

## REINFORCEMENT OF EPOXIDISED NATURAL RUBBER BY PRECIPITATED SILICA NANOFILLER: STUDIES ON CURE CHARACTERISTICS AND RUBBER-FILLER INTERACTION

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**ABSTRACT** : Epoxidised natural rubber, which is produced via modification of natural rubber enhanced the polarity of natural rubber. In this work, the rubber – filler interaction of epoxidised natural rubber (ENR) and precipitated silica nanofiller was investigated. The surfaces of silica are polar and hydrophilic, which normally required a coupling agent to make it more compatible with hydrocarbon polymer. The use of ENR in precipitated silica nanofiller compound eliminates the use of silane coupling agent in the compound formulation since ENR has better compatibility with silica nanofiller. This study presents the rheological behaviour and cure characteristics of silica nanofiller – ENR compounds with different silica contents. For this purpose two different types of silica nanofiller have been compounded with ENR. The rubber-filler via bound rubber measurement shows a high rubber-filler interaction in ENR-silica nanofiller compound. Lower Payne effect was observed resulting from the reduction in filler-filler interaction. This indicates that there is a strong reinforcement mechanism exhibited by silica nanofiller in epoxidised natural rubber compound. The improved mixing enhanced the filler-rubber interaction and increased the nanofiller dispersion as well as reduced the filler-filler interaction.

**KEYWORDS** : Precipitated silica, nanofiller, epoxidised natural rubber, Payne effect, rubber-filler interaction

## INTRODUCTION

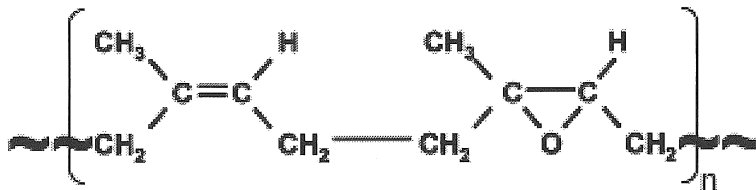
The chemical modification of natural rubber (NR) via epoxidation of natural rubber latex yield a specialty rubber called 'Epoxidised Natural Rubber', (ENR), that has improved properties depending on the degree of epoxidation (Baker, Gelling & Samsuri, 1986; Malaysian Rubber Research and Development Board, 1983; Rubber Research Institute of Malaysia, 1983). The epoxide groups are randomly distributed along the NR backbone (Baker, Gelling & Samsuri, 1986). ENR-10 which has 10 mole percent of epoxidation level has basically similar properties with NR but additionally has higher damping capability. ENR-50 which has 50 mole percent of epoxidation level, behaves differently from NR, with oil resistance and low gas permeability that are comparable to specialty synthetic rubber (Malaysian Rubber Research and Development Board, 1983; Rubber Research Institute of Malaysia, 1983). On the other hand, ENR-25 (25 mole percent of epoxidation level) gives improved wet grip characteristics and low rolling resistance which offers the best balance required in tyre applications (Baker, Gelling & Palmer, 1985; Gelling, 1991).

Epoxidation increases the polarity of natural rubber. The presence of polar epoxide groups in ENR, as shown in Figure 1 makes the rubber compatible with highly polar filler like silica. It is reported that excellent reinforcement of ENR is obtained with silica filler even in the absence of coupling agent (Malaysian Rubber Research and Development Board, 1983; Rubber Research Institute of Malaysia, 1983; Baker, Gelling & Palmer, 1985; Gelling, 1991; Franco, 2002). The main application of silica is in passenger tyre tread. The silica revolution in tyre industry has started with *Green tyre* concept introduced by Michelin in early nineties to give lower rolling resistance and better wet traction tyre, which gives fuel benefit to consumer (Rauline, 1993). The silica-filled tread compound with an optimised amount of silane coupling agent is able to provide good reduction in rolling resistance and improved wet traction (Annemieke ten Brinke, 2002; Dierkes, 2005; Hans-Detlef Luginsland, 2002).

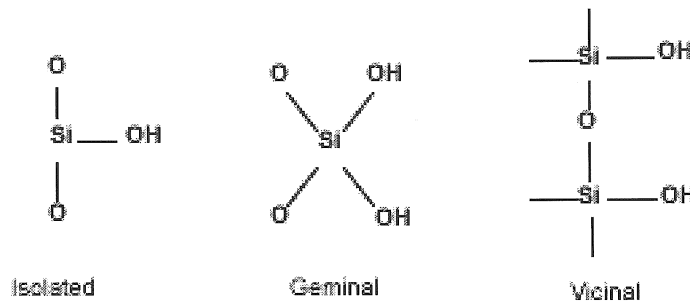
Silica consists of silicon and oxygen arranged in a tetrahedral structure of a three-dimensional lattice (Hans-Detlef Luginsland, 2002; Mark, Erman & Eirich, 1994; Mark, Erman & Eirich, 2005). The surfaces of silica consist of siloxane and silanol groups, which are polar and hydrophilic (Mark, Erman & Eirich, 2005; Norman, 2007), that give strong tendency to absorb moisture and adversely influence the cure process and properties of cured rubber (Ansarifar, Lawton & Nijhawan, 2004; Ansarifar & Holmes, 2005; Ansarifar & Lim, 2006). There are three types of silanol groups (Si-OH) on the surface of silica, namely isolated, geminated and vicinal silanol group as shown in Figure 2. These silanol groups are generally highly associated with hydrogen bonds. The amount of water adsorbed on the surface of silica affects the ionisation of the silanol groups, and in turn affects the curing property (Ansarifar, Lawton & Nijhawan, 2004; Ansarifar & Holmes, 2005; Ansarifar & Lim, 2006; Butler & Freakley, 1992). When high loading of silica is used, the viscosity of the compound increases substantially making the processing more difficult. The increase in

viscosity is attributed to a strong interaction between silica particles (Lin, HergN Rother & Hilton, 2002).

