Utilization of Different Curing Systems and Natural Zeolite as Filler and Absorbent for Natural Rubber/Nitrile Rubber Blend

Tutchawan Siriyong¹ and Wirunya Keawwattana², *

ABSTRACT

The effects of the vulcanization system and natural zeolite loading on the mechanical properties, thermal and oil resistances of a natural rubber (NR) and acrylonitrile-butadiene rubber, also known as nitrile rubber (NBR) blend in the ratio of 20:80 was studied. The vulcanization systems used in this study were conventional vulcanization (CV), efficient vulcanization (EV) and peroxide vulcanization. The amount of natural zeolite filling added was varied from 0 to 60 parts per hundred (phr). The vulcanizates cured with the CV system gave the greatest tensile properties; however, they showed the lowest thermal and oil resistance. Greater thermal and oil resistance was observed in the vulcanizates cured with dicumyl peroxide (DCP). Moreover, the tensile strength and 100% modulus of the vulcanizates increased with an increase in the natural zeolite loading, while there was no substantial change in the compression set. The oil resistance in both diesel and biodiesel blends of the vulcanizates was significantly improved with the natural zeolite content. The vulcanizates containing 40 phr of natural zeolite cured with peroxide showed the lowest swelling and the highest relative tensile strength in oil (diesel and biodiesel). As well as the oil resistance, the optimum mechanical properties were observed in the vulcanizates filled with 40 phr of natural zeolite and cured with peroxide.

Keywords: natural rubber, nitrile rubber, vulcanization systems, natural zeolite, oil resistance

INTRODUCTION

Thailand’s use of petroleum oil is the cause of urgent economic and environmental problems. The only real, long-term solution for this issue is to reduce the dependency on petroleum oil. Material compatibility is a major concern whenever the fuel composition is changed in the fuel system. Hence, changing from diesel to biodiesel and the introduction of alternative fuels often create many problems with the rubber engine parts in the fuel system that are in contact with the biodiesel. However, this is not a problem with B20 blends and below (Joshi and Pegg, 2007).

Throughout the history of fuels development there has been a parallel development of the rubber engine parts used with them. Acrylonitrile-butadiene rubber, also known as nitril rubber (NBR) is known for its superior properties of oil, ozone and chemical resistance. It has been commercially available and exploited in a variety of manufacturing products such as tires, bulb seals, o-rings, gaskets, bumpers and fenders. On the other hand, natural rubber (NR) has excellent mechanical properties and heat build-up, but has poor oil resistance. Hence, it was chosen to be blended with NBR in this experiment to develop new materials possessing...
the best properties from each component and with a low cost of investment. This need in turn requires the ability to predict swelling when placed in a liquid. Koning claimed that melt blends have been employed industrially, but a certain level of blend compatibility was achieved despite great efforts in blend improvements via technical and mechanical tunings (Koning et al., 1998). Many researchers studied the properties of the blend of NR/NBR as a function of blending conditions and blend ratios and found that blend morphology is a significant factor which has an impact on the chemical and mechanical properties (Tinker and Jones, 1998; Hexiang et al., 2005; Moonprasith et al., 2005). Sirisinha and co-workers suggested that the relative tensile strength is an indicator of oil resistance, which was in agreement with research on the blend morphology, indicating that the oil resistance in a 20/80 NR/NBR blend strongly depends on the phase morphology of the blend; the smaller the size of the NR dispersed phase, the higher the oil resistance of the blend (Sirisinha et al., 2003b).

The raw rubber-elastic product must be converted into the final product by means of a vulcanization process. Vulcanization is the process which links the macromolecular chains with each other at their reactive sites. Several vulcanization systems are used in the rubber industry, and each cure system has its own merits. Selection of a cure system is based upon several considerations such as the functional performance desired of the vulcanizate or article and the processing and safety risks of the curing process. The most frequently used systems involve conventional vulcanization (CV) which features a high sulfur/accelerator ratio, resulting in highly flexible polysulfidic networks with good mechanical properties. However, the ageing resistance is very poor due to the temperature susceptibility of polysulfidic linkages. Efficient vulcanization (EV) which features a low sulfur/accelerator ratio shows good heat stability and oxidation resistance, but has a poor resistance to fatigue because of the presence of predominantly monosulfidic and disulfidic crosslinks. The use of dicumyl peroxides (DCP) as the vulcanizing agent generates C-C bonds between the rubber chains. They exhibit low set characteristics, low stress relaxation and good ageing resistance. The peroxide system exhibits the lowest toluene uptake due to the combined effect of rigidity of C-C bonds (Soney et al., 1999). However, vulcanization generally not only restricts the mechanical properties but also the degree of swelling of polymers. The density of chain entanglement and chain ends, crosslink density, compatibility of both the polymer and liquid type and the amount of filler in addition to the viscosity of the penetrant liquid and the functionality of the crosslink are determinants of the molecular transport of organic solvent in rubber vulcanizates (Jianfen and Salovey, 2001). The transport of solvent through polymers is affected by the polymer structure, crosslink density, mode of crosslink, presence of fillers, penetrant size and temperature (Korkuna et al., 2005).

