Effect of vulcanization temperature on curing characteristic, physical and mechanical properties of natural rubber/palygorskite composites

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Abstract. This paper aims to determine the optimum vulcanization temperature on curing characteristic, mechanical and physical properties of natural rubber/palygorskite composites. Three variations of vulcanization temperature (140, 150 and 160°C) were conducted on the samples. Cation-exchanged method used to treat the palygorskite. Rheological measurements and mechanical testing (tear, tensile and fatigue life) were conducted on the composites sample. Scanning electron microscopy (SEM) was used to reveal the dispersion of palygorskite in NR matrix. It was found that the scorch and cure time of NR/Palygorskite decrease with increasing of vulcanization temperature. The tensile strength and fatigue life was optimum at 140°C and slightly decreased with the increasing of vulcanization temperature. The SEM micrograph revealed the strength and weakness in the system. It can be concluded that the optimum properties of NR/Palygorskite composites were at 140°C of vulcanization temperature and most of the mechanical and physical properties were slightly decreased with the increasing of vulcanization temperature.

1. Introduction

Natural rubber (NR) is a unique biomass extracted from a tropical plant (cis-1,4-polyisoprene) and composed of carbon and hydrogen atoms only. The natural property, renewability which making it carbon neural, environmental friendly and biodegradable, has boost its demand around the world [1]. Nowadays, usage of natural rubber alone in rubber product manufacturing is not practical and economic anymore. Hence, the introduction of filler into the rubber compound has increased its mechanical properties while reducing manufacturing cost. One of the earliest and common nanofiller is carbon black that is relatively inert and stable materials [2]. However, with its current high price and its adverse effect toward environmental and human body, many researchers encouraged to find an ecofriendly alternative carbon black. Clay is identified as one of a good alternative for carbon black and many studies have been carried out to improve the performance of clay in a nanocomposite. Structurally, clays have different size and mineralogy compared to other fine-grained soils, which is the behavior, is more to plastic when contain water and become harder when dried it [3]. Palygorskite is a clay mineral type and a crystalline hydrated magnesium aluminium silicate mineral with needle
shape result in unique colloidal properties and give high surface area and porosity particles when thermally activated [4-5]. The hydrophilic behavior of the palygorskite is incompatible and has a poor dispersion in the hydrophobic polymer phase [6]. Therefore, the idea is the organoclay surface need to undergo treatment such as cation exchange surfactant to improve the rubber-filler interaction when the polarity of pure natural clay is modified [7]. Zheng et al., (2004) [8] use trimethyloctadecylamine as cation exchange agent to treat the organoclay and compound it with the rubber matrix at 175°C while Rath et al., (2012) [9], use palygorskite as filler and compared the properties of the treated and untreated nanocomposites at 120°C.

In the present study, the curing characteristic, physical and mechanical properties of the cation treated palygorskite of the natural rubber composite were investigated under different vulcanization temperature (140, 150 and 160°C). The properties of the NR/cation treated palygorskite composites were analyzed and compared with NR/untreated palygorskite composites. Then, the dispersion of the fillers in the rubber matrix was characterized using Field Emission Scanning Electron Microscopy (FESEM) and performed on the fracture surface of the composite.

2. Experimental

2.1. Material

Natural rubber SMR 20 (cis-polyisoprene- the glass transition is -70°C and density of 0.91 g/mL at room temperature), High Ammonia (HA) latex (60% total solid content and specific gravity is 0.95-0.96), zinc oxide, stearic acid, tetramethylthiuram disulphide (TMTD), zinc diethyldithiocarbamate (ZDEC) and sulphur was kindly provided by Zarm & Chemical Supplier Sdn Bhd. While antioxidant, anchoid, octdecylamine, potassium hydroxide (KOH) and calcium chloride was supplied by Sigma Aldrich (M) Sdn Bhd and used as received.

2.2. Methodology

2.2.1. Preparation of Palygorskite Clay.

20 g of clay was added into the 1000mL hot water (80°C) and stirred for 1h (300rpm). Later, mixed hot solution with mixture of 7.5 g of dedocyltriethylamine and 4.2 mL HCl in 500 mL of water and stirred at rpm 400 for another 1 h (80°C). The precipitate filtered and washed with hot distilled water until reached pH7 and dried at 60°C for 36 h before used. After that, the 6 pphr palygorskite clay was mixed with 3 pphr 10% KOH, 5 pphr anchoid and water and stirred for 2 h. Ball mill technique was applied to the dispersion mixture for 2 days to produce aqueous suspension.
2.2.2. Preparation of Master Batch.

200g of natural rubber latex was heated until it reached about 45 to 50°C and poured into the warm latex 20 g of modified palygorskite clay by cation ions exchanged and continuously stirred for 15 minutes at 60°C. Then, 10% of CaCl solution was used to co-coagulate the latex compound and washed with excess distilled water until it reached pH 7. The coagulated latex was cut into small pieces and dried in an oven at 100°C for 2 h.

