Influence of TESPT on Tensile and Tear Strengths of Vulcanized Silica-filled Natural Rubber

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The effect of coupling agent on tensile and tear strengths of vulcanized NR filled with 50 pphr of precipitated silica (VN3) was investigated. The amount of coupling agent was varied from 0, 1, 2, 3, 4, 5 to 8 pphr. In the absence of coupling agent bis[3-(triethoxysilyl)propyl] tetrasulphide (TESPT), the tensile strength of silica-filled vulcanized NR was lower than the tensile strength of unfilled vulcanized NR. The enhancement in the tensile strength was achieved only when TESPT was incorporated into the rubber compound. The dependence of tensile strength on the amount of TESPT showed a similar trend as the dependence of tensile strength on the crosslink concentration. This might imply that varying the amount of TESPT was analogous to varying the crosslink concentration of the rubber network. The effect of TESPT on tearing energy was very striking in silica-filled vulcanized NR. Without Si69, the crack propagated in a steady (smooth) manner where the tearing energy increases with increasing test speed. When TESPT was added into the silica mix, the crack propagated sideways from the intended tear path producing the so called knotty tearing. The tearing energy was about a factor of ten higher than that without coupling agent in particular at low tear rates regions. The results here indicated clearly that in silica-filled vulcanized NR, coupling agent was essential to induce the strength anisotropy necessary for the occurrence of knotty tearing. The result also showed that TESPT also influenced the amount of hysteresis in silica-filled vulcanized NR. Both tensile and tear strengths were affected by the hysteresis.

Key words: Coupling agent; TESPT; tensile strength; tearing energy; hysteresis; silane 69

Reinforcement of elastomers by colloidal fillers, like carbon black or silica, plays an important role in the improvement of the mechanical properties of high-performance rubber materials. The reinforcing potential is mainly attributed to two effects: (i) the formation of a physically bonded flexible filler network and (ii) a strong polymer–filler couplings (Vilgis 2009). Both of these effects arise from a high surface activity and the specific surface of the filler particles. Natural rubber is completely hydrocarbon and non-polar. On the other hand, the silica fillers

are polar in nature which need coupling agent to bond the rubber and silica fillers. Föhlich *et al.* (2005) stated that the silica fillers form a strong filler network with minimal interaction with the polymer chain but form a chemical linkage when a coupling agent is introduced. Coupling agent bis[3-(triethoxysilyl)propyl] tetrasulphide abbreviated as TESPT commonly known as Silane 69 has been found to be very effective. Choi and Kim (2002) reported that silane coupling agent enhanced the bound rubber formation by chemicals bonds between the

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silica and rubber. Vilgis *et al.* (2001) suggested that there are primary and secondary chemical reactions taking place that lead to chemical bonding between the silica fillers and rubber chains via TESPT as shown in *Figure 1*.

It was reported by Park and Choo (2003), and Gent *et al.* (2003) that the organic functional group of silica surface lead to an increase of adhesion at interfaces between silica and the rubber chains resulting in an enhancement of crosslink density. Our concern here is to investigate the effects of the chemical bonding that formed at the filler surface and the rubber chains via TESPT on the mechanical strengths of vulcanized silica-filled NR. It is well established that mechanical properties such tensile and tear strengths are affected by the crosslink concentration. Apart from crosslink concentration, the strength and nature of chemical bonds bridging the filler surface and rubber chains also affect tensile and tear strengths.

EXPERIMENTAL

Table 1 shows the formulations of the natural-rubber silica-filled compound. Natural rubber (SMR L) was used throughout. The amount of precipitated silica was fixed at 50 pphr, and the amount of coupling agent (TESPT) was varied from 1 to 8 pphr. Mix no. 1 was unfilled (gum) compound without any filler. Mix no. 2 served as the control compound containing 50 pphr of precipitated silica but without TESPT. Semi-EV sulphur vulcanization system was used throughout. There was an additional mix with 10 pphr of TESPT for the tear experiment.

