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Effect carbon black and modified kaolin hybrid filler on the curing and physic-mechanical properties of natural rubber-styrene butadiene rubber blends

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Abstract. Carbon black is known as an excellent reinforced filler for rubber compounding, this petroleum based product needs to be substituted using renewable or mineral filler due to some negative adverse. In this paper, natural rubber (NR) – styrene-butadiene rubber (SBR) (50/50) phr binary blends based on polyethylene glycol-modified kaolin (PEG-K) and carbon black CB hybrid filler were synthesized. The rubber formulation was designed for idler roller for charcoal conveyor in open peat mining application. The present study investigates the effect of PEG-K and CB composition on curing, physical, tensile and oil, and acid resistance of the binary blends. The effect was examined by varying the composition of PEG-K/CB as follows: 50/0; 40/10; 30/20; 20/30; 10/40; 0/50 phr/phr of the hybrid filler. The rubber compounding was conducted in accordance with the ASTM D3142, and the testing procedures were analyzed based on international standards. The vulcanizates were prepared by heating press at 140 °C for about 25 minutes. The results showed that the processing-ability of a single filler is easier than the higher hybrid filler. The rheological analysis showed that the higher PEG-K may increase the cure rate index, but the lower PEG-K might improve cross-linking density. The higher loading CB improved the specific gravity and hardness, tensile strength slightly, while there is less significant effect on decreasing compression set, abrasion resistance, and elongation at break. Meanwhile, the higher number CB of binary blends has better oil and acid resistance than the PEG-K. Compared to idler roller specification in the market, the vulcanizates in this research have better quality.

1. Introduction

Generally, some modification has been made to increase the quality of rubber products and some fillers were intentionally mixed. Fillers could be categorized as reinforcing and non-reinforcing based on the size, polarity, affinity, and bonding interaction between its surface and the natural rubber polymers [1,2]. The reinforcing filler strengthens the cross-linking interaction and bonding within the

polymer matrixes, the adequate number of filler and compatibility between filler and polymer are essential keys to enhance the characteristics of rubber products [1-3].

Carbon black has been used widely to reinforce and enlarge the volume of rubber products. While, Calcium Carbonates are also added to the rubber compounding only to enlarge the rubber products [4]. Some mineral such as kaolinite, quartz, and montmorilonite also blended as fillers to reduce production costs [4]. It is reported that reinforcing effects may result from mineral fillers' physical characteristics such as size, porous, and polarity.

Kaolin contains some functional groups and cations held together by van der walls, hydrogen bonds, and electrostatic interaction [5,6]. Kaolin was intentionally used to modify and cheapen the processing of rubber compounding. However, some adverse effects on the physical-chemical properties of kaolin combined within the natural rubber polymer need to be addressed. Some organo-modified clays have been developed as a reinforcing filler for polymers.

Previous research on organo-modified clays compounded in natural rubber has recently developed, but the hybrid filler of modified kaolin is still limited. Some physical and chemical modification has been studied in order to improve the property of filler. For instance, organic modification was done by soaking some chemical solutions with the fillers such as acidic, base, salt, hexadecyl-trimethyl-ammonium bromide, and polyethylene glycol [6]. The modification has been conducted to improve the hybrid filler dispersion and interaction between filler and rubber polymer.

The addition of carbon black, kaolin as a single filler has been compounded with SBR and Natural Rubber resulted in some improvement in the quality of tensile, physic mechanical properties, and processing ability [5-8].

It was found that hybrid filler using nano clay fillers has some strength, particularly in dynamic properties, reinforcing effect, and also physical properties [9]. Some published work only focus on nano-size and this effect may not been studied in terms of the type of rubber polymers [9]. This research will investigate the NR/SBR blending using hybrid filler of kaolin modified PEG and carbon black. This is intentionally designed to improve kaolin's dispersion and intercalation or exfoliation with carbon black in NR/SBR blend. The study would observe the processing ability and the effect of hybrid fillers addition towards its quality. The systematic work reports on the physical, chemical, oil resistance of the NR/SBR blending using hybrid filler of kaolin and modified PEG has been limited. Thus, this paper explains those effects.

