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The Development of Rubber Compound based on Natural Rubber (NR) and Ethylene-Propylene-Diene-Monomer (EPDM) Rubber for Playground Rubber Mat

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ABSTRACT

The development of rubber compound for playground rubber mat by studying the effect of light-colored fillers on cure characteristics, mechanical properties of natural rubber (NR) and ethylene propylene diene monomer (EPDM) rubber blend was investigated. It was found that at the same filler loading (100 phr), $CaCO_3$ filled-rubber showed the lowest cure time (t_{c90}) and also the best mechanical properties compared with other fillers. At various filler loading (50, 100 and 150 phr), rubbers filled with $CaCO_3$ and natural zeolite at 150 phr both showed the lowest cure time and highest hardness, but $CaCO_3$ displayed the lowest values of tensile strength and elongation at break. In addition, the influence of the vulcanization system (conventional vulcanization (CV), semi-efficient vulcanization (semi-EV), and efficient vulcanization (EV)) on the mechanical properties of the 100 phr $CaCO_3$ filled vulcanizates were investigated and discovered that the CV system showed the highest mechanical properties.

Key words: natural zeolite, filler, vulcanization system

INTRODUCTION

Nowadays, rubber is used as a material for playground mat because it has impact-absorbing surface as a result of the lowest rate of injury (U.S. Consumer Product Safety Commission, 2001). In addition, rubber has elasticity and slip resistance properties. Playground mats are mostly used for outdoor applications in which the oxygen, ozone, heat and UV light from environment can not be avoided. Ethylene propylene diene monomer (EPDM) rubber is one of the materials used for the playground rubber mat especially in outdoor application (www.advpolytech.com/Anniversary Presentations/Melos%20EPDM.pdf). EPDM has a light-colored, an excellent aging resistance and ozone resistance. Unfortunately, EPDM rubber shows poor tensile strength because of its low degree of unsaturation and the position of the unsaturation which is not the polymer backbone (Morton 1987; Hofmann 1989). In addition, EPDM is synthetic rubber and very expensive. Therefore, it is of interest to study the properties of the blend of EPDM with highly unsaturated rubber such as natural rubber (NR). NR has excellent mechanical properties, i.e., tensile strength and abrasion resistance. The high strength of natural rubber is certainly due to its ability to undergo strain-induced crystallization (Morton, 1987). In addition, NR can produce in Thailand and has favorable economics.

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Carbon black is normally used as filler in rubber compound. Since carbon black is not an inert filler compound but instead enhances and reinforces various properties of rubber. While carbon black gives rubber many of its durable properties, carbon black also gives rubber its black coloration. There has been an increasing demand for light-colored rubbers in outdoor applications, especially in the playground. The study of replacement of carbon-black with various types of light-colored fillers such as calcium carbonate, clay and silica has thus been emphasized and discovered that it led to the decrease in mechanical properties (Calvo *et al*., 2000).

In this paper, the effects of the amount and type of fillers on the mechanical properties (i.e, hardness, tensile strength, elongation at break, and modulus) in the blend of NR/EPDM (60/40) has been carried out. The influence of vulcanization system, including conventional vulcanization (CV), semi-efficient vulcanization (semi-EV), and efficient vulcanization (EV) on the mechanical properties has also been established.

MATERIALS AND METHODS

Materials

Natural rubber (STR5L) was purchased from S.M.P. RUBBER, Thailand. EPDM (EPT 4969; ENB content 9.8%), and Antilux were purchased from Bayer, Germany. Natural zeolite was obtained from Kasetcenter Co., Ltd. Calcium carbonates ($CaCO_3$), zinc oxide (ZnO), stearic acid were supplied by C.P. Chemical Industry, Global Chemical, and Imperial Industrial Chemical, respectively. Clay was purchased from Talc India, India. *N-tert.* butyl-2-benzothiazole sulfenamide (TBBS), and Wingstay-L were purchased from Flexsys, Germany, and Eliokem, USA., respectively. Sulphur was obtained from Sahapaisal Industry. Rubber Oil was supplied by PSP Speciales. TiO_2, and pigment (Cr_xO_y; green color) were obtained from Dupont, Thailand, and Lucky Four, Thailand, respectively.

Characterization of filler properties

The surface area and pore volume of fillers were determined by the Brunauer-Emmett-Teller (BET) method on Autosorb-1 accelerated surface area and porosimetry system, respectively. Particle size was measured by particle size analyzer (wet sieve). X-ray Fluorescence (XRF) was used to analyze the chemical composition of the fillers.