All rubber mixes were prepared in a laboratory Banbury mixer (capacity 1600 cm³) with the following mixing conditions:

Initial temperature of mixing chamber : 70°C
Rotor speed : 110 rpm
Fill factor : 0.7

Mixing sequence:

0 minute — Rubber

½ minute — All chemicals + ½ silica

1½ minute — Remaining ½ silica + Si69 + DEG

2½ minutes — Sweep

3½ minutes — Discharge.

The weight of each mix was recorded immediately after it was discharged and left overnight. Curatives were added on the 2-roll mill the next day. Mixing on the 2-roll mill was about 5 minutes. The finalized mix compound was sheeted out, cooled and stored at 23°C. The weight loss of all the eight mixes ranged from 0.38% to 1.6%. The recorded discharge temperature of the mixes ranged from 130°C – 140°C. Samples were taken from each mix to determine their Mooney viscosity at 100°C by using Mooney viscometer and cure characteristics by using Monsanto Rheometer at 150°C.

Moulding of the test-pieces was done in an appropriate compression mould in an electrically heated press at 150°C. The cure time of each mix was referred to t₉₅ of the rheometer torque-time chart.

Figure 1. Chemical bonding that formed between rubber chains and silica surface via TESPT (Vilgis et al. (2003)).

Table 1. Natural rubber silica-filled formulations.

Mix no.	1	2	3	4	5	6	7	8
NR (SMR L)	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
Santoflex 13 TM	3	3	3	3	3	3	3	3
Precipitated silica (VN3)	—	50	50	50	50	50	50	50
Si 69 (TESPT)	—	—	1	2	3	4	5	8
DEG	—	—	2	2	2	2	2	2
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

All the ingredients are expressed as parts per hundred of rubber (pphr).

Tensile Test

Tensile strength and elongation at break were done by pulling a dumbbell test-piece at 500 mm per minute at 23°C by using a tensile machine in accordance with *ISO 37*. The mean value from five readings were recorded.

Tear Test

Tearing was carried out by separating the legs of the trouser test-piece using an Instron tensile machine at test speeds ranging from 5 mm per minute to 1000 mm per minute. In the case of constant rate separation method, the tear

rate was half the crosshead speed (extension rate) (Samsuri & Thomas 1988; Greensmith & Thomas 1955). The tearing energy, T for the trouser test-piece was computed using *Equation 1* given by Samsuri and Thomas (1988); and Greensmith and Thomas (1955).

$$T = F(\lambda + 1) / h \quad (1)$$

where, F is the force to propagate tearing, λ is the extension ratio in the legs of the test-piece and h is the average nominal thickness of the test-piece.

Hysteresis Test

The test-pieces $75 \text{ mm} \times 10 \text{ mm} \times 1 \pm 0.2 \text{ mm}$ were prepared by stamping a die on a flat vulcanized rubber sheet of uniform thickness. The test was conducted at $23 \pm 2^\circ\text{C}$. The test-piece was clamped between the two grips of the tensile machine and the gauge length (40 mm) between the grips was noted. The test-piece was stretched to 300% strain and then relaxed it to zero strain. This process was repeated six times

at the test speed of 500 mm per minute. The hysteresis was determined from the area of the hysteresis loop (area bounded by the extension and retraction curves as shown by a schematic diagram in *Figure 2*) of the sixth cycle.

Hardness Test

Hardness is defined as the resistance to surface indentation as measured under specified conditions. The test was done in accordance with *ISO 48*. A cylindrical test-piece (8 mm thick, 25 mm diameter) was placed underneath a spherical indenter where a specific load was applied for a specific time. The hardness reading was displayed electronically by the hardness tester.

RESULTS AND DISCUSSIONS

The Rheological and Cure Characteristics of Silica-filled NR Compounds

The Mooney viscosity and cure characteristics of the silica-filled NR compounds are shown in *Table 2*. The Mooney viscosity of gum

Figure 2. Schematic diagram showing the force-extension and retraction curves. The area bounded by the extension and retraction curves is known as hysteresis (Azemi 2008).

Table 2. Mooney viscosity (M_L (1+4) 100°C) and optimum cure time (t_{95}) of silica-filled NR compounds.

