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Research Paper

Influence of Sepiolite Addition Methods and Contents on Physical Properties of Natural Rubber Composites

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Abstract

The influence of sepiolite loadings (1-10 phr) and sepiolite addition procedures (mill and latex mixing approaches) on properties improvement of natural rubber composites was investigated. The viscosity, curing behavior, and tensile test were used to assess the property changes whereas the rubber-filler interactions was confirmed by using stress relaxation, swelling, Mooney-Rivlin and rheological methods. It was found that the characteristics of rubber composites influenced by both mixing methods and filler contents. Comparing between two different mixing methods, the slower stress relaxation rate and less swelling capability were achieved from mill mixing technique. This method also lowered the strain where the upturn of stress was occurred as suggested by Mooney-Rivlin plot. The greater properties enhancement of composites was obtained from milling method because of the better rubber-filler interactions, probably as a result of the nature of filler used. The greatest tensile strength improvement was achieved at 1 phr sepiolite loading where the smallest damping characteristics ($\tan\delta$) indicating the highest elastic behavior were obtained as revealed by rheological measurements. The simplicity of production and shortened step of milling procedure would be more favorable than the latex mixing approach for fabrication sepiolite filled rubber composites.

Keywords

Composites, Mechanical Properties, Natural Rubber, Physical Properties, Sepiolite

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1. INTRODUCTION

In general, Natural Rubber (NR) that has not unvulcanised cannot be functioned as products due to its soft at high temperatures, and brittle at low temperatures Roberts (1988) unless it was crosslinked (Kim et al., 2020). The unvulcanised NR generally possesses low mechanical properties but vulcanised NR exhibits high degree of elasticity, mechanical strength, and thermal properties (Aprem et al., 2005). This is due to the fact that the vulcanisation reaction inhibits the NR chains from sliding when the load is applied.

Fillers are practically introduced into rubber in order to achieve performance characteristics that are appropriate for the end use applications (Bokobza, 2019). Reinforcing fillers have been included to enhance the performance of rubber products (Noordermeer, 1998) whereas inert filler (non-reinforcing) is used to cheapen the manufacturing cost (Roy et al., 2020). Silica and carbon black appear as the most often used fillers to achieve products with desired properties. However, the production of these fillers usually necessitates a considerable level of energy consumption (Masa et al., 2020). There are many alternative fillers that have been available and used to incorporate in rubbers. However, searching fillers consisting unique characteristics have been always a special choice. Nowadays, the use of sepiolite as filler in rubber composites has been the subject of various research due to sepiolite has a needle-like structure with tunnel-like micropore channels, allowing for the enhancement of mechanical, thermal and barrier performances of composites (Bokobza and Chauvin, 2005; Chen et al., 2007; Bokobza et al., 2009; Zaini et al., 2018). In addition, unlike traditional silica and carbon black, it is naturally occurring and readily available in significant quantities (Di Credico et al., 2019). Sepiolite is a micro-fibrous clay with $Si_{12}Mg_8O_{30}(OH, F)_4]$. $(H_2O)_4 \cdot 8H_2O$

as structural formulation (Masa et al., 2020). It has a typical tetrahedral-octahedral-tetrahedral layer fibrous structure, with magnesium atoms, octahedrally coordinated, joining together two-dimensional layers of tetrahedral SiO_4 units. The length of such fibrous morphology is approximately 2-10 μm. In addition, the sepiolite also has a tunnel-like micro-pore channel in its structure that can react with rubber molecules. Owing to the nano-sized sepiolite with needle-like fibrous structure and high aspect ratio, it can be a potential new filler type for substitution of carbon black or silica, providing advantages of light weight, enhanced physical and dynamic properties, and may find application in electric vehicle and other ultra-performance tires (Mohanty et al., 2021). It has been suggested that sepiolite could be used as a filler in rubber composites (Zaini et al., 2018; Nasution et al., 2020; Bhattacharya et al., 2008). These reports found that incorporation of sepiolite enhanced properties of the composites including, curing, mechanical, thermal, swelling, flammability and morphological properties. However, milling technique was mainly used for preparation the composites. Recently, Di Credico et al. (2019) have demonstrated a new approach for preparation NR/sepiolite composites by using latex-compounding technique. They found that the latex mixing approach provided more uniformity of sepiolite distribution in the rubber matrix, and the dynamic mechanical performances of NR loaded with sepiolites were greater in comparison to materials prepared by conventional milling approach. However, the mechanical properties, i.e., tensile and curing properties were not compared and discussed in details.

