

Use of Epoxidized Natural Rubber as a Compatibilizer in Silica-filled Natural Rubber Compounds

Karnda Sengloyluan^{1,2}, Kannika Sahakaro^{1,2*}, Wilma K. Dierkes² and Jacques W.M. Noordermeer²

¹*Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani 94000 Thailand.*

²*Department of Elastomer Technology and Engineering, Faculty of Engineering Technology, University of Twente, P.O.Box 217, 7500 AE Enschede, The Netherlands.*

Abstract

Silica-filled natural rubber (NR) tire tread compounds with epoxidized natural rubber (ENR) as a compatibilizer were investigated. The ENRs were prepared by an in-situ performic epoxidation reaction and characterized by proton nuclear magnetic resonance spectroscopy. The epoxide levels of 10, 38 and 51 mole% with ENR contents of 2.5-15.0 phr were used as compatibilizers in the silica-filled NR compounds. Cure characteristics, flocculation rate constant, bound rubber contents, and mechanical properties of the silica-filled NR were studied. Increasing the mole% of epoxide and ENR contents increased cure and scorch times of the silica-filled compounds, while silica flocculation decreased, when compared with a silica-filled compound without ENR. Total bound rubber and chemically bound rubber contents of the compounds which indicate interaction/reaction between the epoxide groups of ENR and silanol groups on the silica surface also increased with increasing epoxide levels. The addition of ENR as a compatibilizer decreased the Mooney viscosity of the compounds, which can be related to an improvement of silica dispersion in the compounds. Tensile strength and reinforcing index of the vulcanizates increased with increasing mole% of epoxide and ENR contents up to 7.5-10.0 phr.

Keywords: silica, epoxidized natural rubber, natural rubber, compatibilizer

***Corresponding Author:** K.Sahakaro (skannika@bunga.pn.psu.ac.th)

Introduction

Natural rubber (NR), butadiene rubber (BR) and styrene-butadiene rubber (SBR) are non-polar rubbers which are widely used in tire industry. Recently, silica has been used to replace carbon black to produce fuel saves tire. But due to the silanol groups on its surface, silica is highly polar and incompatible with the non-polar rubbers. Polar functional groups of the silica surface may form hydrogen bonds with some polar components in the rubber compound such as accelerators, and thus affect on cure properties. A successful use of silica for rubber reinforcement therefore requires silane coupling agents to improve silica-filled rubber properties. However, some polar rubbers bearing functional groups which can interact with the silica surface have been studied as alternatives to silane to enhance interaction in silica-filled compounds [1, 2].

Epoxidized natural rubber (ENR) shows a higher polarity than NR due to the epoxide groups in its structure. By its polar functional groups, ENR interacts with hydroxyl groups on the silica surfaces. It has been reported that the mechanical properties of silica-filled

ENR without silane coupling agent were higher than those of silica-filled NR without silane. This was due to improved interaction between the ENR and silica surface via hydrogen bonds [3].

In the present study, ENRs with different mol% epoxide are used as compatibilizers. The effects of ENR contents and mole% of epoxide on the properties of silica-filled natural rubber are investigated.

Experimental

1. Chemicals and compound preparation

The compounding ingredients were natural rubber (RSS 3), epoxidized natural rubbers with 10, 38 and 51 mol% of epoxide denoted as ENR-10, ENR-38 and ENR-51, respectively, highly dispersible silica (Zeosil 1165MP), bis-(3-triethoxysilyl-propyl)tetrasulfide (TESPT), N-cyclohexyl-2-benzothiazole sulfenamide (CBS), diphenyl guanidine (DPG), treated distillate aromatic extract (TDAE) oil, 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), ZnO, stearic acid, and sulfur.

The rubber compounds were prepared using the formulation as shown in Table 1. Mixing was carried out in an internal mixer (Brabender 350s) using an initial mixer temperature setting of 110°C, rotor speed 60 rpm for 15 min. Then the compound was mixed with curatives on a two roll mill for 5 min.