Silica can be divided into three classes, namely conventional silica, semi-highly dispersible silica (semi-HD) or easily dispersible silica and the latest is highly dispersible silica (HDS) (Mark, Erman & Eirich, 2005; Norman, 2007). The primary particle size of reinforcing silica is typically 10 - 45 nanometer (nm) (Norman, 2007; Ansarifar, Lawton & Nijhawan, 2004; Ansarifar & Holmes, 2005; Ansarifar & Lim, 2006; Butler & Freakley, 1992; Lin *et al.*, 2002; Mihara *et al.*, 2007). It is anticipated that the (HDS) silica has higher concentration of geminal silanol groups, whilst the conventional silica has higher amount of isolated silanol groups.



**Figure 1.** Structure of Epoxidised Natural Rubber



**Figure 2.** Types of silanol groups on silica surface

This study was carried out to investigate the reinforcement of ENR with silica nanofillers. The effect of variation of silica nanofillers loading on cure characteristics, as well as rubber to filler interaction from bound rubber measurements, Mooney viscosity and storage shear modulus ( $G'$ ) will be discussed.

## MATERIALS AND METHODS

### Materials

Epoxidised natural rubber of 25 % epoxidation level (ENR-25) produced from Rubber Research Institute of Malaysia (RRIM) was used for this study. Two types of silica nanofillers were used, namely Zeosil 1165MP, the highly dispersible precipitated silica, supplied by Rhodia Silica Korea and silica Ultrasil VN3, the conventional precipitated silica, supplied by JJ-Degussa Chemicals (M). The silica nanofillers analytical properties are summarised in Table 1. The compound ingredients and formulation as expressed based on parts per hundred of rubber (phr) were as follows: ENR (100 phr), silica either Zeosil 1165MP or VN3 (vary), zinc oxide (3 phr), stearic acid (3 phr), calcium stearate (2 phr), N-1,3-dimethylbutyl-N' phenyl-phenylenediamine or 6PPD (1 phr), 1,2-dihydro-2,2,4-trimethylquinoline or TMQ (1 phr), Nytex 840 oil (16 phr), sulphur (1.8 phr) and N-tert- butylbenzothiozole -2-sulphenamide or TBBS (2.4 phr). The silica loadings were varied from 50 phr to 60, 70, 75 and 80 phr.

**Table 1.** Analytical properties of silica nanofillers

Silica type	HDS	Conventional
	Zeosil 1165 MP	Ultrasil VN3
BET Specific surface area, (m <sup>2</sup> /g)	165	170
CTAB Specific surface area, (m <sup>2</sup> /g)	160	165
Primary particle size, (nm)	10	14
Moisture, (2 hrs at 105 °C) (%)	6.4	5.5

### Method

Mixing was carried out in three stages. The first stage mixing was in Banbury 1600 internal mixer. The silica and oil were pre-blended and divided into three different portions prior to mixing. The mixing parameters of 110 rpm rotor speed and starting temperature of 90 °C were used. During the mixing, rubber and powder were first added except for curatives, filler and oil. This was then followed by addition of silica and oil in stages. The mixing was dumped at 165 °C. The second stage mixing was carried out to remill the masterbatch in internal mixer for three minutes. In the final stage, the curatives, sulphur and accelerator were added on 12" x 6" two-roll mill at 55 °C to produce ~2 mm thick sheets.

## Testings

### Mooney viscosity ML (1+4) or MS (1+4) at 100 °C

Mooney viscosity measurements were carried out using the Mooney Viscometer MV2000 (using small or large rotor) at temperature of 100 °C. The sample weights were in the range of 25 - 30 g. The final viscosity was taken after 4 minutes.

### Bound Rubber Content

The bound rubber content (BRC) measurement was done on the samples after 7 days maturation. BRC measurements were performed in duplicate on single piece of each compound weighing between 0.25 g and 0.3 g and placed into a separate Erlenmeyer flask. About 50 cm<sup>3</sup> of toluene was added into each flask. The flasks were kept at room temperature in the dark for seven days. During this period, the flasks were gently swirled to prevent the rubber from sticking at the bottom of the flask. After seven days, the wet (swollen) weights were determined and samples were placed in a drying cabinet (40 °C) for 24 hours. The dried samples were weighed on the following day and bound rubber content values were calculated.

The amount of bound rubber (g/g filler) is calculated by:-

$$BRC(g / g \text{ filler}) = \frac{w_{dry} - w_{insolubles}}{w_o \times \frac{w_{filler, phr}}{w_{total, phr}}} \times 100 \quad (1)$$

where:  $w_o$  is the initial weight of the sample,  $w_{dry}$  is the dry weight of sample,  $w_{insolubles}$  is the weight of insolubles in samples,  $w_{filler, phr}$  is the total filler weight in phr and  $w_{total, phr}$  is the total compound weight in phr.

The ammonia treatment bound rubber content was carried out by storing the flask containing the sample in ammonia atmosphere in dessicator for 7 days and the wet and dry weights were determined as in the standard procedure above. The ammonia treatment on bound rubber according to Wolff and Polmanteer will cleave physically the bound rubber (Vondracek & Pouchelon, 1990; Vondracek & Schatz, 1979).