Thus, the purpose of this study was to further investigate the influence of two alternative mixing methods, milling and latex approaches, on the physical performances of rubber composites containing various sepiolite contents. The property enhancements were discussed based on the viscosity, curing behaviour and mechanical properties whereas the rubber-filler interaction was confirmed by using stress relaxation, swelling, Mooney-Rivlin and rheological methods.

2. EXPERIMENTAL SECTION

2.1 Materials

High-ammonium NR latex (HA) containing Dry Rubber Content (DRC) of 60% and NR graded RSS-3 were used for latex and milling approaches, respectively. These were manufactured by Chalong Concentrated Natural Rubber Latex Industry Co. Ltd., Thailand. Stearic acid bought from Imperial Chemical Co., Ltd., Thailand and zinc oxide (ZnO) purchased from Global Chemical Co., Ltd., Samut Prakan, Thailand were used as activator. Sepiolite filler was received from Hebei DflMinmet refractories Corporation, Shijiazhuang, Hebei, China. Sulfur curing agent was purchased from Siam Chemical Co., Ltd., Samut Prakan, Thailand and N-cyclohexyl-2-benzothiazole sulfonamide (CBS) was manufactured by Flexsys America L.P., West Virginia, USA.

2.2 Preparation of Rubber Compound

Two alternative mixing procedures, latex mixing approach and milling approach, were used to prepare NR composite compounds. Figure 1 shown diagram for compounding preparation of the composites. In the latex mixing approach (see Figure 1(a)), 5 wt% of sepiolite dispersion in water was firstly prepared before adding to HA latex. It was then vigorously stirred at room temperature for 30 minutes prior to drying to obtain NR masterbatch containing $1-10$ part per hundred of rubber (phr) sepiolite. Finally, the NR-sepiolite masterbatches (NR/sepiolite MB) were later mixed with other chemicals including stearic acid, ZnO, CBS and sulfur on two roll mill at room temperature. As for milling approach, all of the chemical components including sepiolite filler were mixed with rubber (RSS-3) on two roll mill in one step as illustrated in Figure 1(b). The composites' formulation as well as the time for mixing are shown in Table 1. When the rubber was mixed on two roll mill, the total mixing time was set at 17 min for all mixing approaches. The compounds were finally vulcanised at 160°C by using compression-molding following their respective curing times. The specimens obtained from latex mixing approach containing sepiolite at 1-10 phr were noted as NRL-S1, NRL-S3, NRL-S5 and NRL-S10, while those composites obtained from milling approach were abbreviated as NR-S1, NR-S3, NR-S5 and NR-S10. The NRL-S0 and NR-S0 were assigned to neat NR sample obtained from latex mixing and milling approaches, respectively.

2.3 Mooney Viscosity and Mooney Stress Relaxation Tests

The changes of composites' viscosity and stress relaxation were evaluated by using a Mooney viscometer, MV 3000 Basic (MonTech, Germany). The tests were carried out at 100°C using a large rotor in accordance with ASTM D1646.

Table 1. Formulation and Mixing Time for Preparation of NR Composites

Chemical	Amount (phr)	Mixing time (min)
NR	100	2
Stearic acid	1	2
ZnO	3	
Sepiolite	0, 1, 3, 5 and 10	10
CBS	1.5	2
S	1.5	1
Total mixing time		**17**

The stress relaxation was fitted with the power law model as shown in Equation (1).

$$\begin{aligned} M &= kt^a \\ \log M &= \log k + a \log t \end{aligned} \tag{1}$$

where, M is the relaxation torque, k is a constant, a is the relaxation rate determined from the slope in a log-log plot of M versus t, and t is the relaxation time.