Table 1 Compound formulations

Chemicals	Amounts (phr)		
RSS 3	100.0	100.0	Variable
ENRs	-	-	Variable
Zeosil 1165MP	55.0	55.0	55.0
TESPT*	-	4.5	-
TDAE oil	8.0	8.0	8.0
ZnO	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0
TMQ	1.0	1.0	1.0
DPG*	1.0	1.0	1.0
CBS	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5

*Amounts of TESPT and DPG were calculated according to the silica CTAB surface area with following equations [4]:

$$\text{TESPT (phr)} = 0.00053 \times Q \times A$$

$$\text{and DPG (phr)} = 0.00012 \times Q \times A$$

Where Q is the amount of silica (phr) and A is the CTAB surface area of the silica (m²/g).

2. Preparation of epoxidized natural rubber

High ammonia latex (HA) with 60 wt% of dry rubber content was used to prepare ENR via an in-situ performic epoxidation reaction [5] at a temperature of 40°C using Teric N30 as a stabilizer. The reaction time of epoxidation was set according to the required level of epoxide groups in the ENR product. ¹H NMR technique was used to analyze the molecular structure of the ENR [6].

3. Mooney viscosity, cure properties, Payne effect and flocculation

Mooney viscosity was tested using Mooney viscometer (MV 2000VS, Alpha Technologies) according to ASTM D1646. Cure properties were studied by using a Rubber Process Analyzer (RPA 2000, Alpha Technologies) at 150°C (ASTM D2084). The Payne effect or filler-filler interaction and the flocculation rate constant (k_a) of the silica-filled compounds before vulcanization were studied by using the RPA 2000 at 100°C. The measurement and calculation of k_a are as detailed by Kaewsakul *et al.* [7].

5. Bound rubber measurement

Uncured masterbatch (without curatives) was put into a metal cage and immersed in toluene at room temperature for 72h (renewed every 24h) in either a normal or an ammonia atmosphere. The sample was finally dried in an oven. The bound rubber content was calculated using the following equation;

$$\text{Bound rubber (\%)} = \frac{(m - m_s)}{m_r} \times 100$$

Where m is the weight of sample after extraction, m_s is the weight fraction of silica in the sample and m_r is the weight fraction of rubber in the sample. The ammonia treatment was to cleave the physical interactions, so that truly chemical interaction could be determined [8].

6. Tensile properties

The rubber sheets were press-cured at 150°C to their optimum cure time and tested at a crosshead speed of 500 mm/min. (ASTM D412) using dumb-bell shaped specimens.

Results and discussion

1. Mooney viscosity and Payne effect

Mooney viscosities of the compounds with ENR-10 as compatibilizer show almost no change (Figure 1a), while ENR-38 and ENR-51 decrease the Mooney viscosities of the compounds to a level similar to that of a TESPT-containing compound.

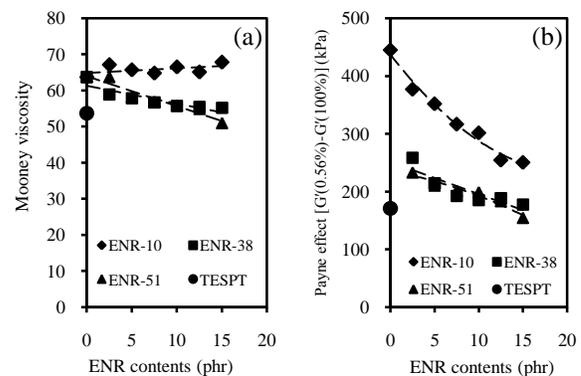


Figure 1 Mooney viscosity (a) and Payne effect (b) of silica-filled natural rubber with ENR as a compatibilizer.

