EFFECTS OF FILLER HYBRIDIZATION ON THE MECHANICAL PROPERTIES OF NR/SBR/EPDM RUBBER BLENDS

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ABSTRACT: Hybridization of active fillers is one of the techniques utilized to enhance rubber properties. This study highlights the effects of filler hybridization on the mechanical properties of an industrial applied natural rubber/styrene butadiene rubber/ethylene propylene diene terpolymer (NR/SBR/EPDM) Rubber Mat compound reinforced by non-black fillers. Initially, three different rubber compounds were prepared; i) calcium carbonate ($CaCO_3$)-filled NR [$CaCO_3$NR] as reference sample, ii) precipitated silica (PSi)-filled NR/SBR/EPDM [PSiBR], and iii) calcined clay (ClCy)-filled NR/SBR/EPDM [ClCyBR]. From these compounds, composites of NR/SBR/EPDM were prepared. The ratio of PSi:ClCy was varied to study the effects of filler hybridization. $CaCO_3$ was added for cost advantage industrially and its level was fixed. It was found that inclusions of ClCy and PSi individually and their hybridizations show higher tensile and tear strengths than the reference sample. Particularly, the largest improvement was found with the amount of ClCy which is higher than PSi. A ratio of PSi:ClCy in this particular range (1:2 to 2:3), seems to provide the optimum packing factor for good interaction between the fillers. SEM analysis suggests that better dispersion and packing of fillers due to size and shape of hybrid fillers play an important role in improving the composite properties.

KEYWORDS: *Natural Rubber, Styrene Butadiene Rubber, Ethylene Propylene Diene Terpolymer, Hybrid Filled System, Non-black Filler*

1.0   INTRODUCTION

Active fillers can enhance the mechanical properties of rubbers [1-4]. The reinforcing mechanism is explained by the partial immobilization of rubber on the filler surfaces due to the undeformable characteristic of fillers, which effectively halts the chains from elastic deformation under an applied tensile load. This contributes to the dissipation of

the strain energy to prevent any possible flaw from spreading [2,5]. Petroleum synthesized carbon black is associated with pollution issues and only suits dark color rubber products [6,7]. Thus, non-black fillers with principally clay, precipitated silica and calcium carbonate are industrially preferable today [8]. Rattanasom et al. [9] claimed that a carbon black-reinforced rubber exhibits higher modulus than a silica-reinforced one but the latter provides a unique combination of tear strength, aging resistance and adhesion properties. Although application of precipitated silica is gaining prominence nowadays, the poor rubber-filler interaction due to the highly polarity of silica impairs the rubber mechanical properties. Generally, organosilane is used to improve the rubber-filler interaction [10,11]. Clays are hydrated aluminium silicates with hexagonal shaped platelet layers [12]. The strong ionic interactions between polymer and silicate layers that generate crystallinity at the interfaces are responsible for reinforcement [13]. The clay layers introduce an extra energy dissipation mechanism contributed by enhanced crystallization under the strains [14].

Hybrid multiphase filler system retains the advantages of all fillers and provides synergistic effect of rubber reinforcement [15]. Rohini Thimmaiah and Siddaramaiah [16] reported that the adding of metakaolin into carbon black-added natural rubber compound at as low as 5 phr can confer optimized tensile properties. Moreover, Liu et al. [14] revealed that clay platelets can construct a hybrid network through physical contact with carbon black that could act as micro-barrier to increase the crack path of rubber vulcanizates.

This study examines the mechanical properties of natural rubber/styrene butadiene rubber/ethylene propylene diene terpolymer (NR/SBR/EPDM) blends filled with different ratios of hybrid non-black fillers i.e. calcium carbonate ($CaCO_3$), precipitated silica (PSi) and calcined clay (ClCy) based on an industrial Rubber Mat formulation. The NR/SBR/EPDM composition and the $CaCO_3$ amount were maintained at 95.9/1.7/2.4 phr and 9.2 phr respectively while the ratio of PSi:ClCy was varied. Prolonged mixing was performed at the presence of silane coupling agent to improve the rubber-filler   interaction.

