisation and activation process are applied to PKS at high temperatures to improve the weaknesses of PKS. The carbonisation process is a thermal decomposition of organic material in the absence of oxygen which can eliminate any volatile matter, develop a porous structure and increase the carbon content (Rugayah *et al*., 2014). It also can create mechanical interlocking between filler and rubber matrix with the presence of their porous structure hence improving the mechanical strength of the composites. Whereas, the carbonisation-activation process is a two-step process in which the material is carbonised at a temperature of around 500°C and activated at a temperature of around 900°C. This process uses higher heating temperatures compared to the carbonisation process. With this higher heating temperature, it has the ability to enhance the properties of palm kernel shells better in terms of carbon content, surface area and development of pores structure (Hamza *et al*., 2015).

Nowadays, many renewable and natural fillers such as rice husk, coconut shell and bamboo have been extensively used in rubber-based applications. One of the renewable and natural fillers sources would be PKS and it has the potential to be used as a bio-filler in the rubber industry due to its high lignin content, along with hemicellulose that could give the fibre toughness and stiffness (Daud *et al*., 2016). PKS also has the ability to be transformed into an enhanced version of bio-filler known as biochar and activated carbon by undergoing carbonisation and activation processes. These processes could improve their specific desirable features such as creating porous structure and increasing the carbon content, which are very important features as part of rubber reinforcement (Farida *et al*., 2019). Previous studies involving palm kernel shell biochar (PKSB) and activated palm kernel shell (APKS) as filler reinforcement in rubber matrices are quite low in number due to a lack of research about it. This study involves the utilisation of PKSB and APKS of high carbon content and porosity as reinforcement in NR composites. Both PKSB and APKS have great, promising potential to be used

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as a semi-reinforcing filler in NR composite. This study could encourage rubber researchers around the world to transform biomass PKS into a value-added additive and incorporate it into rubber matrices. Therefore, this study aimed to analyse the potential and performance of both PKSB and APKS as bio-fillers in natural rubber (NR) by adding different filler loading in comparison with other commercial fillers. The effects of PKSB and APKS on the morphology, cure characteristics and mechanical properties of NR composites were investigated by using a scanning electron microscope (SEM), swelling measurements and tensile test.

MATERIALS AND METHODS

Preparation of Materials

Natural rubber bale (grade SMR-10) was supplied by a local company, Airelastic Industries Sdn. Bhd. while the raw PKS was obtained from the Ulu Kanchong Palm Oil Mill, Ulu Kanchong Estate, Negeri Sembilan, Malaysia. PKS was converted into PKSB and APKS by carbonisation and activation processes following the method from previous studies (Nahrul Hayawin *et al.*, 2017; 2020). This is shown in *Figure 1 a, b* and *c*. PKS underwent a carbonisation process at 500.0°C where approximately 40 kg of PKS was fed into a rotary kiln and the process took around 60 min to form PKSB (Mohd Hasan *et al.*, 2019; Nahrul Hayawin *et al.*, 2020). The PKSB was activated using a 2-in-1 carbonisation activation process at 900.0°C to produce APKS (Nahrul Hayawin *et al.*, 2020). The PKSB and APKS were first washed using distilled water to remove any contaminants and the pH value was checked by using a pH meter until pH 7 was obtained and further dried in an oven for 24 hr at 104.5°C. Since acidity tends to diminish the crosslink density of filler, resulting in a slow vulcanisation cure rate, the pH of the samples must be neutral (Malomo *et al.*, 2020). Both PKSB and APKS were then pulverised into powder form which could be seen in *Figure 1c* and sieved via a vibratory sieve shaker with a mesh size of 240.

Preparation of PKSB- and APKS-filled NR Composites

Figure 2 shows the experimental design of PKSB and APKS as fillers in NR composites. It shows the process starting from the morphological study of PKSB and APKS particles until mechanical testing was conducted. *Table 1* shows the formulation of rubber compounding used in this study, which were F1 (without filler), F2-F7 (PKSB filler) and F8-F13 (APKS filler). The NR (SMR-10) was incorporated in a two-roll laboratory mill at room temperature according to ASTM D3184. The roll was preheated for 1 min, then the rubber was placed into the mill and pre-masticated until it became soft and formed a band around the mill. Following the pre-mastication procedure, the ingredients were added in the following order; zinc oxide, stearic acid, PKSB or APKS, 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), 2-2'-dithiobisbenzothiazole (MBTS), 1,3-diphenyl-guanidine (DPG), tetramethylthiuram disulfide (TMTD), paraffin oil and sulphur. All compounding ingredients were mixed for about 10-15 min. The finalised mixtures were sheeted to about 3 mm thick and cooled for 24 hr at room temperature. The mixtures were then compressed into rubber composites via placement in a mould and pressed between heated plates of the hot press machine at 160°C for curing. The amount of time used for the compression was based on the results of curing characteristics in *Table 4*.

