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Effects of Calcined Clay / Precipitated Silica Hybridization on Cure Characteristics and Mechanical Properties of a Rubber Swimming Fin Compound

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ABSTRACT

Background: Fillers hybridization of calcined clay / precipitated silica in a rubber swimming fin compound of natural rubber / styrene butadiene rubber / ethylene propylene diene terpolymer blend was investigated on the cure characteristics and mechanical properties of composites. Objective: The reinforcement of fillers hybridization is purposed to enhance the mechanical properties of this industrial compound and at the meantime maintaining its feature of low specific gravity of 1 g/cm^3 and below. The fillers hybridization treated with silane coupling agent, 3-triethoxysilyl propyltetrasulfide (TESPT) in a form of filled masterbatch (SiCyMB) was prepared through multiple-stage-prolong melt mixing. SiCyMB was then added into the rubber swimming fin compound at 3 different percentages of 16.5 %, 28.0 % and 37.0 %. Results: The crosslink density of vulcanizates is increased proportionately with the loadings of SiCyMB ascribed to extra linkages formed from the silanization reactions. Increase in crosslink density enhances the hardness of vulcanizates. However the tendency of cure retardation is observed when increasing in the loadings of SiCyMBwhich reduces the values of cure rate index (CRI). The rubber vulcanizates reinforced by using present fillers hybridization have exhibited improved mechanical properties particularly on the tensile strength and tear strength when the dosage of SiCyMB has increased to the proximity of 28 % to 37 %. SEM micrographs reveal the calcined clay and precipitated silica have dispersed and distributed well across the rubber matrix and the rubber-fillers interaction is enhanced which contributes primarily to rubber reinforcement. Conclusion: Adding of hybrid fillers calcined clay / precipitated silica through the processing method, multiple-stage-prolong mixing can improve the mechanical properties of an industrial compound of rubber swimming fin. On the other hand, the low specific gravity feature of this particular compound is maintained through SiCyMB reinforcement.

INTRODUCTION

Rubber fillers are essentially imparting satisfactory vulcanizate properties, processing behaviour and reducing compound cost. Enhancement of properties for the particulate-filled rubber composites depends primarily on the extent of filler dispersion in the rubber, specific surface area, structure, reactivity of filler surface and interface phenomena (Zhang *et al*., 2012; Ahmed *et al*., 2013; Liang, 2013). Precipitated silica and clays are both eco-friendly non-petroleum derivatives and are relatively economy in preparation than the other fillers particularly carbon blacks which are only suitable as the fillers of dark color rubber products and synthesized from petroleum feedstock affiliating with pollution issues. According to Prasertsri and Rattanasom

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(2012), silica imparts better tear strength and abrasion resistance when comparing with carbon blacks in tire application. For calcined clay, it is a special high temperature treated kaolinite at 450-750 ^{0}C that allows removal of bound water and hydroxyls of clay layers of which its application in rubber confers better reinforcing effect (Gamelas*et al.*, 2014). However, high surface polarity of precipitated silica renders it to serious particles agglomeration and strong filler-filler interaction contributed by both hydrogen bonds and Van der Waal forces (Sengloyluan*et al.*, 2014). High polarity and strong filler-filler interaction of precipitated silica limit its compatibility interaction with non-polar rubbers. To ease this limitation, silane coupling agent is usually used to turn the polar filler into a reactive material in rubber compounding through the formation of chemical bonding on filler surfaces via silanization reactions during mixing and thereby enable crosslinking to rubber molecules (Kaewsakul*et al.*, 2013; Pongdong*et al.*, 2015). Moreover, Le et al. (2014) proposed the infiltration of rubber molecules into large filler agglomerates during mixing can increase the distance of filler particles and reduce filler-filler interaction in attainingthe enhanced degree of dispersion. In this connection, extended rubber mixing time confers improved filler dispersion in rubber matrix. Fillers hybridization has drawn the attentions of many researchers attributable to the fact of multiphase-fillers can retain the advantages of all fillers in providing synergism on rubber reinforcement (Liu *et al*., 2010). Fillers hybridization of silica / kaolinite (Zhang *et al*., 2012), carbon black / clay (Rattanasom and Prasertsri, 2012), silica / carbon black (Young and park, 2007), organoclay / calcium carbonate (Ghari and Jalali-Arani, 2016) and marble sludge / silica (Ahmed *et al*., 2014) were among several past research focuses. Particularly for silane grafting silica / clay hybridization that disperses and interacts well with rubber, its reinforcing capability has attracted wide attentions recently.

