Epoxidierter Naturkautschuk –
Modifiziert mit Sepiolite
Kompositen

Epoxidized Natural Rubber/ Modified Sepiolite Composites

1. Introduction

One of the most important phenomena in material science is the reinforcement of rubber by rigid particles, such as carbon black, silica, clays, and calcium carbonate, to name a few [1-3]. It is a well-known fact that the addition of rigid filler particles, even in small amounts, to a rubber, strongly influences its mechanical behavior. Polymer matrices (e.g., thermosets, thermoplastics, elastomers) reinforced by nanofillers have attracted considerable attention in recent times due to their higher mechanical, thermal and physical properties [4-6].

Sepiolite is a microcrystalline hydrous magnesium silicate with \( \text{Si}_4 \text{Mg}_8 \text{O}_{30} (\text{OH}, \text{F})_4 \cdot 8\text{H}_2\text{O} \) as the unit cell formula [7], showing a microfibrous morphology with particle size in the range of 2 – 10 in length. Sepiolite has three main characteristics. Firstly, it has unique needle-like fibrous structure that loose rapidly when dispersed in water or other polar solvent, forming a monomer fiber or small fiber bundles. Secondly, it has a tunnel-like micro-pore channel structure (see Figure 1). Sepiolite shows an alternation of blocks and tunnels that grow in the direction of the fibre. Each structural block is composed of two tetrahedral silicite sheets sandwiching a central sheet of magnesium oxide-hydroxide. This structure provides infinite channels along the fibre axis with a cross section of about 1\( \times \)0.4 nm\(^2\). Finally, the strong adsorption capability of sepiolite, it has very high specific surface area. Such relatively high surface area is from the fibrous morphology and intra-crystalline tunnels of the sepiolite. Due to the great surface area and the existence of siloxane surface and silanol group of the sepiolite, the development of the new composites based on the sepiolite and modified natural rubber is a potant challenge.

Epoxidized natural rubber (ENR) is a derivative of natural rubber produced by chemical modification [9]. Commercial grade ENR comes in two grades, ENR 25 and ENR 50 where the unsaturated backbone has been replaced to an epoxide group at 25 mol% and 50 mol% respectively. Epoxy groups are randomly distributed along the polymer chain of ENR. It shows better oil resistance, damping and low gas permeability compared to natural rubber. The increment in polarity also increased the compatibility with polar rubbers and/or polar fillers.

The idea of this work is to use the sepiolite in ENR matrix. This is to gain the properties enhancement arising from the unique structures of sepiolite in association with the molecular sequence of ENR rubber. It is believe to give the composite with higher compatibility, physical and thermal stability to the composites. A further aim of this study was also carried out through the use of silane coupling agent where a reinforcement mechanism and possible interactions among two components are proposed. To the best of our knowledge, no attempts have been made so far to investigate the potential of sepiolite filled ENR composites. In this article, cure characteristics, mechanical properties, fractured surfaces and their corresponding rubber filler interaction have been investigated.

2. Experimental Details

2.1 Materials

The formulation used for compounding is presented in Table 1. Epoxidized natural rubber with 25% epoxy content (EP-OXYPRENE 25) was used as a matrix which was obtained from Guthrie Group Sdn. Bhd. Malaysia. Sepiolite was obtained from Hebei Dfi Minmet refractories.
Corporation. China. The main constituents of Sepiolite are SiO₂ (45 – 58%), Al₂O₃ (0.2 – 0.4%), MgO (21 – 28%), Fe₂O₃ (0.1 – 0.3%), CaO (33 – 35%), H₂O (9 – 15%) and loss on ignition with 27 – 28%. Silane coupling agent namely N-(3-(Trimethoxysilyl) propyl) ethylenediamine was obtained from Dow Corning Silicons Malaysia Sdn Bhd with the trade’s name of Dow Corning® Z-6032 Silane. The physical properties of the sepiolite were shown in Table 2. Sepiolite is in needle structure (see Figure 2) which indicates high reinforcing structure and suitable to use as reinforcing filler in rubber compounds. Zinc oxide, stearic acid and sulphur were supplied by Zarm & Chemical Supplier Sdn Bhd. N-isopropyl-N’-phenyl-p-phenylenediamine (IPPD), Tetramethylthiuram disulfide (TMTD) and N-cyclohexyl-2-benzothiazolesulphenamide (CBS) were obtained from LANXESS Corporation.