2.2.3. Mixing and Rubber Compounding

Two rubber compounds with different type of filler in the same amount of loading (6pphr) were prepared in semi efficient vulcanization (SEV) system based on summarized formulation (Table 1). After mixing, the compounds undergone compression moulding in order to produce sheet and button form of sample for testing with three different vulcanization temperatures.

| Ingredients          | Gum compound | Untreated Palygorskite Compound | Treated Palygorskite Compound |
|----------------------|--------------|--------------------------------|------------------------------|
| NR rubber            | 100          | 100                            | 100                          |
| Stearic acid         | 2            | 2                              | 2                            |
| ZnO                  | 5            | 5                              | 5                            |
| ZDEC                 | 0.5          | 0.5                            | 0.5                          |
| TMTD                 | 1.5          | 1.5                            | 1.5                          |
| Antioxidant          | 2            | 2                              | 2                            |
| Sulphur              | 1.5          | 1.5                            | 1.5                          |
| Palygorskite         | -            | 6                              | 6                            |

2.2.4. Characterization

Curing characteristics of the rubber compounds were carried out using Monsanto rheometer (140, 150 and 160°C) for 30 min at 25 dNm range of the torque. Tensile test was carried out according to ASTM D412 while tear followed ASTM D624. Fatigue life test was carried out using a Monsanto fatigue to failure tester (FTFT) with dumbbell samples BS type E subjected to cyclic strain 100rpm. The fatigue life was calculated using Japanese Industrial Standard (JIS) average. Hardness test was performed according to ASTM D2240 at room temperature. Swelling test was performed by soaking the sample (30 x 5 x 2mm) in toluene until equilibrium for 72 h at room temperature. The rubber filler interaction, Qf/Qg was calculated using Lorenz and Parks equation [10]. Compression set test is measured the differences of original thickness and thickness after recovery expressed in percentage. FE-SEM was carried out using Zeiss Supra 35V SEM instrument. The samples from the surfaces of tensile testing were coated with a thin layer of gold palladium using a SEM sputter coater to prevent the occurrence of superfluous.
3. Result and Discussion

3.1. Curing Characteristic

The curing characteristics of unfilled and filled compound with untreated palygorskite and cation treated palygorskite obtained from rheometer graph are presented in Table 2. The results show the different cure characteristics due to different type of filler added into rubber composites.

| Compound          | Temperature (°C) | M_L (dNm) | M_H (dNm) | t_1/2 (min) | t_90 (min) | Cure Index (min⁻¹) |
|-------------------|-----------------|-----------|-----------|-------------|------------|-------------------|
| Unfilled          | 140             | 0.14      | 6.32      | 3.75        | 7.14       | 29.5              |
|                   | 150             | 0.15      | 6.03      | 2.04        | 4.43       | 41.84             |
|                   | 160             | 0.11      | 5.65      | 1.28        | 1.99       | 140.85            |
| Untreated palygorskite | 140           | 0.30      | 5.47      | 4.38        | 7.40       | 33.11             |
|                   | 150             | 0.22      | 5.21      | 2.40        | 3.59       | 84.03             |
|                   | 160             | 0.21      | 4.89      | 1.45        | 2.02       | 175.44            |
| Cation treated palygorskite | 140          | 0.27      | 5.53      | 2.40        | 3.81       | 70.92             |
|                   | 150             | 0.25      | 5.34      | 1.50        | 2.17       | 149.25            |
|                   | 160             | 0.23      | 5.11      | 1.06        | 1.51       | 222.22            |

Higher value of minimum torque (M_L) at temperature 140°C for all three compounds was recorded and decreasing with increasing of vulcanization temperature. Theoretically, when curing temperature arise, molecular chain has a tendency to absorbed the heat energy which produced during preheat stage and allowed the molecules to have higher mobility which led to lowering the rubber viscosity. Apart from that, the surface treatment also affected the minimum torque, M_L of rubber compound due to the present of hydroxyl group on the surface of untreated palygorskite tends to form agglomeration and led to increase in M_L of the compound [11]. The value maximum torque (M_H) of cation treated palygorskite/NR composites is higher compared to palygorskite/NR composites due to the formation of hydrogen bonding between amino group in the cation exchange agent (octadecylamine) and hydroxyl groups in the organoclay [12]. The presence of treated palygorskite reduced the scorch time and cure time (t_90) which accelerated the vulcanization prosess. This phenomenon is due to the cation exchange treatment which improve the compatibility of rubber-filler interaction by reduced silanol groups of palygorskite and able to homogenously distributed in the rubber matrix that leads the formation of crosslinking also increase the rate of vulcanization. In contrast, untreated palygorskite is incompatible with rubber matrices and have a high tendency to agglomerate, hence increase the scorch time when more torque needed to shear the agglomeration of filler in the matrix. The surface of hydrogen bond that absorbed basic accelerators and deactivate them is resulting in reducing rate of vulcanization process [13]. Cation treated palygorskite has the highest cure rate index at increased trend for 140, 150 and 160°C respectively and higher compare to the untreated palygorskite
composite. Hence from the viewpoint of cure rate index, it has obeyed the theory like aforementioned in cure time. Where the cation treated palygorskite has reduced silanol groups of palygorskite and hence increases the rate of vulcanization, while for untreated palygorskite composites the acidic hydroxyl, siloxane groups has absorbed the basic accelerators causing it to slow down the degree of vulcanization. The low viscosity of the component tends to form a continuous phase [14].