Present research investigated the rubber reinforcing effect via hybridization of calcined clay / precipitated silica which has not been investigated thoroughly especially in industrial application. A method of industrial feasible multiple-stage-prolong melt mixing to achieve high mixing temperature for silanization and satisfactory disperse the filler aggregates was employed to produce a filled masterbatch compound. This compound was used to reinforce an industrial natural rubber / styrene butadiene rubber / ethylene propylene diene terpolymer blend compound of low specific gravity at 0.95 g/cm^3 in permitting the water floating feature that used in the production of rubber swimming fin.

MATERIALS AND METHODS

Materials:

Natural rubber (NR) (L-grade) with specific gravity (s.g.) 0.92 g/cm^3 was supplied by Hockson Rubber Trading. Ethylene propylene diene terpolymer (EPDM) (Nordel P4520) with Mooney viscosity 20 and s.g. 0.86 g/cm^3 was supplied by Dow Chemical. Styrene butadiene rubber (SBR) (Intol 1502) with Mooney viscosity 52 and s.g. 0.94 g/cm^3 was supplied by Polimeri Europa UK Ltd. 3-triethoxysilyl propyltetrasulfide (TESPT) was supplied by Innova Chemical Co. Ltd. Precipitated silica with surface area of 161-190 m^2/g and s.g. 2.00 g/cm^3 was supplied by Euro Chemo Sdn. Bhd. Calcined clay with surface area of 12-16 m^2/g and s.g. 2.77 g/cm^3 was supplied by Tangshan Madison Kaolin Co. Ltd. Other rubber ingredients of zinc oxide (ZnO), stearic acid, polyethylene glycol (PEG), phenolic antioxidant, paraffinic oil, metal soap, homogenizing resin, mercaptobenzothiazole disulfide (MBTS), diphenyl guanidine (DPG) and sulfur were the grades of customarily used in rubber industry.

Formulations and Mixing:

A filled masterbatch compound of hybridized precipitated silica / calcined clay treated with TESPT of rubber system NR / EPDM / SBR blend (SiCyMB) was prepared as the formulation in Table 1. Besides, an industrial compound referring to a rubber swimming fin formulation (FIN) was prepared as shown in Table 1.SiCyMB was prepared through multiple-stage-prolong mixing in four stages. The first 3 stages of compound mixing were completed by using a two wings tangential 110 liter internal mixer (X(S)N-110/30) from Dalian ChengXin Rubber & Plastics Machinery Co. Ltd., China with a friction ratio of 1.22 and the final 4th stage was accomplished by using a two-roll-mill from WuXi Rubber & Plastics Machinery Co. Ltd., China with a friction ratio of 1.25. The mixing sequence and parameters in producing SiCyMB are exhibited in Table 2.

Table 1: Formulation of SiCyMB and FIN

Ingredient	SiCyMB (phr[a])	FIN (phr[a])
NR	67.65	66.23
EPDM	19.03	19.87
SBR	13.32	13.91
Paraffinic oil	6.09	6.36
Precipitated silica	10.66	-
Calcined clay	19.79	-
Homogenizing resin	3.04	-
Metal soap	3.81	-
TESPT	6.09	-
Phenolic antioxidant	-	1.59
ZnO	-	3.18
Stearic acid	-	4.77
Polyethylene glycol	-	0.48
MBTS	-	3.18
DPG	-	0.32
Total	149.48	119.89

[a] Part per hundred rubber

Table 2: The mixing sequence and parameters of SiCyMB

1st cycle internal mixing
- Incorporated rubber blend. - Mixing time (minute): 4 - Mixing temperature (^{0}C): 65
2nd cycle internal mixing
- Incorporated paraffinic oil, homogenizing resin, metal soap, 5 kg precipitated silica, 5 kg calcined clay and TESPT in sequence. - Mixing time (minute): 4 - Mixing temperature (^{0}C): 110
3rd cycle internal mixing
- Incorporated the balance precipitated silica and calcined clay. - Mixing time (minute): 6 - Mixing temperature (^{0}C): 130
4th cycle two-roll-mill mixing
- Roller nip (mm): 5 - Mixing time (minute): 6 - Mixing temperature (^{0}C): 80