### Rheometry

The compounds were tested for cure characteristics using a Monsanto MDR Rheometer at 172 °C for 15 minutes with oscillation amplitude of 0.5 arc.

### Rubber Processing Analyser (RPA)

The storage shears modulus ( $G'$ ) of uncured rubber compounds were measured using RPA2000 (Alpha Technology). Triple strain sweep test was set at 1 Hz in a range of 2.79% - 139% at 60 °C.

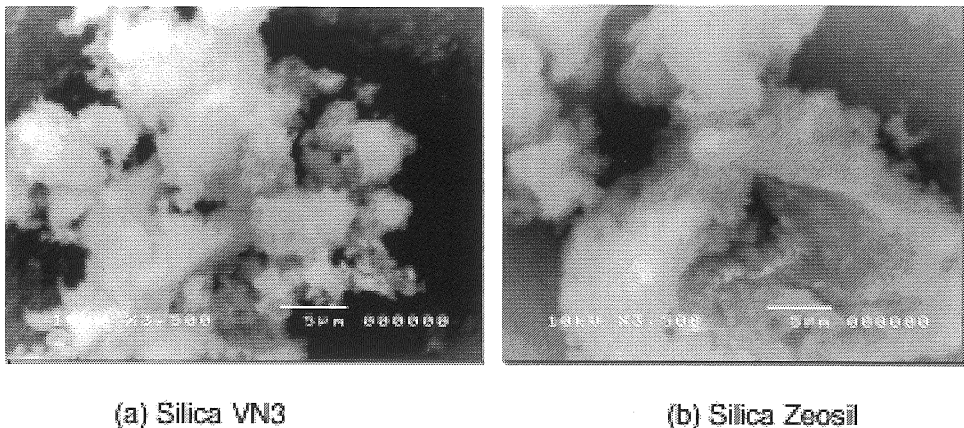
### Scanning Electron Microscope (SEM) examination

The SEM analysis was carried out using JEOL SEM JSM-5300 Scanning Electron Microscope operated at 10 kV with 14 mm working distance. The specimens were prepared for examination by evaporative coating with ultra-thin layer of gold under high vacuum.

## RESULTS AND DISCUSSION

### Silica nanofiller morphology

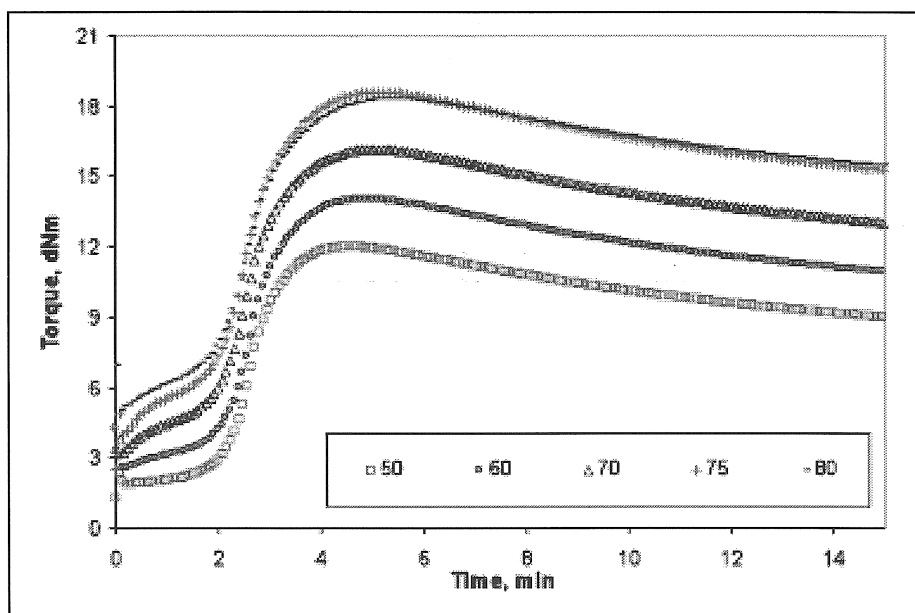
The morphology of precipitated silica nanofillers is demonstrated in Figure 3. The morphology of both silica nanofillers VN3 and Zeosil are constituted by small, branched aggregates which are mainly spherical, forming quite a dense agglomerate. It appears that silica Zeosil has a more 'lumpy-like' and larger agglomerate structure as compared with silica VN3.



**Figure 3.** SEM images of silica nanofiller agglomerates (a) silica VN3, (b) silica Zeosil

## Cure characteristics

Figure 4 presents the variation of cure or rheometer curves of ENR-silica compounds with increasing silica Zeosil loading. At the beginning of the curing, there is a delay or induction period before the torques begin to rise appreciably to optimum cure time. After the optimum cure, the torque increases slowly to maximum torque, and then there is a reversion period which can be seen with the decrease in torque. The minimum and maximum torques (ML and MH) of ENR-silica compound increase with increasing loading of silica Zeosil. The increase in MH is clearly observed with the increase in silica Zeosil loading.



**Figure 4.** Rheometer curve of ENR filled with Silica Zeosil at various loadings

It can be seen from Figure 4, that there are two types of induction period for ENR-silica compound. For compound with silica loading at 50 phr, the rheometer curve shows the normal induction period as seen for rubber compound. Nonetheless, for ENR-silica compound at higher loading of silica at 60, 70, 75 and 80 phr, the induction period in the rheometer curve shows an interesting behaviour where there is a sign of initial torque rise, which shall be denoted as initial torque rise. This initial torque rise is observed to increase with increasing silica Zeosil content.