Although fillers such as CaCO₃, talcum, clay and rice husk ash have been used as rubber-filler, not much work was found in the literature related to the use of natural zeolite as filler. Natural zeolites have been utilized in ion-exchange and sorption processes since their discovery two centuries ago. The breakthrough on natural and synthesized zeolites thirty years ago has had a great impact on adsorption process technology, and perhaps more importantly, on catalytic process technology throughout the petroleum and chemical industries. Over the years, the utilization of zeolite has not only saved money, but also provided a new flexibility in the design of products and processes. The following properties make zeolite attractive as a catalyst, absorbent and ion-exchanger: a well-defined crystalline structure, high internal surface area, uniform pores with one or more discrete sizes, good thermal stability, highly acidic sites when used as an ion-exchanger with protons and the ability to absorb and concentrate hydrocarbon (Dixit and Prasada-Rao, 1999). However, it
was scarcely utilized in the rubber industry. Thus, it is of interest to study the influence of vulcanization systems and natural zeolite as filler on the mechanical properties of the vulcanizates, especially on the oil resistance (to both diesel and biodiesel) to evaluate natural zeolite as an alternative filler in oil resistant products.

**MATERIALS AND METHODS**

**Materials**

Natural rubber (NR) was purchased from S.M.P Rubber, Thailand. Acrylonitrile rubber (NBR) having 33% acrylonitrile content was supplied by Multi-Chemical & Engineering Co., Ltd, Thailand. Natural zeolite as a filler was supplied from the Kasetscenter, Thailand. Dicumyl peroxide (DCP), 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), zinc oxide (ZnO) and stearic acid were supplied by Imperial Industrial Chemicals, Thailand. Sulfur was obtained from Sahapaisal Industry Co. Ltd., Thailand. Rubber Oil was supplied by PSP Specials. N-tert. butyl-2-benzothiazole sulfenamide (TBBS) was purchased from Eliokem, USA.

**Characterization methods of natural zeolite**

The surface area and pore volume of the fillers were determined by the Brunauer-Emmett-Teller (BET) method (Fagerlund, 1973) on an Autosorb-1 accelerated surface area and porosimetry system, respectively. Particle size was measured using a wet sieve particle size analyzer (Autosorb-1series; Quantachrome Co. Ltd.; London, United Kingdom). X-ray fluorescence spectroscopy (XRF; Siemens SR S3400; Bruker AXS GmbH; Karlsruhe, Germany) was used to analyze the chemical composition of the fillers.

**Compounding and sample preparation**

The rubber formulations are given in Table 1. NR was first masticated on a two-roll mill for 6 min at 50 °C before blending. The mixing was carried out in both an internal mixer and on the two-roll mill. All other ingredients, except the sulfur, were mixed with the natural rubber and acrylonitrile rubber in a internal mixer (Brabender Plasti-Corder; Brabender GmbH & Co. KG; Duisburg, Germany). Mixing was done at a temperature of 50 °C at 55 rpm for 11 min. Thereafter, the curatives were added and mixed

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Peroxide system</th>
<th>CV system</th>
<th>EV system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Nitrile rubber</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Natural zeolite</td>
<td>Variable a</td>
<td>Variable a</td>
<td>Variable a</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>-</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>-</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Rubber oil</td>
<td>-</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>TMQ</td>
<td>-</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>TBBS</td>
<td>-</td>
<td>0.6</td>
<td>2.4</td>
</tr>
<tr>
<td>Sulfur</td>
<td>-</td>
<td>2.0</td>
<td>0.2</td>
</tr>
<tr>
<td>DCP b</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

phr = Parts per hundred.

a Variable at 0, 20, 40 and 60 phr.