2. Materials and method

2.1. Material

Polymer: Standard Indonesian Rubber Type 10 (Crumb Rubber – PT Badja Baru); Styrene-Butadiene Rubber Krylnax 5706 (PT Asri Petrochemical). Fillers: Kaolin (Obtained and extracted from Bangka Island, PT Renergi Indonesia); Carbon Black N-550 (PT Sumi Asih). Chemicals: Zinc Oxide; MBTS; Stearic Acid; Curative Agent Sulphur; IPPD; PEG mass molecule 6000-7000kg/mol (Merck).

Table 1. Rubber formulation.

Chemicals	Formula (phr)					
SIR 10	50					
SBR	50					
PEG-K	50	40	30	20	10	0
CB (Carbon Black N-550)	0	10	20	30	40	50
ZnO	5					
MBTS	1					
Stearic Acid	1					
Sulfur	2.0					
IPPD	1					
Other chemicals	as required					

2.2. Methods
2.2.1 Kaolin Modification and Rubber Compounding. Kaolin from Bangka Island was obtained and purified. Firstly, kaolin was ground and sieved at 200 mesh, then it was washed and soaked in a PEG using water for 5 days. For better intercalation between kaolin and PEG, the soaking process was conducted in very excessive water and stirred. After that, to obtain PEG-K (Kaolin exfoliated PEG), the solution was centrifuged and decanted to separate the kaolin from the solution. Finally, PEG-K was dried at 70 °C for 24 hours or until 0.5% water content (w/w).

The rubber was compounded in accordance with the ASTM D 3182 using open mill/ two roll XK 160 (Shanghai Rubber-China), speed rotor of 50-60 rpm at 40°C by employing cold water circulation to prevent pre-heated and pre-vulcanization. SIR-10 and SBR were masticated for about 3-5 minutes until plasticized; PEG-K and CB as formulated in table 1 was added simultaneously with the stearic acid and ZnO. The mixture was then compounded for about 7-8 minutes until finely dispersed. After that some chemicals MBTS, IPPD and other chemicals and curative agent sulfur were added in the last rubber compounding. The rubber compounded sheet was rolled into 2 mm thickness sheet and stored at about 25 °C temperature before testing.

2.3. Testing Procedures
Rheological characteristics were determined based on ASTM 5289 using Rotorless Cure Meters. The equipment: Rheometer (UR2010 from U-CAN Dynatex) u/l setting at of 155 °C, curing 5 minutes pressure 4.8 kg/cm². The rheological properties were evaluated.

The vulcanizates were cut using dumb-bell shape to obtain the specimens of tensile properties. Tensile properties were tested at speed (cross head) 500-580 mm/min UTM Instron 3366; the testing was conducted based on ASTM D412.

The density of compounded rubber was tested after pressing and heating at 120 °C for 30 minutes; ASTM D395 at 25-30°C. Similarly, according to ASTM D2240-05 (2010), hardness was measured using KURO KR-14A (30-100 Shore A) at room temperature by preparing 6 mm thickness of pressed and heated vulcanizates priorly. The compression set was tested ASTM D1817 with 25% deflection, 70°C for 22-24 hours. Abrasion resistance was tested based on g BS 903, Pt.A.9 Method C.

Acid and oil resistance was tested using ISO/TR 7620. The 2 mm thick test pieces specimens are completely immersed in 10% sulphuric acid; 10% hydrochloric acid (w/v); ASTM oil No 1; and ASTM Oil No 2 in a closed vessel. At a room temperature, the vessel has been observed for 72 hours.