The occurrence of initial torque rise in the cure characteristic of high loading silica-ENR compounds are believed to be associated with silica flocculation or the reagglomeration of silica particles after rubber compounding (Cataldo, 2002). The reagglomeration results in more silica-silica network or filler to filler interaction. Hence, at higher loading of silica

Zeosil, with flocculation, there is an increase in filler-to filler interaction, which leads to the decrease in rubber to filler interaction.

On the other hand, comparison to silica VN3 can be observed in Figure 5 which shows the variation of rheometer curves of ENR-silica compound with increasing silica VN3 loading. Generally, as observed for silica Zeosil compound, the minimum and maximum torques (ML and MH) of ENR-silica compound increase with increasing loading of silica VN3. However, the increase in MH variation is not too obvious as compared to silica Zeosil. The MH of compound for 60 and 70 phr of silica VN3 is almost comparable. Nonetheless, compound of 75 phr silica loading shows slightly lower MH. For ENR-silica VN3 compound, the initial torque rise is also observed starting from 60 phr silica loading and it is clearly seen for 80 phr silica. However, in contrast to silica Zeosil compound, at 60, 70 and 75 phr silica VN3 loading, the rise in the initial torque is almost comparable. The initial torque rise indicates reagglomeration occurs with increasing silica VN3 in the compound but to a less extent comparable to silica Zeosil compound. As compared to silica VN3 which is conventional silica, it is anticipated that silica Zeosil has higher amount of geminal silanol groups, which is more reactive and may interact with other neighbouring silanol groups via hydrogen bonding.

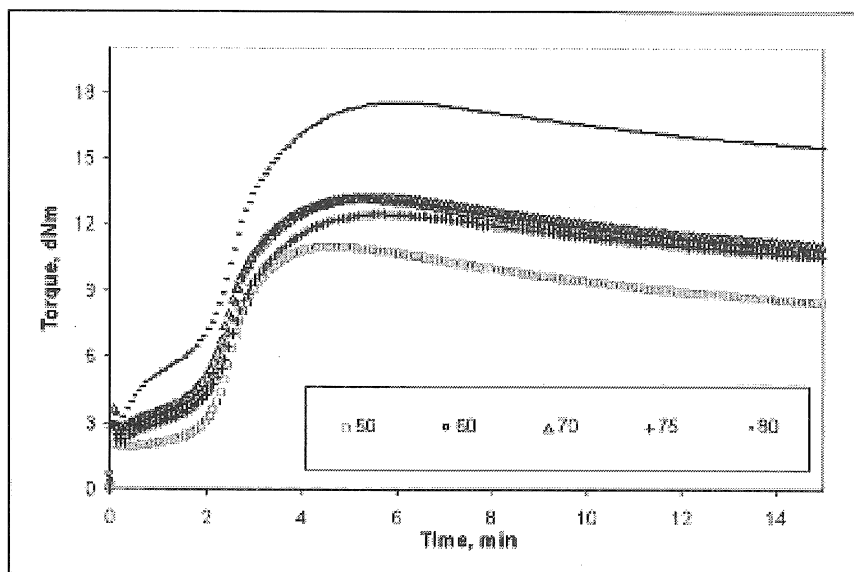
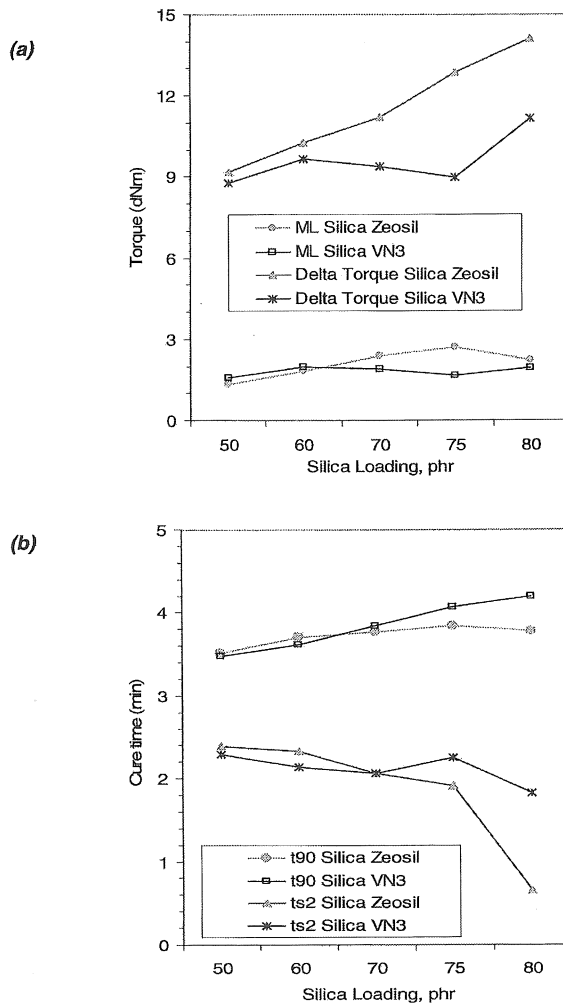


Figure 5. Rheometer curve of ENR filled with Silica VN3 at various loadings



It is observed from Figure 6 (a) that the torque difference of ENR-silica Zeosil compound increases with increasing silica loading, however the torque difference for ENR-silica VN3 compound tend to drop after 70 phr silica VN3 loading but bounce back at 80 phr silica loading. The torque difference is indirectly related to the crosslink density of the compound. Hence, it is postulated that higher loading of silica contributes to better crosslinking in the compound. Figure 7 illustrates the relationship between the toluene swelling index,  $1/Q$  with increasing silica loading. As the silica loading increases, the  $1/Q$  value also increase, which shows that silica loading has an effect on crosslink density.