2.2 Preparation of composites
Simultaneous incorporation of ENR 25, silane coupling agent and the entire amount of additives were mixed on a laboratory-sized two-roll-mill (model XK-160) at ambient temperature. The total mixing time was kept to a minimum to avoid sticking of the rubber compound on the mill rolls. The compounds without the silane coupling agent were also prepared as reference. For the discussion here, the composites with and without silane coupling agent will be designated as US for the untreated and TS for the silane-treated sepiolites. The resulting compounds were later tested for its curing characteristics using a Monsanto Moving Die Rheometer (MDR 2000). The compounds were subsequently compression-molded using a stainless steel mould at 150°C with a pressure of 10 MPa using a laboratory hot-press based on respectively curing times.

2.3 Curing characteristics
Curing Characteristics such as torques, scorch time and cure time of sepiolite filled ENR composites was determined by using a Monsanto Moving Die Rheometer (model MDR 2000) according to ISO 3417:2008, at 150°C and test time was set for 30 minutes with range of the torque at 25 dNm.

2.4 Measurement of tensile properties
Dumbbell-shaped samples were cut from the moulded sheets according to ISO 37:2011. Tensile tests were performed at a cross-head speed of 500 mm/ min. Tensile tests were carried out with a universal tensile machine Instron 3366 to determine the tensile properties in terms of tensile strength, stress at 100% elongation (M100), stress at 300% elongation (M300) and elongation at break.

2.5 Measurement of tear behaviour
Tear strength of the vulcanizates were determined using Instron Universal Testing Machine according to ISO 34-1:2015 with cross-head speed of 100 mm/min and the two “trouser legs” were fixed to the jaws of the tensile machine. The tear strength was evaluated from the averages of the five repeated tests for each compound.

2.6 Assessment of rubber-filler interaction
Cure test pieces of dimension 30 x 5 x 2 mm³ were swollen in toluene until equilibrium, which took 72 h at room temperature. The samples were taken out from the liquid, the toluene was removed from the samples’ surface and the weight was determined. The samples were then dried in the oven at 60°C until the constant weights were obtained.

The Lorenz and Parks equation was used to study the rubber-filler interaction (Qf/Qg)

\[
Qf = \frac{\text{Swollen weight}}{\text{Dried weight}} \times \frac{\text{Original weight}}{\text{Formula weight (filled vulcanizate)}}
\]

(1)

Fig. 1: Schematic model representing the sepiolite structure [8].
Q is defined as grams of solvent per gram of rubber hydrocarbon, the subscripts \( f \) and \( g \) in equation refer to filled and gum vulcanizates, respectively. The higher the \( Q_f/Q_g \) values, the lower the rubber-filler interaction.

\[
Q_q = \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Original weight} \times \text{formula weight of gum vulcanizate}}
\]

(2)

\[
\text{Rubber-filler interaction} = \frac{Q_f}{Q_g}
\]

(3)

The fractured specimens were collected and the fractured surface was observed using Field Emission Scanning Electron Microscope (FESEM) ZEISS SUPRA 35VP. The fractured pieces were coated with layer of gold palladium with BIO-RAD Polaron Division SEM to eliminate electrostatic charge build-up during examination.

**3. Results and Discussion**

**3.1 Curing characteristics**

The curing characteristics of the US and TS filled ENR composites are listed in Table 1. Maximum torque (MH) is a measure of stiffness or shear modulus of the completely vulcanized test specimens at the curing temperature. The MH was found to increase consistently with increasing sepiolite loading. It is known that sepiolite used is a hard solid powder, thus, increasing of sepiolite loading gives rise to a reduction in the deformable rubber portion in the compounds, which is known as the dilution effect [10]. The addition of filler restricts the flow of rubber compounds resulting an increase in viscosity. According to Mittal et al. [11], the maximum torque (MH) was generally correlated with the durometer hardness and modulus. This also indicated that the incorporation of sepiolite increases the stiffness of the rubber. Similar observations were also made for torque difference (MH-ML), which is a measure of the difference between stiffness or shear modulus of the fully vulcanized and unvulcanized test specimens taken at the lower point of the vulcanizing curve. The MH-ML value is indirectly related to the physical and chemical crosslinking. Therefore, it can be concluded that the incorporation of sepiolite has contributed to the better interaction between sepiolite and ENR matrix. As for the TS, the MH and MH - ML of TS filled ENR composites were slightly higher than that of US filled ENR composites. This was attributed to the higher degree of rubber-filler interaction, arising from the silane coupling agent. As a result, the chemical linkages between the silane and the sepiolite together with the ENR-25 matrix are formed.