Sample preparation

The rubber compound formulas are given in Table 1. NR was first masticated on two-roll mill for 4 min. Then masticated NR was mixed with EPDM. Requisite amount of filler, ZnO, stearic acid, Antilux, Wingstay-L, TiO_2, pigment and rubber oil were added sequentially in a Brabender plasticorder at a rotor speed of 40 rpm

Table 1 Compound formula.

Ingredients	phr[a]
Natural rubber (NR)	60
EPDM	40
Filler[b]	50,100,150
ZnO	5
Stearic acid	1
Antilux	5
Wingstay-L	1
TiO_2	3
Pigment	1
Rubber oil	10
TBBS[c]	0.75[d],1.80[e],2.50[f]
Sulfur	2.25[d],1.20[e],0.50[f]

[a] phr, part per hundred of rubber

[b] filler, various filler ($CaCO_3$, Clay, and Zeolite)

[c] TBBS, accelerator; N-tert.butyl-2-benzothiazole sulfenamide

[d] 0.75,[d]2.25, amounts of TBBS, and sulfur, respectively in the CV system

[e] 1.80,[e]1.20, amounts of TBBS, and sulfur, respectively in the semi-EV system

[f] 2.50,[f]0.5, amounts of TBBS, and sulfur, respectively in the EV system

for 10 min. The mixing temperature was 120°C. The accelerator and curative were added into the mixes on two-roll-mill at temperature 70°C for 7 min. The mixes were then sheeted with two-roll-mill and kept at room temperature for 24 hr before testing.

Prior to vulcanize the rubber compounds, vulcanization time was determined by means of Moving Die Rheometer (MDR). The compounds were then compression molded using a hydraulic hot press at 150°C, under pressure of 15 MPa.

Mechanical properties

Tensile properties (tensile strength, elongation at break, and modulus) were determined using a tensile testing machine (Instron model 5569) according to ASTM D412-92. Hardness measurement of samples was done according to ASTM D2240-97 (Shore A).

RESULTS AND DISCUSSION

Filler properties characterization

Physical properties and chemical composition of $CaCO_3$, clay and natural zeolite are presented in Table 2 and Table 3, respectively.

It can be seen that particle sizes of calcium carbonate and natural zeolite are not significantly different and appear to be smaller than clay. The surface area of calcium carbonate is low compared to that of natural zeolite and clay. Pore volume of all fillers shows no significant difference as seen in Table 2.

As presented in Table 3, it can be seen that the chemical composition of all fillers exhibits that clay and natural zeolite are mainly composed of silica, while calcium oxide (CaO) is the major component in $CaCO_3$.

Table 2 Physical properties of fillers.

Filler	Particle size (mm)	Surface area (m^2/g)	Pore volume (cc/g)
$CaCO_3$	45	3.07	0.0013
Natural zeolite	45	14.59	0.0059
Clay	>150	11.68	0.0034

Table 3 Chemical composition of $CaCO_3$, clay, and natural zeolite.

Chemical composition (%)	Filler types		
	$CaCO_3$	Clay	Natural zeolite
SiO_2	7.06	76.76	69.88
Al_2O_3	1.39	15.90	24.87
Na_2O	-	-	2.20
MgO	-	0.34	0.46
K_2O	-	2.19	0.42
CaO	91.46	0.33	0.07
TiO_2	-	1.05	1.20
Fe_2O_3	0.09	3.37	0.90
CuO	-	0.04	-
ZnO	-	0.02	-

Effect of amount and type of filler on the cure characteristic of vulcanizates.

Rubber compound was mixed in Brabender plasticorder at a rotor speed of 40 rpm at 120°C. Moving die rheometer (MDR) was used to study the cure characterization of the rubber compounds with various amounts and types of fillers, showing the result of minimum torque (M_L), maximum torque (M_H), scorch time (t_{s2}) and optimum cure time (t_{c90}) as seen in Table 4.