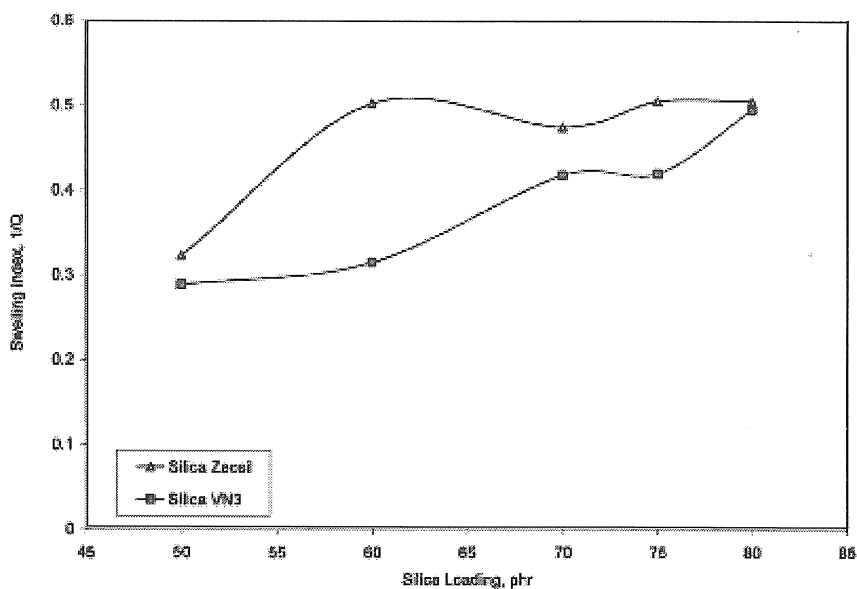


**Figure 6.** Cure characteristic of ENR-silica compound with increasing silica loading

Figure 6 (b) illustrated that the optimum cure time ( $t_{90}$ ) of ENR-silica VN3 becomes longer with silica loading, whilst the  $t_{90}$  of ENR-silica Zeosil only increases slightly with increasing silica loading. The scorch time ( $t_{s2}$ ) of ENR-silica Zeosil compound shows a declining trend with increasing silica loading with a large reduction of scorch time at 80 phr silica. For ENR-silica VN3 compound, the  $t_{s2}$  only becomes marginally shorter with increasing silica loading.

### Mooney viscosity

The changes in Mooney viscosity of ENR-silica compound with increasing silica loading is presented in Figure 8. It is observed that for silica Zeosil compound, the Mooney viscosity increases steadily with increasing silica loading, whilst for silica VN3 compound, the Mooney viscosity seems to increase with increasing silica loading with an exception at 75 phr loading where there is a slight reduction in Mooney. This observation corresponds with the MH of rheometer curve of silica VN3 compound at 75 phr that is lower than 60 and 70 phr silica loading.



**Figure 7.** Swelling index of ENR-silica compound at various silica loadings

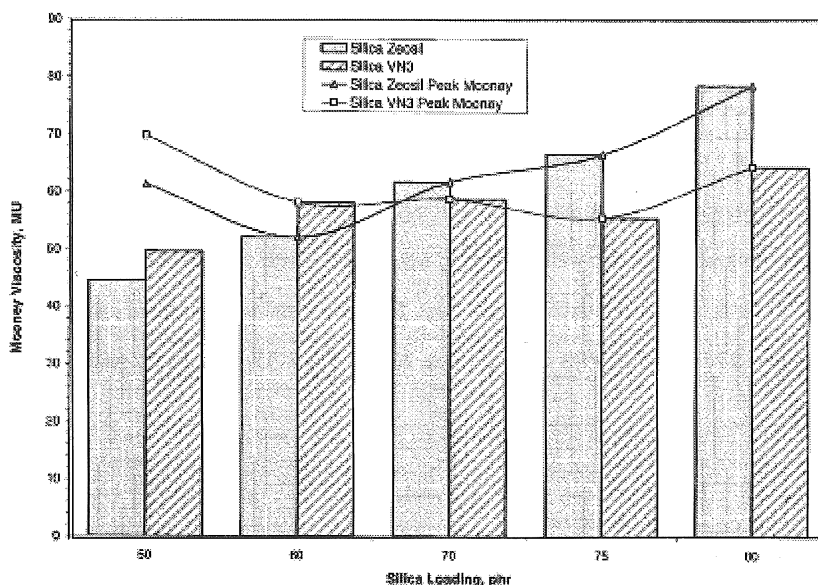


Figure 8. Changes in Mooney viscosity with increasing silica loading

### Rubber-Filler Interaction

The bound rubber content (BRC) of compounds filled with silica Zeosil and silica VN3 are shown in Figure 9 and Figure 10 respectively. In the case of ENR-silica Zeosil compound, the bound rubber content (%) increases with increasing silica loading and the specific bound rubber g/g silica marginally decreases with the increase of silica Zeosil loading up to 70 phr, and it seems to plateau with further increase in silica loading to 75 phr and 80 phr. The bound rubber g/g filler is not much affected with increasing filler loading, which indicates strong rubber to filler interaction. This is resulting from the flocculation or reagglomeration that occurs with increasing filler loading, where more silica-silica networks are formed. Interestingly, the strength of the rubber-filler interaction as indicated by  $V_r$  measurement shows a steady increase with increasing silica Zeosil loading. The increase in  $V_r$  indicates that there is a strong ENR and silica interaction or coupling in the compound which leads to permanent bound rubber. The observation also indicates that there is an increase in the interaction sites between bound rubber ENR and silica, with increasing silica loading.