Scorch time (\( t_s \)) was an important parameter to the rubber processor, as a short \( t_s \) may lead to fasten the premature vulcanization. As can be seen in Table 3, the control sample had the highest \( t_s \) which was 0.91 min. Then, the \( t_s \) slowly decreased with increasing sepiolite loading. The decrement of \( t_s \) can be associated to the filler related parameters such as surface area, moisture content, and metal oxide content. In particular, the magnesium oxide contents in the sepiolite itself. As widely accepted that, the magnesium oxide is usually used as cure activator for the rubber compounds [12], it is able to act as a cation at the double bond to activate the crosslinking process. This probable reason also influenced the cure time (\( t_{c90} \)) of the composites. The optimum (\( t_{c90} \)) had reduced when sepiolite was added to the rubber compounds.

Another reasonable explanation might be due to the ENR itself. In general, ENR has a tendency to stick on the surface of mill. This makes the rubber remained a period of time on the mill during mixing. As sepiolite loading increases and consequently, generates more heat due to additional friction. It is interesting to be highlighted that the epoxidation plays an important role in the curing process of the compounds. Gelling and Morrison [13] have reported that the epoxide groups of ENR can also activate the adjoining double bonds. As a result, fasten cure rate is observed for ENR compounds.

At similar sepiolite loading, the presence of a silane coupling agent has decreased the \( t_s \) and \( t_{c90} \) of the ENR composites. This was due to the better dispersion of the TS in the ENR matrix as compared to untreated sepiolite. De et
al., [14] stated that the silane coupling agent generally favors the curing process of the rubber compounds. Well-dispersed filler would induce heat during the shearing force between rubber matrix and filler. As a result, the $t_s$ and $t_c$ eventually reduced.

**Mechanical properties**

The effect of sepiolite loading on the stress at 100% elongation ($M_{100}$) and at 300% elongation ($M_{300}$) of US and TS filled ENR composites are shown in Table 4. It can be seen that the $M_{100}$ and $M_{300}$ increased gradually with an increase of sepiolite loading. As more sepiolite particles get into the rubber, the elasticity of the rubber is reduced, resulting in more rigid, stiffer, and harder vulcanizates. Furthermore, the increment of tensile modulus with increasing sepiolite loading may be due to the effect of strain amplification, resulting from the fact that the sepiolite is in the rigid phase at tested temperature, which cannot be deformed.

As a consequence, the intrinsic strain of the polymer matrix is higher than the external strain yielding a strain independent contribution to the modulus which is well-known as hydrodynamic effect [15]. This result is corresponding to the maximum torque (MH) observed in the preceding section. Ishak et al. [16] mentioned that three factors affected the composites modulus were filler modulus, filler loading and aspect ratio. High stiffness composite required filler particle of high modulus and high aspect ratio and preferably at high filler loading.

As expected, the tensile modulus of TS filled ENR composites showed higher tensile modulus than untreated composites. This result is distinctly different for the stress at 300% elongation. Fu et al. [17] have noted that the three main factors affecting the composites’ modulus were filler modulus, filler loading, and filler aspect ratio. High stiffness composite requires filler particles of high modulus and high aspect ratio (the ratio of the major to the minor dimension of a particle), and preferably at high filler loading. Since all of those factors have been kept more or less constant in the present study, it can be inferred that the presence of coupling agents have led to a significant improvement in the filler–matrix interfacial bonding. This will obviously results in an increase in the efficiency of stress transfer from the matrix to the filler, which consequently gives rise to higher modulus.

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**Figure 3** shows tensile strength of US and TS filled ENR composites. It shows that the tensile strength increases with more sepiolite loading. The tensile strength however decreases after 5 phr and 2.5 phr of the US and TS filled composites respectively. The small particle size of sepiolite generates a large surface area that can interact with the rubber and diminish particle-to-particle distance. The
surface area is one of the important characteristics in reinforcing fillers because the particles with larger surface areas increase the properties of the polymer [18-19]. Stronger bonding occurs with more contact area available to react with the polymer matrix. Apart from that, the higher rubber-filler interaction of sepiolite and ENR matrix play an important role on the properties enhancement. This can again be attributed to interactions between the hydroxyl and siloxane groups available on the sepiolite and epoxide groups of ENR through hydrogen bonding and/or chemical bonding that occur after possible ring opening of the epoxy ring during mixing or compression moulding, as previously proposed by Manna et al. [20] and Rocha et al. [21]. A possible mechanism for bonding between the ENR and sepiolite is proposed in Figure 4. The enhancement of this interaction improves the wetting and adhesion of the polymer to the filler and consequently allows better stress transfer in the composites. Comparing the tensile strength of US and TS filled ENR composites; the TS provides significant improvement to the tensile strength of the composites. As can be seen from the result, it is obviously observed that only 2.5 phr of TS is adequate to give the highest tensile strength to the ENR composites. This shows that the treatment of 2.5 phr of sepiolite gives rise to shear strength at the filler interface and forms strong adhesion between treated sepiolite and rubber matrix. As a consequence, such shear stress was comparatively transferred from the matrix to filler, allowing the filler fully interacted to the ENR matrix and improved rubber-filler interaction at the event of lower amount sepiolite in comparison to that untreated one.