3. Result and discussion
3.1. Rheological Analysis
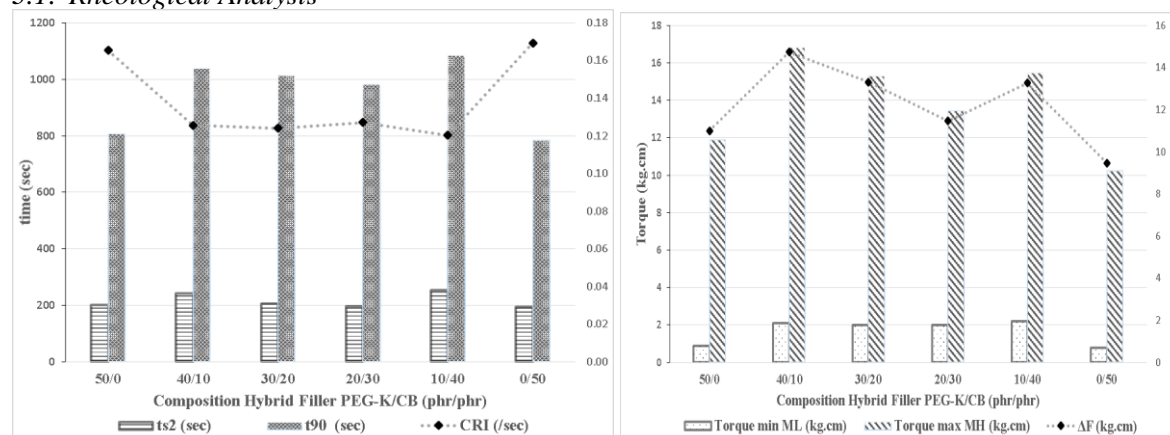
Figure 1. The effect of hybrid filler composition of PEG-K and carbon black towards its CRI and cross linking density.

The processing-ability of the kaolin modified PEG hybrid with carbon black fillers within the NR-SBR binary blending matrix is shown in figure 1. The ΔF (MH-ML) calculated as the bonding strength

between filler and rubber polymer is affected by the composition of PEG-K and CB. The cross linking density were varied by the number of PEG-K and CB. It could be implied that the more homogenous the filler within the polymer, the cross-linking density tended to be more stable. Carbon from petroleum derivatives has less polarity surface within the cavity. While kaolin may have some OH groups that could improve the hydrogen bonding or networking filler rubber [7]. In addition, organic modified kaolin using PEG may result in more van der walls effect to disperse more fine and blending in the polymer [10, 11]. This similar description was wrote by Azizli, Abbasizadeh [12]. The bonding between SBR-NR and carbon and kaolin-modified PEG was observed by its composition in Figure 1. Compared with the single filler either CB or Kaolin modified PEG with smaller size and high homogeneity according to ΔF values, the cross linking density had the lowest value. Conversely, the cure rate index of the melting and processing process had the highest value.

Figure 1 shows that the higher MH indicates the high viscosity of the rubber composites, as shown that the more heterogeneous composition of K-PEG and CB may have the higher MH. NR and SBR had huge molecular weight along with the PEG exfoliated in kaolin. Thus, it needed more energy to mix and masticate between carbon black and modified kaolin filled. The chemical dispersion within the polymer matrixes was also affected by the polarity of the filler. Due to the existing functional groups such as hydroxyl and huge surface area in CB PEG-K filler may improve or exhibit the chemical dispersion in the rubber compounding [3,13,14]. The characteristics of hybrid filler, PEG-K and carbon black may adsorb and interact by hydrogen bonding with sulphur, ZnO, MBTS in rubber compound [1, 15, 16]. In some extent, excessive curative agents and MBTS also may span the curing process. The higher viscosity of hybrid filler in huge NR-SBR polymer composites may also shorten the curing and scorch time due to less mobility sulfur in very heterogeneous polymer matrixes [3,11,13].