Prolonged mixing at high temperature was aimed to achieve sufficient silanization reactions of TESPT with fillers and reached uniformity dispersion of filler aggregates. FIN compound was prepared by using the similar internal mixer through two stages mixing at 4 minutes and 65 ^{0}C for each stage. Three different combinations of SiCyMB / FIN (SC16.5%, SC28.0%, SC37.0%) and a pure FIN (SC0%) compound served as a control sample were homogeneously mixed as displayed in Table 3 by using a laboratory two-roll-mill for a mixing time of 5 minutes. Each sample was then added with 2 phr of sulfur after the compounds were rested for 24 hours at ambient temperature (24-28 ^{0}C). Three replications for each sample were prepared. The curatives added for four samples were made equal against the contents of rubbers for the final mixtures. When increasing in the dosage of SiCyMB, it increases the compound specific gravity (s.g.). By purpose of maintaining the swimming fin compound at 1.00 g/cm^3 and below to keep it floating on water, the maximum percentage of SiCyMB was fixed at 37.0 % as indicated in Table 3. The s.g. of each compound was determined by dividing the total weight of added ingredients over the sum of each volumetric value of ingredient.

Table 3: Different combinations of SiCyMB and FIN in percentages

Compound	SiCyMB (%)	FIN (%)	Compound specific gravity (g/cm^3)
SC0%	0.00	100.00	0.95
SC16.5%	16.50	83.50	0.98
SC28.0%	28.00	72.00	0.99
SC37.0%	37.00	63.00	1.00

Determination of Cure Characteristics:

Cure characteristics of samples were determined by using an oscillating rotorless rheometer (UR2010) from U-CAN Dynatex Inc., Taiwan. The temperatures of upper and lower dies were set to 165 °C with a pressure of 4.5 kg/cm^2 for a test time of 240 sec. in compliance with ASTM D5289. The data of cure characteristics for scorch time (T_2), 90 % cure time (T_{90}), cure rate index (CRI) and torque difference (Δ torque) were recorded. CRI, which is a measure of cure reaction (Sabzekar*et al.*, 2015) is given as Eq. 1:

$$CRI = \frac{100}{T_{90} - T_2} \tag{1}$$

Δ torque represents the shear dynamic modulus, which is indirectly related to the crosslink density of rubber (Jovanovic*et al.*, 2014) is given as Eq. 2:

$$\Delta \text{ torque} = MH - ML \tag{2}$$

where MH and ML are maximum and minimum torque, respectively.

Testing and Analysis of Vulcanizates:

Hardness test was performed by using a hardness meter (Bareiss HPE II) according to ASTM D2240. Tensile and angle tear test were performed by using a universal testing machine (Shimadzu EZ-500NLX) according to ASTM D412 and ASTM D624, respectively. In addition, crosslink density was determined by using solvent penetration method. The specimens of dimension 30 mm × 20 mm × 0.55 mm were immersed in 100 ml toluene (density 0.865 gml^{-1}, boiling point 110 ^{0}C) for 5 consecutive days at room temperature to achieve an appropriate rubber-solvent equilibrium. The molecular weight of polymer between crosslinks was determined by using the Flory-Rehner Equation as below (Ahmed *et al.*, 2014):

$$M_c = \frac{-\rho_r V_s(\phi_r^{\frac{1}{3}} - \frac{\phi_r}{2})}{\ln(1-\phi_r) + \phi_r + \chi\phi_r^2} \tag{3}$$

whereρ_r is the density of rubber, *V*s is the molar volume of toluene determined at 106.52 cm^3mol^{-1}, Φr is the volume fraction of rubber in the swollen gel and χ is the Huggins polymer–solvent interaction parameter fixed at 0.3795. The crosslink density (υ_e) was then determined from Eq. 4 (Ahmed*et al.*, 2014):

$$\upsilon_e = \frac{1}{2M_C} \tag{4}$$

Scanning electron micrographs (back scattered electron)by using a field emission SEM machine JEOL, JSM-6701F operated at accelerating voltage of 20 kV and 1000x were used to characterize the microstructures of precipitated silica and calcined clay powders. Besides, scanning electron micrographs (secondary electron imaging) of angle tear fracture surfaces at the crack tips of SC0% and SC28.0% were obtained by using a Hitachi SUI510 scanning electron microscope with an accelerating voltage of 15 kV under a magnification of 2000x. The samples were subjected for evaporative vacuum sputter coating to deposit an ultra-thin layer of gold onto the surface of specimens to prevent electrostatic charging.

RESULTS AND DISCUSSION

Cure Characteristics:

Cure characteristics of compounds are depicted in Table 4.