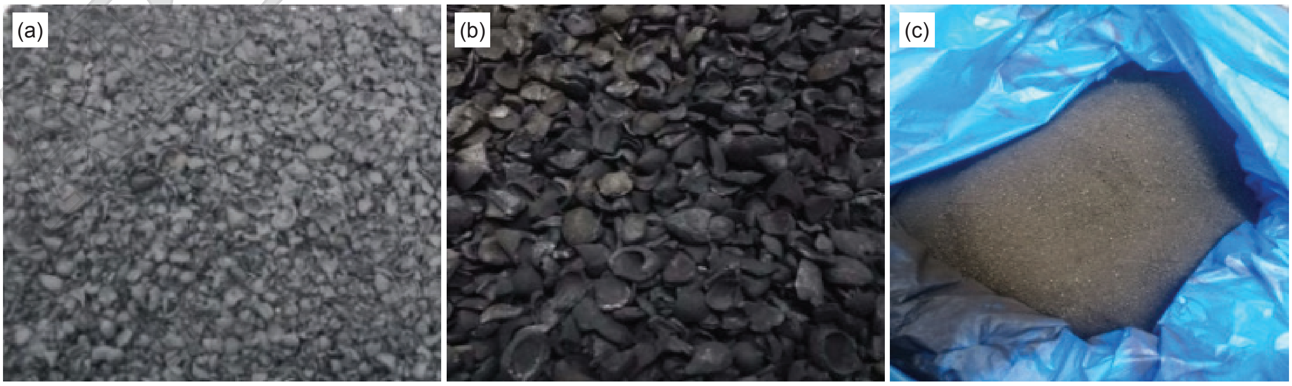

Figure 1. (a) Palm kernel shell biochar (PKSB), (b) activated palm kernel shell (APKS) and (c) fine PKSB and APKS powder after pulverised.

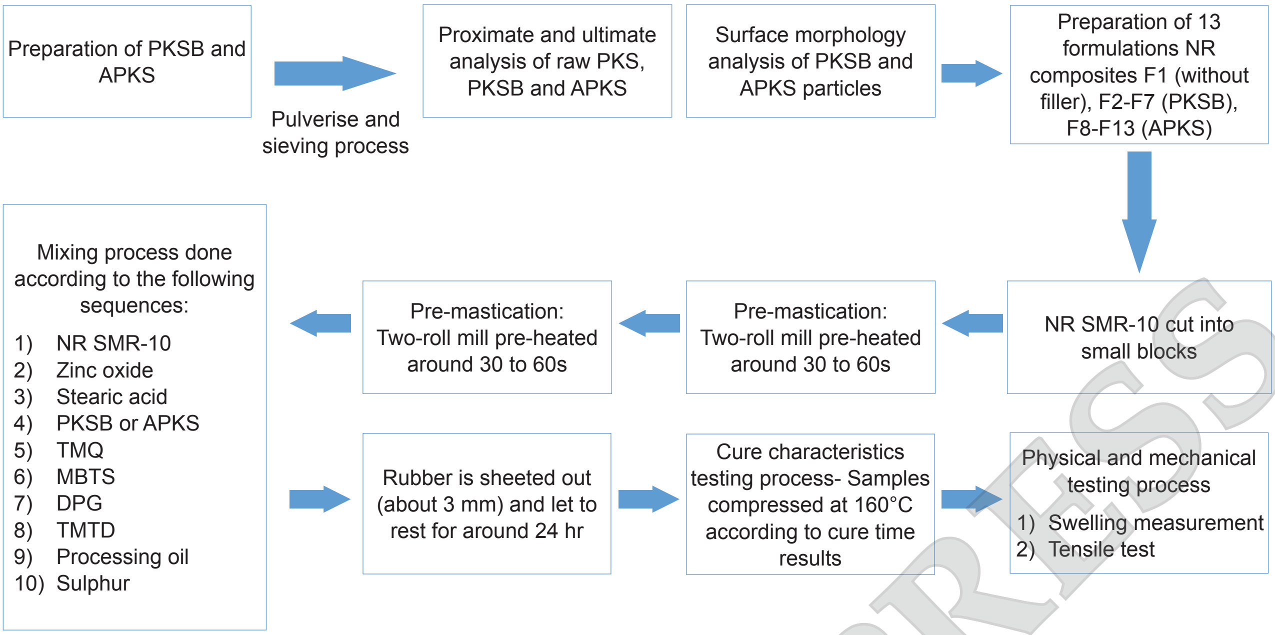

Figure 2. Experimental design of PKSB- and APKS-filled NR composites.

