

COMPARATIVE STUDY ON VISCOSITIES, STRESS RELAXATION, CURING AND MECHANICAL PROPERTIES OF SEPIOLITE AND SILICA FILLED NATURAL RUBBER COMPOSITES

(Kajian Perbandingan Mengenai Kelikatan, Kelonggaran Tekanan, Penyembuhan dan Sifat Mekanikal Komposit Getah Asli dengan Sepiolit dan Silika)

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Abstract

In the present study, natural rubber composites filled with sepiolite and silica were prepared. The effects of the two fillers by loading (1–10 phr) on viscosities, stress relaxation, curing, and mechanical properties of the composites were investigated. Viscosity of rubber usually increased with filler loading about 7–22% with sepiolite and about 3–37% with silica, depending on filler content. Smaller rate of stress relaxation was found with sepiolite filler in comparison with silica filler. Furthermore, shorter curing cycle with greater crosslink density and hot temperature reversion resistance were achieved through the use of sepiolite filler in NR. Lorenz-Parks and Kraus models utilized for assessing rubber-filler interactions revealed stronger interactions of sepiolite filler with the rubber matrix. As a result of the good interactions between sepiolite filler and rubber matrix, larger reinforcement indexes and tensile strengths were achieved with sepiolite filler in comparison with silica filler. This was due to the higher aspect ratio of sepiolite (~5.32) compared to that of silica (~1.09) as demonstrated by SEM analysis. The highest tensile strength was achieved at 1 phr sepiolite loading which was about 17% improvement over unfilled sample.

Keywords: composites, fillers, rubber, sepiolite, silica

Abstrak

Komposit getah asli yang diisi dengan sepiolit dan silika telah disediakan dalam kajian ini. Kesan kedua-dua pengisi dengan memuatkan (1-10 phr) pada kelikatan, kelonggaran tekanan, tempoh pematangan dan sifat mekanikal komposit telah disiasat. Kelikatan getah biasanya meningkat dengan pengisi yang memuatkan dari 7-22% dengan sepiolite dan kira-kira 3-37% dengan silika, bergantung kepada kandungan pengisi. Kadar kelonggaran tekanan yang lebih kecil didapati dengan sepiolit berbanding

dengan pengisi silika. Juga, tempoh pematangan yang lebih pendek dengan ketumpatan sambung silang yang lebih tinggi dan rintangan perkembalian suhu panas dicapai dengan menggunakan pengisi sepiolit dalam getah asli. Model Lorenz-Parks dan Kraus yang digunakan untuk menilai interaksi pengisi getah mendedahkan interaksi yang lebih kuat dari pengisi sepiolit dengan matriks getah. Indeks pengukuhan yang lebih tinggi dan kekuatan tegangan dicapai dengan pengisi sepiolit daripada pengisi silika. Ini disebabkan oleh interaksi pengisi getah yang lebih baik yang timbul daripada nisbah aspek sepiolit yang lebih tinggi (~ 5.32) daripada silika (~ 1.09) seperti yang kemudiannya didedahkan oleh analisis SEM. Kekuatan tegangan tertinggi dicapai pada 1 phr pemuatan sepiolite iaitu kira-kira 17% peningkatan berbanding sampel yang tidak diisi.

Kata kunci: komposit, pengisi, getah, sepiolit, silika

Introduction

Generally, introducing one or more fillers is a strategy for improving the properties of natural rubber (NR). The use of a filler is convenient, effective, and relatively cheap for enhancing the properties of rubber [1, 2]. Among the different properties, modulus, tensile strength, tear strength, abrasion resistance, and service life of rubber can be improved, depending on size and shape of filler particles as well as the filler-matrix interactions [3, 4]. Various types of filler have been applied in rubber composites, and carbon black and silica are the most commonly used fillers in the rubber industries [5, 6]. Several studies have tested sepiolite filled rubber composites since sepiolite has unique needle-like particle shape with tunnel-like micropore channels, possibly improving the thermal, mechanical, and barrier properties of the composites [7-11].

Sepiolite belongs to nontoxic phyllosilicates, is abundant in the nature, and has a low cost. Regarding its chemical structure, sepiolite comprises microcrystalline-hydrated magnesium silicate with the unit cell formula $\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH},\text{F})_4 \cdot (\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$ [11]. It is microfibrillar with 2–10 μm particle length and tunnel-like micropore channels, providing efficient adsorption and high specific surface area for strong interaction with the rubber matrix. Comparative studies of sepiolite with other fillers, assessing reinforcing abilities, have been conducted recently [7, 9, 12-14]. Bokobza et al. [7, 9] investigated the relation of filler shape (silica particles and sepiolite fibers) with the mechanical properties of NR and styrene butadiene rubber (SBR), prepared by sol-gel process. They demonstrated that the sepiolite filler imparted more reinforcement in comparison with the spherical silica particles in NR. However, it had less interaction with

SBR because the sepiolite interacts less with SBR than NR, leading to poor interaction between the rubber and filler and poor dispersion in the SBR matrix. Bhattacharya et al. [12] investigated the impact of various nanofillers, namely, montmorillonite clay, sepiolite, hectorite, carbon nanofiber, and expanded graphite, and their dispersion methods on the properties of NR nanocomposites. They found that the mechanical and physical properties, including modulus, tear, and tensile strength, depended strongly on specific surface area, aspect ratio, filler volume fraction, and dispersion of filler. Lowe et al. [13] prepared NR nanocomposites reinforced with unmodified and modified clay and sepiolite. They observed that overall better properties were obtained for nanocomposites filled with clay. In case of sepiolite filler, the modified sepiolite exhibited relatively small improvements (only 3%) compared to the neat sepiolite. Winya and Hansupalak [14] compared the effects of sepiolite and silica on mechanical properties and thermal stability of NR/EPDM blend. They reported that both properties were similar for the two fillers, in the loading range investigated (0–12.5 phr), but the sepiolite was preferred over silica, as a lower loading achieved comparable mechanical and thermal properties.

Up to now, there is little work studying property changes of sepiolite and silica filled NR composites in the literature. The objective of the current study was to understand the effects of the two types of filler (i.e., sepiolite and silica) by small loading level on mechanical properties of NR composites. The study results are discussed considering certain properties, including viscosity, stress relaxation, curing, and tensile properties. The rubber-filler interactions are discussed based on Lorenz-Parks and Kraus models.