Table 4: Cure characteristics of compounds

Samples	T_2 (Sec.)	T_{90} (Sec.)	M_L (dNm)	M_H (dNm)	Δ Torque (dNm)	CRI (min^{-1})
SC0%	146.67 ± 2.50	217.17 ± 4.96	1.83 ± 0.13	13.70 ± 0.17	11.87 ± 0.12	85.23 ± 3.57
SC16.5%	148.83 ± 4.83	230.33 ± 6.12	1.88 ± 0.09	15.00 ± 0.66	13.12 ± 0.59	73.66 ± 1.76
SC28.0%	137.50 ± 3.73	222.00 ± 5.97	1.94 ± 0.12	16.31 ± 0.14	14.36 ± 0.19	71.17 ± 3.74
SC37.0%	142.67 ± 2.94	232.83 ± 5.60	1.93 ± 0.10	16.76 ± 0.27	14.83 ± 0.28	66.64 ± 2.73

Rate of cure reaction which is represented by CRI value shows a reduction trend as a function of SiCyMB loading. The decreasingtrend may due to the absorption of cure accelerators and soluble Zn by the silanol side groups of fillers. Although the silane coupling agent, TESPT can reduce the number of hydroxyl groups, the temperature of internal mixing for SiCyMB reached at maximum 130 ^{0}C seems unlikely to create sufficient silanization reactions to prevent cure retardation completely. Although Reuvekamp*etal.* (2002) claimed that a minimal mixing temperature of 130 ^{0}C is necessary for silanization, Zloczower (2009) and Kaewsakul*et al.*, (2013) suggested other higher practical ranges of silanization temperatures at 120-145 ^{0}C and 135-145 ^{0}C, respectively. However, high mixing temperature at 140 ^{0}C or above may post to the risk of premature vulcanization forSiCyMB especially after prolonged storage which is undesirable industrially. In terms of Δ torque which represents the crosslink level of rubber vulcanizate, it increases when rising in the dosages of SiCyMB. Numerous researchers (Pattanawanidchai*et al.*, 2014; Theppradit*et al.*, 2014; Ge *et al.*, 2015; Pongdong*et al.*, 2015) observed the increasing trend of crosslink density as a result of enhanced silane-filler linkages in the presence of organosilane. Apart from preventing cure retardation, organosilane yields extra crosslinks with rubber matrix which can enhance further the crosslink density (Prasertsri and Rattanasom, 2012). It seems that SiCyMB increases the crosslink density of compounds through the certain level of reduction in cure retardation as well as the tendency in forming extra silane-rubber crosslinks during vulcanization.

Hardness and Crosslink Density:

Hardness values of vulcanizates are apparently enhanced proportionally with the Flory-Rehner crosslink density values when the loadings of SiCyMB are increased as manifested in Fig. 1.

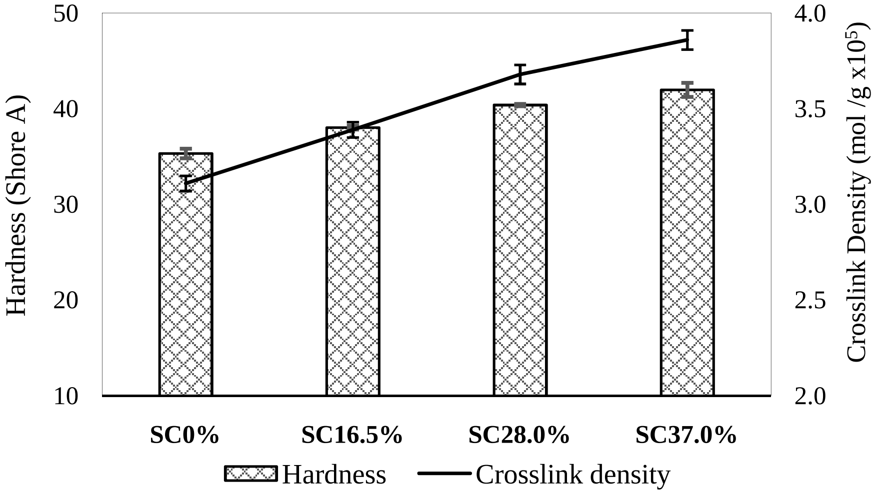


Fig. 1: Hardness and crosslink density of vulcanizates

The crosslink density of rubber increases in corresponding to the hardness value (Moonchai*et al.*, 2012; Choi and Kim, 2015; Pornprasit*et al.*, 2016). Moreover, the rubbers added with higher loadings of filler are more rigid attributed to the reduction of rubber chain elasticity (Zuber *et al.*, 2014). From this standpoint, enhancement of crosslink density and inclusion of rigid fillers instigated by SiCyMB have effectively restricted the chain motions within the dense network which contributed to extra stiffening effect of vulcanizates.