It can be seen that at the same filler loading (100 phr), the cure time of $CaCO_3$-filled rubber compound is faster than that of clay and natural zeolite, possibly due to the fact that clay and natural zeolite are mainly composed of silica. This is commonly explained by the surface of silica (SiO_2) groups, which has hydrolyzed to silanols (-SiOH). These silanol groups behave as acid and are chemically active. The higher surface area fillers have more silanols available and are thus more reactive. Some of the reactions with silanols can have a profound effect on the properties of the rubber compound, especially where the chemical involved is an important part of the cure system. Most of the accelerators used in sulfur cure systems contain an amine group. Strong adsorption or reaction with filler particles can decrease the amount of accelerator available for vulcanization reactions. This can give slower cure rates and a reduced state of cure (Fred, 1993). The effect can result from the reaction of zinc ions with filler particles. Costa *et al.* (2003) suggested that the most plausible explanation for the specific deceleration effect of silica would be the occurrence of an ion exchange reaction on the silica surface between silanol groups and zinc stearate, with the liberation of stearic acid (see Figure 1). In addition, the cure time of natural zeolite-filled rubber compound is slightly slower than clay-filled rubber compound. This may be attributed to the greater surface area of the natural zeolite (Table 2).

For all fillers, the results show that increasing the filler loading in rubber compounds increases both of maximum torque and minimum torque. This indicates that the processability of the compounds becomes a little more difficult with the increase in filler loading. The increase could be due to the agglomeration of filler in the natural rubber matrix (Ismail *et al.*, 2002).

Generally, the addition of filler reduces not only scorch time, but also optimum cure time. It can be seen that the higher the filler loading, the lower the curing time is. This is clearly seen in $CaCO_3$ and natural zeolite. For clay, however, the cure time tends to increase slightly at very high loading. This is possibly due to the reduction of accelerator in the rubber matrix, as it is trapped on the silica surface which is the main component of clay as discussed earlier (Figure 1) (Sae-Oui *et al.*, 2002). Even though natural zeolites are also mainly composed of silica, their cure time seem to decrease slightly with increasing filler loading, possibly due to their smaller particle size.

Effect of amount and type of filler on the mechanical properties of vulcanizates

Rubber compound is mixed in Brabender

Table 4 Cure characteristics of rubber compounds.

Cure characteristic	$CaCO_3$			Clay			Natural zeolite		
	50	100	150	50	100	150	50	100	150
Minimum torque (ML), lb-in	0.26	0.34	0.65	0.38	0.40	0.70	1.32	1.47	0.98
Maximum torque (MH), lb-in	3.15	3.85	4.52	2.67	2.85	3.27	2.02	2.13	2.42
Scorch time (ts2), min	8.93	7.39	5.58	19.98	21.43	17.21	N/A	N/A	N/A
Optimum cure time (tc90), min	12.90	12.63	9.02	21.26	26.68	28.03	32.07	29.06	21.37

N/A = Not available

plasticorder. The compound is then compression molded using a hydraulic hot press at 150°C, under pressure 15 MPa. After that, the mechanical properties, i.e., tensile properties, and hardness are tested.

The effect of fillers on hardness of vulcanizates is represented in Figure 2. Hardness of filled vulcanizates with all types of filler increases with filler loading. This is simply due to the fact that incorporation of more rigid filler particles into rubber reduces elasticity of the rubber chains, leading to more rigid rubber vulcanizates (Costa *et al.*, 2000). At the same amount of filler loading, $CaCO_3$-filled vulcanizate gives the