Materials and Methods

Materials

Table 1 summarizes the details of the various chemical ingredients utilized in compound preparation and their quantities expressed in part(s) per hundred parts of rubber (phr). All the ingredients were used as received.

Preparation of composites

The composites of NR with sepiolite or silica filler were prepared on a laboratory-sized two-roll mill with a 1.5 mm nip and a 12 cm guide. The chemical ingredients were added in the sequence displayed in

Table 2. NR was firstly masticated for 2 min, followed by incorporation of ZnO and stearic acid, and milled for 1 min. The filler (sepiolite or silica) was then added to the mix and milled for 9 min. Next, MBTS was fed to the mix and milled for 2 min. Finally, sulfur was added to the mix and milled for 1 min. After completion of the mixing with total mixing time of 15 min, the rubber compounds were then vulcanized through compression molding with a hydraulic press at 160 °C following their respective curing times (t_{90}) in order to obtain 1 mm thick vulcanized sheets.

Table 1. Formulation of the NR compounds

Chemical	Supplier
NR (Standard Thai Rubber graded 5L, STR 5L)	Chalong Concentrated Natural Rubber Latex Industry Company Limited, Songkhla, Thailand
Zinc oxide (ZnO)	Imperial Chemical Company Limited, Pathumthani, Thailand
Stearic acid	Global Chemical Company Limited, Samut Prakarn, Thailand
2,2'-Dithiobisbenzothiazole (MBTS)	Shanghai Rokem Industrial Company Limited, Shanghai, China
Sulfur	Siam Chemical Company Limited, Samut Prakan, Thailand
Sepiolite clay	Guangzhou Billion Peak Chemical Technology Company Limited, Guangzhou, China
Precipitated silica (Ultrasil VN3)	Evonik Industries AG, Essen, Germany

Table 2. Formulation of the NR compounds

Chemicals	Quantity (phr)		Mixing time (min)
	NR/sepiolite	NR/silica	
NR	100	100	2
Stearic acid	1	1	1
ZnO	3	3	
Sepiolite clay	0, 1, 3, 5, and 10	-	9
Silica	-	0, 1, 3, 5, and 10	
MBTS	1.5	1.5	2
Sulfur	1.5	1.5	1
Total mixing time (min)			15

Mooney viscosity and Mooney stress relaxation measurement

Mooney viscosity and Mooney stress relaxation of the different rubber composite samples were investigated through the use of a Mooney viscometer, MV 3000 Basic (MonTech, Germany), according to ASTM D1646. The tests were carried out at 100 °C using the large rotor. The stress relaxation was fit with the power law model in equations 1 and 2:

$$M = kt^a, \quad (1)$$

$$\log M = \log k + a \log t, \quad (2)$$

where M refers to the torque during relaxation, k is a constant, t is the relaxation time, and the relaxation rate a denotes the slope visible in a log-log plot of M versus t.

Curing characteristics

The curing characteristics of the NR compounds, in terms of maximum torque (M_H), torque difference ($M_H - M_L$), cure time (t_{90}), and cure rate index (CRI), were determined at 160 °C through the use of a moving die rheometer (Montech MDR 3000 BASIC, Buchen, Germany). The CRI was defined by equation 3.

$$CRI = \frac{100}{t_{90} - t_{s1}} \quad (3)$$

Reversion resistance

The measurement of the reversion resistance of the composites at elevated temperature was performed using the percentage of reversion in the rubber compound after 300s, from the time at maximum torque (R_{300}), as shown in equation 4 [15, 16]:

$$R_{300} = \frac{M_H - M_{300}}{M_H} \times 100, \quad (4)$$

where M_H is the maximum torque in the curing curve and M_{300} is the torque at 300s after M_H .

Rubber-filler interactions

The extent of these filler-matrix interactions was estimated through the use of the Lorenz-Parks [17] and Kraus models [18]. The Lorenz-Parks model is as follows:

$$\frac{Q_f}{Q_g} = ae^{-z} + b, \quad (5)$$

where Q is the amount of solvent absorbed, f and g indexes refer to filled and gum rubber vulcanizates, a and b are constants (the model parameters tuned to fit data), and z denotes the weight fraction of filler. The Q can be obtained via equation 6 [19]:

$$Q = \frac{\text{Swollen wt.} - \text{Dried wt.}}{\text{Original wt.}}. \quad (6)$$

The Kraus equation is as follows:

$$\frac{V_{ro}}{V_{rf}} = 1 - m \left(\frac{f}{1-f} \right), \quad (7)$$

where V_{ro} and V_{rf} refer to the volume fractions of elastomer in the solvent swollen gum vulcanizate and filled sample, f is the volume fraction of filler, and m is the rubber-filler interaction parameter. V_{rf} is expressed by the equation of Ellis and Welding [20], as follows:

$$V_{rf} = \frac{(W_d - fW_0) / \rho_r}{(W_d - fW_0) / \rho_r + A_s / \rho_s}, \quad (8)$$

where W_d and W_0 are the deswollen and the initial weights of the composite samples, f is the volume fraction of filler in the composite, ρ_r is the density of rubber, A_s is the content of solvent absorbed, and ρ_s is the density of solvent. V_{ro} is given by equation 9:

$$V_{ro} = \frac{(W_d - W_f / \rho_r)}{(W_d - W_f / \rho_r + W_s / \rho_s)}, \quad (9)$$

where W_f denotes the weight of filler in the composite sample.

Tensile properties

The tensile properties including tensile strength, elongation at break, and reinforcement index (the ratio of the moduli at 300 and 100% elongations, or M300/M100, RI) of crosslinked NR composites were studied through the use of a universal tensile testing machine, LR5K Plus (LLOYD Instruments, UK) in accordance with ISO 37. The averages of five dumbbell-shaped specimens are reported, and the test was conducted at ambient temperature with a crosshead speed of 500 mm/min. The RI was defined by equation 10 [21-23]:

$$\text{Reinforcement Index, RI} = \frac{M_{300}}{M_{100}} \quad (10)$$

where M300 and M100 refer to the stresses at 100% and 300% strains, respectively.

Morphological test

The dispersion of sepiolite and silica fillers throughout the rubber matrix was investigated through the use of a scanning electron microscope (SEM; FEI Quanta 400 FEG, the Netherland). All composite specimens were immersed in liquid nitrogen and subsequently fractured before sputter-coating with gold in order to eliminate electrostatic charge buildup during examination. The SEM photomicrographs of cut surfaces were taken at magnification of 500x.