From the amount of silane’s point of view, it can be concluded that the use of 2 phr of silane with 2.5 phr of sepiolite is sufficient to give the composites greatest tensile strength. This shows that the efficiency of silane in coupling with sepiolite is significantly superior in comparison to other loadings. When silane is used, there are two reaction mechanisms competitively taking place during compound mixing or compression moulding. These mechanisms are all temperature dependent: (1) the silane-to-sepio-lite or silanization/hydrophobation reaction and (2) the silane-to-rubber or coupling reaction as shown in Figure 5. The reduction in tensile strength with loading beyond 5 phr of sepiolite loading is simply due to the dilution effect [10]. When more sepiolite particles are integrated into the ENR matrix, the sepiolite particles tend to interact with each other, known as filler–filler interaction or agglomeration. Nielsen and Landel [22] and Jordhamo et al., [23] reported that the filler-polymer interphase discontinuity is created in the particulate filled composites due to poor stress transfer which generates weak structure. Agglomeration of the filler particles and de-wetting of the polymer at the interphase aggravate the situation by creating stress concentration points which account for the weakness in the composite.

The elongation at break of the US and TS filled ENR composites is shown in Figure 6. Increasing sepiolite loading results in an increase in the flexibility of ENR composites. The larger surface area and the softer characteristic of sepiolite loaded material lead to better interfacial interactions between sepiolite and ENR. The homogenous dispersion of sepiolite inside the ENR is responsible for the higher ductility of the composites. It is interesting to highlight that the elongation at break of the composites is improved by the addition of silane coupling agent. This is clearly attributed to the improved interfacial interaction between sepiolite and ENR matrix. However, with the presence of highly contained sepiolite in the ENR composites, it resulted in decrease of the elongation at break. The flexibility of the composites decreases due the agglomeration occurs, creating the partially separated micro spaces between the filler and the matrix and finally leading to increase the ruptures. When considering the amount of sepiolite use, it was found that the decreasing trend of TS filled ENR composites was found earlier than those...
of US counterparts. This is clearly due to the less efficiency of silane coupling agent at higher filler loading as discussed earlier in term of tensile strength.

The tear strength of US and TS filled ENR composites is shown in Figure 7. It can be seen that the addition of sepiolite had successfully increased the tear strength. The particle size of the sepiolite is small enough to gain higher contact area to the ENR matrix, which results in a better interaction between the ENR matrix and the sepiolite. In addition to that, strong rubber-filler interaction obtained from ENR and sepiolite is also responsible to the higher energy required to cause the tearing failure. Therefore, the tear strength is improved upon the use of sepiolite. The decreasing trend of tear strength when the sepiolite is over 5 phr is simply due to the agglomeration of sepolite which caused to poorer rubber-filler interaction. The increment of tear strength of treated sepiolite filled ENR in comparison to the untreated one is due to the formation of hydrogen bonding and improvement in the interfacial interactions between sepiolite and ENR matrix. This enhancement in the tear strength is corresponding to the tear strength and elongation at break observed in the previous section.

3.3 Rubber-filler interaction

The reinforcement of a rubber by filler was associated with a strong interaction between the filler surface and the rubber [24]. Thus, swelling test was important testing for the rubber processor to determine the rubber-filler interaction of the rubber composites. As the rubber composites were immersed in toluene, toluene was penetrated into the free volume between crosslink causing swelling of rubber composites. The weight of test specimen was keep increasing up to a maximum point in which the space between crosslink points had been fully filled by toluene. Figure 9 shows the rubber-filler interaction of US and TS filled ENR composites. It is well accepted that the lower the $Q_f/Q_g$ value, the higher the rubber-filler interaction. Increasing sepiolite loading resulted in a strong interaction between sepiolite and the ENR matrix. From the $Q_f/Q_g$ values, it is evidently shown that it is correspondence to the tensile strength, elongation at break and tear strength observed in the previous study, indicating that strong rubber-filler interaction is observed at the certain amount of sepiolite and after using the silane coupling agent. The higher rubber-filler interaction observed is simply because of high surface activity and, consequently, high affinity of sepiolite to interact to rubber as proposed in Figures 4 and 5.