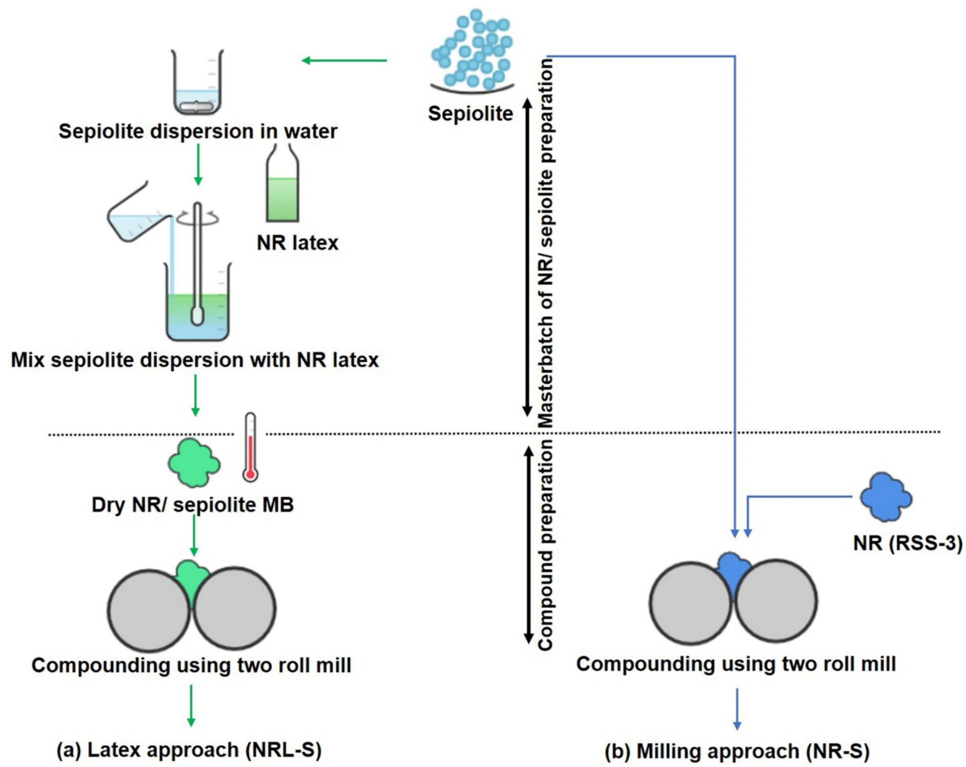

Figure 1. Preparation Steps of Rubber Composites; (a) Latex and (b) Milling Approaches

2.4 Measurement of Curing Characteristics

Curing properties including scorch time (t_{s1}), curing time (t_{90}) and torque differences ($M_H - M_L$) were examined by using a moving die rheometer, MDR 3000 Basic (Montech, Germany) at 160°C for 20 minutes. The t_{90} was estimated from Equation (2).

$$t_{90} = M_L + 0.9(M_H - M_L) \quad (2)$$

2.5 Measurement of Swelling Uptake

The equilibrium swelling test was used to calculate the swelling characteristic of rubber composites. The vulcanizates with and without sepiolite addition obtained from both mixing methods were submerged in toluene solvent for 3 days at room temperature. The swelling degree was calculated by using Equation (3).

$$\text{Swelling (\%)} = \frac{W_s - W_i}{W_i} x100 \quad (3)$$

where W_i is the initial sample weight (g), whereas W_s is the swollen sample weight (g).

The result of the swelling test were further used for estimation the extent of filler-matrix interactions by applying the Lorenz-Parks (Lorenz and Parks, 1961). The Lorenz-Parks model is presented in Equation (4).

$$\frac{Q_f}{Q_g} = ae^{-z} + b \quad (4)$$

where, Q assigns to the quantity of absorbed solvent, g and f refer to gum and filled rubber vulcanizates, whereas a and b are constants (the model parameters tuned to fit data), and z assigned to the filler weight fraction.

The Q can be obtained by applying Equation 5 (Swapna et al., 2016).

$$Q = \frac{\text{Swollen wt. - Dried wt.}}{\text{Original wt.}} \quad (5)$$

2.6 Tensile Property Measurements

The maximum stress at break (tensile strength), tensile stress and strain at break (elongation at break) of the composite specimens were determined at 500 mm/min according to ASTM D412 by using a universal testing equipment, LR5K Plus (LLOYD Instruments, UK), while tear strength was measure according to ASTM D624.

2.7 Dynamic Mechanical Property Tests

The filler-rubber interaction of NR matrix and sepiolite filler in the unvulcanised composites was estimated by means of a

Rubber Process Analyzer (RPA), model D-RPA 3000 (Mon-Tech, Germany). The tests were carried out at 60°C under a strain sweep ranging from 1 - 100% with a frequency of 10 Hz. The damping factor (tan δ) and storage modulus (G') were collected.