Results and Discussion

Mooney viscosity and Mooney stress relaxation measurement

The Mooney viscosities of the NR composite compounds filled with sepiolite or silica are shown in Figure 1. It is observed that in general the Mooney viscosity increased with filler loading. This is usually attributed to hydrodynamic effects, following the Guth and Gold equation [24].

$$\eta_{\text{rel}} = \frac{\eta_f}{\eta_u} = 1 + 2.5\phi + 14.1\phi^2 \quad (11)$$

where η_{rel} is the relative Mooney viscosity, η_f refers to the Mooney viscosity of filled rubber composite, η_u denotes the Mooney viscosity of neat rubber compound, and ϕ is the volume concentration of filler. As the filler loading increases, the viscosity should increase. However, a reduction of viscosity after adding 5 phr silica was observed, which was probably attributed to the formation of large silica aggregation as will be discussed later.

Figure 2 illustrates the Mooney stress relaxation rates of the composite compounds. The filler content had a great effect on the rate of relaxation, and the relaxation rates of sepiolite filled NR composites were slower than those of the silica filled ones. It has been reported that the choice of filler and its interactions with the polymer matrix considerably impacted the rate of stress relaxation. Interactions between filler particles and rubber chains hindered the molecular mobility, thus decreasing the relaxation rate [25, 26]. Considering the type of filler, composites filled with sepiolite relaxed slower than the silica filled ones. Since stronger interactions between filler and rubber matrix could better retard the relaxation rate as mentioned earlier, it is assumed that sepiolite gave stronger filler-matrix interactions than silica. The stronger filler-rubber interaction of sepiolite was attributed to the smaller size with higher aspect ratio of sepiolite dispersion in the rubber matrix as will be discussed later in the morphological observation part. The higher aspect ratio provided the higher surface area to interact with the rubber through chain entanglement and physical adsorption of rubber molecules onto the filler surfaces. It is well accepted that surface area is a major factor in the rubber composite structure. The larger the surface area of the filler is, the higher the possibility of filler-rubber contact takes place, resulting in efficient retardation of rubber molecules during relaxation.

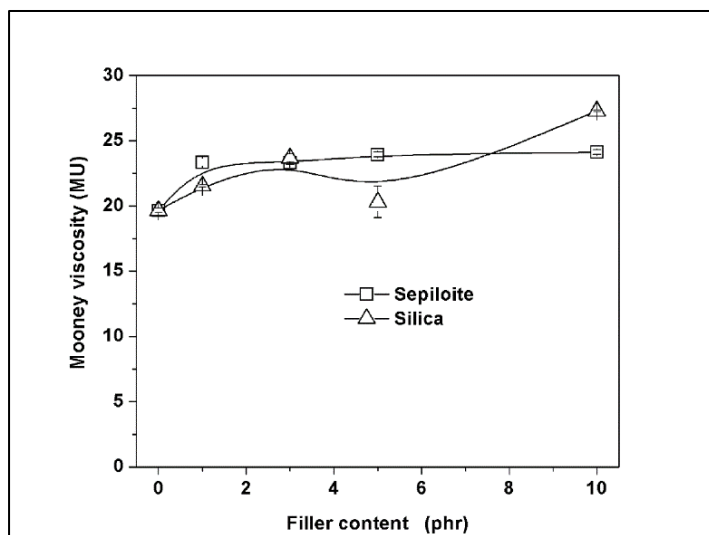


Figure 1. Mooney viscosities of NR compounds filled with sepiolite or silica

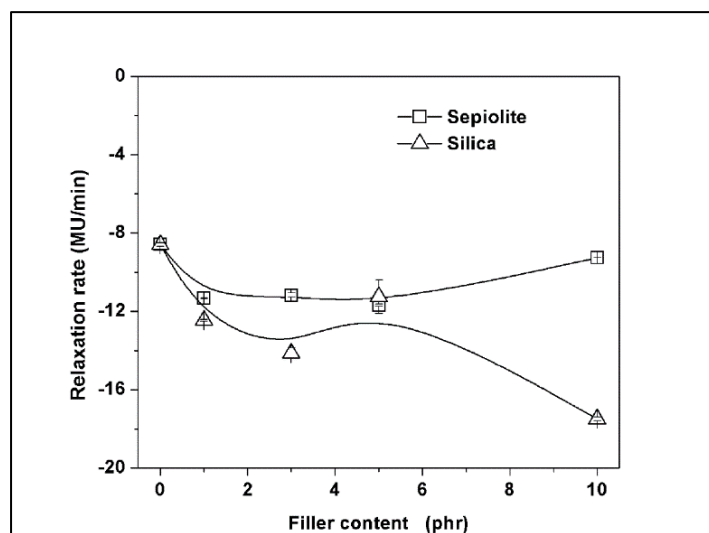


Figure 2. Mooney stress relaxation rates of NR compounds filled with sepiolite or silica

Curing characteristics

Curing properties in terms of M_H , M_H-M_L , t_{90} , and CRI, obtained from rheometric tests of the different rubber compounds, are presented in Figure 3(a)–Figure 3(d). It is noticed that the changes in curing properties were more pronounced for the sepiolite filled compounds in comparison with those for the silica filled ones. The M_H and M_H-M_L (Figures 3(a) and 3(b)) tended to increase with sepiolite loading, while they were approximately constant when silica was incorporated to

the NR compounds. It is well known that M_H and M_H-M_L are related to molecular rigidity and crosslink density, respectively, for rubber compounds. The higher molecular rigidity and crosslink density were achieved with sepiolite filler because of the larger aspect ratio and surface area for contacting with the rubber molecules. The adsorbed rubber chain fragments on filler surfaces forming physical interaction restrict the chain mobility in the rubbery matrix and serving as additional crosslinks in the

composites. Consequently, the rigidity and crosslink density of the composites were improved. It has been reported that large improvements in M_H and M_H-M_L for composites with small filler loadings are attributed to stronger rubber-filler interactions [27-29]. Therefore, stronger interactions of rubber and filler can be assumed for sepiolite compared to those for silica in filled NR compounds.