TMQ = 2,2,4-Trimethyl-1,2-dihydroquinoline; TBBS = N-tert. butyl-2-benzothiazole sulfenamide

b DCP = Dicumyl peroxide content in natural rubber/nitrile rubber (20/80) blend according to Sirisinha et al. (2003a).
with the compounds on the two-roll-mill at 50 °C for 5 min. Then, the mixes were sheeted out and kept at room temperature for 24 hr before testing.

All other ingredients of the peroxide system were mixed in the Brabender plasticorder and sheeted out on a two-roll-mill and then the mixes were kept at room temperature for 24 hr before testing. The resultant rubber compound was then compression molded to a 90% cure with a hydraulic press at 15 MPa with a 150 °C cure temperature to produce vulcanized rubber. The cure time used for any individual compound was predetermined by a moving die rheometer (TechPro MD+; CG Engineering Ltd.; Bangkok, Thailand) before the vulcanization process proceeded.

Measurement of mechanical properties

The tensile properties of the dumbbell-shaped (punched out using Die C, ASTM D 412-92) test specimens were measured according to ASTM D638-08 (2008) using a tensile tester (Instron 5569; Instron Industrial Products; Pennsylvania, United States of America) at a crosshead speed of 500 mm.min⁻¹ with a load cell of 1 kN. The compression set was measured according to ASTM D395-03 (2008). Accelerated thermal ageing tests were followed in the present investigation. The thermal ageing experiment was performed in a closed oven at 100 °C for 22 hr. The aged samples were allowed to rest at room temperature for 30 min and the changes in tensile strength of specimens were used to determine the thermal resistance. For oil resistance, the dumbbell-shaped test specimens were immersed in oil at room temperature for 70 hr. Thereafter, the specimens were removed from the oil and quickly dipped in acetone. The changes in the tensile strength of specimens measured after oil immersion were used to determine the oil resistance. The relative tensile strength was calculated from the ratio of tensile strength after oil immersion to that before oil immersion.

Morphological study

The phase morphology of the blend was studied using scanning electron microscopy (SEM; model JSM-5410 LV; JEOL Ltd; Tokyo, Japan). The samples of the blends were broken in liquid nitrogen to avoid any possible deformation of phases. The samples were further dried. Thereafter, the dried surfaces of the samples were gold coated and then examined by SEM.

RESULTS AND DISCUSSION

Cure characteristics

Table 2 represents the cure characteristics of the rubber compounds. It can also be seen that the minimum torque (ML) of the NR compounds increased with increasing filler loading. This indicates that the presence of filler in the rubber matrix has reduced the mobility of the macromolecule chains of the rubber (Hanafi, 2003). The maximum torque (MH) can be taken as a measure of crosslinking density. Theoretically, it is known that the torque difference (MH - ML) shows the shear dynamic modulus which is indirectly related to the crosslink density of the compound (Poh and Ng, 1998). It can be seen that the value of MH and the torque difference of the NR compound increased with increasing natural zeolite loading. Therefore, it can be concluded that incorporation of natural zeolite in the rubber matrix produced a better crosslink density.

However, from Table 2, it can also be seen that the scorch time (ts2) of the natural zeolite-filled compounds decreased, probably due to the interaction between the components of the cure system and the natural zeolite surface (López-Manchado et al., 2003), whereas the cure time at 90% crosslink (tc90) increased with the increasing natural zeolite content due to the acidity effect of natural zeolite. This result can be explained by the fact that natural zeolite is mainly composed of silica and three possible associated reasons. First, the filler-filler interactions occurred because silica has a number of hydroxyl groups on its surface;
second, there was accelerated adsorption on the silica surface and third, there was a reduction in the zinc-complex formation. Therefore $t_{90}$ became longer (Sombatsompop et al., 2004).

For the different curing systems under investigation, it should be noted that regular variation torques, $t_{90}$ and $t_{2}$ were observed only in case of the sulfur systems (CV and EV) as shown in Table 2. It is evident from Table 2 that the rubber compounds with the CV system gave higher values of both $M_L$ and $M_H$, than those with the EV system. This was due to the compound cured with CV having a much greater crosslink density than that cured with EV as seen in Table 2. In general, the CV system was less effective than the EV system. Thus, the optimal cure time of the compound cured with CV should be longer than that cured with the EV system. From the evidence in Table 2, the compound cured with CV had a much greater crosslink density than that cured with EV. Moreover, as seen in Table 1, the amount of sulfur in the EV system was too little. This might also cause vulcanizate undercure, thus leading it to have a longer optimal cure than the CV system.