3.2. Tensile Properties
Figure 1 shows tensile strength and elongation at break of unfilled NR, NR/untreated palygorskite and NR/cation treated palygorskite composite at different vulcanization temperatures. The results show for treated palygorskite composite a decreasing trend while for unfilled NR and untreated palygorskite showed a quite same trend for 3 vulcanization temperatures. It can assume that, the high vulcanization temperature has deteriorated the mechanical properties of the rubber composite. Besides that, overall tensile strength of cation treated palygorskite is higher than untreated palygorskite rubber composite. This is because of the surface treatment was enhance the mechanical properties of the rubber composite by increase it compatibility and interfacial bonding with the rubber matrix at the same time causing the elongation at break become limited. This treatment lower down the surface energy and improves the wetting characteristic of the rubber matrix, and resulting in larger interlayer spacing. Additionally, the cation can provide functional group that can initiate the polymerization of monomers to improve the adhesion between the palygorskite and rubber matrix and the filler-rubber interaction and its mechanical properties.

![Figure 1](image1.png)

**Figure 1.** The effect of unfilled NR, NR/Cation Treated and Untreated Palygorskite/NR composite at different vulcanization temperature on (a) tensile strength (b) elongation at break.

The modulus showed higher value for treated palygorskite compared to untreated palygorskite in increasing trend with increasing temperature. According to Olad (2011) [15], when added rigid filler to the soft polymer matrix, it will carry the major ration of applied load to the polymer matrix under stress condition, if the interfacial interaction between the filler and matrix is adequate [16]. The good
compatibility and the present of amine group on the surface of palygorskite has led to better interaction of filler-matrix phase, resulting a higher stiffness. On the contrary untreated filler composite will have high tendency to slippage since the compound just need to break the crosslinkage, physical entanglement and matrix-matrix interaction compared to the treated palygorskite. The modulus properties reduced might be due to deterioration of the rubber chains when increasing the vulcanization temperature, resulting a phenomenon called chain scissoring.

![Figure 2](image2.png)

**Figure 2.** Tensile modulus of rubber composites at different vulcanization temperature, (a) Unfilled NR, (b) NR/ Cation Treated Palygorskite and (c) NR/untreated palygorskite

### 3.3. Tear Properties

Figure 3 shows the highest tear strength recorded at 150°C for NR/cation treated palygorskite. This could be explained by the ability of the crosslinks and rubber chains to crystalline upon the applied of tearing force which that turns the amorphous rubber into a semi crystalline material. This crystallite is highly oriented and act like filler crosslinks. Furthermore, due to the local reinforcement of strain-induced crystallites at highly strained crack tip, the crack growth resistance in natural rubber increased, resulting higher tear strength [17].

![Figure 3](image3.png)

**Figure 3.** Tear strength of unfilled NR, NR/cation treated palygorskite, and NR/palygorskite composites at different vulcanization temperature
Based on the result, unfilled NR shows the lowest tear strength at 140°C followed by 150°C and 160°C respectively. It is because of low resistance in the gum rubber that prevent the rubber from resisting the slippage that occurred due to the stress concentration compared to the composite filled with nano filler which is able to reinforce the compound and form a surrounding layer of immobilized polymer.

3.4. Fatigue Life Properties
Figure 4 illustrates that fatigue life increases from 140°C (92.39 kcycles) to 150°C (100.64 kcycles), and decreases at temperature 160°C (86.17 kcycles). The decreasing of fatigue life properties from 150 to 160°C is due to the elevated temperature as stated by Gupta (2004) [18], where it was proven that higher curing temperature is not only decreased the curing time but also decreased the properties of the static strength and fatigue life. The fatigue to failure process involves initiation of microcracks and propagation of microscales and naturally occurring flaws due to combination of factors such as fillers, contaminants or void in the matrix, non-homogenous dispersed compound ingredients and surface flaws [19-20]. Besides, the main reason that affects fatigue life properties is crosslink density, which undergoes the reversion with increasing the vulcanization temperature. These crosslinks comprise two general types, which are monosulphide and disulphide crosslinks, and polysulphide crosslinks, which impart various properties to the rubber matrix. Polysulphide crosslink chain may break at higher vulcanization temperature and formed monosulphide crosslink chain.