Considering t_{90} of both sepiolite and silica filled compounds (Figure 3(c)), different phenomena are observed based on the filler type. Incorporation of sepiolite in NR tended to reduce t_{90} , while silica slightly prolonged it. A reduction of the t_{90} in sepiolite filled composites can be explained by the magnesium oxide (MgO) contained in the sepiolite structure. It is generally accepted that MgO is an activator of vulcanization reaction in rubber compounds, as it acts as a cation activating the crosslinking process at the diene backbone of the rubber [30]. On the contrary, the slight increase in t_{90} noticed for the silica filled compounds was probably a result of the highly polar nature of silica, leading to the absorption of the curing ingredients, including ZnO, stearic acid, and accelerators, and thereby resulting in a delayed curing process [31, 32].

The influence of metal oxide in sepiolite filled compounds on vulcanization process was later confirmed by increased CRI (Figure 3(d)), which indicated that curing reactions occurred faster with sepiolite filler than with silica filler. The CRI is a measure of rate of vulcanization based on the difference between cure time and scorch time. The higher the value of cure index, the faster the curing process [30].

Reversion resistance

Reversion resistances, R_{300} , for the composites with sepiolite or silica filler in NR vulcanizates were estimated by exposing the rubber composites to shear at an elevated temperature for a certain period of time. A larger R_{300} indicates more reversion [15, 33]. Figure 4 illustrates the reversion resistances of NR composites filled with sepiolite and silica. It is observed that the filler type and loading had a

considerable effect on R_{300} within the experimental range probably because of relatively small filler loading. However, a larger R_{300} was seen for the silica filled NR composites, indicating that they had poorer reversion resistance in comparison with sepiolite filler. This can be because the greater sepiolite dispersion and better rubber-filler interactions improved the crosslink density of sepiolite filled NR composites. The better filler dispersion to gather with the higher overall crosslinking degree retarded the mobility of the rubber chains, and this enhanced the thermal stability of the rubber composites [8]. Furthermore, sepiolite itself could contribute to thermal stabilization and flame retardant properties of the filled polymer, as it served as a heat quencher and an initiator for formation of char on the polymer surface, inhibiting diffusion of oxygen [10].

Rubber-filler interactions

In order to evaluate the extent of interactions between rubber and filler, Lorenz-Parks and Kraus models were employed. Figure 5 presents Lorentz-Parks plot for the NR composites filled with sepiolite and silica. The value of rubber-filler interaction (Q_f/Q_g) generally reduced with sepiolite content but remained almost constant for the silica filled composites. Since the Q ascribed to the amount of solvent absorbed by rubber sample, the reduction of Q_f/Q_g was due to the better restricted diffusion of solvent molecules through the rubber matrix, resulting from greater extent of interaction between rubber and filler. The smaller value of Q_f/Q_g denotes stronger filler-matrix interactions [19, 28, 34, 35]. Since the Q_f/Q_g of sepiolite filled NR composites was below that of the silica filled composite at each loading level, the stronger rubber-filler interactions were achieved in the sepiolite filled composites. In contrast, the constant value of Q_f/Q_g in the composites filled with silica implies less interaction between silica and rubber matrix.

The rubber-filler interactions were further confirmed through the use of the Kraus model (plot of volume fraction ratio (V_{ro}/V_{rf}) versus volume ratio of filler ($f/1-f$)), and the results are displayed in Figure 6. It was observed that V_{ro}/V_{rf} decreased with filler loading. The negative slope in the plot of V_{ro}/V_{rf} versus $f/1-f$ is an

indication of a good reinforcing effect [19, 28]. The negative slope was due to strong rubber-filler interaction, resulting from a reduction of the solvent uptake (solvent sorption) in the rubber composites. Consequently, the V_{rf} value decreases, resulting in a reduction in V_{ro}/V_{rf} value (V_{ro} is constant). More negative slope is noticed for the composites with sepiolite filler, implying that sepiolite was more effective in reinforcing the composite than the silica. Based on the Lorenz-Parks and Kraus models, it is confirmed that sepiolite provided stronger rubber-filler

interactions of the two fillers, leading to greater reinforcement within the range tested in the present study. The good interactions between sepiolite and rubber were attributed to the fact that the rubber chains can easily interact with the narrow channels in the sepiolite structure [9, 36]. Moreover, the larger specific surface area of sepiolite ($364 \text{ m}^2/\text{g}$) [36] over silica ($175 \text{ m}^2/\text{g}$) [37] may facilitate the rubber-filler interactions.

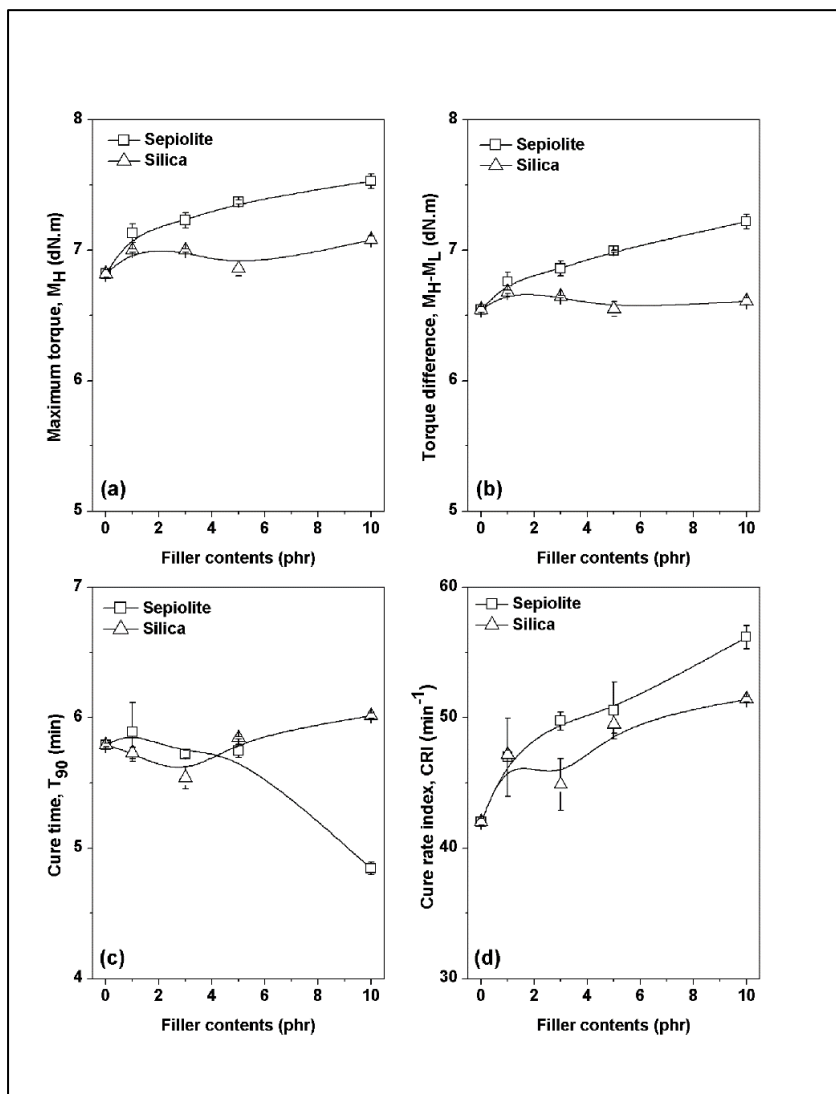


Figure 3. Curing properties in terms of (a) maximum torque, (b) torque difference, (c) cure time, and (d) cure rate index for the NR composites filled with sepiolite or with silica