Mix number	1	2	3	4	5	6	7	8
M_L (1+4) 100°C	29.6	44.9	61.3	65	63.9	62	58.7	54.4
t_{95} (minutes) at 150°C	18	22	15	15	17	18	19	20

compound (Mix 1) was very low since there was no filler in the compound apart from ingredients necessary for vulcanization. Mixes 2 to 8 contained the fixed amount of filler (VN3) but varying amount of TESPT. It could be seen that Mix 2 produced higher Mooney viscosity by about 52% than the unfilled compound. This increase was associated with the hydrodynamic effect. The addition of TESPT increased the Mooney viscosity of the compound ranging from 22% to 40% depending on the level of TESPT. This further increase might be associated with the enhancement in the rubber-filler interaction that occur during mixing (Luginsland *et al.* 2021). The addition of silica increased the optimum cure time from 18 minutes (Mix 1, unfilled) to 22 minutes (Mix 2) because of the tendency of the silica

filler to absorb curatives associated with its surface ruggedness. Mixes 3 to 8 contained diethylene glycol (DEG) to minimize absorption of curatives by the filler. Consequently, the cure time is shortened.

Effect of TESPT on Hardness of Vulcanized Silica-filled NR

Before discussing the mechanical strengths (both tensile and tear), it is useful also to look at the hardness of the vulcanized rubber since it can be used to measure the degree of reinforcement. The hardness of gum (unfilled) vulcanized NR is 40.1 IRHD for this particular semi-EV system. The addition of 50 pphr of silica increased the hardness markedly to 70 IRHD as shown in *Figure 3*. The results indicated that hardness increased progressively with

Figure 3. Effect of TESPT on hardness of vulcanized silica-filled NR.

increasing amount of TESPT. The mechanism by which filler enhances the hardness and modulus is reasonably well understood, at least in qualitative terms. The stiffening is in part attributed to the absence of deformation within the rigid filler particles, and in part with the immobilization of the rubber at the interface between the rubber matrix and the filler particles as a consequence of two-network formation, plus the hydrodynamic effect (Ligginsland *et al.* 2001; Vilgis *et al.* 2009). According to Vilgis *et al.* (2009) coupling agents such as TESPT have triethoxysilyl functions which can react with the silanol groups on the silica surface. This chemical reaction is known as ‘silanization reaction’. During the reaction, one ethoxy group of each Si-unit reacts with an accessible silanol group on the silica surface and, therefore, links chemically to the filler (Vilgis *et al.* 2009). The hardness increased with increasing amount of TESPT because of the enhancement of the two-network formation since the level of accessible silanol group was always high.

Influence of TESPT on Tensile Strength

The coupling agent TESPT showed very

marked influence on the tensile strength of vulcanized silica-filled NR as shown in Figure 4. The tensile strength of gum (Mix 1) vulcanized NR is relatively high (22 MPa) because of its ability to strain crystallize during stretching. Indeed the tensile strength of gum vulcanizate was greater than silica-filled NR without coupling agent (Mix 2). At first sight, it is unthinkable that silica-filled vulcanized NR gives lower tensile strength than unfilled vulcanized NR. This is a perfect example of the compound nature of the mechanism of reinforcement of particulate fillers in vulcanized rubber. In the absence of efficient bonding or interaction at the rubber-filler interface, the expected reinforcement cannot be achieved. In the presence of coupling agent, silica-filled vulcanized NR gave markedly higher tensile strength than that of without coupling agent. This indicated the significant influence of coupling agent to enhance the rubber-filler interaction. It was interesting to note that the tensile strength increased with increasing amount of TESPT until it reached an optimum level. Above this optimum level of TESPT, the tensile strength decreased similarly as the

Figure 4. Plot of tensile strength vs TESPT showing the influence of TESPT on tensile strength.

dependence of tensile strength on the crosslink concentration of the rubber network as shown in *Figure 5*. The same explanation might be put forward to explain the dependence of tensile strength on TESPT. The effect of increasing the amount of TESPT is analogous to increase the crosslink concentration. Azemi and Che Mohd (2013) found that the volume fraction, v_r , of the rubber in the swollen gel increases with increasing TESPT as shown in *Figure 6*. The reduced swelling of silica-filled vulcanizates can reflect an increase in crosslinking efficiency of the vulcanizing system and hence a greater degree of actual crosslinking, or adhesion of rubber to filler particles, causing reduced

swelling near the particles even when the degree of crosslinking is unchanged (Gent & Hartwell 2003).