### Mechanical properties of filled natural rubber/nitrile rubber

For natural zeolite-filled NR/NBR Vulcanizes with various vulcanization systems, it was found that tensile strength improved with an increased natural zeolite loading up to 40 phr as shown in Figure 1. This is possibly explained by the fact that natural zeolite is mainly composed of 68.88% silica which could show its ability to improve the mechanical properties of the vulcanized rubber. Beyond 40 phr of natural zeolite loading, the tensile strength reduced, because of the inability of the filler to support the stresses and there may have been poor dispersion of the filler in the rubber.

Figure 1 illustrates that the tensile strength of all vulcanizates filled with various natural zeolite loadings under different vulcanization systems decreased in the order of CV > peroxide > EV, respectively. Sulfur vulcanization (CV) can accommodate more stress and exhibited higher tensile strength than the EV and peroxide systems because the high flexibility of the S-S linkages makes them capable of withstanding high

### Table 2  Cure characteristics of rubber compounds with different contents of natural zeolite under conventional vulcanization (CV), efficient vulcanization (EV).

<table>
<thead>
<tr>
<th>System</th>
<th>Zeolite (phr)</th>
<th>$M_L$ (Nm)</th>
<th>$M_H$ (Nm)</th>
<th>$\Delta M$ (Nm)</th>
<th>$t_{s2}$ (min)</th>
<th>$t_{90}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV</td>
<td>0</td>
<td>0.03 ± 0.03</td>
<td>0.43 ± 0.12</td>
<td>0.40 ± 0.10</td>
<td>5.65 ± 0.35</td>
<td>17.09 ± 1.03</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.04 ± 0.09</td>
<td>0.49 ± 0.15</td>
<td>0.45 ± 0.06</td>
<td>5.50 ± 0.32</td>
<td>17.91 ± 1.13</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.05 ± 0.04</td>
<td>0.72 ± 0.20</td>
<td>0.67 ± 0.16</td>
<td>4.27 ± 0.38</td>
<td>18.63 ± 1.22</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.05 ± 0.06</td>
<td>0.77 ± 0.21</td>
<td>0.72 ± 0.15</td>
<td>3.90 ± 0.40</td>
<td>19.77 ± 1.30</td>
</tr>
<tr>
<td>EV</td>
<td>0</td>
<td>0.02 ± 0.01</td>
<td>0.13 ± 0.08</td>
<td>0.11 ± 0.07</td>
<td>24.11 ± 1.08</td>
<td>26.12 ± 1.03</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.03 ± 0.02</td>
<td>0.21 ± 0.09</td>
<td>0.18 ± 0.07</td>
<td>25.21 ± 1.21</td>
<td>27.48 ± 1.22</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.04 ± 0.05</td>
<td>0.26 ± 0.15</td>
<td>0.22 ± 0.10</td>
<td>26.88 ± 0.98</td>
<td>28.89 ± 0.89</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.03 ± 0.04</td>
<td>0.32 ± 0.18</td>
<td>0.29 ± 0.14</td>
<td>27.35 ± 1.01</td>
<td>29.39 ± 1.08</td>
</tr>
</tbody>
</table>

phr = Parts per hundred; Values are ± SD.

$M_L$ = Minimum torque achieved during the vulcanization.

$M_H$ = Maximum torque achieved during the vulcanization.

$\Delta M$ = Difference between the maximum and the minimum torque.

$t_{s2}$ = Scorch time or time in which there is an increase of 2% of initial torque.

$t_{90}$ = Curing time to get 90% of crosslink.
stresses. Therefore, the vulcanizates of the EV system containing mainly C-S linkages resulted in poorer tensile properties than for the CV systems. However, the lower tensile strength in the peroxide system was probably due to the presence of short and rigid C-C bonds between the macromolecular chains (Habeeb et al., 2005).

The morphology of the NR/NBR vulcanizates with and without natural zeolite was studied by SEM as shown in Figure 2. It can be seen that the natural zeolite particles were not clustered and uniformly dispersed in the matrix filled with 40 phr natural zeolite. It is clear that an increase in the natural zeolite loading beyond 40 phr had a substantial influence on the dispersion, resulting in clustering of the natural zeolite which can be explained based on the agglomeration effect.