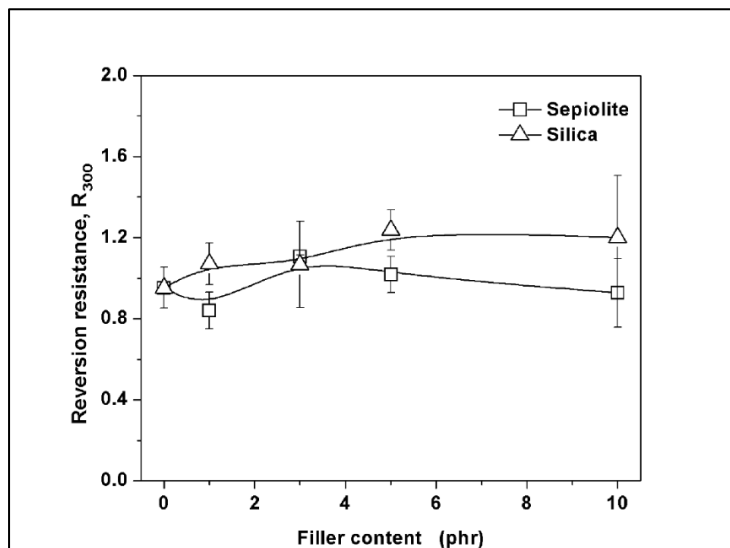


Figure 4. Reversion resistances of NR composites filled with sepiolite or with silica

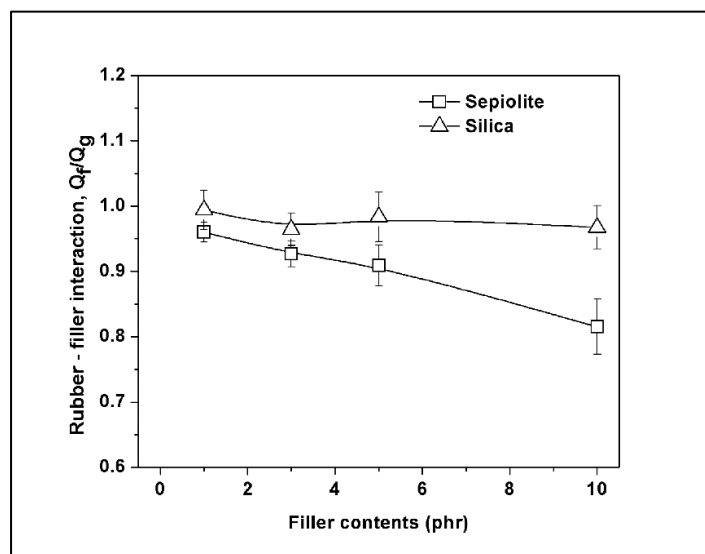


Figure 5. Lorentz-Parks plot of NR composites filled with sepiolite or silica

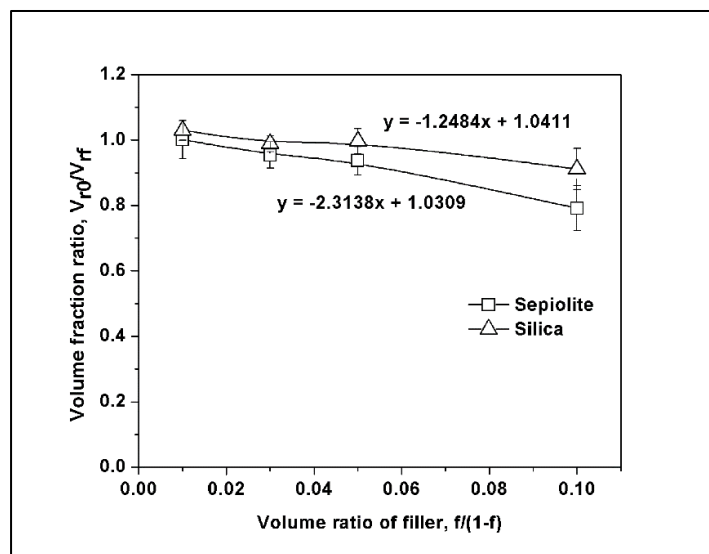


Figure 6. Kraus plot of NR composites filled with sepiolite or silica

Tensile properties

Figure 7 displays reinforcement index (M300/M100) for the NR composites filled with the two tested fillers. It is generally observed that the reinforcement index of sepiolite filled NR composite was greater than that of the silica filled composite. This was simply due to the stronger interactions between rubber and sepiolite filler, as previously discussed. The tubular-shaped with high specific surface area of sepiolite may act as stress transferring agent, which would increase the reinforcing index. This finding is in agreement with previous literature [5, 7, 9, 38], reporting that sepiolite fibers provided more reinforcement than spherical silica particles due to their high aspect ratio. The aspect ratios of sepiolite and silica found in the current study were approximately 5.32 and 1.09, respectively, which are in line with the previous report [38].

Figure 8 displays the variation in tensile strength of NR composites filled with sepiolite and silica. It can be clearly noticed that incorporation of sepiolite provided slightly higher tensile strength than silica, because of the better rubber-filler interactions. The highest tensile strength was about 17% improvement over unfilled sample found at 1 phr sepiolite loading, probably due to the greatest rubber-filler interactions as previously suggested by the stress relaxation and filler-rubber

interaction results (Figures 2, 5, and 6). As a result of filler incorporation, the extensibility of rubber usually decreases due to either good rubber-filler interactions, restricting the movements of rubber chains, or poor filler dispersion, with agglomerates serving as stress concentration points. Thus, the elongation at break of composites reduced with filler loading, as presented in Figure 9. Similar observation was found in previous report [30]. The better rubber-filler interactions of sepiolite provided a slightly superior extension capability, particularly at low filler loadings.