The same trend is observed for ENR-silica VN3 compound where the specific bound rubber g/g silica tend to reduce with increasing silica Zeosil loading. The occurrence of reagglomeration with increasing filler loading will decrease the rubber- filler interaction and subsequently reduce the bound rubber of the compound. As observed with ENR-silica Zeosil compound,

the  $V_r$  of ENR-silica VN3 compound increases with silica loading. This shows that a strong coupling exist between ENR and silica in the compound.

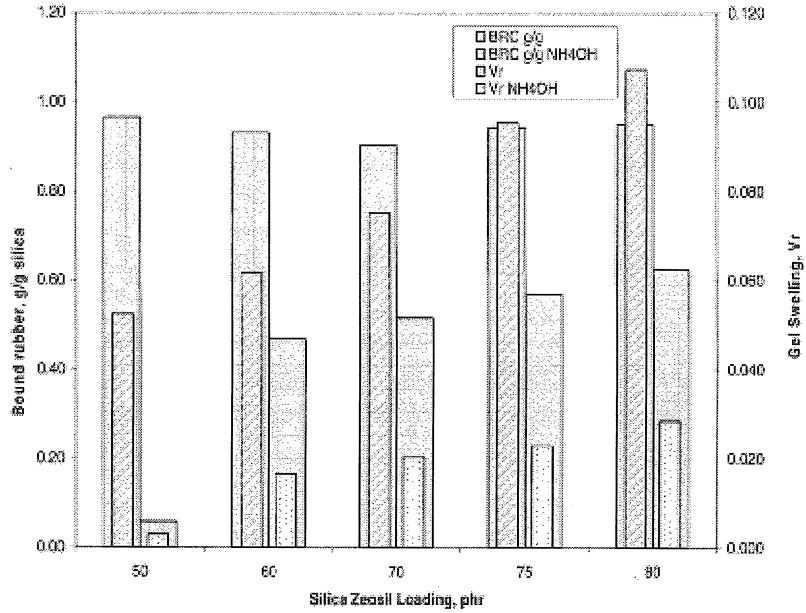


Figure 9. Bound rubber g/g silica and gel swelling, Vr of ENR-silica Zeosil compound

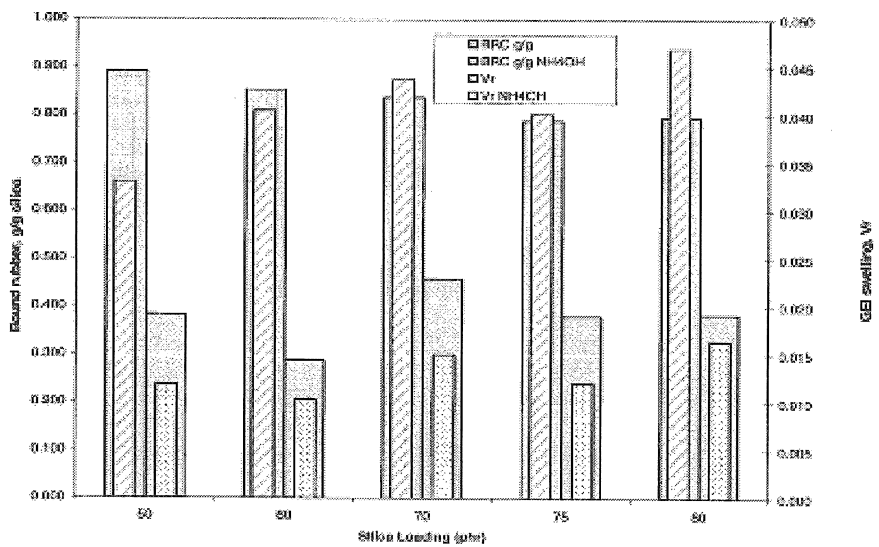
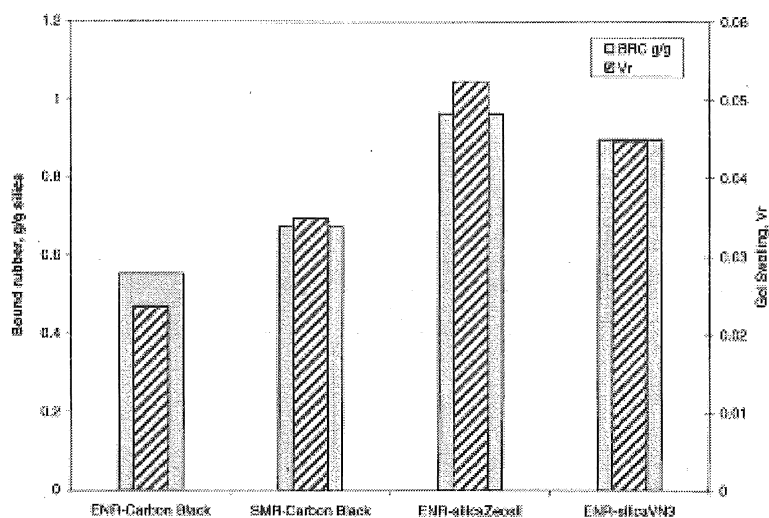