2.8 Morphological Property Test

The dispersion of sepiolite filler in the NR matrix was investigated using a Scanning Electron Microscope (SEM), model Quanta 400 (Thermo Fisher Scientific, Czech Republic). To minimise electrostatic charge buildup during testing, the samples were sputter-coated with gold after fracturing in liquid nitrogen.

3. RESULT AND DISCUSSION

3.1 Mooney Viscosity and Mooney Stress Relaxation

Figure 2 depicts the influence of sepiolite addition and contents on the viscosity of NR composites. The NR viscosity apparently enhanced with the incorporation of sepiolite filler due to a substantial limitation the mobility of the molecular chains that was caused by the strong interaction between sepiolite and the rubber molecules (Arayapranee and Rempel, 2013). For both preparation methods, the highest level of viscosity was seen at 1 phr sepiolite filled composites, implying that the strongest adhesion between filler and rubber matrix was achieved at this loading. Increased addition of filler higher than 1 phr lowered the viscosity, yielding from poor filler dispersion. The milling samples possessed lower viscosity than those of samples obtained from latex mixing approach. The smaller viscosity indirectly indicated a good process ability and flow properties due to lower elastic property of rubber mixes (Zaeimoedin et al., 2014).

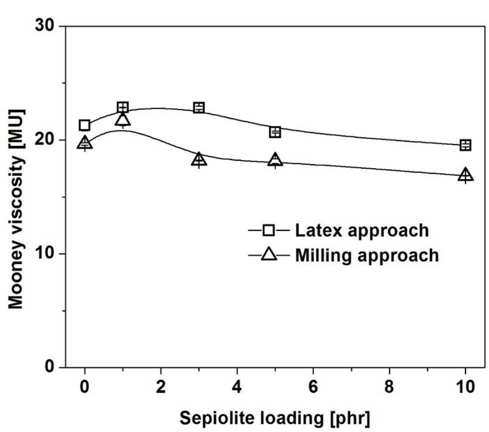

Figure 2. Variation of Mooney Viscosity Values of NR Composites Made by Different Sepiolite Addition Methods

Figures 3(a) and 3(b) presents stress relaxation of the NR composites loaded with sepiolite made by latex and milling approaches, respectively. It is well accepted that, strong interaction between filler particle and rubber chains influenced the stress relaxation rate (Maria et al., 2014). This is an indirect method for assessing the rubber-filler interaction. Higher interaction is frequently associated with a lower relaxation rate. Since the type of filler used was fixed, thus the difference of relaxation behaviour was surely attributed to the presence of interaction between rubber matrix and sepiolite filler. Lower stress relaxation rate had been found in the rubber composites achieved from milling approach (see Figure 3(b)). The lowest relaxation rate was seen from NR-S1 where the slope is about -3.1. Therefore, the interaction of rubber with sepiolite filler was stronger in the sample made from milling approach. In contrary, the relaxation rate of composites obtained by latex mixing approach was steeper and varied with sepiolite loading. The faster rate of stress relaxation in the latex mixing process suggested lesser interactions between filler and rubber molecules. This was due to the fact that sepiolite cannot swell in either water or organic solvents or exfoliate like other type of clay (Locatelli et al., 2020). Therefore, less ability of rubber molecules to interaction with filler during latex mixing that having water as medium.

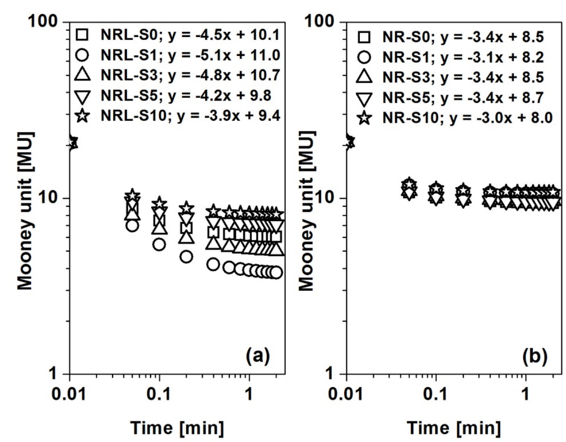

Figure 3. Variation of Stress Relaxation of NR Composites Made by (a) Latex and (b) Milling Approaches