Clearly, it can be seen from Figure 3 that the %elongation at break of vulcanizates cured with the CV and peroxide systems slightly decreased with increasing filler loading. Again, the explanation is based on the elasticity effect from the filler particles in the rubber. However, the %elongation at break of the EV system gradually increased with increasing zeolite loading. The explanation is based on the high specific area of natural zeolite (14.59 m².g⁻¹) that changes the stress focus in the rubber matrix, and the yielding deformation of the rubber around the natural zeolite.

![Figure 1](image1.png)

**Figure 1** Tensile strength of natural zeolite-filled natural rubber/nitrile rubber vulcanizates under conventional vulcanization (CV), efficient vulcanization (EV) and peroxide vulcanization (phr = Parts per hundred; Errors bars show ± SD).

![Figure 2](image2.png)

**Figure 2** Scanning electron microscopy micrographs of cross sections of natural zeolite-filled natural rubber/nitrile rubber vulcanizates cured using the conventional vulcanization system: (A) without natural zeolite; (B) 40 parts per hundred (phr) natural zeolite; (C) 60 phr natural zeolite.
zeolite can absorb some energy of deformation, thus helping to reach the reinforcement goals. In this way, the extensibility and elasticity of rubber composites are improved (Qinfu et al., 2008). Compared to sulfur systems (CV and EV), the vulcanizates with the peroxide system showed the lowest %elongation at break. By contrast, the rubber compounds with the peroxide system showed the highest modulus at 100% strain (Figure 4). The result could be explained by the effect of the rigid C-C bonds in the rubber chains (Daniel, 1984) and natural zeolite can improve the stiffness of all vulcanizates. The explanation is based on the reinforcing effect. As more filler particles are introduced into rubber, the elasticity of the rubber chains is reduced, resulting in higher stiffness properties. (Hishman and El-Nashar, 2004)

The more natural zeolite introduced into the rubber, the more the elasticity of the rubber chains is reduced and the interaction with

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**Figure 3**  % Elongation at break of natural zeolite-filled natural rubber/nitrile rubber vulcanizates under conventional vulcanization (CV), efficient vulcanization (EV) and peroxide vulcanization (phr = Parts per hundred; Errors bars show ± SD).

**Figure 4**  100% Modulus of natural zeolite-filled natural rubber/nitrile rubber vulcanizates under conventional vulcanization (CV), efficient vulcanization (EV) and peroxide vulcanization (phr = Parts per hundred; Errors bars show ± SD).
rubber-filler is decreased, resulting in a higher compression set as shown in Figure 5. That is to say, the increase in the compression set is attributed to the dilution effect. It can be seen in Figure 5 that all vulcanizates filled with 60 phr of natural zeolite showed the lowest elasticity. Furthermore, the vulcanizates under the peroxide system showed low compression set characteristics, followed by EV and CV, respectively. This is simply due to the fact that the crosslink structure in the peroxide system is mainly a C-C crosslink which is stronger and more thermally stable than sulfidic crosslinks which are mainly found in the sulfur systems.

Thermal resistance of filled natural rubber/nitrile rubber

The physico-mechanical properties of the vulcanizate are generally improved in the presence of filler. The tensile strength of filled-vulcanizate with different amounts of filler was measured. The results indicated that the vulcanizates with natural zeolite possess the greatest relative tensile strength throughout the ageing period (Figure 6). This can be attributed to the reinforcing effect and thermal stability of the silica present in the natural zeolite besides the interaction between the silica and polar CN groups present in NBR (Mark et al., 2005). The relative tensile strength increased progressively with the increased amount of natural zeolite.

As presented in Figure 6, the peroxide vulcanizates exhibited greater relative tensile properties than the CV and EV vulcanizates. This is attributed to the better heat stability of the C-C networks in the peroxide vulcanizates than the mono- and poly sulfidic ones in the sulfur systems. However, the EV vulcanizates exhibited greater thermal resistance than the CV vulcanizates which can be explained on the basis of the heat stability of the sulfidic network in the order of EV (monosulfidic) > CV (polysulfidic).

Oil resistance of filled natural rubber/nitrile rubber vulcanizates

In Thailand, oil from palm fruits is the highest potential source of biodiesel. Diesel (donated by Diesel PTT Alpha-X from PTT Public Co., Ltd., Thailand) was mixed with 5% of palm oil biodiesel (AI Energy Co., Ltd., Thailand) and the blend was tested to evaluate its impact on the performance of vulcanizates.

