

**Verwendung von epoxydierem Naturkautschuk als Verträglichkeitsvermittler in Zusammensetzungen aus kieselsäuregefülltem Naturkautschuk für Reifenlaufflächen**  
**Use of Epoxidized Natural Rubber as a Compatibilizer in Silica-Filled Natural Rubber Tire Tread Compounds**

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### Abstract

Silica-reinforced natural rubber (NR) tire tread compounds with epoxidized natural rubber (ENR) as a compatibilizer are investigated. ENR contents of 2.5-15.0 phr, with epoxide levels of 10, 38 and 51 mol%, are used. The addition of ENRs, especially ENR-38 and ENR-51, as compatibilizers decreases the Mooney viscosity and Payne effect (i.e. filler-filler interaction), which implies an improvement of silica dispersion in the compounds. Chemically bound rubber contents of the compounds, indicative for interaction/reaction between the epoxide-groups of the ENR and silanol-groups on the silica surfaces, also increase with higher epoxide-contents of the ENR. Raising the ENR contents and mole% of epoxide prolongs cure and scorch times of the silica-filled compounds, when compared with a silica-filled NR-compound without ENR. Tensile strength of vulcanizates is improved with increasing mole% of epoxide, and an optimum value is observed when 7.5 phr of ENR-51 was used. The results show overall, that the properties of silica-reinforced NR can be substantially improved by adding ENR as a compatibilizer, when compared with a compound without.

**Keywords:** silica, epoxidized natural rubber, natural rubber, compatibilizer, tire compounds.

### 1. Introduction

Silica shows high polarity and a hydrophilic surface due to the silanol groups on its surface. Thus, silica is not compatible with non-polar rubbers such as natural rubber (NR), styrene-butadiene rubber (SBR) and butadiene rubber (BR). It is better compatible with polar rubbers such as chloroprene rubber (CR)<sup>1</sup> and acrylonitrile butadiene rubber (NBR)<sup>2</sup>. Polar functional groups of the silica surface may form hydrogen bonds with some polar components in the rubber compound such as accelerators. So, basic accelerators can easily be adsorbed on the acidic surface of

silica and thus effect on cure properties. A successful use of silica for rubber reinforcement therefore requires silane coupling agents to improve silica-rubber interaction and silica dispersion as well as to prevent accelerator adsorption on the silica surface. 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.

Epoxidized natural rubber (ENR) shows a higher polarity than NR due to the epoxide groups in its structure. The

chemical and physical properties of ENR change according to the epoxide contents. 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 claimed to be due to improve interaction between the ENR and silica surface *via* hydrogen bonds<sup>3</sup>.

In the present study, ENRs with different mol% epoxide are used as compatibilizers at 2.5-15wt% of rubber. The effects of ENR contents and mole% of epoxide on the properties of silica-filled natural rubber are investigated.

## 2. Experiments

### 2.1 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-triethoxysilylpropyl)tetrasulfide (TESPT), N-cyclohexyl-2-benzothiazole sulfenamide (CBS), diphenyl guanidine (DPG), treated distillate aromatic extract oil (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 using an internal mixer (Brabender 350s) using an initial mixer temperature setting of 110°C, rotor speed 60 rpm, according to a mixing procedure shown in Table 2.

### 2.2 Mooney viscosity and cure properties

Mooney viscosity was tested using Mooney viscometer (MV 2000VS, Alpha Technologies) at 100°C according to ASTM D1646.

Cure properties of the compounds were studied by using a Rubber Process Analyzer (RPA 2000, Alpha Technologies) at 150°C for 30 min.

Table 1 Compound formulations

Chemicals	Amount (phr)		
RSS 3	100.0	100.0	variable
ENRs	-	-	variable
Zeosil 1165	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
Sulphur	1.5	1.5	1.5

\*Amounts of TESPT and DPG were calculated according to the silica CTAB surface area with following equations<sup>4</sup>:

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

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

Where Q is the amount of silica (phr) and A is the CTAB surface area of the silica (m<sup>2</sup>/g).

Table 2 Two-step mixing procedures

Mixing procedures	Time (min)
<i>Step 1: Internal mixer</i>	
- Mastication	2
- Addition of a half of silica	5
- Addition of a second half of silica and TDAE oil	5
- Addition of stearic acid, ZnO and TMQ	3
<i>Step 2: Two roll mill</i>	
- Addition of DPG, CBS and Sulfur	5

### 2.3 Payne effect

The Payne effect or filler-filler interaction of the silica-filled compounds were studied by using the RPA 2000 at 100°C, frequency 0.5 Hz and strain sweep at 0.56 to 100%, before vulcanization.