In case of NR composites filled with silica, the highest tensile strength was found at 5 phr (about 12% over neat NR) which was considered to be optimum. Further increase in the silica incorporation slightly reduced the tensile strength because of the increment of silica aggregation, as will be discussed later in the morphological part. The aggregation of silica served as stress concentration point, resulting in a reduction of elongation at break. It is also found that the tensile strength of NR composites filled with sepiolite and silica was not much different due to relatively small filler loading. However, smaller loading of sepiolite required to obtain maximum tensile strength than silica would be benefited for preparation of rubber composite containing small filler loading.

Morphological property

Figure 10 presents the SEM micrographs of cryo-fractured surfaces of sepiolite (Figures 10(a) and 10(b)) and silica (Figures 10(c) and 10(d)) filled NR composites. It is noticed that the morphology of rubber composites comprises different sizes and shapes of filler dispersion, based on loading and type of filler. In the composites filled with sepiolite (Figures 10(a) and 10(b)), small size of filler with tubular-shaped was dispersed throughout the rubber matrix. The length (L) and diameter (D) of sepiolite in NR/Sepiolite 1 were about 1.34 - 3.15 μm and 0.34 - 0.91 μm , respectively. Meanwhile, they were about 2.45 - 5.50 μm and 0.45 - 1.12 μm , respectively, in NR/Sepiolite 5. Thus, the average aspect ratios of rubber composites filled with 1 and 5 phr sepiolite were about 5.32 ± 3.44 and 4.88 ± 3.36 , respectively. Less amount of tubular-shaped particulates was observed in sample containing 1 phr sepiolite due to small amount of sepiolite added. However, such dispersion is sufficient to assist the stress transfer to each other. Large size of sepiolite aggregation was seen when the sepiolite loading was up to 5 phr. Such dispersion would be responsible for a reduction in tensile strength and elongation at break.

Considering the composites filled with silica, the L and D of silica in NR/Silica 1 (Figure 10(C)) ranged within 0.46 - 3.02 μm and 0.44 - 2.80 μm , respectively, whereas they were within 1.34 - 6.72 μm and 1.12 - 7.05 μm , respectively, for NR/Silica 5 sample (Figure 10(D)), resulting in the aspect ratio of about 1.06 ± 0.04 for NR/Silica 1 and 1.03 ± 0.2 for NR/Silica 5. It was also found that the size of silica dispersion increased with filler loading, suggesting that filler-filler interaction was preferred at high silica loading. Smaller aspect ratio of silica dispersion than those of sepiolite can be confirmed which was in well agreement with previous report [39].

Based on the SEM observation, it is clearly evident that the aspect ratio of sepiolite dispersion was greater than that of silica. The higher aspect ratio created larger surface area contact between rubber and filler, providing better stress transfer between the components. Therefore, the better restricted chain relaxation and the higher tensile properties were obtained with incorporation of sepiolite.

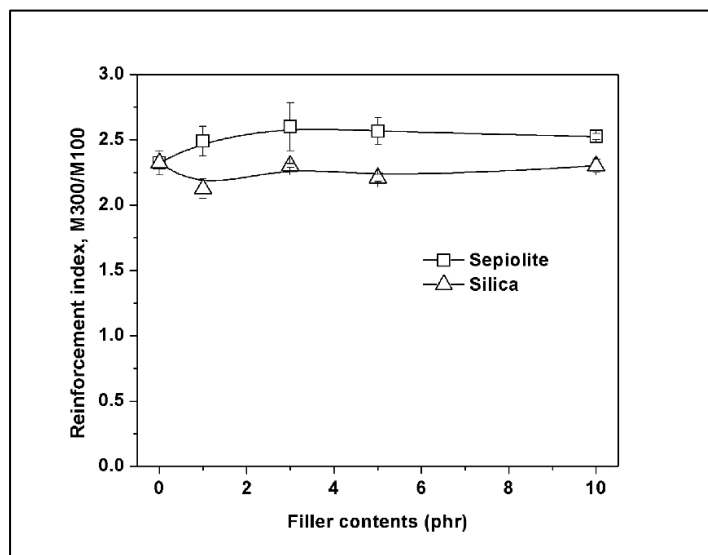


Figure 7. Reinforcement index (M300/M100) of NR composites filled with sepiolite or silica