TABLE 1. RUBBER COMPOUNDING FORMULATIONS

Ingredients (phr)	Formulation												
	1	2	3	4	5	6	7	8	9	10	11	12	13
NR	100	100	100	100	100	100	100	100	100	100	100	100	100
PKSB	0.0	5.0	10.0	20.0	30.0	40.0	50.0						
APKS								5.0	10.0	20.0	30.0	40.0	50.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Zinc oxide	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
TMQ	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Oil	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	50	5.0	5.0	5.0	5.0
DPG	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Sulphur	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
TMTD	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
MBTS	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25

Characterisation of PKSB, APKS, PKSB- and APKS-filled NR Composites

Ultimate and proximate analysis. The elemental components which consist of carbon, hydrogen, nitrogen and sulphur content in raw PKS, PKSB and APKS were analysed using a CHNS analyser (LECO, CHNS932, USA) according to the ASTM D5291 method. The proximate analysis was done using a thermogravimetric analyser (TGA) Mettler Toledo, TGA/SDTA 851 (USA) according to ASTM D5142 to determine moisture content, volatile matter, fixed carbon and ash content of raw PKS, PKSB and APKS particles (Nahrul Hayawin *et al*., 2017).

Morphological study. The surface morphology of PKSB and APKS were analysed and characterised using a scanning electron microscope (Leica Cambridge S-360 SEM) to determine the porous structure and shape of the pores for PKSB and APKS.

Cure characteristics. The PKSB-filled rubber and APKS-filled NR composites were cut between 8-10 g and cure assessment was carried out at 160°C within a test period of about 30 min using a ZME-1005A rubber rheometer ZME tester. Cure time (t_{90}), maximum torque (M_H), minimum torque (M_L), and scorch time (t_{s2}) were obtained from the torque versus time rheographs. The delta torque (ΔM) of the vulcanized rubber composites was calculated by using Equation (1):

$$\Delta M = M_H - M_L \tag{1}$$

Swelling measurement. The swelling test was performed in toluene to determine the rubber-filler interaction and degree of swelling for the PKSB- and APKS-filled NR composites according to ASTM D3616. The cured rubber sheet was cut into two pieces with a dimension of 1 × 1 cm and the initial weight of each sample was recorded. The sample was immersed in toluene for 72 hr at room temperature. Then, the swollen sample was removed from toluene after 72 hr, wiped and weighed again until it reached equilibrium weight. The degree of swelling (Q) and the volume fraction of rubber (Vr) were determined using Equations (2) and (3), respectively:

$$Q\ (\%) = \frac{W_2(g) - W_1(g)}{W_2(g)} \times 100 \tag{2}$$

where W_1 is the weight of the un-swelled composite and W_2 is the swollen weight.

$$Vr = \frac{V_R}{(V_R + V_S)} \tag{3}$$

where V_R is the volume of rubber and V_S is the molar volume of the solvent (toluene).

Tensile test. The tensile test on the PKSB- and APKS-filled NR composites was carried out using a dumbbell-shaped test piece with a width of 4.051 mm and the thickness of the samples was measured. The tensile properties were determined according to ASTM D412 using Instron Universal tensile testing machine (model 5569) at a speed rate of 500 mm/min. The test was repeated 5 times for each formulation and the average value was calculated. The tensile properties such as tensile strength, elongation at break and modulus at 100 and 300 were generated by the software. The reinforcement index of PKSB- and APKS-filled NR composites were calculated using Equation (4):

$$\text{Reinforcement index (RI)} = \frac{\text{Modulus 300 (M300)}}{\text{Modulus 100 (M100)}} \tag{4}$$

RESULTS AND DISCUSSION

Ultimate and Proximate Analysis

Table 2 shows the elemental constituents of raw PKS, PKSB and APKS obtained from the ultimate analysis. The carbon content (C) of PKSB and APKS increased while a decrease in hydrogen (H), nitrogen (N) and sulphur (S) contents were recorded in comparison with raw PKS. This might be due to the high temperature applied for the carbonisation process in PKSB at 500°C and the carbonisation-activation process in APKS at 900°C. This also could be associated with the release of volatile materials in PKSB and APKS that did not affect the carbon content (Hamza *et al.*, 2015). The release of the hydroxyl group may be responsible for the decrease in H content, while the thermal decomposition of lignocellulose components such as lignin, cellulose and hemicellulose may have contributed to the decrease in the N and S contents (Zainal *et al.*, 2018).