3.2. Physical-Mechanical Properties

Table 2 lists the effect of kaolin modified and carbon black composition as hybrid filler in NR-SBR rubber polymer towards hardness, specific gravity, tensile strength, compression set, abrasion resistance. The single filler as PEG modified kaolin had the lowest hardness, specific gravity, and tensile strength listed in table 2. The modified kaolin might fill the rubber polymer but was less reinforced compared to carbon black. The hybrid fillers might improve the physical and tensile performance of the rubber polymer by increasing the carbon black number. It was predicted that the slight improvement might be caused by compatibility, processing-ability, and cross-linking density, as explained in the rheological analysis. It is believed that the CB as reinforcing filler may dominate the physical and mechanical performance of the rubber composites. The same result with other research, the massive volume carbon black in rubber may increase the physical properties such as hardness and density [17-19]. In other words, the hardness reflected the strength of reinforcing filler. While, the PEG-K was expected to be reinforced filled hybrid with carbon black in NR-SBR rubber polymer matrixes. Based on the physical and mechanical performance, the PEG-K might slightly improve the rubber products' reinforcing effect.

The remarkable enhancement of the tensile properties were affected by the hybrid fillers and rubber during compounding and dispersing. It was predicted that less homogeneous hybrid filler of PEG-modified kaolin and carbon black may cause the mastication to be less dispersed. Some research using homogenizer has been conducted to improve the NR SBR blending to get fine dispersion of hybrid filler in rubber matrix polymer [19].

Similarly, the elongation at break also slightly decreased due to the higher loading CB less than PEG-K. The aggregation and agglomeration of weaker PEG-K and Carbon black might decrease tensile properties [19,20]. Table 2 shows the compression set and abrasion resistance experience a slight decrease by the less loading PEG-K, the carbon black still dominates the reinforcing effect in the composites. Thus, it could be inferred that the PEG-K could contribute positively as carbon black hybrid filler for NR-SBR binary blending.

Table 2. The effect of PEG-K and carbon black hybrid filler in NR/SBR binary blends towards physical-mechanical properties.

Hybrid Filler (PEG-K/CB) (phr/phr)	Hardness (Shore A)	Specific gravity (g/cm^3)	Tensile Strength (MPa)	Compression Set A	Abrasion Resistance DIN.mm^3	Elongation At break (%)
50/0	65	1.123	10.1	35	450	440
40/10	68	1.124	10.2	32	410	430
30/20	72	1.134	10.3	30	400	430
20/30	74	1.138	10.4	27	400	420
10/40	76	1.141	11.8	25	390	400
0/50	78	1.150	12.4	20	340	390

Rubber filler interaction might improve the effective strong bonding if the filler dispersion was homogenous [18,19]. In a certain number, the optimum PEG-K and carbon black as hybrid filler might be obtained by its good tensile properties. An excessive number of filler, aggregation hybrid filler and its rubber matrix may happened and caused the deterioration of the vulcanizates [20, 21]. Hence, morphology of hybrid filler in SBR/NR binary blends needs to be investigated using SEM and PSA analysis.

Table 2 shows that the compression set increased by adding reinforced filler of carbon black. The same explanation was described by some researchers [17,18,22]. The higher loading CB improved the stiffness of the rubber products. Compared to hybrid filler, single filler, either CB or PEG-K, has low compression set value. Conversely, the polar PEG-K might result in a higher compression set value due to the glycol and hydroxyl in rubber blends. The PEG-K and carbon black were strong bonded so the value compression set could be minimized, and some deformation decreased.

Table 2 shows the trend of decreasing tensile properties due to the less carbon black added than the PEG-K in rubber polymer. It weakened the cross-linking bonding and some erosion within the polymer [19,23,24]. The hybrid filler of PEG-K and CB does not as homogenous as single filler. Susanto and Marlina [25] also reported a similar finding that has blended SBR and NR using carbon black filler; Bach, Vu [26] blends NR/NBR filled by silica. It is a fact that the less dispersion and low affinity of carbon black among binary blends that have different polarity may result in decreasing tensile properties [17,19,21].

3.3. Acid and Oil Resistance Properties

Some deterioration during the usage of rubber products could be avoided. Table 3 shows the hardness, volume, tensile strength, and surface changes due to oil acid and oil immersion for 3 days at room temperature. The immersion of chemical solution was based on ISO/TR 7620:2005 to examine some hardening, surface attack, degradation of the rubber products [25,27,28]. It is known that the minimum changes indicate the better quality of rubber products.

