The silica-filled natural rubber in presence of epoxidized natural rubbers: curing, swelling and tensile properties

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Abstract. The two types of epoxidized natural rubbers (ENR-25 and ENR-50), having 25 and 50 moles of epoxidation, were used to study the influences of their incorporations on optimum curing time, swelling and tensile properties of silica-filled natural rubber (NR) compounds. The NR vulcanizates were filled by silica filler at a fixed loading at 30.0 phr and the ENRs were incorporated separately into the filled NR compounds with varied concentration i.e 5, 10, 15, 20 and 25 phr. The filled-NR compounds were prepared based on a semi-efficient cure formulation and cured at 150 °C. From the results, it was revealed that both the ENRs acted as curatives and compatibilizers. They increased the optimum curing time and crosslinks level of the silica-filled NR compounds. The higher the ENRs loadings; the higher was the optimum curing time and crosslinks level. It was also revealed that the tensile moduli and tensile strength were raised; the elongations at break were reduced as the ENRs incorporations were raised to 25 phr of concentration. At a similar concentration, the ENR-25 exhibited a less pronounced curative and compatibilization affections than ENR-50.

1. Introduction
Generally, in the making of rubber products or rubber articles, raw elastomers/rubbers, other rubber chemicals are compounded with fillers to extend their applications in engineering aspects. Fillers must be not expensive and they are mixed in a relatively large concentration to rubbers concerning processing and mechanical properties [1].

As one of the most popular fillers in a commercial rubber factory, silica is an excellent filler with a large surface area and also low density. It has some advantages in providing final properties such as decreasing in resistance of tire roll and loss in hysteresis that significantly effect to fuel expense [2]. One of the disadvantages of silica is the difficulty of dispersing the filler inside the matrix of natural rubber (NR) and hence, formulations for silica-filled NR compounds must have one compatibilizing agent [3] to make stronger rubber to filler interactions. The previous paper [4], epoxidized natural rubbers, ENR-50 and ENR-25, were added into silica-filled NR compounds and it was found that they acted as compatibilizing and curative materials. They increased the cure/scorch times and also change in torque of silica-filled NR compounds. They also compatibilized the NR and the silica which resulted in improving the filler distribution and interactions between rubber and filler of the compounds of silica-filled NR.
In elaboration the curative and compatibilizing affections of ENRs on compounds of silica-filled NR; the present study was aimed to investigating the influences of ENR-25 or ENR-50 on curing, swelling and tensile properties of compounds of silica-filled NR.

2. Chemicals and methodology

2.1. Chemicals
ENR-25, NR, ENR-50, precipitated silica, MBTS-accelerator, sulfur-crosslinker, stearic acid-co activator, ZnO-activator and IPPD-antioxidant were supplied by rubber lab, Engineering School of USM, Malaysia.

2.2. Preparation of compounds of NR
Semi efficient was chosen as the compounding formulation/recipe. Compounding procedure was based on ASTM (D3184 – 80) and was held on one 2 roll-Model: XK-160 and, the recipe of NR compounds plus ENRs is tabulated in Table 1.

| Materials               | Concentration in phr |
|-------------------------|-----------------------|
| Nat. rubber             | 100                   |
| MBTS                    | 1.5                   |
| Silica                  | 30                    |
| ZnO                     | 5                     |
| Sulfur                  | 1.5                   |
| Stearic acid            | 2                     |
| IPPD                    | 2                     |
| ENR-25 or ENR-50        | 0; 5; 10; 15; 20; 25   |

2.3. Optimum curing time and tensile properties
The optimum curing time of compounds of silica-filled NR in the presence of ENR-25 or ENR-50 were ruled by the Monsanto Moving Die – 2000 Rheometer which based on ASTM D2084/11. All compounds samples were cured at 150 °C.

2.4. Percentage of swelling
The percentage of swelling was ruled in the solution of toluene, based on ISO1817. The (30 mm x 5 mm x 2 mm) sized of vulcanizates of silica and ENRs filled NR were weighed using one balance and swollen inside toluene for 3 days at room temperature. Compounds samples were cleaned from all residue of toluene and the weight was determined. The swelling percentage is mass change:

Swelling percentage (%) = 100% \( \frac{(W_2 - W_1)}{W_1} \) \tag{1} 

In which \( W_1 \) is the beginning mass (gr.) and \( W_2 \) is the mass (gr.) after immersion in toluene.