Figure 10. Bound rubber g/g silica and gel swelling, Vr of ENR-silica VN3 compound



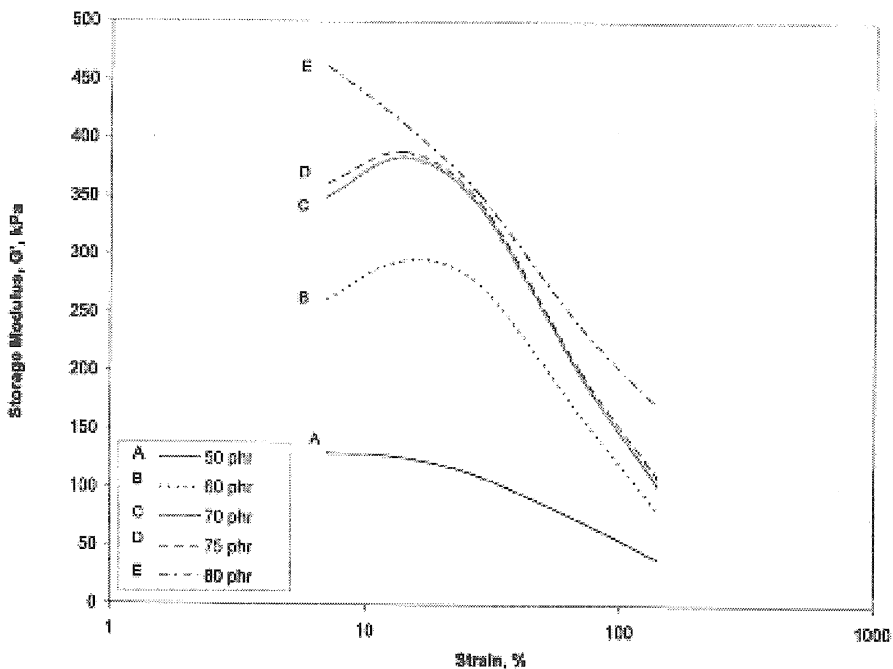
**Figure 11.** Comparison of bound rubber g/g silica and gel swelling, Vr of silica-filled ENR compound with carbon black- filled compound

Ammonia treatment BRC on the compounds was also carried out. It is reported that ammonia treatment of bound rubber measurement will cleave the physically bound rubber (Polmanteer & Lentz, 1975; Vondracek & Pouchelon, 1990; Vondracek & Schatz, 1979). Hence, the ammonia modified bound rubber measurement can be used to estimate hydrogen bonding between rubber and silica in ENR-silica compound. It is observed that there is a considerable reduction in bound rubber after ammonia treatment. This shows that significant amount of interaction between ENR and silica is formed through hydrogen bonding. This is due to the hydrophilic characteristic of silica surface. The modified bound rubber measurement was also carried out on the finalized compound. Interestingly most of the bound rubber of the finalized compounds is completely destroyed after ammonia treatment. This again shows that most of the interactions in the ENR-silica compound are based on the strong hydrogen bonding between ENR and silica.

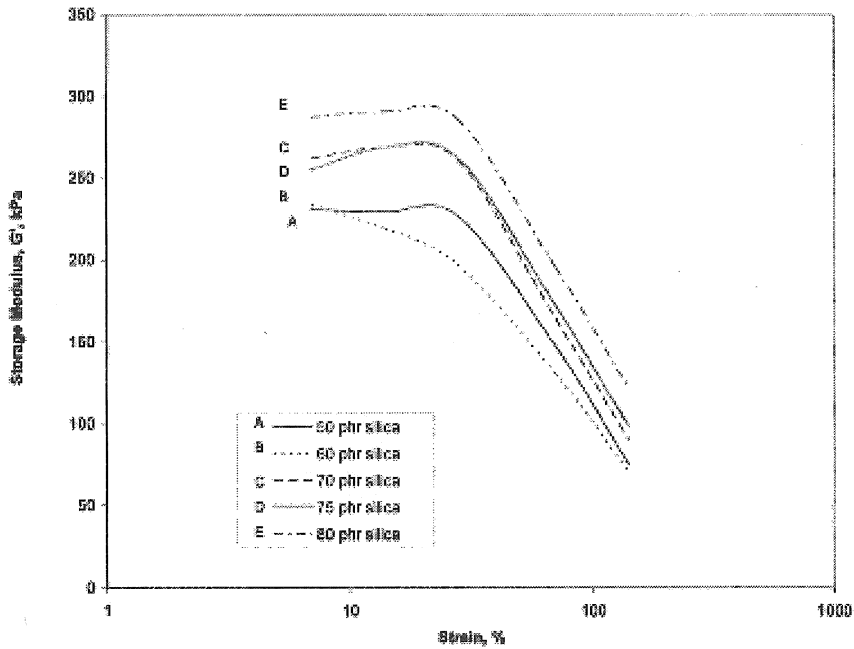
The strong interaction of ENR and silica is due to its polar nature of ENR, where in this case, the ENR contains 25 mol % of epoxy group, which has better interaction with silanol groups on silica surfaces. This strong coupling of ENR and silica is even higher than carbon black-filled natural rubber compound as supported with higher bound rubber g/g filler and Vr in ENR-silica compound as compared to ENR-carbon black and SMR-carbon black compound as shown in Figure 11. In addition to epoxy groups, ENR also contains a small proportion of ring opening species (about 1 mol % as measured from  $^1\text{H}$  NMR) that constitutes of hydroxyl and furan functionality (Chapman, 2007; Gelling, 1991). It is postulated that these polar

groups also interact with silanol groups of silica through hydrogen bonding which add to the strong coupling of ENR and silica in the compound as observed in bound rubber measurement.