Table 3 shows the changes in properties of binary blends with hybrid fillers ternary blends become smaller due to the high loading CB. As the better dispersion and the good processing-ability of the hybrid fillers as shown as the increasing of carbon black addition, the acid resistance also improved [8]. Similarly, the oil resistance also experienced the same trends.

It was shown that the composition of hybrid filler PEG-modified kaolin and carbon black does not influence the volume or size after immersion. The acid solution might be adsorbed in the binary blends, the usage of hybrid filler might not significantly affect this adsorption. Therefore, some deterioration may be avoided by not forming the new surface crack [28]. The oil immersion may affect more rigorous than chemical since the oil may facilitate swelling or shrinkage the rubber blends [17,25]. Hydrochloric acid immersion may results the formation of impermeable surface of binary blends due to chlorination process, thus it increase the hardness by Hadi and Kadhim [28]. Conversely, sulphuric

acid may destroy more robust relatively and accelerate the corrosion in the rubber blends as reported by Kashani, Ngo [29].

Table 3. The effect of PEG-K and carbon black hybrid filler in NR/SBR binary blends towards acid and oil resistance.

Hybrid Filler (PEG-K/CB) (phr/phr)	Change In	10% H2SO4	10% HCl	ATM Oil No 1	ASTM Oil No 2
50/0	Volume (%)	0.3	0.3	1.2	1.4
	Tensile Strength (MPa)	-1.1	-1.3	-2	-2.3
	Hardness (Shore A)	-4	-1	**-6**	-7
	Surface	slightly crack	slightly crack	slightly crack	slightly crack
40/10	Volume (%)	0.4	0.4	1.3	1.5
	Tensile Strength (MPa)	-1.3	-1.6	-2.3	-2.4
	Hardness (Shore A)	-5	-2	**-7**	-7
	Surface	slightly crack	slightly crack	slightly crack	slightly crack
30/20	Volume (%)	0.4	0.5	1.5	1.6
	Tensile Strength (MPa)	-1.3	-1.4	-2.2	-2.4
	Hardness (Shore A)	-5	-2	**-7**	-7
	Surface	slightly crack	slightly crack	slightly crack	slightly crack
20/30	Volume (%)	0.4	0.5	1.3	1.5
	Tensile Strength (MPa)	-1.3	-1.4	-2.2	-2.4
	Hardness (Shore A)	-5	-2	**-7**	-7
	Surface	slightly crack	slightly crack	slightly crack	slightly crack
10/40	Volume (%)	0.4	0.5	1.3	1.6
	Tensile Strength (MPa)	-1.3	-1.3	-2.3	-2.3
	Hardness (Shore A)	-4	-2	**-7**	-7
	Surface	slightly crack	slightly crack	slightly crack	slightly crack
0/50	Volume (%)	0.2	0.3	1	1.1
	Tensile Strength (MPa)	-1	-1	-1.5	-2
	Hardness (Shore A)	-2	1	-3	-3
	Surface	no crack	no crack	no crack	no crack

4. Conclusion

PEG-modified kaolin was successfully synthesized and used as a reinforced filler hybrid with carbon black. Hybrid filler of PEG-K and CB has successfully filled into NR/SBR polymer. The composition of PEG-K and CB was studied towards some physical, mechanical, tensile and chemical resistance. The rheological analysis of the composites showed that the hybrid filler of PEG-modified kaolin and carbon black were not as easily mixed as single filler, either PEG-K or carbon black. Thus, the composition of fillers influenced the CRI and cross-linking density of rubber composites. The higher loading of CB than PEG-K might improve some properties such as hardness, specific gravity, tensile strength. Meanwhile, it decreased the performance of abrasion resistance, compression set and elongation at break. To some extent, the PEG-K contributed positively to sulphuric acid and hydrochloric acid resistance, the decreasing or increasing of volume, hardness, tensile properties may be reduced by the hybrid filler. The hybrid filler PEG-K and carbon black in binary blend NR/SBR may be observed its morphology. To improve the processing-ability of the composites, some homogenizer needs to be added.

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