2.0   METHODOLOGY

NR (L-grade) was supplied by Hockson Rubber Trading, EPDM (Nordel P4520) at 50 % ethylene and 5 % diene was supplied by Dow Chemical Company. SBR (Intol 1502) with MV of 52 was supplied by Polimeri Europa UK Ltd. PSi with surface area of 161-190 m^2/g was supplied by Euro Chemo Sdn. Bhd. ClCy with surface area of 12-16 m^2/g was supplied by Tangshan Madison Kaolin Co. Ltd., while Organosilane, 3-triethoxysilylpropyltetrasulphide (TESPT) was supplied by Innova Chemical Co. Ltd. Other ingredients include $CaCO_3$, ZnO white, stearic acid, mercaptobenzothiazole disulphide (MBTS), diphenyl guanidine (DPG), polyethlene glycol, phenolic antioxidant, homogenizing resin, Zn soap, parafinic oil and sulfur were the grades customarily used in rubber industries. Compounding was performed by using a laboratory two-roll mill according to ASTM D3182. The First stage mixing involved preparations of three initial compounds; (i) $CaCO_3$-filled NR ($CaCO_3$NR), ii) PSi-filled blend rubber (PSiBR), and (iii) ClCy-filled blend rubber (ClCyBR). The blend rubber consists of NR, SBR and EPDM. $CaCO_3$NR was referred to an industrial Rubber Mat formulation which was used as a reference sample in the present study. For PSiBR and ClCyBR, prolonged mixing were performed at temperature of 70-80 °C for 120 min at 1 mm of roller nip in order to improve the dispersion and distribution of fillers and to attain complete silanization of TESPT. The formulations of the compounds in part per hundred rubber (phr) are listed in Table 1.

Table 1: Formulation of the initial compounds

Ingredients	$CaCO_3$NR	PSiB	ClCyBR
NR	100.00	68.00	68.00
SBR		13.00	13.00
EPDM		19.00	19.00
$CaCO_3$	10.00	3.81	3.81
Precipitated		30.44	
Calcined clay			30.44
Phenolic	0.50		
Zinc oxide	5.00		
Stearic acid	3.00		
Polyethylene	3.00		
DPG	0.20		
MBTS	4.00		
Paraffinic oil	0.50	6.09	6.09
Metal Soap	0.42	3.81	3.81
Homogenizing		3.04	3.04
TESPT		6.09	6.09

The Second stage involved mixing of 5 compounds in different combinations of PSiBR and ClCyBR with fixed percentage of CaCO$_3$NR as depicted in Table 2. These combinations represent the ratios of rubbers and fillers as shown in Table 3.

Table 2: Different combinations of the initial compounds

Sample No.	CaCO$_3$NR (%)	PSiBR (%)	ClCyBR (%)
1	85.37	-	14.63
2	85.37	5.12	9.51
3	85.37	7.32	7.32
4	85.37	9.51	5.12
5	85.37	14.63	-

Table 3: Compositions of hybrid-filled rubber composites

Sample No.	NR (phr)	SBR (phr)	EPDM (phr)	CaCO$_3$ (phr)	PSi (phr)	ClCy (phr)
1	95.9	1.7	2.4	9.2	-	3.8
2	95.9	1.7	2.4	9.2	1.3	2.5
3	95.9	1.7	2.4	9.2	1.9	1.9
4	95.9	1.7	2.4	9.2	2.5	1.3
5	95.9	1.7	2.4	9.2	3.8	-

The composites were then added with sulphur and the final vulcanizates were prepared by using compression molding at 165 °C and pressure of 150 kg/cm^2. Tensile and trouser tear test were performed by using a universal testing machine (Zwick Roell, Z005) according to ASTM D412 and ASTM D624, respectively. Morphological analyses at the tear tips of gold-sputter-coated tear test specimens were performed by using scanning electron microscope (Zeiss EVO50) operated at accelerating voltage of 15 kV under a magnification of 1000 x.

3.0   RESULTS AND DISCUSSION

The percentage of changes for ultimate tensile strength (σ_u) as the function of PSi and ClCy fractions against the CaCO$_3$NR reference sample is shown in Figure 1.
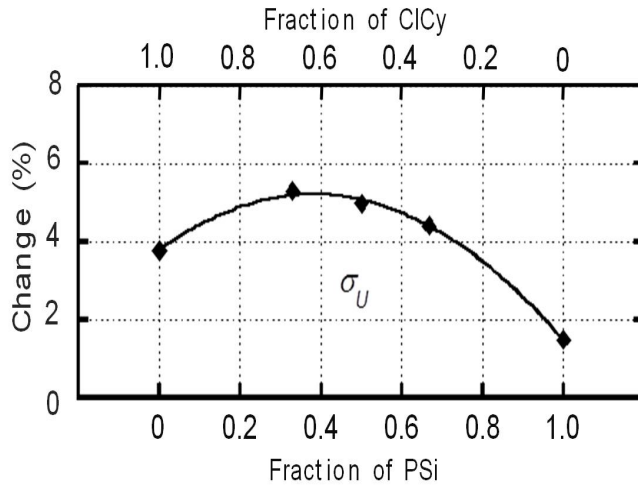
Figure 1: Relation between changes of σ_u in PSi/ClCy/CaCO$_3$-filled composites as the function of PSi/ClCy ratios