The results of the proximate analysis on raw PKS, PKSB and APKS are shown in *Table 3*. The moisture content of PKSB and APKS decreased as the temperature of carbonisation increased due to the release of the hydroxyl group (-OH) on the surface of raw PKS when high heat was applied (Rugayah *et al.*, 2014). The same trend could also be seen for the volatile matters of PKSB and APKS, where the thermal decomposition in raw PKS released more volatile materials when the temperature increased (Nahrul Hayawin *et al.*, 2017). For fixed carbon, PKSB and APKS showed increasing values compared to raw PKS because both particles had undergone carbonisation and carbonisation-activation processes at high temperatures, which produced more C-C bonds, resulting in the formation of highly carbonaceous molecules (Mohd Hasan *et al.*, 2019; Sallau *et al.*, 2021). The ash content of PKSB and APKS also increased compared to PKS. Previous studies have stated that the increase in the ash content might be related to the increase in pH value or indicate low purity of the carbon material (Mohd Hasan *et al.*, 2019; Rugayah *et al.*, 2014).

TABLE 2. ULTIMATE ANALYSIS OF RAW PKS, PKSB AND APKS

Sample	Carbon, C (%)	Hydrogen, H (%)	Nitrogen, N (%)	Sulphur, S (%)
Raw PKS	60.90 ± 0.20	12.76 ± 0.02	0.66 ± 0.33	0.19 ± 0.01
PKSB	69.20 ± 0.10	3.30 ± 0.08	0.61 ± 0.01	0.04 ± 0.00
APKS	74.38 ± 2.19	2.03 ± 0.24	0.33 ± 0.01	-

TABLE 3. PROXIMATE ANALYSIS OF RAW PKS, PKSB AND APKS

Sample	Moisture content (wt. %)	Volatile matter (wt. %)	Fixed carbon (wt. %)	Ash (wt. %)
Raw PKS	9.55 ± 0.40	53.38 ± 0.21	18.84 ± 0.02	0.87 ± 0.01
PKSB	6.01 ± 0.10	13.08 ± 1.00	75.02 ± 3.30	4.61 ± 2.50
APKS	5.72 ± 0.98	9.35 ± 3.50	80.21 ± 2.00	2.72 ± 0.97

Morphological Properties of PKSB and APKS

The SEM images of PKSB and APKS particles were observed at different magnifications of 1000×, 2000× and 3000× as shown in *Figure 3*. *Figure 3a* and *3b* show that PKSB has many large pores on the surface of the primary particle due to the pyrolysis process that caused the organic material around the particles to decompose. The gradual decomposition of organic materials such as hemicellulose, cellulose and lignin inside PKSB particles may be responsible for the increase in surface and pore volume at 500°C (Wang *et al.*, 2019; Zhao *et al.*, 2017). The surface of PKSB also looked slightly rough with irregular pore sizes ranging from 11 to 133 m^2/g that developed due to the loss of volatile substances after the carbonisation at high temperatures (Hamza *et al.*, 2015).

However, the morphology of APKS particles was quite different compared to PKSB since APKS particles have very tiny and more-developed pores as well as rougher surfaces as shown in *Figure 3d* and *Figure 3e*. The changes in morphology and formation of rough surfaces of APKS may be attributed to the widened pores created during the physical activation and the carbonisation process at 900°C (Malomo *et al.*, 2020). Since APKS has more porous structure, this resulted in more surface area of contact for rubber-filler interaction and promoted mechanical interlocking between APKS and NR phases. The surface roughness observed on the surface of APKS also contributed to the enhanced adhesion of APKS towards NR rubber chains (Daud *et al.*, 2017). This stronger rubber-filler adhesion led to a higher tensile strength of the composite, which helped to enhance the properties of composites. Besides that, both PKSB and APKS had irregular shapes of the primary particle as seen in *Figure 3c* and *Figure 3f* which could be due to the mechanical crushing process using a pulveriser (Nabil *et al.*, 2013).

Cure Characteristics

Table 4 summarises the cure characteristics of rubber composites without the presence of filler (F1) which acts as a control, PKSB filler (F2-F7) and APKS filler (F8-F13). M_H and M_L evaluate the viscosity of the rubber composites to indicate its processability while ΔM measures the stiffness and