3. Results and discussion

3.1. Optimum curing time
The influences of ENRs incorporations on optimum curing time of compounds of silica-filled NR are visualized in Fig. 1. As visualized, incorporation of 5 phr of ENR-25 or ENR-50 into control compound (a compound with no ENR) caused in raising the optimum cure time. It was an indication of the action
of the ENRs as materials of curative that affected optimum curing time. Presumably, groups of epoxide reacted with silanol of silica and hence, the reaction needed a longer time to finish the curing process.

![Figure 1. Influence of ENRs concentration on optimum curing time](image)

It was also observed that the bigger the ENR-25/ENR-50 concentration, the longer the optimum curing times were. It was because of the bigger amount of groups of epoxide presented inside the filled-NR compounds. The more the epoxide groups, the longer the time to finish the curing process.

At a similar concentration of ENR, optimum curing time of ENR-25 was shorter than that of ENR-50. Naturally, it was because of level of epoxidation of ENRs and hence, ENR-25 got fewer epoxide groups.

3.2. Swelling properties

Fig. 2 visualized the influence of ENR-25 or ENR-50 on swelling percentages of vulcanizates of silica-filled NR. Since swelling percentage reflects the crosslinks level of rubber compounds [5] in which, with bigger amount/concentration of toluene did penetration into compound sample meant a higher swelling percentage; indicating a lower level of crosslinks [6]. The ENRs incorporation at 5.0 phr. reduced the swelling percentage or raised crosslink density. The raising of crosslinks was attributed to the epoxide groups - silanol groups reactions and also intercalation and exfoliation processes [7]. The latter processes enhanced the rubber to filler interactions.

Normally, the overall crosslinks of a rubber vulcanize are the sulphide and physical [8-9]. Since the ENRs may undergo several acid catalyst ring-opening reactions through some ether type crosslinks in curing process; causing in crosslinks raising [10]. As a consequence, total crosslinks of vulcanizates of silica-filled NR in the presence of ENR-25 or ENR-50 might have crosslinks of physical, ether and sulphide types.

Bigger concentration of ENRs produced higher crosslinks level. It was because of action of ENR-25/ENR-50 as compatibilizing and curative materials. During the process of curing, a combination of other curatives and ENRs enhanced the crosslinks forming include ether and sulphide crosslinks. Together, they mininished the agglomerations of filler particles and raised interactions of rubber to filler, respectively and, interactions of rubber to filler is known as crosslinks of a physical type [11].

At a similar concentration of ENR, crosslinks level of ENR-25 system was fewer than that of ENR-50 system. Repeatedly, it was an indication of epoxidation degree that has performed a significant function in process of curing upon the compounds of silica-filled NR. The ENR-25 system with fewer epoxide yielded a lower level in extra crosslinks of ether type.
3.3. Elongations at break, tensile moduli and strength

The influences of ENRs on tensile properties such as M300/M100 (tensile moduli), EBs (elongations at break) and TS (tensile strength) are visualized in Figs. 3-6. As visualized in Figs. 3 and 4, an incorporation of 5 phr of ENRs raised tensile moduli and, increases the ENRs concentration further raised the tensile moduli. Since the tensile moduli depend on crosslinks level [10], the raising of tensile moduli was because of the crosslinks enhancement.

At a similar concentration of ENR, the tensile moduli of ENR-25 system were lower than those of ENR-50 system. It was associated with a fewer level of ether type crosslinks of ENR-25 system than ENR-50 system.
Fig. 5 visualized that an incorporation of 5 phr of ENRs reduced EB and, the bigger the ENRs concentration, the lower were the EBs. It was because of the raising of crosslinks level which immobilized the movements of NR chains.

At a similar concentration of ENR, EBs of ENR-25 system were longer than those of ENR-50 system. It was because of the lower crosslinks level of ENR-25 system which mobilized the NR chains more freely.

From Fig. 6, an incorporation of 5 phr of ENRs raised TS and TS was further raised slightly up to 25 phr of the ENRs incorporations. The raising TS was because of the higher level of crosslinks.

At a similar concentration of ENR, the TS of ENR-25 system was lower than that of ENR-50 system. Positively, it was because of fewer crosslinks of ENR-25 system than ENR-50 system.
4. Conclusions
The curative affection of epoxidised natural rubbers raised optimum curing times of compounds of silica-filled natural rubber. The compatibilizing affection of epoxidised natural rubbers raised crosslinks level and tensile properties. The raising of crosslinks and tensile properties by forming the ether crosslinks and improving rubber to filler interactions. The bigger the epoxidised natural rubbers concentrations inside the compounds of silica-filled natural rubber; causing in a more significant were affections of curative and compatibilization.

At a similar concentration; crosslinks level, tensile moduli and strength of epoxidised natural rubber with 25 percent of moles epoxidation were lower than epoxidised natural rubber with 50 percent of moles epoxidation.

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