Filler-rubber interaction of the filled compounds as indicated by the Payne effect in Figure 1b, decreases when the ENR content is increased. The lower Payne effect indicates less silica-silica interactions, i.e. better dispersion of silica in the matrix. The compounds with ENR-38 and ENR-51 in the range of 7.5-15 phr show similar Payne effects compared to the compound with

TESPT. The reduction of filler-filler interaction in the presence of ENR in silica-filled NR compounds can again be attributed to interactions between the silanol groups of silica and epoxide groups of ENR through hydrogen bonding and/or a chemical bonding, molding after a possible ring opening of epoxy ring which may have occurred during mixing and compression, as previously proposed by Manna *et al.* [9].

2. Flocculation

The silica-filled compounds with neither ENR nor TESPT show the highest flocculation rate constant (k_a) compared to other compounds. This is because of a strong hydrogen bonding between silica aggregates. After ENRs were added into silica-filled compounds, improvement of k_a was observed. The compounds with ENR-51 in the range of 7.5-15 phr show the same level of k_a compared to the silica-filled compound with TESPT. The use of ENR as compatibilizers can clearly reduce filler-filler interaction in the compounds leading to less re-agglomeration or flocculation phenomena.

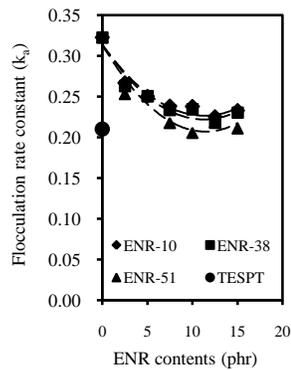


Figure 2 Flocculation rate constant (k_a) of silica-filled natural rubber with ENR as compatibilizer.

3. Filler-rubber interaction

Chemically bound rubber contents of the silica-filled NR significantly increase while physically bound rubber contents slightly decrease by increasing ENR contents and mole% of epoxide of ENR, as shown in Figure 3. The use of TESPT coupling agent leads to a remarkably high chemically bound rubber content, compared to the one without. However, the addition of ENR into the NR compounds without TESPT clearly improves bound rubber content, i.e. filler-rubber interaction. These results prove that ENR can generate chemical interaction and/or reaction in silica-filled NR.

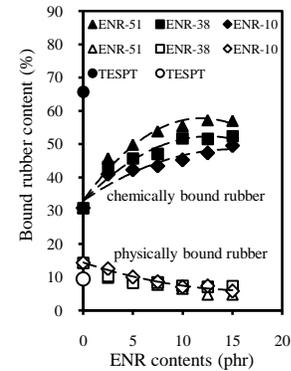


Figure 3 Physically and chemically bound rubber contents of silica-filled NR with ENR as compatibilizer.

4. Cure properties

Both scorch and optimum cure times of the compounds are prolonged when ENR contents and mole% of epoxide are increased (Figure 4). This is due to the high polarities of ENR and silica which interfere with the vulcanization. Even though part of the silanol groups are assumed to have interacted epoxide groups, the unreacted silanol groups can assume hydrogen bonding with polar accelerators, causing accelerator adsorption on the silica surface.

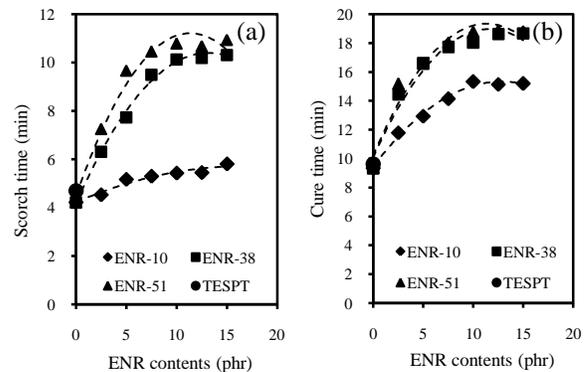


Figure 4 Scorch (a) and optimum cure times (b) of silica-filled NR with ENR as compatibilizer.