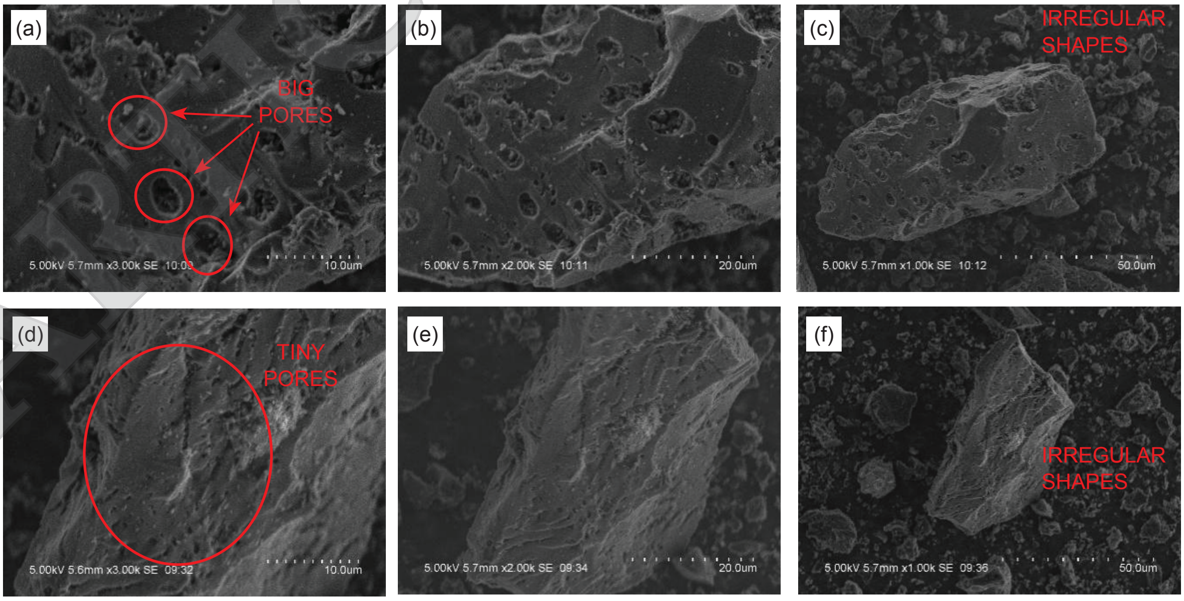

Figure 3. SEM images of PKSB at different magnifications (a) 1000×, (b) 2000×, (c) 3000× and APKS at different magnifications (d) 1000×, (e) 2000×, (f) 3000×.

the rigidity of the material due to the extent of cross-linking and the reinforcement by fillers (Mohamad *et al*., 2008; Sianturi and Surya, 2018). Both M_H and M_L of PKSB-filled NR composites increased as the PKSB loading increased as seen in *Table 4*. This may have been due to the increment of the PKSB content which increased the viscosity of the rubber composites and restricted the molecular motion of the macromolecules (Tomczyk *et al*., 2020; Wang *et al*., 2019). ΔM of formulation 1 showed the lowest value, which could be partly due to the absence of APKS and PKSB. Whereas, the ΔM of PKSB-filled NR composites showed an increasing trend as the filler loading increased which may be due to the formation of cross-linking between filler and rubber phases. Based on the SEM images of PKSB which displayed its porous structure, the pores provided sites for crosslink formation which caused ΔM of PKSB-filled NR composites to increase, thus improving the stiffness of the composites (Abdelsalam *et al*., 2021; Kim *et al*., 2020; Ngamsurat *et al*., 2011). The incorporation of PKSB in the NR matrix did not affect the scorch time (t_{s2}) and the curing time (t_{90}). Meanwhile, the addition of APKS in the NR matrix did not change much on the M_H, M_L, ΔM, t_{s2} and t_{90} values as shown in *Table 4*. Hence, it could be said that the incorporation of APKS in NR composites regardless of any loading ratio was able to maintain the M_H, M_L, ΔM, t_{s2} and t_{90} values which would indicate appropriate processing safety, crosslink formation and cure time as there were only minor differences in curing characteristics between each formulation in APKS-filled NR composites (Sianturi and Surya, 2018). The torque values (M_H, M_L, ΔM) in APKS-filled NR composites showed minor differences which indicated that the filler loading between 5 phr to 50 phr had similarities in terms of crosslinking sites that contributed to the filler-rubber matrix interactions. While t_{s2} and t_{90} for APKS also showed minor differences because the filler loading has similarity in terms of the heat distribution in the matrix due to the incorporation of filler (Mente and Motaung, 2016).

Swelling Properties

The degree of swelling (Q) and the rubber volume fraction (Vr) of the PKSB- and APKS-filled NR composites are shown in *Table 5* and *Table 6*. The absorption of toluene by rubber composites until the swelling equilibrium was achieved at room temperature was used to determine the Q values. The Vr value is the volume fraction of the equilibrium swollen rubber with filler, reflecting the rubber-filler interaction (Ismail and Shaari, 2010). *Table 5* displays the decreasing trend of Q and the increasing trend of Vr for PKSB-filled NR composites. The Q value for formulation 1 was higher due to the absence of filler meanwhile PKSB-filled rubber composites showed a decreasing trend in swelling percentage, which could indicate high crosslink density, resulting in better rubber-filler adherence properties. The reduction of Q values also might be due to the mobility of polymer chains that restricted the penetration of toluene into the 3D network structure of composites. The increasing trend of Vr reflects the enhancement of PKSB-NR matrix attachments (Kim *et al*., 2020; Nabil *et al*., 2013). Meanwhile, the APKS-filled NR composites showed that the Q values fluctuated and the Vr values did not differ much as shown in *Table 6*. This occurred due to the formation of strong filler-filler interaction which influenced the immobilisation of rubber chains, thus giving better-swelling properties (Kim *et al*., 2020).