Additions of PSi and ClCy fillers enhance σ_u of vulcanizates. As shown in Figure 1, the changes of σ_u follow a positive quadratic model of polynomial second order, with the coefficient of determination value of R^2 = 0.998. This means that hybrid-filled composites yields higher values than those added with only PSi or ClCy. The result can be attributed to the synergistic reinforcing effects of the simultaneous presence of PSi and ClCy. From the curve, the largest improvement is achieved when the ratio of PSi:ClCy is about 2:3. This may render to efficient physical interlocking between hybrid fillers and matrix when the amount of PSi was lesser than ClCy. It is in good agreement with a study conducted by Freeman et al. [17] which found that clay is useful to partially replace silica while maintaining acceptable physical properties of rubber composites. The smaller improvement of σ_u shown by the composite added with only PSi compared to that added with only ClCy may be due to the insufficient silanization of bulky silanol groups of PSi with rubber matrix ascribed to lower mixing temperature of 70-80 ^{0}C that caused failure in rubber-filler linkages formation. It has been reported that at least 130 ^{0}C mixing temperature is necessary to ensure desired silanization reactions in rubber matrix [18]. Thus, the increase of rubber σ_u as observed in this study is thought to be predominantly contributed by the enhanced fillers dispersion and distribution through prolonged mixing time of 120 min at small 1 mm roller nip when preparing PSiBR and ClCyBR with a lesser contribution from organosilane linkages. Besides, addition of PSi/ClCY is also effective

to improve the rubber tear strength compared to the CaCO$_3$NR reference sample as shown by the positive changes in Figure 2.
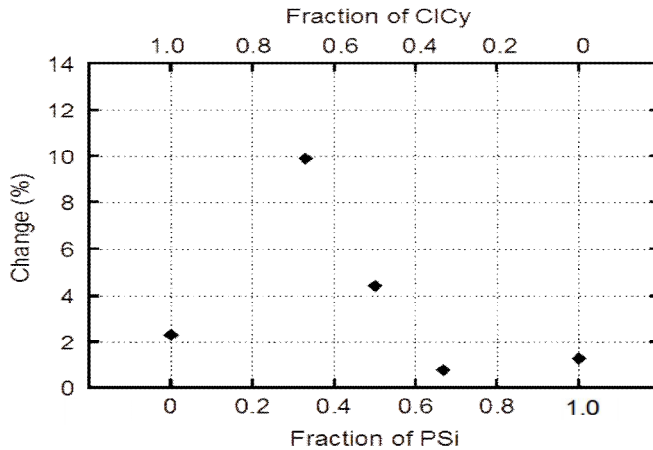

Figure 2: The changes in the tear strength of PSi/ClCy/CaCO$_3$-filled composites as the function of PSi/ClCy ratios.

Similar to the result observed for σ_u, the composite added with higher amount of ClCy and lesser PSi shows the largest improvement in tear strength. This is due to the efficient interlocking between hybrid fillers and matrix that acts as physical barrier perpendicular to the tear direction which subsequently delays the crack growth. The ratio of 1:2 between PSi and ClCy hybridization seems to provide the optimum packing factor for good fillers interaction. The clay layers may construct a dual phase filler network with precipitated silica aggregates to enhance the tear resistance as reported by Liu et al. in the case of clay/carbon black hybridization [14]. The filler networks divert effectively the tear propagation path through a more tortuous path which consumes more energy for propagation.

The distinct morphologies of tear ruptured surfaces of the composites with different filler compositions are depicted in Figure 3.
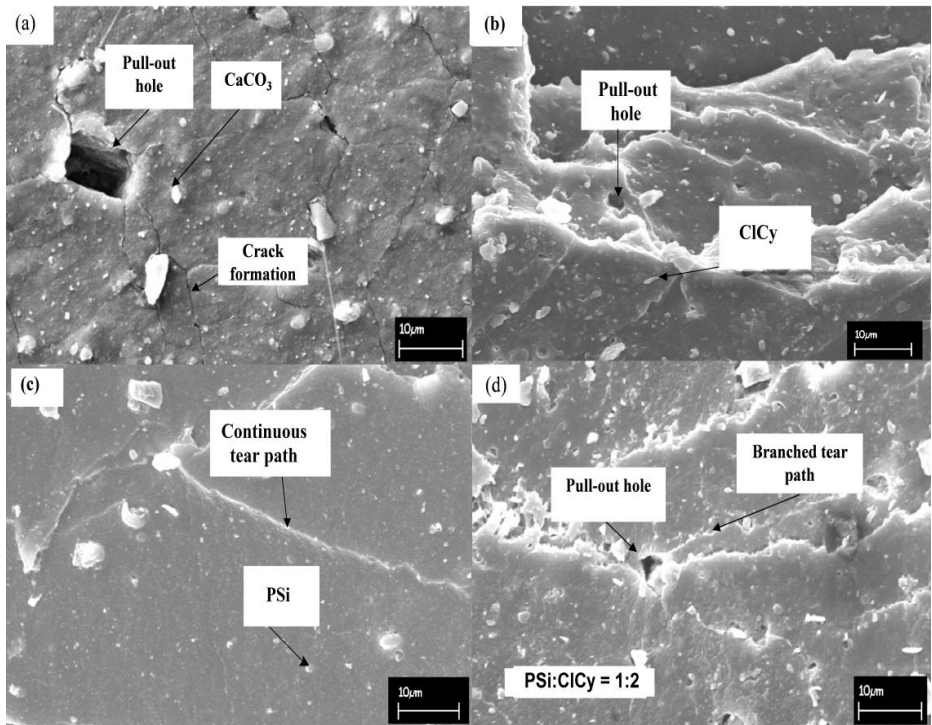
Figure 3: SEM secondary electron micrograph on the fractured surfaces at magnification of 1000 x for (a) $CaCO_3NR$, (b) ClCy/$CaCO_3$-filled composite (Sample 1), (c) PSi/$CaCO_3$-filled composite (Sample 5) and (d) PSi/ClCy/$CaCO_3$-filled composite (Sample 2).