At optimum TESPT, the network structure was already completed, and further insertion crosslink could only result in the tightening of the network. This, in turn, imposed an increasing number of restrictions on any molecular segment attempting to orientate and aligned with neighboring segments. The overall effect was that the degree of oriented crystallization fell and consequently the tensile strength decreased.

Figure 5. Dependence of tensile strength on crosslink concentration. Black-filled vulcanized NR (Samsuri 1989).

Figure 6. Effect of cyclic pre-stressing (10 cycles at 10MPa) on volume fraction of rubber in the swollen gel of silica-filled vulcanized NR containing different amounts of coupling agent, Si69 (TESPT) – (Azemi & Che Mohd 2013).

Influence of TESPT on Tear Strength

Figure 7 shows the influence of coupling agent on the tearing energy of silica-filled vulcanized NR. Without the coupling agent, the tearing strength of silica-filled vulcanized NR was relatively low, particularly at the low tear rates. In the absence of coupling agent, knotty tearing was not produced. Instead, the crack propagated in a steady (smooth) manner, and the tearing energy was strongly dependent on the tear rate. The tearing strength increased with increasing tear rate since the energy dissipation increased with the rate as well. However, in the presence of coupling agent knotty tearing was produced. The tearing energy was about a factor of ten higher than that without coupling agent in particular at low tear rates regions. The results here indicated clearly in the silica-filled vulcanized NR; and coupling agent was essential to induce the strength anisotropy necessary for the occurrence of knotty tearing. Without coupling agent the rubber-filler interaction was very weak that the stress was dissipated before it is high enough to cause the orientation of filler structure. In the presence of coupling agent, the rubber-filler interaction is strong sufficiently to support high stresses to

cause the orientation of filler structure and hence the strength anisotropy was necessary for the occurrence of knotty tearing. Figure 10 indicates that 5 pphr appears to be the optimum quantity of coupling agent to produce high tearing energy over the whole range of tear rates. At 10 pphr of TESPT, the tearing energy decreased particularly at the fast rate. This might be attributed to the tightening of network structure at the rubber-filler interface that might interfere with the development of strength anisotropy. Silica-filled NR gave higher tearing energy than that of black-filled NR. Without coupling agent, tearing energy of silica-filled NR was lower than that of black-filled NR.

Influence of TESPT on Hysteresis

Figure 8 shows that the hysteresis increases steadily with increasing amount of TESPT. Hysteresis or energy dissipation affects a number of physical and mechanical properties such as rolling resistance, skid resistance, damping, tensile and tear strengths. The increase in tensile and tear strengths with increasing TESPT could be partly related to the increase in hysteresis. When hysteresis is high, more energy input is required to do external work.

Figure 7. Influence of coupling agent on tearing energy of silica-filled vulcanized NR.

Figure 8. Effect of TESPT on hysteresis (6th cycle).

CONCLUSIONS

The extent of reinforcement in silica-filled vulcanized natural rubber was affected by the amount of coupling agent TESPT. At 50 pphr of precipitated silica, the hardness increased progressively with increasing amount of TESPT.

There was an optimum level of TESPT to achieve high tensile strength and high tearing energy. This optimum level was at 4 pphr for tensile strength and 5 pphr for tearing energy. In the case of tensile strength, beyond 4 pphr of TESPT the crosslink network becomes tight and tensile strength decreases (Azemi 2014). In the case of tearing energy, without TESPT the tear behaviour was predominantly associated with steady tearing that produced low tearing energy. TESPT was necessary to produce high tearing energy associated with an occurrence of knotty tearing.

The hysteresis increased with increasing TESPT. This increase in hysteresis was also responsible for the increase in tensile and tear strengths.

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