TABLE 4. CURE CHARACTERISTIC OF PKSB AND APKS-FILLED NR COMPOSITES

No. of formulation	M_H (dN.m)	M_L (dN.m)	ΔM (dN.m)	t_{s2} (min)	t_{90} (min)
F1	11.62	0.58	11.04	1:17	2:30
F2	14.60	0.86	13.75	1:28	3:19
F3	15.86	0.75	15.11	1:10	2:36
F4	17.84	0.94	16.90	1:15	2:44
F5	20.16	1.43	18.73	1:26	3:14
F6	22.78	1.59	21.19	1:23	3:10
F7	23.05	1.39	21.67	1:25	3:17
F8	14.70	0.93	13.77	1:10	2:32
F9	15.05	1.17	13.88	1:09	2:22
F10	14.18	1.23	12.95	1:11	2:12
F11	14.33	1.64	12.69	1:39	3:21
F12	15.22	1.33	13.89	1:29	3:13
F13	13.19	2.20	10.99	2:05	4:45

TABLE 5. SWELLING PROPERTIES OF PKSB-FILLED NR COMPOSITES

No. of formulation	Q (%)	Vr
F1	363.10	0.15
F2	329.16	0.16
F3	310.00	0.17
F4	292.93	0.18
F5	288.57	0.18
F6	232.91	0.22
F7	225.53	0.22

TABLE 6. SWELLING PROPERTIES OF APKS FILLED NR COMPOSITES

No. of formulation	Q (%)	Vr
F8	315.19	0.17
F9	316.77	0.17
F10	329.84	0.16
F11	318.21	0.17
F12	305.46	0.17
F13	335.56	0.16

Tensile Properties

The tensile strengths of PKSB-filled NR composites are illustrated in *Figure 4a*, showing the increasing trend of tensile strength from 6 to 14 MPa as the filler loading increased. The porous structure of PKSB initiated better mechanical interlocking between PKSB and NR phases which could enhance the stress transfer from the rubber matrix to filler particles, resulting in restricted mobility of polymer chains (Egwaikhide *et al.*, 2007; Lay *et al.*, 2020; Romli and Mamauod, 2017). Meanwhile, the tensile strength of APKS-filled NR showed the same trend as PKSB rubber composites at F8 (16 MPa) until F11 (18 MPa) as seen in *Figure 4b*. However, the tensile strength of APKS-filled NR composites was higher than PKSB-filled NR composites due to the wide porous surface area of APKS. The rough surface of APKS led to the enhancement of the rubber-filler adhesion via physical interaction. Up to F11, tensile strength started to deteriorate at high APKS loading which might be due to the aggregation of APKS particles. The aggregation of APKS particles led to producing weak points in the composites and hence decreased the tensile properties (Abdelsalam *et al.*, 2021).

Figure 4c and *4d* show the effect of PKSB and APKS loading on the elongation at break for NR composites. It could be seen that the increasing PKSB and APKS loadings decreased the elongation at break. The decreasing trend was caused by the presence of PKSB and APKS in the NR composites, restricting the mobility of NR chains and therefore causing composite failure at lower elongation. This also can be explained by the porous structure between PKSB and APKS in which the stress applied to filler-rubber matrix interfacial adhesion until at one time the stress was too much for a filler-rubber matrix that could cause the rupture to happen (Mente and Motaung, 2016).