## 2.4 Bound rubber measurement

0.25 g of uncured masterbatch (without curatives) was put into a metal cage and immersed in toluene for 72 h (renewed every 24 h). The sample was removed from the toluene, dried at 50°C for 24 h, then immersed in toluene again for 72 h at room temperature in either a normal or an ammonia atmosphere. The ammonia treatment was to cleave the physical linkages between rubber and silica in order to determine the true chemically bound rubber. The sample was finally dried at 50°C for 24 h. The bound rubber content was calculated using the following equation<sup>5</sup>;

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

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.

## 2.5 Tensile properties

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

## 3. Results and discussion

### 3.1 Mooney viscosity and Payne effect

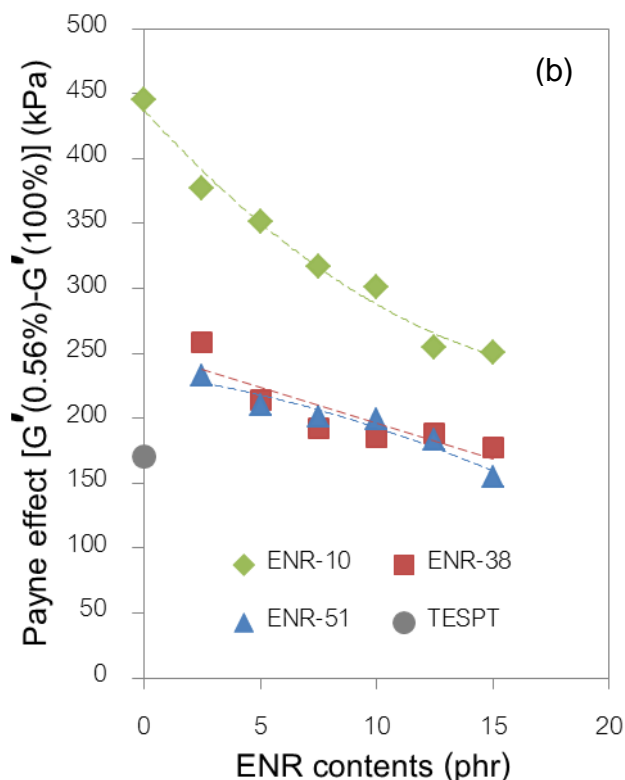
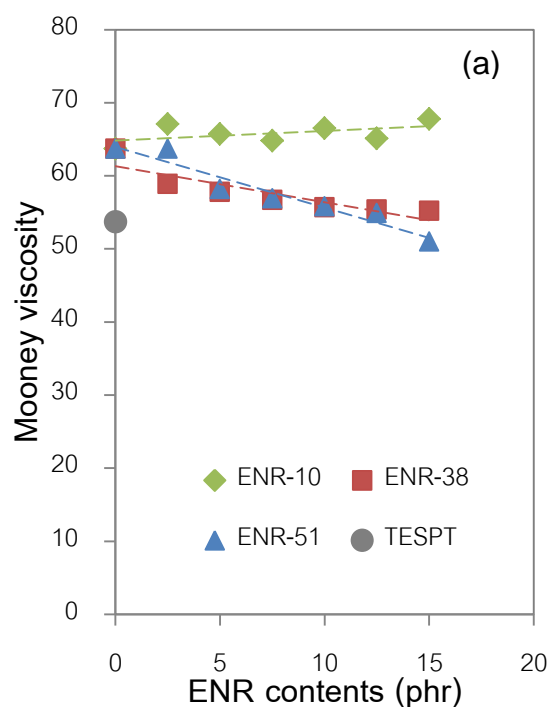
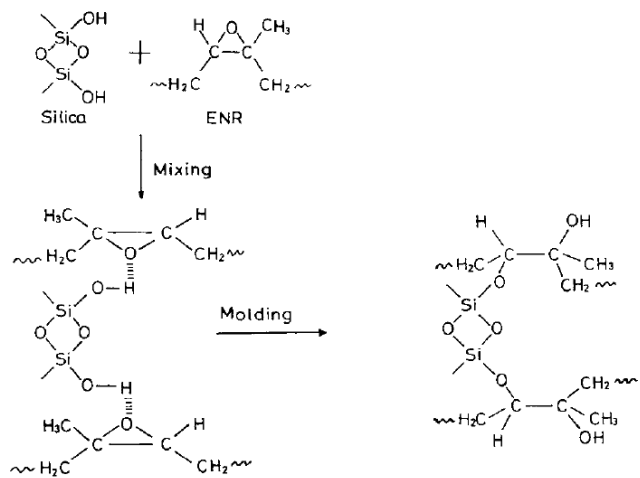


Figure 1 Mooney viscosity (a) and Payne effect (b) of silica-filled natural rubber with ENR as a compatibilizer.