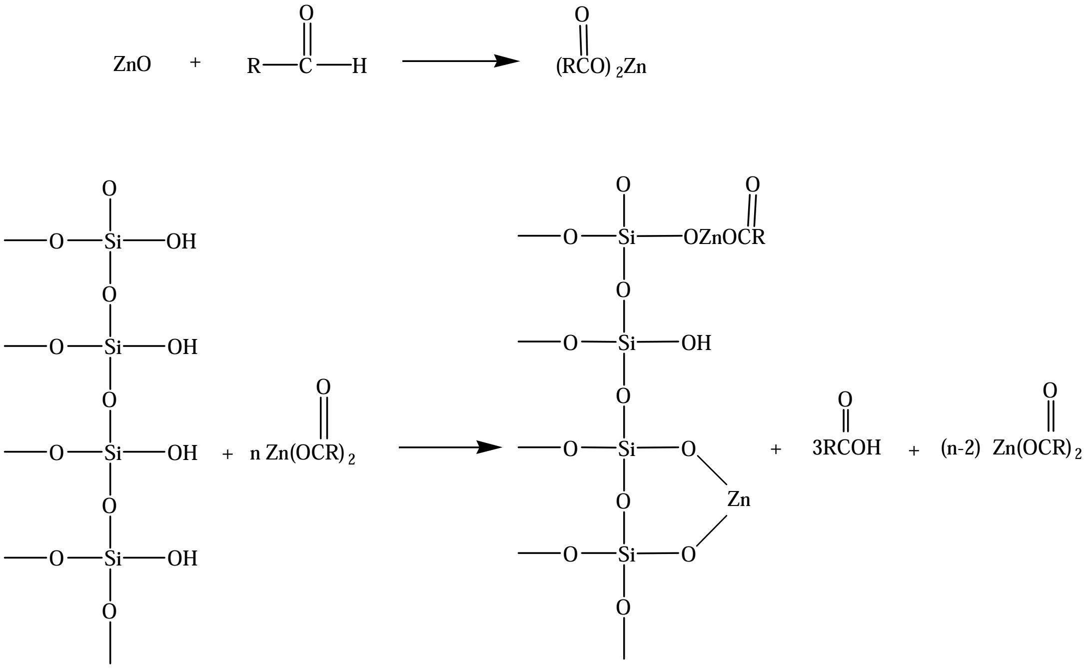

Figure 1 Ion exchange between silanol groups and zinc stearate on sililca surface.

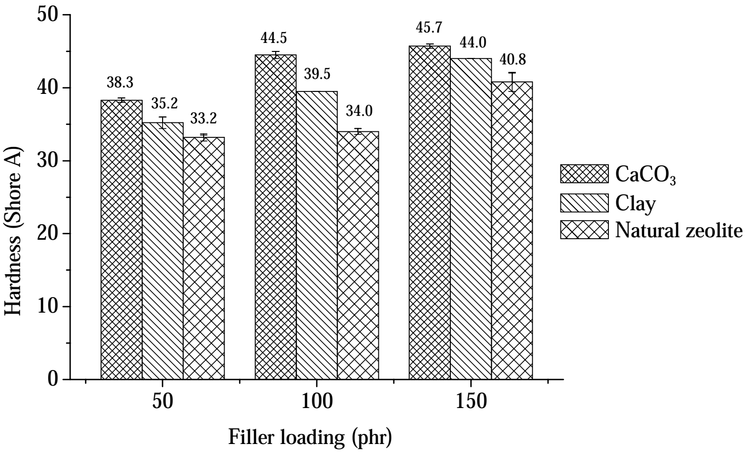

Figure 2 Effect of fillers on the hardness (shore A).

highest hardness value, following by clay-filled and then natural zeolite-filled vulcanizate. The modulus shows the similar trend except that at 150 phr loading clay-filled vulcanizate presents the highest value of modulus as seen in Figure 3. In other word, the modulus of $CaCO_3$-filled vulcanizate increases with the increase in $CaCO_3$ up to 100 phr, whereas it decreases with further loading the amount of $CaCO_3$ to 150 phr.

Figure 4 represents tensile strength of filled vulcanizates. It is found that at the same filler loading, $CaCO_3$ -filled vulcanizate shows the highest value of tensile strength, followed by clay and natural zeolite. This is possibly explained that the clay and natural zeolite composed of silica, resulting in the low rubber-filler interaction leading to low tensile strength as seen in Figure 4. In addition, tensile strength tends to decrease with increasing filler loading at all types of filler (Ismail and Mega, 2001).

Similarly, elongation at break decreased with increasing filler loading at all kinds of filler, as shown in Figure 5. It possibly was because the incorporation of filler particles into rubber could reduce the elasticity of the rubber chains (Ismail and Mega, 2001). It was also discovered that, at

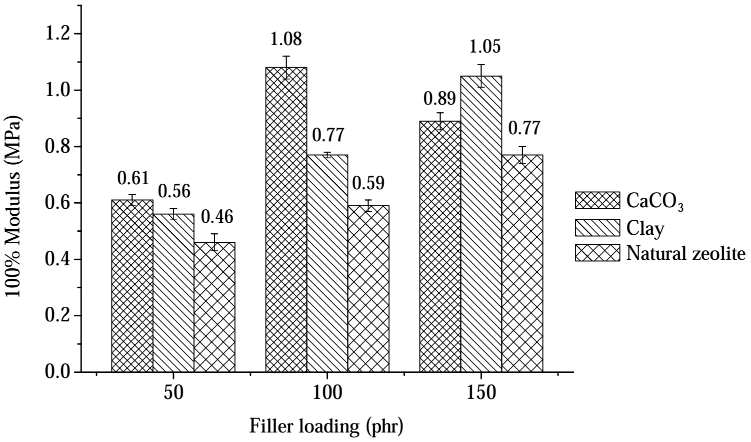

Figure 3 Effect of fillers on the 100% modulus.