Mechanical Properties:

Fig. 2 shows the marked improvements of mechanical properties for the rubber vulcanizates reinforced with increased loadings of SiCyMBmeasured in modulus, elongation at break, tensile strength and tear strength.Significant increases of modulus 200% and modulus 300% are ascribed to increased crosslink density of vulcanizates when increasing in the loadings of SiCyMB that forms tight networks in rubber to restrict chain motions. However, such restrictions of chain mobility at high crosslink levels have reduced the elongation at break of vulcanizates when increasing in the dosages of SiCyMB. When the crosslink density of rubber is increased, the modulus isenhanced but theelongation at break is diminished (Jovanovic*et al.*, 2014; Choi and Kim, 2015; Pongdong *et al.*, 2015). Besides, the reduction of elongation at break for a filled polymer can be caused by the stiffening effect of matrix by the filler which enhances the hardness of vulcanizate(Kadhim*et al.*, 2015; Majid *et al.*, 2015; Motawie*et al.*, 2016). Apparently, tensile strength values of filled vulcanizates especially SC16.5% and SC28% are improved by the reinforcement of SiCyMB. In this context, it is deduced that the good dispersion of finely dispersed hybrid fillers through the shearing effect of multiple-stage-prolong mixing of SiCyMB and improved rubber-fillers interaction bysilanization have promoted effectively thefillers reinforcement. Many researchers (Kaewsakul*et al.*, 2013; Zhong*et al.*, 2015) reported the enhancements of rubber mechanical properties through the aid of silane coupling agents. Moreover, Ismail and Mathialagan (2012) proposed synergistic fillers hybridization can enhance the fillers dispersion effectively and improve the rubber reinforcement. However, the tensile strength is level off after SC28% as observed in SC37%. This result may be attributed to excessive high crosslink density of SC37% hasreduced the capability of rubber to dissipate the stressenergy effectively and rendered brittle fracture behaviour at low elongation. It is deduced that SC28% has achieved the desired levels of fillers dosage and crosslink density in rubber reinforcement. The reinforcement of SiCyMB instigates higher tear strength of vulcanizates appreciably. The improved tear strength is supported by hybrid fillers that interlock well with rubber matrix forming the physical micro-barriers perpendicular to the direction of tear to delay the crack growth.It is reasonably to infer that the clay layers may construct dual-phase fillers networks with silica aggregates to enhance the tear resistance in this perspective.