Mooney viscosities of the compounds with ENR-10 as compatibilizer show almost no change (Figure 1a) when the amount of ENR-10 is increased from 2.5 to 15 phr. However, ENR-38 and ENR-51 decrease the Mooney viscosities of the compounds to a level similar to that of a TESPT-containing compound. The decrease of compound viscosity when ENR is used implies an improvement of silica dispersion due to the interactions between epoxide groups and silanol groups of silica which result in better compatibility.

Filler-rubber interaction, as indicated by the Payne effect in Figure 1b also, of the filled compounds decreases when the ENR content is increased. The compounds containing ENR-10 as compatibilizer show the highest filler-filler interaction, while the compounds with ENR-38 and ENR-51 show much lower and similar values. 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, which may have occurred during mixing and compression molding, as previously proposed by Manna *et al.*<sup>6</sup> Scheme 1.



Scheme 1 Probable mechanism of bonding between ENR and silica<sup>6</sup>.

### 3.2 Filler-rubber interaction

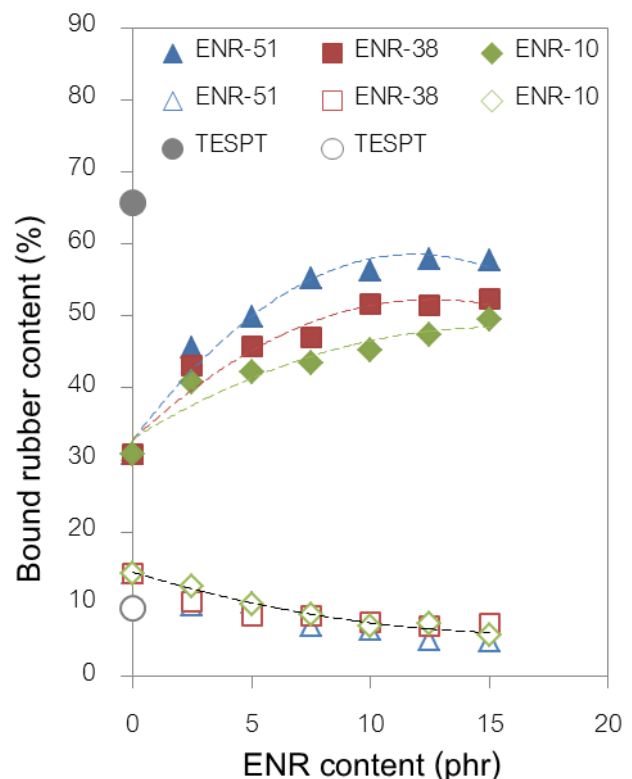


Figure 2 Physically and chemically bound rubber contents of silica-filled NR with ENR as compatibilizer.

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 2. When pure NR was used, 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. The use of ENR-51 in the range of 7.5-15 phr results in the optimum chemically bound rubber content.