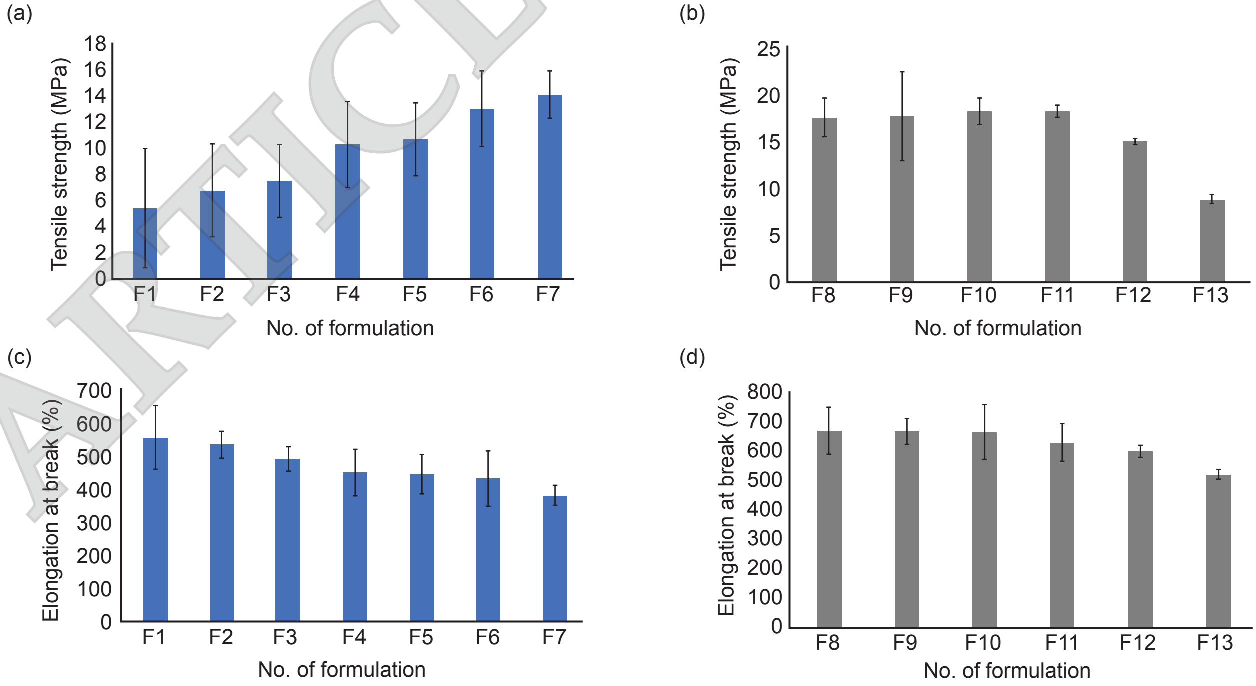

Figure 4. Tensile strength of rubber composites (a) PKSB-filled NR, (b) APKS-filled NR and elongation at break (c) PKSB-filled NR, and (d) APKS-filled NR composites.

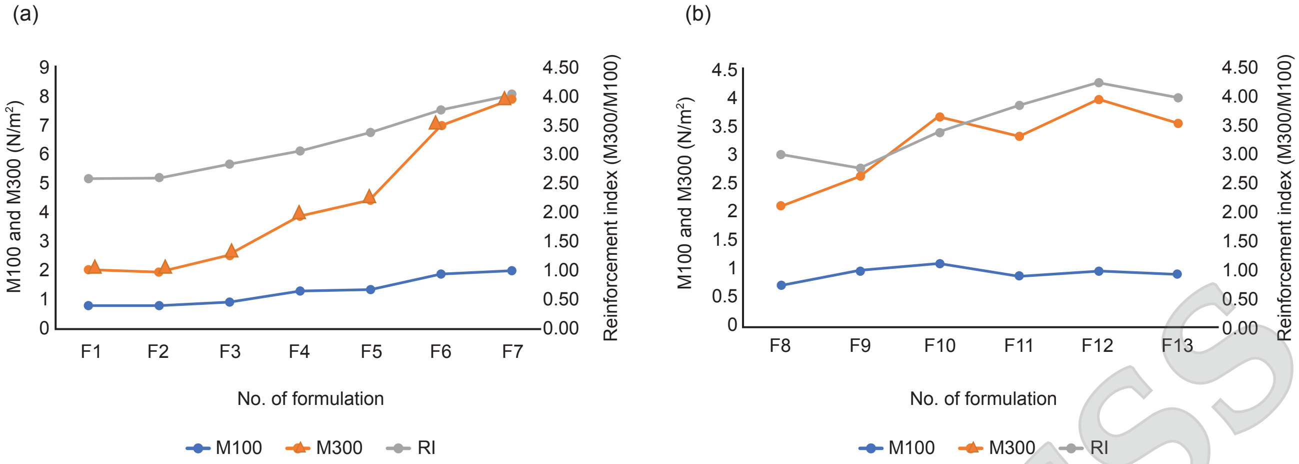

Figure 5. M100, M300 and RI. (a) PKSB-filled NR composites, and (b) APKS-filled NR composites.

The modulus at 100% (M100), 300% (M300) and the reinforcement index (RI) of PKSB- and APKS-filled NR composites are shown in *Figure 5a* and *5b*. In both figures, M100, M300 and RI of PKSB- and APKS-filled NR composites increased as the filler loadings increased. This occurred due to filler-filler and rubber-filler interactions that contributed to the stiffness of composites (Ismail and Shaari, 2010; Lin *et al.*, 2016; Sobhy and Maziad, 2003). High filler content increased the probability of physical interaction between rubber, PKSB and APKS, leading to better reinforcement.