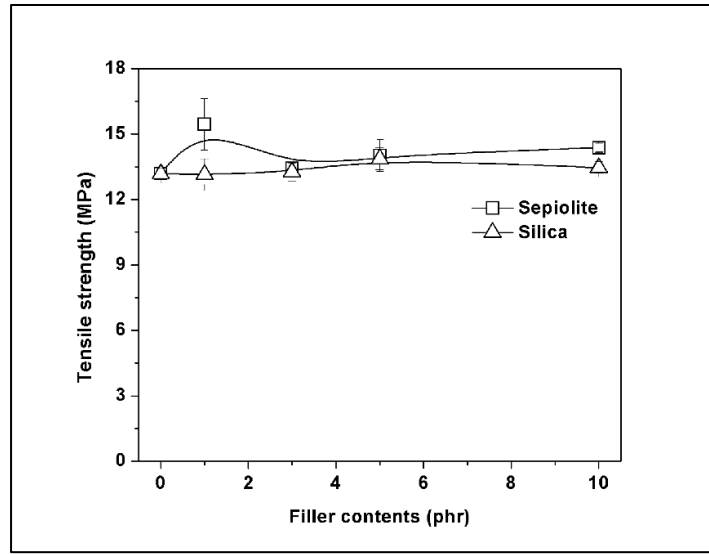


Figure 8. Tensile strength of NR composites filled with sepiolite or silica

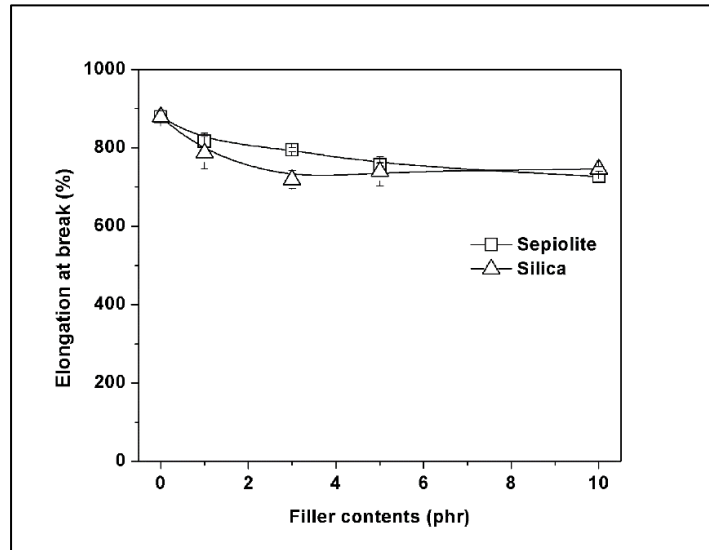


Figure 9. Elongation at break of NR composites filled with sepiolite or silica

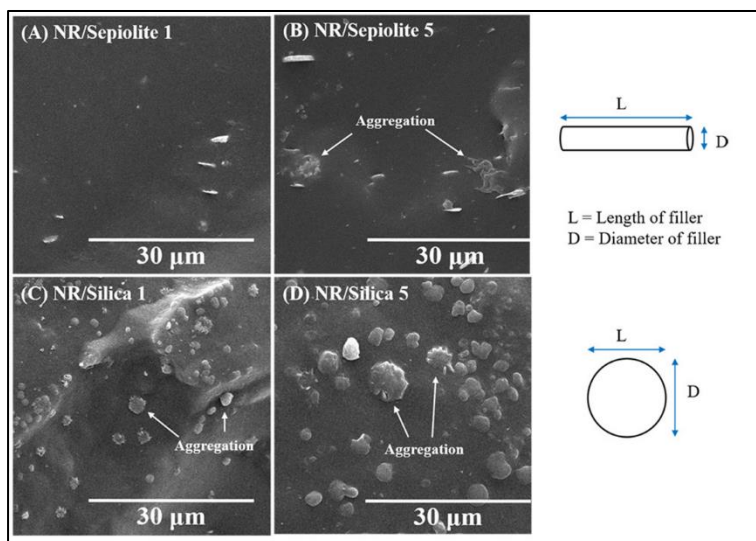


Figure 10. SEM micrographs of NR composites: (a) NR/Sepiolite 1 phr, (b) NR/Sepiolite 5 phr, (c) NR/Silica 1 phr, and (d) NR/Silica 5 phr at 500x

Conclusion

Composites of NR filled with sepiolite or with silica were prepared in the present study, and the influence of filler type and loading level on properties of the composites was investigated. From Mooney viscosity, stress relaxation, and rheometric tests, the results revealed that sepiolite filled NR exhibited a slower relaxation rate with larger torque difference and better reversion resistance than that with the silica filled compounds, suggesting better rubber-filler interactions than in silica filled composites. Increased addition of filler improved the viscosity of rubber by approximately 7 - 22% with sepiolite and approximately 3 - 37% with silica, depending on filler loading. The stronger rubber-filler interactions in the sepiolite filled composites were later confirmed through the use of the Lorenz-Parks and Kraus models. The greater extent of interaction between rubber and filler resulted in the greater restricted diffusion of solvent molecules through the rubber matrix. As a result of the good interactions between sepiolite filler and rubber matrix, larger reinforcement indexes and tensile strengths were achieved with sepiolite filler than with silica filler in the composites. This was due to the higher aspect ratio of sepiolite (~5.32) compared to that of silica (~1.09) as revealed by SEM analysis. The

highest tensile strength was achieved at 1 phr sepiolite loading which was about 17% improvement over unfilled sample.

Acknowledgement

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References

1. Chang, B. P. P., Gupta, A., Muthuraj, R. and Mekonnen, T. (2021). Bioresourced fillers for rubber composites sustainability: current development and future opportunities. *Green Chemistry*, 23: 5337-5378.
2. Maslowski, M., Miedzianowska, J. and Strzelec, K. (2019). Natural rubber composites filled with crop residues as an alternative to vulcanizates with common fillers. *Polymers*, 11(6): 972.
3. Bokobza, L. (2017). Mechanical and electrical properties of elastomer nanocomposites based on different carbon nanomaterials. *Journal of Carbon Research*, 3(2): 10.