3.2 Curing Properties

The effects of fabrication method on curing properties including t_{s1}, t_{90} and M_H-M_L of sepiolite filled NR are summarised in Table 2. With independent of mixing methods, the t_{s1} and t_{90} values reduced marginally as the sepiolite loading was increased. A decrease of both t_{s1} and t_{90} was caused by the metal oxides such as magnesium oxide found in the sepiolite structure. It is well acknowledged that metal oxides was used as activators for the rubber compounds, speeding up the sulfur vulcanization of NR (Masa et al., 2020; Mittal et al., 2011). Thus, shortening the t_{s1} and t_{90}. In addition, it was also found that the M_H-M_L increased with introduction of sepiolite filler. The M_H-M_L values are widely considered to be related to the stiffness of the composite. The result clearly suggested that the incorporation of sepiolite filler enhanced the rigidity of rubber composites.

Table 2. Curing Characteristics of NR Composites Made by Different Sepiolite Addition Methods

Sample	t_{s1}	t_{90}	M_H-M_L	Sample	t_{s1}	t_{90}	M_H-M_L
NRL-S0	1.93	3.91	6.57	NR-S0	3.41	5.60	6.62
NRL-S1	1.60	3.49	6.67	NR-S1	2.61	4.44	6.69
NRL-S3	1.69	3.58	6.66	NR-S3	2.51	4.48	6.65
NRL-S5	1.60	3.68	6.88	NR-S5	2.46	4.31	6.73
NRL-S10	1.40	3.15	7.15	NR-S10	2.21	3.99	7.22

3.3 Swelling Property and Filler-Matrix Interactions

Influence of sepiolite addition methods on swelling behavior of NR composites containing numerous sepiolite loadings is demonstrated in Figure 4(a). The swelling uptake was found to be decreased with increasing filler concentration, implying lesser solvent penetration into the composite samples. A reduction of swelling degree can be explain by two reasons. First, the sepiolite filler particle acts as a barrier to the diffusing molecule. As filler loading enhances, greater hindrance was created to the diffusing molecule (Fernandez and Kunchandy, 2013). Second, it has been reported that a reduction of swelling degree in rubber composites was partially due to increasing rubber-filler interactions (Ismail et al., 2003). In comparison to the composites obtained from latex mixing method, the swelling degree of samples obtained from milling approach approach showed smaller swelling uptake. This finding implies that more rubber-filler interactions were obtained from milling approach method, especially with 1 phr sepiolite loading.

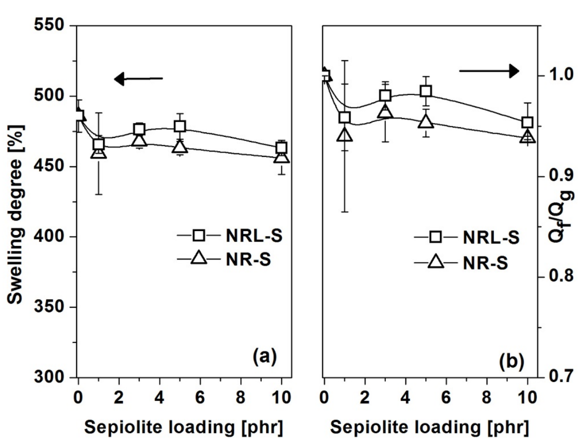

Figure 4. (a) Swelling and (b) Filler-Rubber Interaction of NR Composites Made by Different Sepiolite Addition Methods

To understand the extent of filler-rubber interactions, Lorenz-Parks model was applied and the result is shown in Figure 4(b). It is well accepted that smaller Q_f/Q_g values indicate the greater extent interaction between rubber and filler (Swapna et al., 2016;Ismail et al., 2011). As expected, the value of Q_f/Q_g generally decreased with sepiolite content and the decrease was the lowest at 1 phr. This implied that the highest rubber-filler interactions were achieved with 1 phr sepiolite loading. Considering the technique of sepiolite addition, it was discovered that the Q_f/Q_g values of rubber composites made through milling approach was smaller than those of samples achieved from latex mixing approach. Thus, the stronger rubber-filler interactions in mill-mixed composites over latex-mixed composites can be substantiated.