Figure 5  Percentage of compression set of natural zeolite-filled natural rubber/nitrile rubber vulcanizates under conventional vulcanization (CV), efficient vulcanization (EV) and peroxide vulcanization (phr = Parts per hundred; Errors bars show ± SD).
The equilibrium swelling of the NR/NBR vulcanizates in a range of biodiesel blends with a base fuel (B0, B5, B25, B50, B75 and B100, where 0, 5, 25, 50, 100 represent the percentage of biodiesel in the blend with diesel) was studied using the immersion/weight gain method (Harogoppad and Aminabhavi, 1991). Table 4 shows that the percentage of swelling in the various compositions of biodiesel of the NR/NBR vulcanizates progressively increased with the increasing biodiesel content in the base fuel.

The percentage of swelling was the highest in the B100 blend due to the fact that there are more methyl groups in B100 compared to those in B75, B50, B25, B5 and B0. The higher number of methyl groups can build up polarity in the fuel, resulting in an increase in the percentage occurrence of swelling in the NR/NBR vulcanizates, which can be explained based on the polarity effect (Joshi and Pegg, 2007).

Different quantities of natural zeolite as adsorbent and filler were added to the rubber compounds. It was found that as the dosage of adsorbent was increased, the percentage of swelling of all vulcanizates in both oils also decreased, as shown in Table 3. Two main factors are responsible for the result of the effect of natural zeolite on oil resistance in the blends—namely, the dilution effect of rubber and the absorption of natural zeolite. The internal porosity of the natural zeolite also creates adsorption forces as well as an adsorption-surface area. It can be explained by the fact that both chemisorption and physisorption can be distinguished by chemical and physical interaction. The chemical heterogeneity of zeolites (arising from substitution of Si by Al) and surface curvatures give rise to chemisorption and physisorption sites, respectively (Korkuna et al., 2005). Thus, the higher amount of diesel and biodiesel adsorbed by the natural zeolite indicates a higher accessible micropore volume in these vulcanizates compared to the unfilled vulcanizates.

A similar trend was discovered in terms of the relative tensile strength. In general, the relative tensile strength of filled vulcanizate with different amounts of fillers could be affected by the dilution effect of rubber and the absorption of natural zeolite. As can be seen, the addition of filler increased the relative tensile strength of vulcanizates (Figure 7) and thus the oil resistance. The tensile behavior of swollen vulcanizates is governed by two types

![Figure 6](image-url)  
**Figure 6** Relative tensile strength of natural zeolite-filled natural rubber/nitrile rubber vulcanizates under conventional vulcanization (CV), efficient vulcanization (EV) and peroxide vulcanization after thermal aging (phr = Parts per hundred; Errors bars show ± SD).
Table 3  Percentage of swelling of natural zeolite-filled natural rubber/nitrile rubber vulcanizates after immersing in various amounts of biodiesel added to diesel under conventional vulcanization (CV), efficient vulcanization (EV) and peroxide vulcanization.