### 3.3 Cure properties

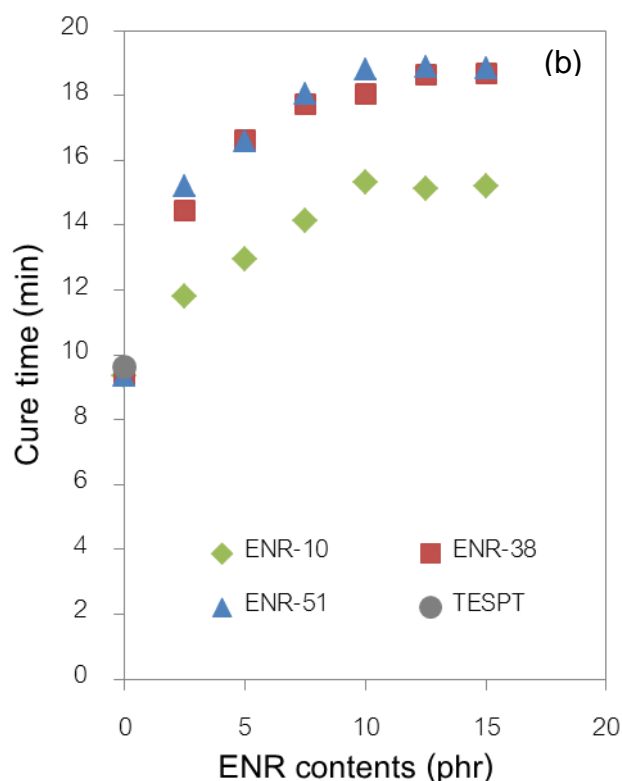
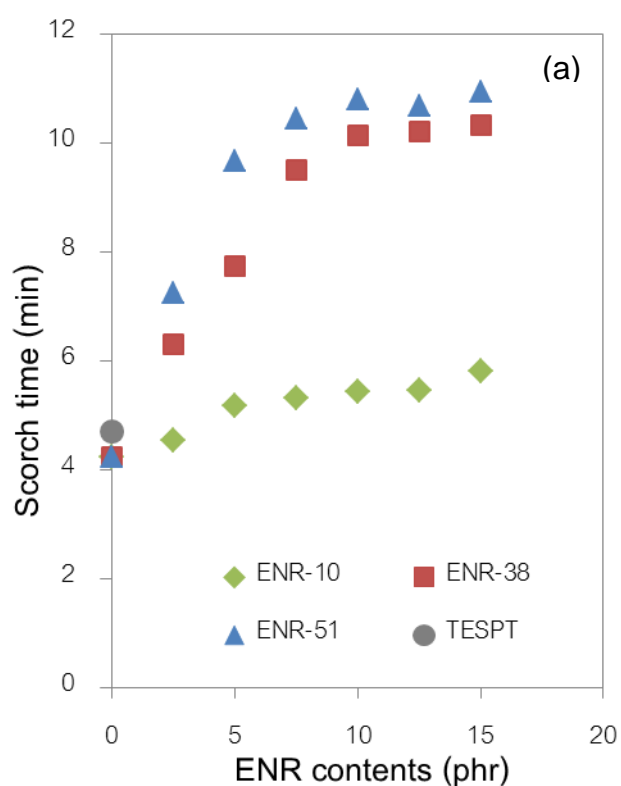


Figure 3 Scorch (a) and optimum cure times (b) of silica-filled NR with ENR as compatibilizer.

Optimum cure time ( $T'_{c90}$ ) and scorch time ( $T_{s1}$ ) of the compounds are shown in Figure 3a and 3b. Both cure and optimum scorch times of the compounds are prolonged when ENR contents and mole% of epoxide are increased. 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 with epoxide groups, the silanol groups which are still free can assume hydrogen bonding with polar accelerators, causing accelerator adsorption on the silica surface. In addition, due to the polarity difference between NR and ENR, the more polar curatives can migrate into the ENR phase, and so cause a delay of the vulcanization reaction in the NR matrix. For the silica filled-compound with TESPT,

because TESPT itself can act as sulfur donor and optimized mixing conditions were employed to ensure a good silanization reaction, the compound therefore displays short scorch and cure times.