Comparative Study on PKSB, APKS and Other Biomasses

Table 7 displays the comparison in cure characteristics of PKSB and APKS with different types of biomass fillers used in rubber compounding which are coconut fibre, untreated kenaf and bamboo charcoal powder (BCP). PKSB recorded the highest maximum torque value compared to the other renewable fillers because the macromolecular rubber chain mobility decreased as the filler loading increased, resulting in more rigid rubber composites. The M_H values of APKS, coconut fibre and kenaf were slightly lower due to the particle size and the surface area of the biomass fillers, which may affect the results obtained (Egwaikhide *et al.*, 2007; Ismail *et al.*, 2010). However, untreated kenaf and BCP showed longer curing times (t_{90}) compared to the other fillers. This may be due to the low viscosity of the fibres, hence low energy was needed to enhance the adhesion between the filler and rubber matrix (Ibrahim *et al.*, 2018; Ismail *et al.*, 2010).

Table 8 shows the comparison of PKSB, APKS and other biomass fillers in terms of swelling percentage, Q. PKSB showed a slightly lower swelling percentage, while APKS and coconut fibre had the highest Q value, compared to bamboo charcoal due to their large surface area and porous structure. A previous study stated that, as the filler loading in the rubber matrix increased, more impediments were formed for the diffusing molecule, reducing the amount of solvent penetrated (Egwaikhide *et al.*, 2007).

TABLE 7. COMPARISON OF PKSB AND APKS WITH OTHER RENEWABLE FILLER IN CURE CHARACTERISTICS

Types of filler	M_H (dN.m)	t_{s2} (min)	t_{90} (min)	References
PKSB	11.62-23.05	1:10-1:28	2:30-3:19	-
APKS	14.70-15.22	1:09-2:05	2:12-4:45	-
Coconut fibre	9.48	0:30-0:40	0:40-1:00	Egwaikhide *et al.* (2007)
Untreated kenaf	7.00-22.00	2:00-4:50	3:90-6:80	Ismail *et al.* (2010)
BCP	-	1:20-1:30	5:00-6:00	Ibrahim *et al.* (2018)

TABLE 8. COMPARISON OF PKSB AND APKS WITH OTHER RENEWABLE FILLERS IN SWELLING PROPERTIES

Types of filler	Swelling percentage, Q (%)	References
PKSB	226-329	-
APKS	305-336	-
Coconut fibre	262-398	Egwaikhide *et al.* (2007)
Bamboo charcoal	270-320	Chen *et al.* (2019)

The comparison between PKSB, APKS, coconut fibre, bamboo charcoal and untreated kenaf is shown in *Table 9*. APKS-filled NR composites had higher tensile strength and elongation at break compared to other fillers. This is because APKS possesses a higher carbon content that could provide a greater reinforcement effect between the filler and rubber matrix. The tensile strength and the elongation at break of other renewable fillers are lower due to their nature and the inability of the filler to adhere as well as to support the stress transferred from the polymer matrix (Egwaikhide *et al.*, 2007). For M100, the results obtained for every filler were almost similar and this might have contributed to the stiffness of the rubber composites.

TABLE 9. COMPARISON OF PKSB AND APKS WITH OTHER RENEWABLE FILLERS IN TENSILE PROPERTIES

Types of filler	Tensile strength (MPa)	Elongation at break (%)	M100	References
PKSB	5-14	385-561	0.74-1.97	-
APKS	8-18	519-669	0.70-1.08	-
Coconut fibre	1-6	300-850	1.00-2.00	Egwaikhide *et al.* (2007)
Bamboo charcoal	6-8	450-600	0.50-1.20	Ibrahim *et al.* (2018)
Untreated kenaf	4-21	210-1 100	0.90-4.00	Ismail *et al.* (2010)

CONCLUSION

The overall findings of PKSB and APKS as potential bio-filler compared with other biomass such as coconut fibre, kenaf and BCP were able to be investigated. The SEM images showed APKS-filled NR composites produced a well-developed porous structure with a rough surface area than PKSB-filled rubber composites, which could improve the mechanical interlocking of rubber-filler, providing better mechanical properties for the rubber composites. PKSB-filled rubber composites had higher torque values compared to other biomass fillers like coconut fibre, kenaf and BCP in terms of curing properties, and could provide more rigid and stiff composites. However, APKS-filled NR composites had better processability than PKSB since t_{s2} and t_{90} were not affected by the filler loadings. PKSB had slightly better-swelling percentages compared to APKS and other fillers as the filler loadings increased, which indicated better rubber-filler interaction and the formation of a crosslinked network between rubber and filler bases. For mechanical properties, APKS possessed higher tensile strength and elongation at break with lower modulus compared to other fillers. This shows good interfacial adhesion between the rubber and the PKS filler. The optimum loading for APKS-filled NR composites is at 40 phr. Therefore, APKS has a high potential to be used as a semi-reinforcing bio-filler in the rubber industry due to its enhanced properties in comparison with other biomass fillers.

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