The influence of silica Zeosil and silica VN3 loading on storage modulus ( $G'$ ) of ENR-silica compound under varying strain deformation as measured using Rubber Processing Analyser (RPA) is depicted in Figure 12 and Figure 13 respectively. The filler-filler interaction can be characterized by 'Payne Effect' or a decrease in storage modulus upon increasing strain. In both cases of silica Zeosil and silica VN3, the Payne effect is observed to increase with increasing silica loading, which indicates high filler-filler interaction or silica network. This is expected as flocculation occurred in high loading of silica as seen in rheological study and this contributes to an increase in silica-silica network.



**Figure 12.** Influence of silica Zeosil loading on storage modulus (RPA at 60 °C and 1 Hz)

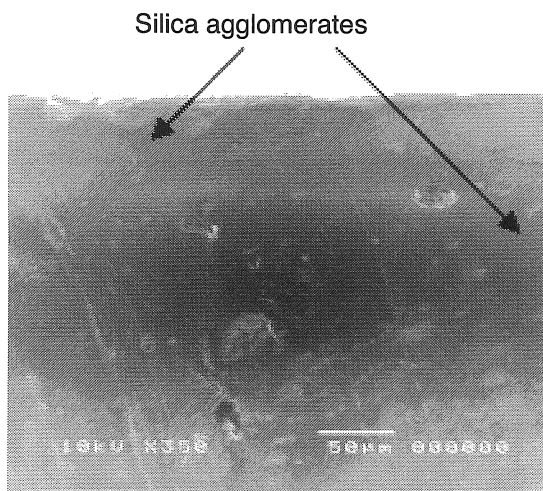


**Figure 13.** Influence of silica VN3 loading on the storage modulus (RPA at 60 °C and 1 Hz)

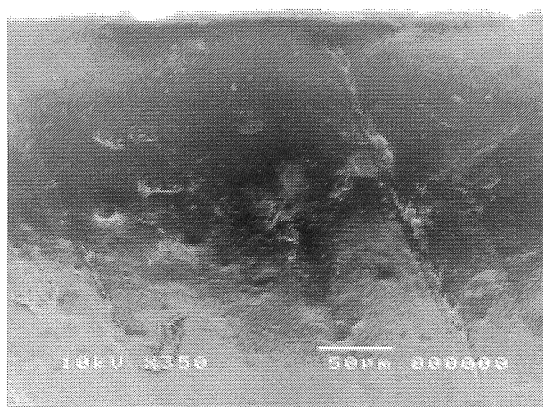
It is also observed that at high loading of silica in the compound there is an increase in modulus. Due to strong silica-silica interaction, rubber is trapped in the silica-silica network resulting in the immobilization of rubber in the structure of silica agglomerate. The immobilization of rubber on the surface of silica and in the silica network structure, correlated with the increase in the strength of bound rubber,  $V_r$  with increasing silica loading. High  $V_r$  was observed for ENR-silica compound especially at high loading silica of 75 phr and 80 phr. Most of the interaction of ENR and silica, but not all, in the compound is associated with hydrogen bond. The rubber immobilization in the ENR-silica compound resulting in the 'in-rubber structure' leads to the strong increase in modulus.

### Morphology of vulcanisates

Figures 14 (a) and (b) pictured the morphology of silica-filled ENR vulcanisate containing 80 phr of silica Zeosil and silica VN3 respectively as studied by Scanning Electron Microscopy (SEM). It can be seen at high loading of 80 phr silica in the compound, the silica agglomerates are clustered as a result of flocculation that occurred as observed from rheological study.



(a) Silica Zeosil vulcanisate



(b) Silica VN3 vulcanisate

**Figure 14.** Photographs of silica-filled vulcanisate at 80 phr silica loading, (a) Silica Zeosil vulcanisate, (b) Silica VN3 vulcanisate



## **CONCLUSION**

The cure characteristic of silica-filled ENR compound showed interesting behaviour with the initial torque rise, observed for ENR-silica compound at silica loading of 70 phr and above. The initial torque rise also increases with increasing silica content. The initial torque rise indicates the flocculation or re-agglomeration which occurs in the ENR-silica compound at high loading of silica. In addition, there is an increase in Payne effect with increasing silica loading in ENR-silica compound as observed from the changes of storage modulus ( $G'$ ) under varying strain deformation. The increase in Payne effect illustrates the filler-filler interaction is higher at high loading of silica as a result of re-agglomeration. The bound rubber measurement shows an increase in bound rubber content (%) with increasing silica loading. The strength of bound rubber as indicated by gel swelling also showed a steady increase with an increase in silica loading. The strong interaction of ENR and silica is due to the polar nature of ENR, which has better interaction with silanol groups on silica surfaces. This strong coupling of ENR and silica in silica-filled ENR compound is observed to be even higher than carbon black-filled natural rubber compound.

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