4. Anand, A., Nussana, L., Sham Aan, M. P., Ekwipoo, K., Sangashetty, S. G. and Jobish, J. (2020). Synthesis and characterization of zno nanoparticles and their natural rubber composites. *Journal of Macromolecular Science, Part B*, 59(11): 697-712.
5. Bokobza, L. (2019). Natural rubber nanocomposites: a review. *Nanomaterials*, 9(1): 12.
6. Roy, K., Debnath, S. C. and Potiyaraj, P. (2020). A critical review on the utilization of various reinforcement modifiers in filled rubber composites. *Journal of Elastomers and Plastics*, 52(2): 167-193.
7. Bokobza, L. and Chauvin, J. P. (2005). Reinforcement of natural rubber: use of in situ generated silicas and nanofibres of sepiolite. *Polymer*, 46(12): 4144-4151.
8. Chen, H., Zheng, M., Sun, H. and Jia, Q. (2007). Characterization and properties of sepiolite/polyurethane nanocomposites. *Materials Science and Engineering: A*, 445-446: 725-730.
9. Bokobza, L., Leroy, E. and Lalanne, V. (2009). Effect of filling mixtures of sepiolite and a surface modified fumed silica on the mechanical and swelling behavior of a styrene-butadiene rubber. *European Polymer Journal*, 45(4): 996-1001.
10. Zhan, Z., Xu, M. and Li, B. (2015). Synergistic effects of sepiolite on the flame retardant properties and thermal degradation behaviors of polyamide 66/aluminum diethylphosphinate composites. *Polymer Degradation and Stability*, 117: 66-74.
11. Zaini, N. A. M., Ismail, H. and Rusli, A. (2018). Thermal, flammability, and morphological properties of sepiolite filled ethylene propylene diene monomer composites. *Malaysian Journal of Analytical Sciences*, 22(5): 899-905.
12. Bhattacharya, M., Maiti, M. and Bhowmick, A. K. (2008). Influence of different nanofillers and their dispersion methods on the properties of natural rubber nanocomposites. *Rubber Chemistry and Technology*, 81(5): 782-808.
13. Lowe, D. J., Chapman, A. V., Cook, S. and Busfield, J. J. C. (2011). Natural rubber nanocomposites by in situ modification of clay. *Macromolecular Materials and Engineering*, 296(8): 693-702.
14. Winya, N. and Hansupalak, N. (2016). A comparison between the effects of sepiolite and silica on mechanical properties and thermal stability of NR/EPDM blend. *MATEC Web of Conferences*, 6: 04003.
15. Khang, T. H. and Ariff, Z. M. (2012). Vulcanization kinetics study of natural rubber compounds having different formulation variables. *Journal of Thermal Analysis and Calorimetry*, 109(3): 1545-1553.
16. Hayeemasae, N. and Masa, A. (2020). Relationship between stress relaxation behavior and thermal stability of natural rubber vulcanizates. *Polímeros*, 30(2): e2020016.
17. Lorenz, O. and Parks, C. R. (1961). The crosslinking efficiency of some vulcanizing agents in natural rubber. *Journal of Polymer Science*, 50(154): 299-312.
18. Kraus, G. (1965). Interactions of elastomers and reinforcing fillers. *Rubber Chemistry and Technology*, 38 (5): 1070-1114.
19. Swapna, V. P., Stephen, R., Greeshma, T., Sharan, D. C. and Sreekala, M. S. (2016). Mechanical and swelling behavior of green nanocomposites of natural rubber latex and tubular shaped halloysite nano clay. *Polymer Composites*, 37(2): 602-611.
20. Ellis, B. and Welding, G. N. (1964). Techniques of polymer science. society of the chemical industry, London: pp. 46-46.
21. Lee, J. Y., Kim, S. M. and Kim, K. J. (2015). Observation of interfacial adhesion in silica-nr compound by using bifunctional silane coupling agent. *Polymer Korea*, 39(2): 240-246.
22. Saramolee, P., Sahakaro, K., Lopattananon, N., Dierkes, W. K. and Noordermeer, J. W. (2015). Compatibilization of silica-filled natural rubber compounds by combined effects of functionalized low molecular weight rubber and silane. *Journal of Elastomers and Plastics*, 48(2): 145-163.
23. Mohamad Aini, N. A., Othman, N., Hussin, M. H., Sahakaro, K. and Hayeemasae, N. (2019). Hydroxymethylation-modified lignin and its effectiveness as a filler in rubber composites. *Processes*, 7(5): 315.

24. Sajjayanukul, T., Saeoui, P. and Sirisinha, C. (2005). Experimental analysis of viscoelastic properties in carbon black-filled natural rubber compounds. *Journal of Applied Polymer Science*, 97(6): 2197-2203.
25. Maria, H. J., Lyczko, N., Nzihou, A., Joseph, K., Mathew, C. and Thomas, S. (2014). Stress relaxation behavior of organically modified montmorillonite filled natural rubber/nitrile rubber nanocomposites. *Applied Clay Science*, 87: 120-128.
26. Gabriel, D., Karch, A., Drechsler, D., Gutmann, J., Graf, K. and Kheirandish, S. (2016). Bound rubber morphology and loss tangent properties of carbon-black-filled rubber compounds. *Colloid and Polymer Science*, 294: 501-511.
27. Honorato, L., Dias, M. L., Azuma, C. and Nunes, R. C. R. (2016). Rheological properties and curing features of natural rubber compositions filled with Fluoromica ME 100. *Polimeros*, 26(3): 249-253.
28. Mondal, D., Ghorai, S., Rana, D., De, D. and Chattopadhyay, D. (2019). The rubber-filler interaction and reinforcement in styrene butadiene rubber/devulcanize natural rubber composites with silica-graphene oxide. *Polymer Composites*, 40(S2): E1559-E1572.
29. Lopez-Manchado, M. A., Arroyo, M., Herrero, B. and Biagiotti, J. (2003). Vulcanization kinetics of natural rubber-organoclay nanocomposites. *Journal of Applied Polymer Science*, 89(1): 1-15.
30. Masa, A., Krem-ae, A., Ismail, H. and Hayeemasae, N. (2020). Possible use of sepiolite as alternative filler for natural rubber. *Materials Research*, 23(4): e20200100.
31. Sridharan, H., Guha, A., Bhattacharyya, S., Bhowmick, A. K. and Mukhopadhyay, R. (2019). Effect of silica loading and coupling agent on wear and fatigue properties of a tread compound. *Rubber Chemistry and Technology*, 92(2): 326-349.
32. Ansarifard, M. A., Chugh, J. P. and Haghghat, S. (2000). Effects of silica on the sure properties of some compounds of styrene-butadiene rubber. *Iranian Polymer Journal*, 9(2): 81-87.
33. Kok, C. M. (1987). The effects of compounding variables on the reversion process in the sulphur vulcanization of natural rubber. *European Polymer Journal*, 23(8): 611-615.
34. Wu, X., Lin, T. F., Tang, Z. H., Guo, B. C. and Huang, G. S. (2015). Natural rubber/graphene oxide composites: effect of sheet size on mechanical properties and strain-induced crystallization behavior. *eXPRESS Polymer Letters*, 9(8): 672-685.
35. Ismail, H., Omar, N. F. and Othman, N. (2011). Effect of carbon black loading on curing characteristics and mechanical properties of waste tyre dust/carbon black hybrid filler filled natural rubber compounds. *Journal of Applied Polymer Science*, 121(2): 1143-1150.
36. Bhattacharya, M. and Bhowmick, A. K. (2008). Polymer-filler interaction in nanocomposites: New interface area function to investigate swelling behavior and Young's modulus. *Polymer*, 49(22): 4808-4818.
37. Kaewsakul, W., Sahakaro, K., Dierkes, W. K. and Noordermeer, J. W. (2013). Optimization of rubber formulation for silica-reinforced natural rubber compounds. *Rubber Chemistry and Technology*, 86(2): 313 - 329.
38. Locatelli, D., Pavlovic, N., Barbera, V., Giannini, L. and Galimberti, M. (2020). Sepiolite as reinforcing filler for rubber composites: from the chemical compatibilization to the commercial exploitation. *KGK Kautschuk Gummi Kunststoffe*, 73: 26-35.
39. Abdul Salim, Z. A. S., Hassan, A. and Ismail, H. (2018). A review on hybrid fillers in rubber composites. *Polymer-Plastics Technology and Engineering*, 57(6): 523-539.