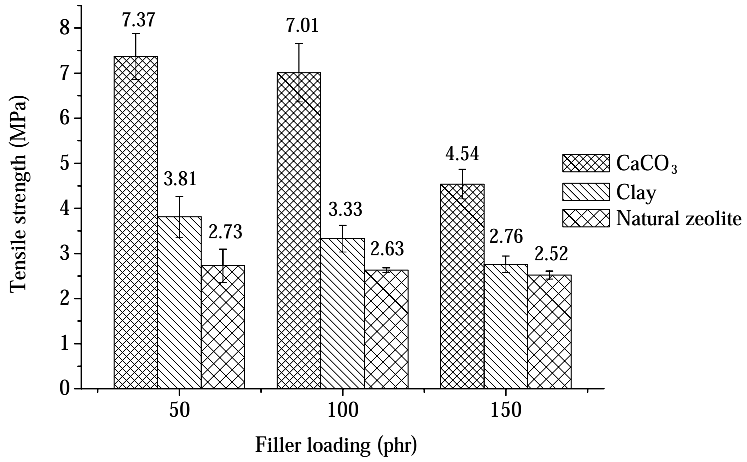

Figure 4 Effect of fillers on the tensile strength.

the same filler loading, vulcanizates filled with $CaCO_3$ showed the highest value of elongation at break compared to those filled with clay and natural zeolite.

Effect of vulcanization system on the mechanical properties of vulcanizates.

The influence of the vulcanization system (conventional vulcanization (CV), semi-efficient vulcanization (semi-EV), and efficient vulcanization (EV)) on the mechanical properties of the vulcanizates was investigated. The amount of accelerator and sulfur for various vulcanization systems is shown in Table 5.

The mechanical properties such as hardness, tensile strength, elongation at break, and 100% modulus of 100 phr $CaCO_3$ filled vulcanizates with various vulcanization systems (CV, semi-EV, and EV) were represented in Figures 6, 7, 8, and 9, respectively.

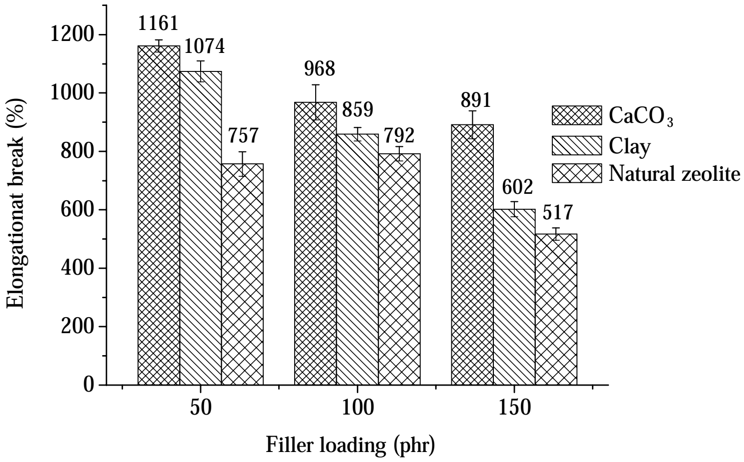

Figure 5 Effect of fillers on the elongation at break.

Table 5 The amount of accelerator and sulfur.

Ingredients	Vulcanization systems		
	CV	Semi-EV	EV
TBBS	0.75	1.80	2.25
Sulfur	2.25	1.20	0.75

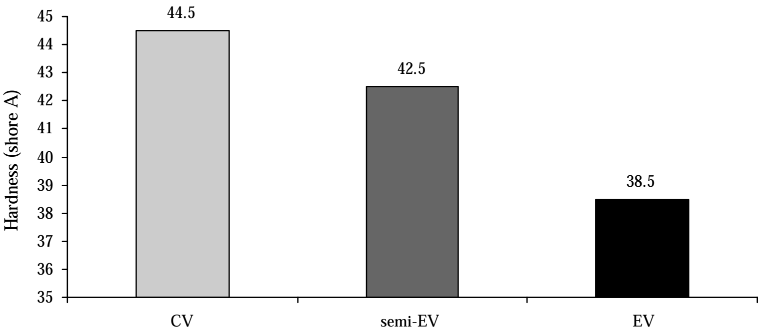

Figure 6 Effect of vulcanization systems on the hardness (shore A).