### 3.4 Mechanical properties

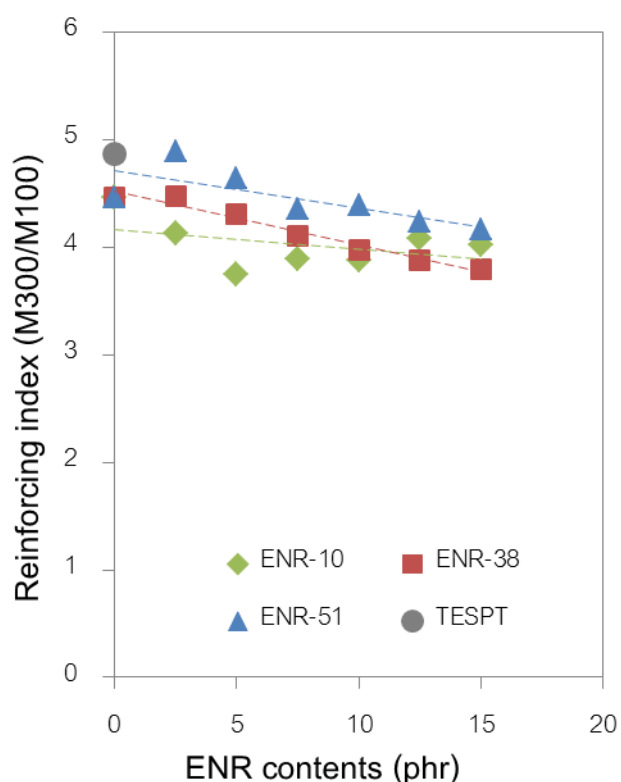
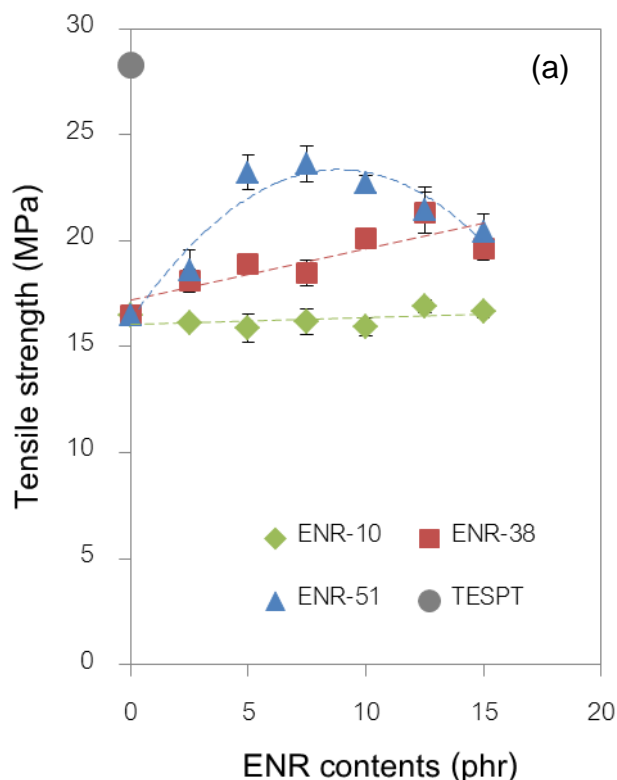


Figure 4 Reinforcing index of silica-filled natural rubber with ENR as compatibilizer.

The silica-filled NR with TESPT shows higher reinforcing index (M300/M100) when compared to the compounds with ENRs as compatibilizers (Figure 4), indicating a greater extent of interactions between the silica and rubber phases when a silane coupling agent is used. When compared amongst the ENR types, the use of ENR-51 gives the highest reinforcing index. 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.

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 5a). Increasing mole% of epoxide and ENR contents increases tensile strength; the optimum value is observed for ENR-51 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 2 and the decreased elongation at break as shown in Figure 5b.



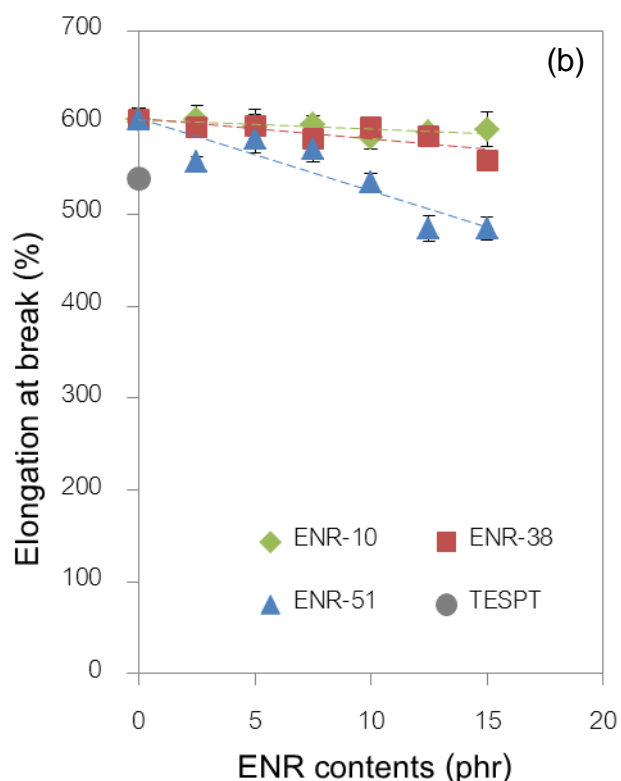


Figure 5 Tensile strength (a) and elongation at break (b) of silica-filled natural rubber with ENR as compatibilizer.

#### 4. 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 increase of ENR content and molar% of epoxide group increases the interactions between silica

and rubber, and so overall 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 TESP silane coupling agent.

#### 5. References

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