Table 3. 100% and 300% Modulus (100M and 300M), Tensile Strength (TS) and Elongation at Break (EB) of NR Composites Made by Different Sepiolite Addition Methods

Sample	100M (MPa)	300M (MPa)	TS (MPa)	EB (%)
NRL	0.58 ± 0.02	1.23 ± 0.01	11.29 ± 1.30	713 ± 34
NRL-S1	0.58 ± 0.01	1.33 ± 0.02	13.56 ± 1.12	694 ± 48
NRL-S3	0.56 ± 0.03	1.32 ± 0.01	12.75 ± 1.58	704 ± 18
NRL-S5	0.64 ± 0.06	1.44 ± 0.10	12.60 ± 0.16	614 ± 73
NRL-S10	0.65 ± 0.03	1.44 ± 0.14	10.81 ± 1.51	617 ± 37
NR	0.57 ± 0.03	1.22 ± 0.01	11.32 ± 0.02	723 ± 34
NR-S1	0.57 ± 0.03	1.27 ± 0.09	15.14 ± 0.02	706 ± 26
NR-S3	0.60 ± 0.02	1.34 ± 0.10	14.15 ± 0.02	708 ± 25
NR-S5	0.63 ± 0.03	1.46 ± 0.02	14.23 ± 0.02	621 ± 43
NR-S10	0.60 ± 0.04	1.47 ± 0.16	12.96 ± 0.02	636 ± 15

3.4 Tensile Property

Figures 5(a) and 5(b) illustrate stress-strain curves of NR composites made by milling and latex approaches, respectively. Average values of modulus at 100% strains and 300% strains, stress at break and strain at break are summarised in Table 3. It can be seen from Figure 5(a) and (b) that addition of sepiolite clearly shifted the point of strain at which the stress upturn occurs towards lower strain. Such observation was more pronounced with increasing sepiolite loading in both mixing method. This finding implied that adding sepiolite to NR changed its stress-strain behavior by shortening the strain at the stress upturn take places. In addition, the region below the stress–strain curve was examined in order to evaluate the toughness of a material (Nun-anan et al., 2020). A greater area below the curve is associated with the higher toughness. Therefore, addition of sepiolite resulted in a greater toughness of rubber composites than the unfilled ones.

It was also found that the modulus at 100% and 300% strains were found to increase slightly with addition sepiolite (see Table 3). This might be due to the fact that incorporation of sepiolite reduced the flexibility of the rubber chains because of the diluting effect (Pasbakhsh et al., 2009), hardening of the composites, as previously suggested by the M_H-M_L values. Considering the stress at break of composites, the highest value of stress at break was achieved when the loading of sepiolite was 1 phr in both cases. The enhancement was about 20% and 34% over the neat NR vulcanizates for the sample from latex mixing and milling approach, respectively. The tensile at break or tensile strength of the composites was destroyed as the sepiolite loading was increased which was attributed to

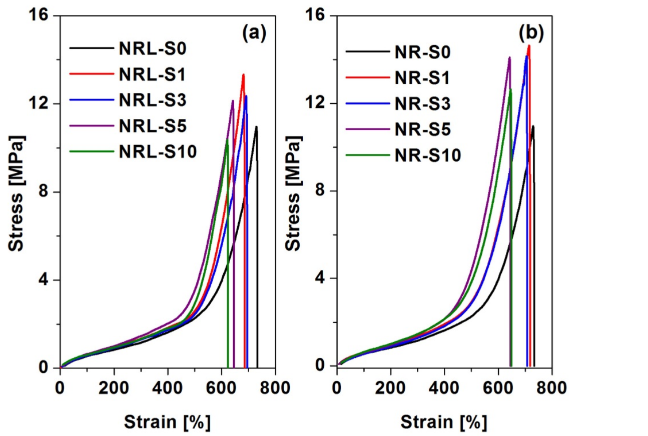

Figure 5. Stress-Strain Curves of NR Composites Made by (a) Latex and (b) Milling Approaches