5. Mechanical and dynamic properties

The silica-filled NR with TESPT shows higher reinforcing index (M300/M100) when compared to the compounds with ENRs as compatibilizers (Figure 5). An increase of ENR content tends to decrease the reinforcing index slightly. This may be caused by the presence of two different rubber phases in the system.

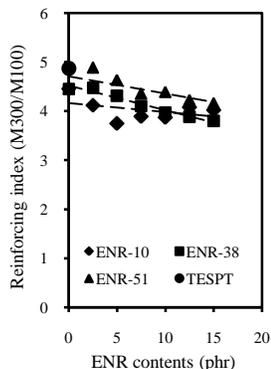


Figure 5 Reinforcing index of silica-filled natural rubber with ENR as compatibilizer.

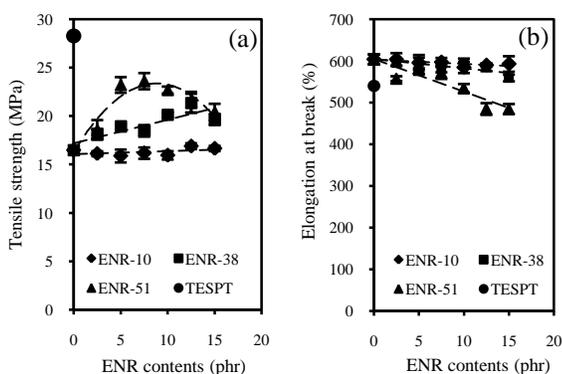


Figure 6 Tensile strength (a) and elongation at break (b) of silica-filled natural rubber with ENR as compatibilizer.

The use of ENR-10 shows no positive effect on tensile strength of the silica-filled NR, but the addition of ENR-38 and ENR-51 enhance the tensile strength, compared to the one without any compatibilizer (Figure 6a). Increasing mole% of epoxide and ENR contents increases tensile strength and the optimum value is observed when ENR-51 was used at 7.5 phr. The results support that the epoxide functional groups improve silica-rubber interaction in the compounds, in accordance with

the increased bound rubber content in Figure 3 and the decreased elongation at break as shown in Figure 6b.

Conclusions

Epoxidized natural rubber (ENR) can be used as a compatibilizer in silica-filled natural rubber, as it results in improved filler-rubber interaction, silica dispersion and tensile strength. The increasing of ENR contents and mole% of epoxide groups increase the interactions between silica and rubber, and so improves the properties. The addition of ENR-51 at 7.5 phr shows the best overall properties, however still lower when compared to a compound with TESPT silane coupling agent.

Acknowledgements

The authors acknowledge the financial support from the Dutch Natural Rubber Foundation (Rubber Stichting), the Netherlands.

References

1. A. Das; S.C. Debnath; D. De; and D.K. Basu *J. Appl. Polym. Sci* 2004, 93, 196.
2. S.-S. Choi *J. Appl. Polym. Sci* 2001, 79, 1127.
3. F. Cataldo *Macromol. Mater. Eng.* 2002, 287, 348.
4. L. Guy; S. Daudey; P. Cochet; and Y. Bomal *Kautsch. Gummi Kunstst.* 2009, 7, 383.
5. C. Nakason; A. Kaesaman; T. Wongkul; and S. Kiatkamjornwong *Plast. Rubb. Compos.* 2001, 30, 154.
6. I.R. Gelling *Rubber Chem. Technol.* 1985, 58, 86.
7. W. Kaewsakul; K. Sahakaro; W.K. Dierkes; and J.W.M. Noordermeer *Rubber Chem. Technol.* 2012, 85, 277.
8. S. Wolff *Rubber Chem. Technol.* 1982, 967, 55.
9. A.J. Manna; P.P. De; D.K. Tripathy; S.K. De; and D.G. Peiffer *J. Appl. Polym. Sci.* 1999, 74, 389.