<table>
<thead>
<tr>
<th>Zeolite (phr)</th>
<th>CV system</th>
<th>EV system</th>
<th>Peroxide system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 20 40 60</td>
<td>0 20 40 60</td>
<td>0 20 40 60</td>
</tr>
<tr>
<td>B0 (Diesel)</td>
<td>25.94 ± 0.22 21.34 ± 0.28 20.52 ± 0.23 15.83 ± 0.17</td>
<td>27.8 ± 0.16 20.67 ± 0.26 18.17 ± 0.21 15.88 ± 0.19</td>
<td>18.47 ± 0.21 12.55 ± 0.21 11.18 ± 0.17 9.23 ± 0.34</td>
</tr>
<tr>
<td>B5*</td>
<td>27.44 ± 0.23 21.41 ± 0.29 20.77 ± 0.34 17.24 ± 0.26</td>
<td>24.92 ± 0.34 23.67 ± 0.23 19.23 ± 0.16 16.23 ± 0.21</td>
<td>17.44 ± 0.21 13.01 ± 0.28 12.18 ± 0.21 9.72 ± 0.22</td>
</tr>
<tr>
<td>B25</td>
<td>32.45 ± 0.25 24.33 ± 0.32 23.32 ± 0.22 18.99 ± 0.19</td>
<td>29.32 ± 0.16 21.78 ± 0.27 20.14 ± 0.33 17.18 ± 0.27</td>
<td>19.98 ± 0.26 19.14 ± 0.19 13.21 ± 0.22 11.88 ± 0.18</td>
</tr>
<tr>
<td>B50</td>
<td>35.21 ± 0.21 30.11 ± 0.12 26.88 ± 0.18 19.54 ± 0.21</td>
<td>30.91 ± 0.22 23.54 ± 0.23 22.33 ± 0.19 18.29 ± 0.25</td>
<td>21.22 ± 0.22 20.92 ± 0.24 16.43 ± 0.12 13.84 ± 0.27</td>
</tr>
<tr>
<td>B75</td>
<td>38.56 ± 0.43 30.87 ± 0.23 28.34 ± 0.16 22.22 ± 0.23</td>
<td>31.67 ± 0.17 24.94 ± 0.26 23.83 ± 0.34 20.07 ± 0.44</td>
<td>22.05 ± 0.28 23.34 ± 0.25 18.22 ± 0.25 15.32 ± 0.21</td>
</tr>
<tr>
<td>B100</td>
<td>42.91 ± 0.34 32.93 ± 0.29 32.45 ± 0.29 24.33 ± 0.17</td>
<td>33.01 ± 0.30 26.13 ± 0.20 25.98 ± 0.32 21.89 ± 0.23</td>
<td>22.91 ± 0.22 24.72 ± 0.12 19.92 ± 0.27 16.97 ± 0.25</td>
</tr>
</tbody>
</table>

phr = parts per hundred; B0, B5, …B100 represent blends of 0%, 5% … 100% biodiesel in the fuel sample; * = Normal blend used in Thailand; Values are ± SD.

The use of natural zeolite as a sorbent filler produced considerable changes in the oil resistance capability in both diesel and biodiesel.

CONCLUSION

The transport properties of polymers are strongly dependent on the type and extent of the crosslinks in them. It is very clear that the rubber-solvent interaction is at its minimum and hence there is a total change in the equilibrium swollen chain entanglements. In the equilibrium swollen state, the rubber-rubber interaction is at its maximum and the rubber-solvent interaction is at its minimum and hence there is a total change in the equilibrium swollen chain entanglements. This gives rise to the abrupt decrease of tensile strength of swollen rubber.

The percentage of swelling was in agreement with the relative tensile strength of all vulcanizates.

The percentage of swelling was in agreement with the relative tensile strength of all vulcanizates. The percentage of swelling in the equilibrium swollen state is at its maximum and the rubber-rubber interaction is at its maximum and the rubber-solvent interaction is at its minimum and hence there is a total change in the equilibrium swollen chain entanglements. This gives rise to the abrupt decrease of tensile strength of swollen rubber.
It was observed that the natural zeolite loading had a strong influence on the cure characteristic of the rubber compounds. The $M_H$ and torque difference of the NR compound increased with an increase in the natural zeolite loading because the incorporation of natural zeolite in the rubber matrix contributed to better crosslink density. However, the $t_{90}$ decreased, while the $t_{c90}$ increased with increasing natural zeolite content due to the interaction between the components of the cure system and the natural zeolite surface, and the acidity effect of natural zeolite, respectively. The cure system (CV system) gave a higher value of both $M_L$ and $M_H$, than did the EV system. Meanwhile, the amount of sulfur in EV was too little which might also have caused the vulcanizate undercure, thus resulting in it having a longer optimal cure than the CV system.

The natural zeolite loading affected not only the cure characteristics but also the mechanical properties of the vulcanizates in which the optimum content of natural zeolite was 40 phr. The tensile properties of vulcanizates increased with increasing natural zeolite content up to 40 phr. Beyond 40 phr of natural zeolite loading, the tensile strength reduced because of agglomeration of the additional filler being loaded into the systems, leading to poor dispersion. The %elongation at break of the peroxide vulcanizates decreased whereas the compression set of all vulcanizates increased with increasing filler loading. Moreover, natural zeolite showed considerable variability not only in the capability of oil resistance improvement in both diesel and biodiesel but also in thermal resistance.

At the particular natural zeolite loading used with various vulcanization systems, it was found that the natural zeolite-filled vulcanizates cured with peroxide gave greater oil resistance than those cured with the sulfur systems (CV and EV). It is interesting to note that natural zeolite has potential to improve the inferior properties of rubber goods with low cost, especially with regard to oil resistance.

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filled with nanokaolin and precipitated silica.