3.4 Tensile and tear fractured surfaces

Figure 9 illustrates the SEM micrographs of tensile fractured surfaces of US and TS filled ENR composites at 100x magnification. Figure 9A shows the fractured surfaces of gum vulcanizate. Smooth and soft surfaces were observed because no rigid filler was incorporated into the matrix. Figures 9B, 9C, and 9D show the fractured surfaces of US filled ENR composites at 2.5, 5, and 10 phr of sepiolite respectively. The roughness and frequency of tearing in US filled ENR composites were visible when sepiolite was added into the matrix. This indicates that more energy is needed to break the sample. A slight increment in the matrix’s roughness with increased levels of US is in agreement with the tensile results observed. However, when US is incorporated beyond 5 phr, the US tends to agglomerate, due to the strong filler–filler interaction as well as the detachment of sepiolite. This is shown in Figure 9D, indicating that less energy is required to cause failure in the materials. The high filler–filler interaction of sepiolite in ENR matrix causes a reduction of tensile strength. The tensile fractured surfaces of the TS filled ENR composites are also illustrated in Figures 9E, 9F and 9G. With the addition of TS in concentrations up to 2.5 phr, an augmentation in surface roughness occurs as well as compared to the fractured surface with loading at 5 phr of US (see Figure 9C) and materials with gum vulcanizate (see Figure 9A), which shows less tearing lines leading to
lower ultimate tensile value. Better homogeneity in TS filled ENR composites indicates a coherence of the TS and the ENR phases. The uniform dispersion of TS in the ENR matrix alters the crack path, which leads to resistance from crack propagation and hence results in higher tensile strengths and improved mechanical properties.

Figure 10 displays the tear fractured surfaces of US and TS filled ENR composites at 100x magnification. With the addition of US in concentrations up to 5 phr (see Figures 10A, 10B and 10C), the failure surfaces show feature of well-developed interfacial interaction and low pull-out of US on the fracture surface was seen. An augmentation in surface roughness and a homogeneous pattern are more pronounced for the TS filled ENR composites (see Figures 10E, 10F and 10G), indicating a coherence of the TS particles and the ENR phases. However, for the 10.0 phr of US and TS were added (see Figures 10D and 10G), it can be seen that there were a lot of voids on the fracture surface. This showed that it was easily pulled out sepiolite when amount of the filler was exceed optimum amount which cause filler agglomeration happened.

4. Conclusions

The following conclusion can be presented:

1. SEM image of sepiolite particles clearly showed that sepiolite particles are in needle structure, indicating that high contact area and reinforcement can be attained by incorporating sepiolite.

2. The addition of sepiolite resulted in faster scorch (ts) and curing times (tc90) where MH increased consistently with the increase of sepiolite loading due to the highly restricted molecular motion of macromolecules when sepiolite was incorporated.

3. The tensile strength of sepiolites filled ENR composites shown optimum value at 5 phr and 2.5 phr for the US and TS respectively. SEM images exhibited more surface roughness for the composites at 5 phr sepiolite loading. As a result, higher energy is needed to cause a failure to the sample.

4. The rubber-filler interaction between the sepiolite and ENR matrix was enhanced by the addition of silane coupling agent where two major factors are concerned i.e., the hydrogen bonding between the hydroxyl available on the sepiolite and epoxide groups of ENR through and/or chemical bonding that occur after possible ring opening of the epoxy ring either during mixing or compression molding.

![Fig. 9: Tensile fractured surfaces obtained from SEM of untreated (US) and silane-treated (TS) sepiolites filled ENR composites at 100x magnification: Control (A), US2.5 (B), US5 (C), US10 (D), TS2.5 (E), TS5 (F) and TS10 (G).](image-url)
5. References


Fig. 10: Tear fractured surfaces obtained from SEM of untreated (US) and silane-treated (TS) sepilotes filled ENR composites at 100x magnification: Control (A), US2.5 (B), US5 (C), US10 (D), TS2.5 (E), TS5 (F) and TS10 (G).