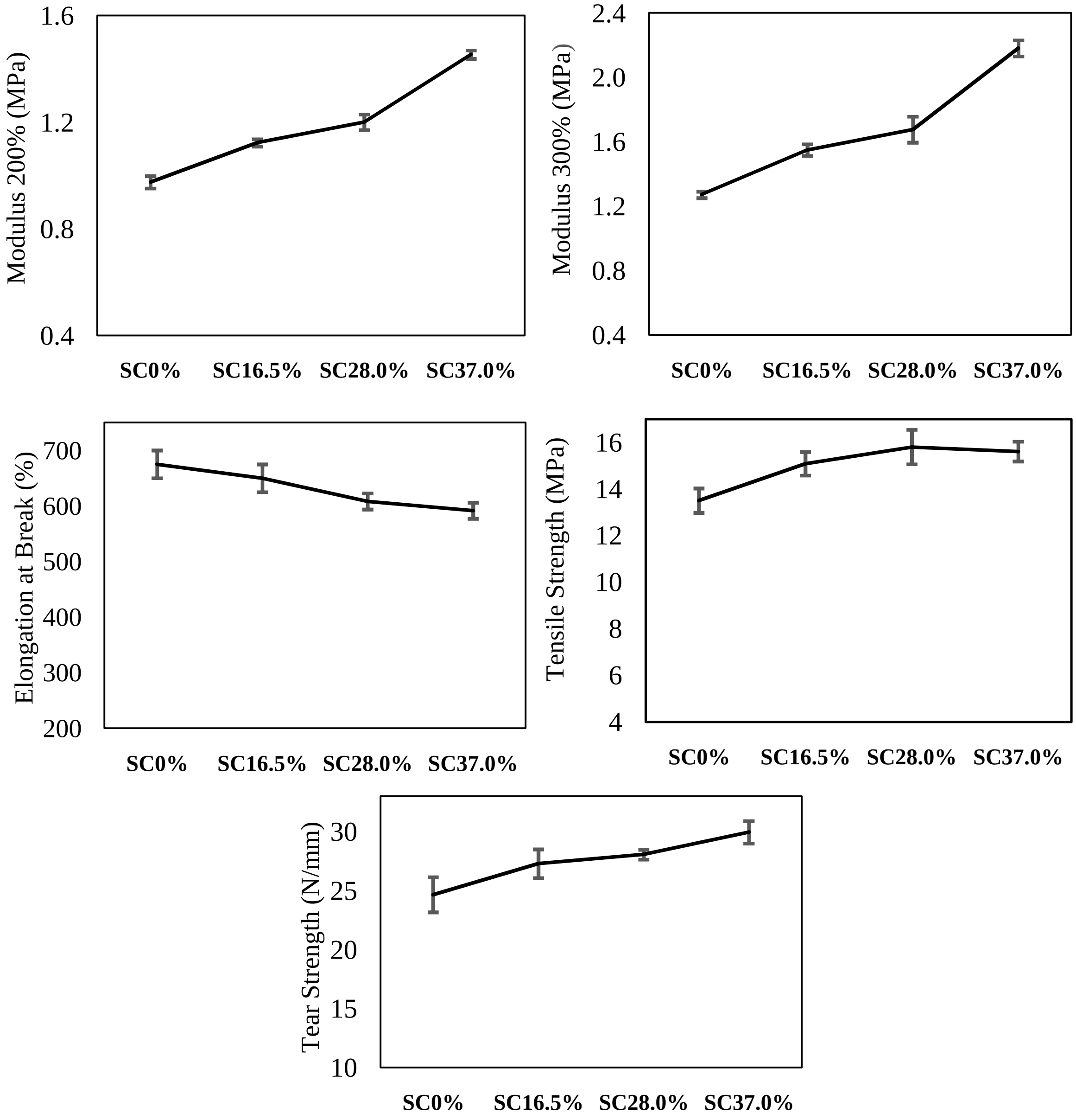
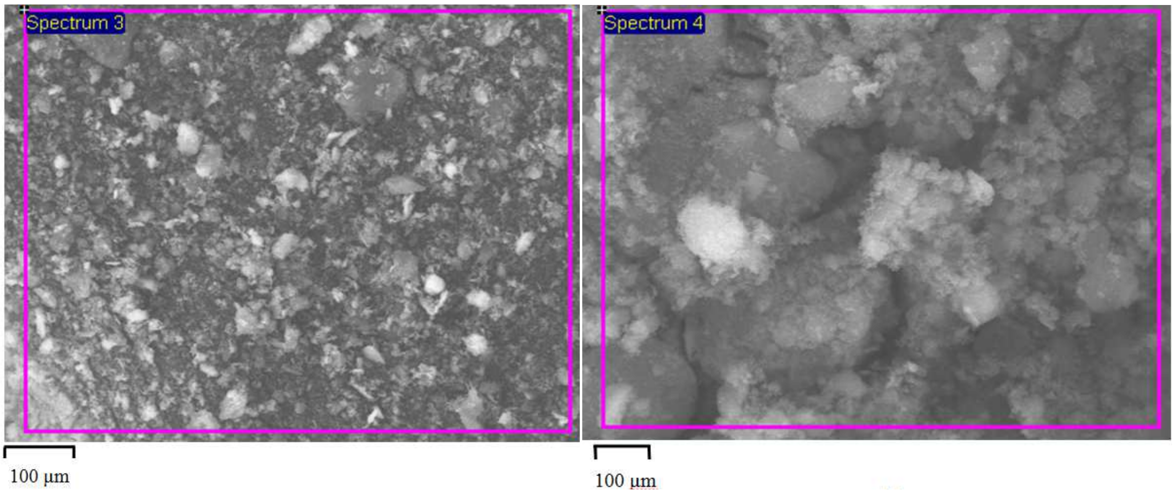


Fig. 2: Modulus 200%, modulus 300%, elongation at break, tensile strength and tear strength.