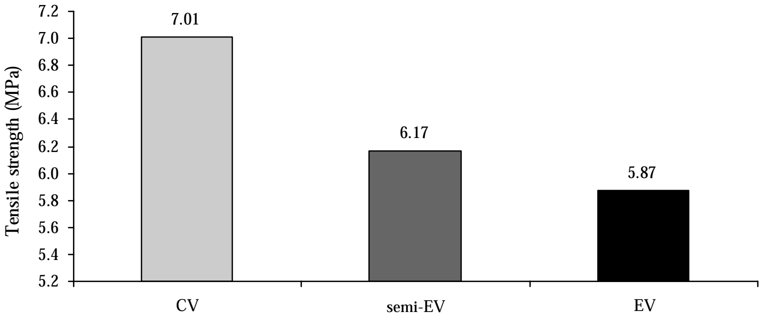

Figure 7 Effect of vulcanization systems on the tensile strength.

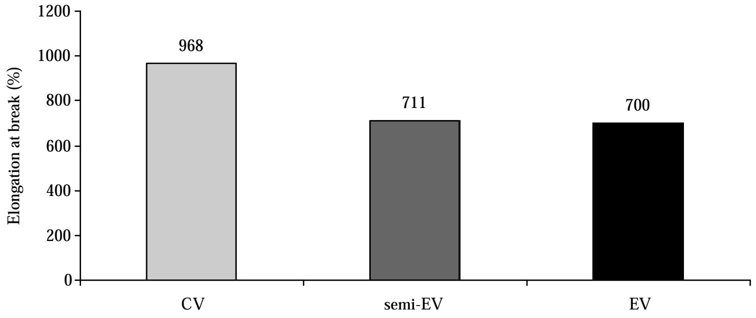

Figure 8 Effect of vulcanization systems on the elongation at break.

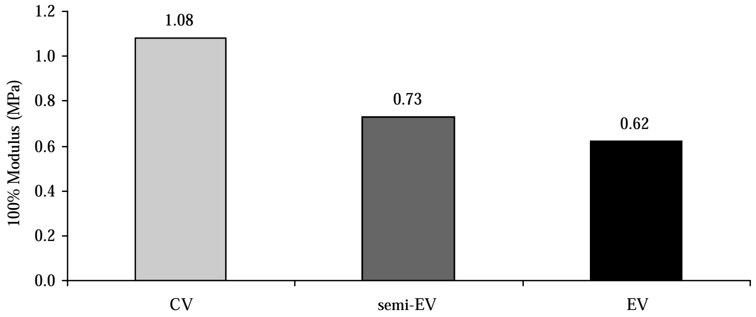

Figure 9 Effect of vulcanization systems on the 100 % modulus.

It can be seen from the figures that conventional vulcanization system showed the strong effect on the mechanical properties of the vulcanizates by showing the highest value of their mechanical properties compared to that of semi-EV and EV systems. This is simply due to the higher crosslink density of the vulcanizates in the CV system because there is more sulfur available for crosslink formation as polysulfidic into compound rubber, resulting in the increase in elasticity of rubber (Pal *et al.*, 1983). Rubbers vulcanized in CV system could have good mechanical properties (tensile strength, elongation at break, and modulus) and dynamic properties, however, aging resistance is not good as EV system in which crosslink of EV system is monosulfidic or disulfidic (AKiba, and Hashim, 1997).

CONCLUSION

The study on the incorporation of various light-colored fillers ($CaCO_3$, clay, and natural zeolite) in rubber compounds for playground rubber mat was investigated. It was found that at a similar filler loading, vulcanizate filled with $CaCO_3$ showed the shortest cure time and the highest properties. The greater the filler loading in rubber compounds filled with $CaCO_3$ and natural zeolite the shorter the cure time was. In contrast, clay filled rubber showed the opposite trend. Moreover, it was found that the hardness of vulcanizates filled with all kind of filler increased with increasing the filler loading, however, the tensile strength and elongation at break decreased. The mechanical properties of vulcanizates obtained in conventional vulcanization (CV) system showed the best values compared to those of semi-EV and EV system. It is to say that there is the possibility of using light-colored fillers, including $CaCO_3$, clay, and natural zeolite for playground rubber mat.

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