Figure 3(a) shows the ruptured surface of pure $CaCO_3NR$ reference sample that is observed to have large $CaCO_3$ particles distributed throughout the smooth surface of rubber matrix. They are approximately having the size of raw $CaCO_3$ (~8 µm), while some are agglomerated into larger sizes (~10 µm) as shown by the pull-out hole. The presence of large particles $CaCO_3$ can weaken the rubber by creating structural flaws to deteriorate the tear strength. Furthermore, profuse microvoids are found on the fractured surface indicating poor rubber-filler interaction renders to debonding of fillers from the rubber matrix. Moreover, numerous secondary cracks perpendicular to the principle surface of the reference sample are also observed. The formation of grooves and deep cracks are correlated with inefficient energy transfer mechanism between matrix and reinforcing fillers [19].

In comparison to the smooth fractured surface of $CaCO_3NR$, the fractured surface of the ClCy/$CaCO_3$-filled composite demonstrates

rougher web-step profile as shown in Figure 3(b). Rougher failure surface indicates that the fillers in the rubber matrix have effectively enhancedthe reinforcement in the rubber vulcanizates to allow better stress transfer and improve the mechanical properties [20]. The fractured surface shows limited debonding between the fillers and the rubber matrix and fewer microvoids compared to that of the reference sample. Furthermore, it is observed that ClCy particles (~3 μm) are distributed evenly in the rubber matrix with no excessive agglomeration indicating good filler dispersion. The fracture surface of PSi/CaCO$_3$-filled composite is shown in Figure 3(c). There are continuous tear paths observed on the fractured surface from one end to another with lesser surface roughness compared to the ClCy-loaded vulcanizate. The presence of unrestricted tear paths from one end to the other of the fractured surface indicates poor tear strength [20]. This explains why the tear strength of the composite added with only PSi is inferior to that added with only ClCy as discussed above. However, it is observed that PSi aggregates with diameter around 0.5-1 μm are well-distributed evenly in the rubber matrix which imparts better tear strength than the reference sample of CaCO$_3$NR. The small aggregate of PSi is beneficial to enhance the rubber mechanical properties due to increased rubber-filler interfacial but on the contrary, large agglomerates act as stress concentrators to decrease the properties of products [21,22]. The fractured surface of hybrid PSi/ClCy/CaCO$_3$ composite added with PSi/ClCy at ratio 1:2 which shows high values of tensile and tear strengths is shown in Figure 3(d). The surface exhibits aggregates of PSi and ClCy are inter-dispersed and distributed across the rubber matrix. A rough fractured surface with short branching of tear paths is observed. The rough fractured surface, i.e. the so called cross-hatched pattern, composed of numerous webs and steps in different sizes is an indication of blunt tear, while a smooth indicates a sharp tear [14]. Thus, it is reasonable to postulate that the achievement of tear strength enhancement relates to the formation of subsidiary cracks induced by the hybridization of PSi and ClCy.

4.0   C O N C L U S I O N S

This study has shown that adding of PSi/ClCy fillers. The increases in the tensile and tearstrengths show the positive effect of filler

hybridization. It can be said that a ratio of PSi:ClCy in this particular range (1:2 to 2:3), seems to provide the optimum packing factor for good interaction between the fillers. The platelets of ClCy are inter-dispersed evenly through the rubber matrix in the mixture with smaller particle size of PSi. We can conclude that better dispersion and packing of fillers due to size and shape of hybridization fillers play an important role in improving the rubber properties.

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