SEM Analysis:

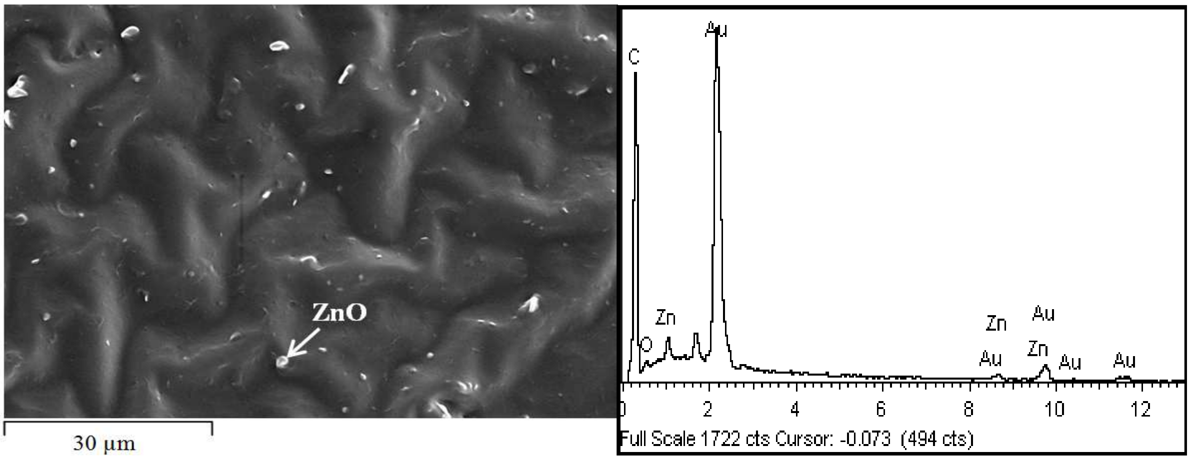
Fig. 3 exhibits the SEM micrographs of calcined clay (a) and precipitated silica (b) raw powders in characterizing the microstructures of both fillers at a magnification of 1000x.Calcined clay manifests the irregular shaped particulates which are consistence to Rattanasom and Prasertsri (2012) who claimed that the calcination process can alter the size and shape of clay into irregular structures of high aspect ratio and promote effectively the rubber-filler interfacial contact. Referring to the SEM micrograph of precipitated silica, it is apparently showing an intense agglomeration of this filler. This is in agreement with the serious agglomeration of precipitated silica contributed by both hydrogen bonds and Van der Waal forces that form strong filler-filler interaction (Sengloyluan*et al.*, 2014).



(a) (b)

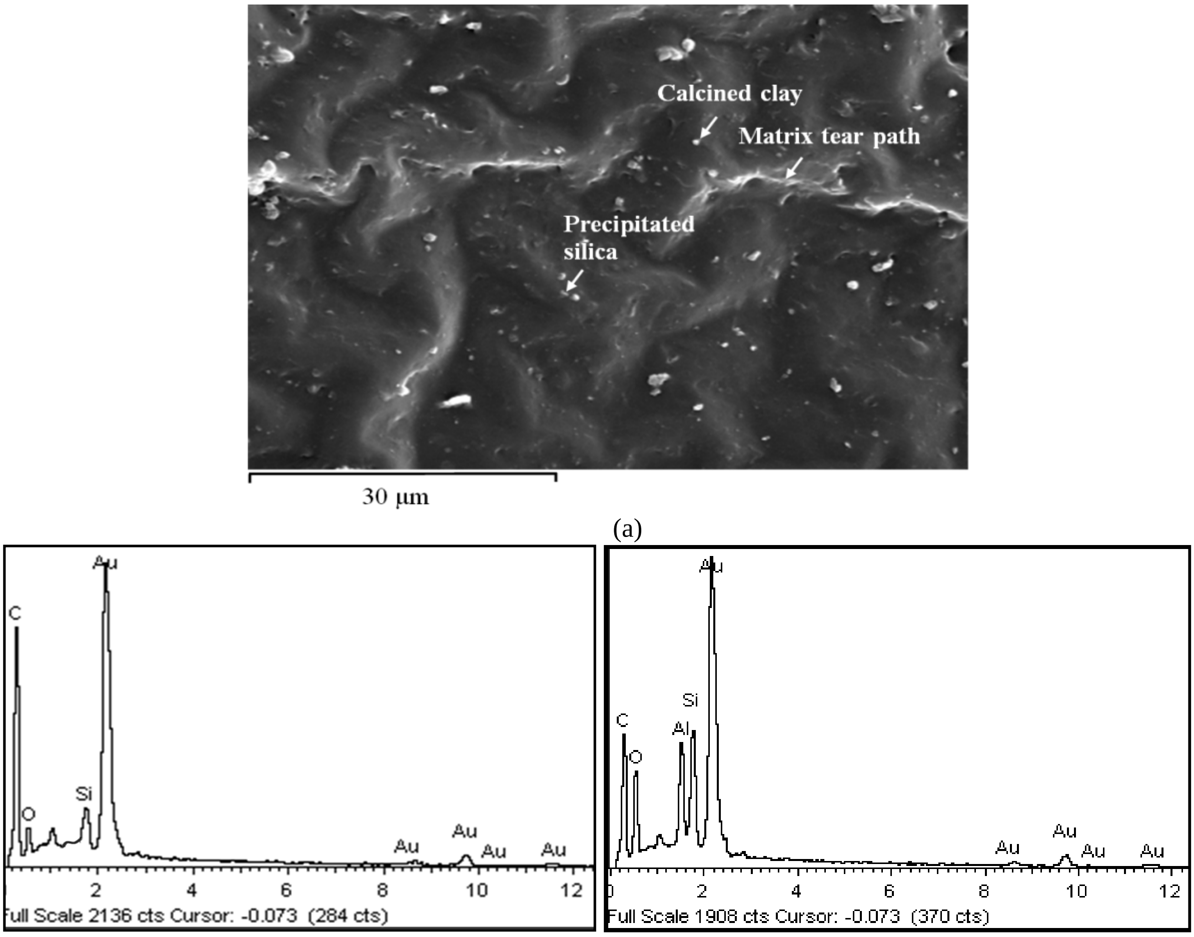
Fig. 3:SEM back scattered micrographs of calcined clay (a) and precipitated silica (b) raw powders with magnification of 1000x