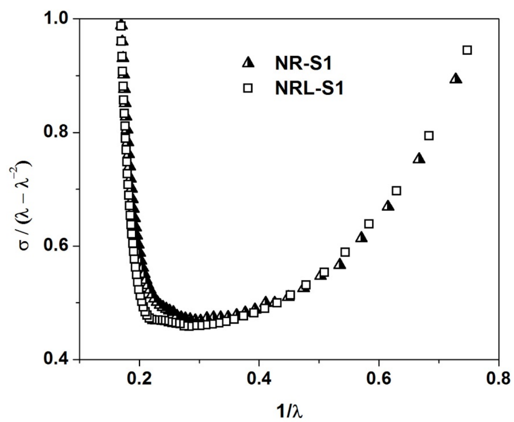

Figure 6. Mooney−Rivlin Plots of NR Composites at 1 phr Sepiolite Loading

lower filler-rubber interactions, probably resulting from filler aggregation with high loading. The milling sample yielded greater values of tensile strength than the sample made from latex approach, owing to improved interactions between the filler and the rubber matrix, as demonstrated by relaxation characteristic (see Figure 3) and swelling properties (see Figure 4). On the contrary, the NR composites' strain at break reduced (see elongation at break) with increased sepiolite concentration as a result of stiffening effect from sepiolite incorporation.

Based on the tensile properties, it is clearly spotted that the stress-strain response of NR vulcanizates changes with incorporation of sepiolite and the highest tensile strength was achieved at 1 phr sepiolite loading, in particular when the composite was prepared from milling approach method. To gain more details of reinforcement between these two alternative preparation methods, the stress-strain curves of NR containing 1 phr sepiolite clay were converted into Mooney-Rivlin plots and the result is shown in Figure 6. It can be found that at the $\sigma/\lambda - \lambda^{-2}$ of rubber composite shows a steep upturn at low $1/\lambda$ due to the strain-induced crystallization (Wu et al., 2013). The $\sigma/\lambda - \lambda^{-2}$ of composites obtained by milling approach show an upturns at a slight larger $1/\lambda$ (or smaller deformation) than that of the sample made from latex mixing approach, suggesting that the milling approach is more favourable than the latex approach. The strong interaction between rubber and filler accelerated the strain-induced crystallization process (Masa et al., 2016), leading to the enhancement of mechanical property.

3.5 Tear Strength

Figure 7 depicts the influence of mixing approaches on tear strength of NR composites with varied sepiolite contents. As can be seen, the maximum tear strength value was observed at 1 phr sepiolite content in both techniques of mixing. However, the greater improvement of tear strength at 1 phr sepiolite loading was seen from milling approach method. The tear strength was found to be at the same level as observed for tensile strength. This was almost certainly owing to the improved rubber-sepiolite interaction as mentioned earlier.

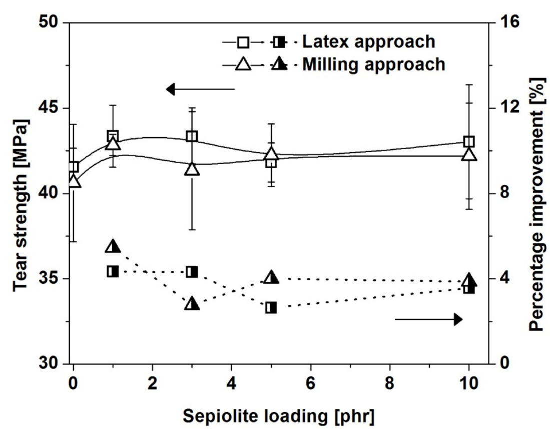

Figure 7. Tear Strength and Percentage of Improvement of NR Composites

3.6 Dynamic Mechanical Properties

To further confirm the interaction between sepiolite and rubber matrix, the rubber composites obtained from milling approach method containing various sepiolite contents were selected as representative and were evaluated by using RPA. The plot of G' and tan δ as a function of shear strain for NR composites with different sepiolite loadings is presented in Figures 8(a) and 8(b), respevtively. Focusing the composites containing sepiolite lower than 10 phr, the 1 phr sepiolite (symbol ◯) containing composite showed a higher G' values over other loadings entire range of shear strain amplitudes, indicating that a considerable reinforcement has occurred. In addition, the lowest value of damping characteristics or tan δ (see Figure

8(b)) was found in the composite filled with 1 phr sepiolite. The smaller value of tan δ indicates higher elastic behavior (Fröhlich et al., 2005). The composites with 1 phr sepiolite loading displayed the highest elastic behavior due to the greatest rubber-filler interaction that was in agreement well with the results shown in Figure 3 and Figure 5. This is the reason why at 1 phr sepiolite loading provide the highest tensile strength.