Figure 4. Fatigue life of Unfilled NR, NR/untreated Palygorskite and NR/Cation Treated Palygorskite composite at different vulcanization temperature

Figure 5 shows the rubber-filler interaction, \( Q_f/Q_g \) values on different composites at different vulcanization temperature. The higher values of the \( Q_f/Q_g \) indicate the lower the rubber-filler interaction.
The treated filler has better filler interaction than untreated filler composite due to the surface modification that replaced by some quartenary ammonium compound with a long hydrophobic tail enhances the compatibility between the filler and matrix. This method changes the behaviour of the filler from hydrophilic filler to hydrophobic filler.

3.5. Hardness Properties

Figure 6 shows at 140°C, unfilled NR shows the highest hardness compared to NR/ cation treated palygorskite and NR/ palygorskite, which reflects the lowest elongation at break 840% at the same temperature. Such result indicates that, at 140°C, the rubber composites achieved an optimum curing characteristic, where the results obtained was corresponded with one another. Besides temperature 140°C, cation treated palygorskite shows the highest hardness compared to the other two compounds. This is due to lower surface energy and larger interlayer spacing of cation treated palygorskite, which depends on presence of hydrophobic groups of surfactants, which enhanced the intercalate ability of palygorskite while improving physical and mechanical properties [20]. Elevated cure temperature produces a network with lower degree of crosslink density (thermal breakdown of monosulfide crosslink) and an increase in the extent of sulfidic main chain modification cause a reduction in modulus [21].
3.6. Swelling Properties

Figure 7 shows the crosslink density of the compounds at different vulcanization temperature. The crosslink density of the NR/ cation treated palygorskite composite samples was higher than NR/ palygorskite and unfilled NR composite at the same vulcanization temperature. This is because of there are many crosslinks produced in the rubber matrix when rubber matrices are swelled in toluene. The crosslink density showed a decreasing trend from 140 to 160°C. At vulcanization temperature of 140°C, highest values of crosslink density recorded which were $6.34 \times 10^{-5}$ g/mol, $6.10 \times 10^{-5}$ g/mol and $6.88 \times 10^{-5}$ g/mol of the crosslink density for unfilled NR, NR/ untreated palygorskite and cation NR/ cation treated palygorskite composites respectively. Vulcanization temperature has significant effect on crosslink structure. Optimum properties are obtained when curing is done at the lowest possible temperature. However, to increase productivity, higher temperatures are frequently used.

![Figure 7. Crosslink density of the unfilled NR, NR/ untreated Palygorskite and NR/ Cation Treated Palygorskite composites at different vulcanization temperatures](image)

3.7. Field Emission Scanning of Electron Microscope (FESEM)

Figure 8 shows the micrograph of tensile fracture surface of all three composite. Figure 8(a) shows the image surface of natural rubber composite without filler. It clearly shows that the surface has a small dot due to presence of additive like antioxidant, vulcanizing agent etc, which indicates that all ingredients homogenously distributed in the rubber matrices. Furthermore, Figure 8(b) shows the image of NR/palygorskite composite. The presence of needle shapes fillers shows homogenously dispersed and adhered perfectly to the matrix. This might be due to the good processing parameter and latex compounding method that allowed the palygorskite to reinforce the adjacent matrix and enhanced physical and mechanical properties. In contrast, Figure 8(c) shows rougher surface of NR/ cation treated palygorskite composite compare to Figure 8(a) and (b). It obviously shows the successfully effect of surface modification to improve the interaction with the presence of many tear lines on the fracture surface. It was proven that the composite needed a high energy to break the chain and it was designated the effect of better interaction between chains and has higher strength properties.
Furthermore, the uniform tear lines in one direction presence on the NR/ cation treated palygorskite composite shows that the modified palygorskite undergo isotropic failure.

![Figure 8](image-url)

**Figure 8.** FESEM micrograph at 500 X magnification of (a) unfilled NR, 5000 X magnification (b)NR/ untreated palygorskite composite and (c) NR/ cation treated palygorskite composite

4. Conclusion

The result of NR/ cation treated palygorskite composite cured at 140°C demonstrated the optimum properties among others. These are corresponding with the expected outcome where the cation treated palygorskite have enhanced the compatibility and homogeneity in the rubber matrix. The improvement caused by the mobility of the rubber chains constrained. Furthermore, the investigation on morphology of cation treated palygorskite give strong evident and positive impact of the cation treated palygorskite to mechanical properties of rubber composite. Therefore, surface modification which using to modified surface of palygorskite clay was enhanced the mechanical properties of the composites. This method was improved filler – matrix interfacial interaction hence increases the mechanical properties.

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