The SEM micrographs on the fractured surfaces of angle tear samples for SC0% and SC28.0% were compared as illustrated in Fig. 4 and Fig. 5respectively. The mechanical properties of vulcanizates can correlate well with the topography of failure surfaces expressed through the SEM micrographs. The fractured morphology of SC0%in Fig. 4 exhibitsa continuity matrix surface with the particles of ZnO served as a cure activator distributed across the fractured surface.The relative smooth topography of SC0% compared to SC28.0% with obvious matrix tear paths (Fig. 5) represents better tear strength of the latter. A rubber of fracturedsurface with matrix tearing lines requires higher energy to failure, which contributes to better tear performance (Arayapranee and Rampel, 2013; Mohamad *et al*., 2013; Surya *et al*., 2013;Soh*et al*., 2015;Zhong*et al*., 2015). In addition for SC28.0%, filler aggregates of precipitated silica and calcined clay measured at approximately 1-3 µm are dispersed and distributed evenly across the rubber matrix evident the multiple-stage-prolong mixing is effective to overcome the serious agglomeration of precipitated silica as displayed in Fig. 3(b). It seems likely that silanization reactions have improved the fillers-rubber interaction which is evident bygood attachment of filler aggregates on the rubber matrix without inferior pull-out holes. As highlighted by numerous researchers (Ismail and Mathialagan, 2012; Ahmed *et al*., 2015; Ge *et al*., 2015), detachment of filler aggregates from the polymer fractured surface attributed to poor matrix-filler interaction is usually related to poor filler reinforcement.



(a) (b)

Fig. 4:SEM fractured surface micrograph (SEI) of SC0% (a) with magnification of 2000x, accelerating voltage of 15 kV and EDX analysis on ZnO (b)



(a)

(b) (c)

Fig. 5: SEM fractured surface micrograph (SEI) of SC28.0% (a) with magnification of 2000x, accelerating voltage of 15 kV and EDX analysis on precipitated silica (b) and calcined clay (c)

Conclusions:

The fillers hybridization of precipitated silica / calcined clay by using the filled masterbatch concept can improve the hardness, crosslink density and mechanical properties of a NR / SBR / EPDM blend compound used to produce the rubber swimming fin. The filled masterbatchSiCyMB produced through multiple-stage-prolong mixing can disperse and distribute the hybrid fillers effectively and promote the silanization reactions up to a desirable level. Adding of SiCyMB at the proximity of 28 % to 37 % is proven a practical way to enhance the mechanical properties of the industrial rubber swimming fin compound and at the same time to maintain the water floating feature of low specific gravity at 1 g/cm^3 and below.However, the cure rate index shows a reduction with the addition of SiCyMB. As a whole, this project has contributed to knowledge of understandings on the rubber reinforcement by fillers hybridization through an industrial feasible processing method that enhanced the mechanical propertiesand insight on the cure characteristics.

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