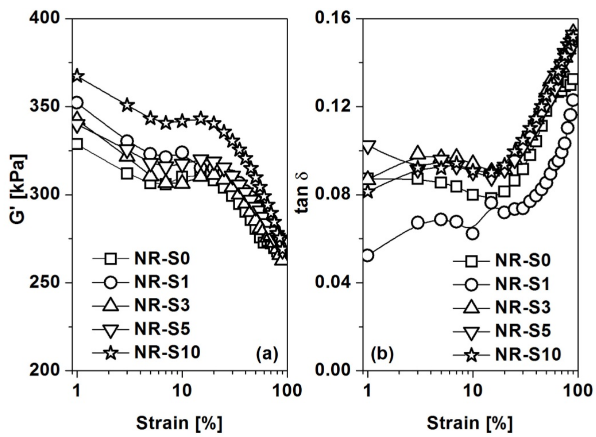

Figure 8. Plot of (a) Storage Modulus (G') and (b) Damping Characteristics (tan δ) Versus Strain of NR Composites

It is apparent that the composites obtained from the milling approach provide the greater properties improvement than those obtained by latex approach, probably due to the nature of sepiolite itself. In term of rubber composites fabrication, the simplicity of production with the shortened step of milling procedure would be more favorable than the latex mixing approach. The obtained result showed the opposed suggestion to the previous report (Di Credico et al., 2019) which was mainly due to the different type of sepiolite used in this study.

3.7 Morphological Property

To gain deeper understanding the dispersion of sepiolite in NR matrix, SEM analysis was performed, and the imagesare shown in Figures 9(a) and (b). In this study, the NR composites filled with 1 phr was selected due to the highest tensile strength was achieved at this loading level. The lighter dispersed phases are the sepiolite filler whereas the rubber matrix is visible in the darker background area. It was found that the mixing method has drastically affected the dispersion of sepiolite filler. A tubular shaped of sepiolite platelets (diameter of about 0.70-1.20 μm) with more homogeneous distribution was observed with the sample prepared by milling approach (Figure 9(b)), whereas a large aggregation of sepiolite as marked by circle (diameter of about 6.70-13.90 μm) was obtained from latex mixing (Figure 9(a)). Large aggregation of sepiolite filler in latex mixing method was due to the sepiolite cannot swell in water like other type of clay as previously mentioned (Locatelli et al., 2020). Such large aggregation destroyed adhesion between rubber and filler. This may cause a reduction of mechanical properties such as tensile at break and tear resistance of the samples prepared by latex mixing approach.

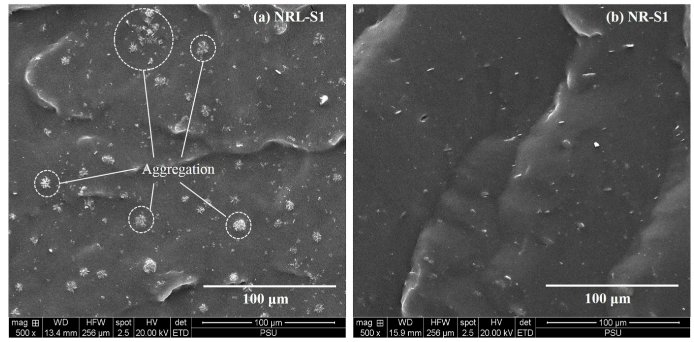

Figure 9. SEM Micrographs of NR Composites Filled Sepiolite (a) NRL-S1 and (b) NR-S1

4. CONCLUSION

In this study, two different mixing procedures were used to prepare NR composites with different sepiolite concentrations (1-10 phr), namely, milling approach and latex mixing approach. Influences of preparation methods and sepiolite loadings on processability and mechanical properties were assessed by the viscosity, curing behaviour, tensile and tearing properties, while the rubber-filler interaction was estimated by using stress relaxation, swelling, Mooney-Rivlin and rheological methods. The viscosity and mechanical properties were found to be influenced by the mixing method and filler content. Addition of 1 phr sepiolite loading yielded the highest viscosity, tensile strength and tear strength in both mixing approaches. The greater improvement of all properties test were seen from milling approach due to the better rubber-filler interaction as confirmed by stress relaxation, swelling, Mooney-Rivlin and rheological tests. The results clearly indicated that the milling approach method provides better mechanical performance than the latex mixing method.

5. ACKNOWLEDGEMENT

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