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Silica-Reinforced NR Compounds

By Wisut Kaewsakul[1,2], Kannika Sahakaro[1,2], Wilma K. Dierkes[2]
and Jacques W.M. Noordermeer[2,*]
(1) Prince of Songkla University, Dept. of Rubber Technology and Polymer
Science, Pattani 94000, Thailand
(2) University of Twente, Dept. of Elastomer Technology and Engineering,
7500AE Enschede, the Netherlands

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Wisut Kaewsakul[1,2], Kannika Sahakaro[1,2], Wilma K. Dierkes[2] and Jacques W. M. Noordermeer[2]

[1]Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani 94000, Thailand; Fax: (+66) 73 331 099; E-mail: skannika@bunga.pn.psu.ac.th

[2]Department of Elastomer Technology and Engineering, University of Twente, P.O. Box 217, 7500AE Enschede, the Netherlands

The dispersion stability of silica aggregates in the rubber matrix is one of the concerns for silica-filled compounds. Silica aggregates tend to flocculate due to their poor compatibility with the rubbers and consequent strong tendency for self-association. The flocculation process can occur during compound storage as well as at the onset of vulcanization. This present work studies the kinetics of the flocculation process in silica-reinforced natural rubber (NR) compounds by following the changes of the storage modulus during thermal annealing under conditions applied for vulcanization. The results demonstrate that silica flocculation can be effectively suppressed by increasing compound dump temperature and amount of silane, as these result in a better degree of dispersion, higher degrees of hydrophobation and filler-rubber interaction. The compounds containing highly dispersible silicas exhibit greater filler-rubber interaction, but their flocculation processes develop faster when compared to the compounds filled with conventional silicas. Epoxidation of NR clearly influences the filler-rubber interaction, but shows no clear evidence of a change of flocculation rate.

Keywords: rubber; silicas; compounding; flocculation; reinforcement

INTRODUCTION

Most high performance rubber products are reinforced by reinforcing fillers, mostly by either carbon black or silica. After the introduction of "Green Tire Technology" by Michelin in 1992, silica has been increasingly used in tire tread compounds. Silica significantly

reduces rolling resistance and improves wet traction of tire tread compounds, compared to carbon black.[1] However, a major drawback associated with the use of silica is the processing difficulties derived from poor compatibility between highly polar silica and non-polar general purpose rubbers. Silica particles have a high surface energy due to a high concentration of silanol groups on their surface and tend to self-associate via hydrogen bonding, leading to the formation of a strong filler-filler network which results in a poor dispersion in the rubber matrix.[2,3] Mixing of silica-filled compounds needs to be optimized in combination with use of a silica surface modifying agent or coupling agent to ensure a good dispersion of silica in the rubber compounds.

Since the processability and properties of the silica-filled rubber compounds are strongly dependent on filler microdispersion and filler-rubber interaction, the self-association of the silica has to be minimized. There are several approaches towards improved silica dispersion and enhanced filler-rubber interactions, such as an optimization of mixing procedures,[4] silica surface treatments,[5] newly developed silicas,[6,7] and the use of polar-functionalized rubbers as a compatibilizer.[8] The most widely used method to maximize the reinforcing efficiency of silica is by use of bifunctional organosilanes as coupling agents. Under optimal conditions the silanes will chemically bond with silica during mixing and later couple with rubber during vulcanization stages.[9,10] Even though coupling agents are applied, silica re-agglomeration, so-called flocculation can be taken place during compound storage and at the onset of vulcanization.[11-13] This phenomenon is dependent on thermal annealing and compound storage time. The reformation of silica agglomerates has an adverse effect on both processability and end use properties.[3,14] This flocculation process has been verified in both carbon black- and silica-reinforced compounds. The determinations of flocculation kinetics can be carried out by using storage modulus data,[11-13] and in the case of carbon black electrical measurements[15] of the uncured compounds.

In this work, the flocculation process in silica-filled NR system was investigated by determining the change in storage modulus of uncured compounds at a low strain amplitude under simulated vulcanization conditions, according to the procedure described by Mihara *et al*.[13] The effects of mixing parameters, i.e. dump temperature and silica-silane-rubber mixing interval; type and quantity of silane coupling agents, i.e. bis-(triethoxysilylpropyl)tetrasulfide (TESPT) and bis-(triethoxysilylpropyl)disulfide (TESPD); silica type; and epoxidized natural rubber (ENR) are studied. The correlations of filler-filler, filler-rubber interactions and flocculation rate constant are discussed.

EXPERIMENTAL

Materials

The natural rubber used was Ribbed Smoked Sheet 3 (RSS3), locally produced in Pattani (Thailand). Epoxidized natural rubbers (ENRs) with the epoxide content in a range of 10-50 mol% were prepared in-house by using the performic epoxidation reaction, as described elsewhere.[16] The compounding ingredients were zinc oxide (Global Chemical, Thailand), stearic acid (Imperial Chemical, Thailand), treated distillate aromatic extract or TDAE oil (Hansen & Rosenthal, Germany), sulfur (Siam Chemical, Thailand), polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), N-cyclohexyl-2-benzothiazolesulfenamide (CBS), and diphenylguanidine (DPG) (all from Flexsys, Belgium). Two types of silane coupling agents were used: TESPT (Zhenjiang Wholemark Fine Chemicals, China), and TESPD (Si-266, Evonik GmbH, Germany) with sulfur contents of 22.0 and 14.4 wt%, respectively. The five grades of silica used are detailed in Table 1.

Compound preparation

Rubber Formulations.– As suggested by Guy *et al.*,[7] the quantities of TESPT and DPG applied for silica-filled rubber compounds should be based on the CTAB specific surface area of the silica and can be calculated by using the Equation (1) and (2)[7] as follows:

$$\text{Amount of TESPT (phr)} = 0.00053 \text{ x Q x CTAB} \qquad (1)$$

$$\text{Amount of DPG (phr)} = 0.00012 \text{ x Q x CTAB} \qquad (2)$$

where Q is the silica content (phr) and CTAB is the specific surface area of the silica used (m^2/g).

The compound based on NR, Ultrasil 7005 and TESPT at 5.0 phr (as calculated) was considered as a reference formulation, as detailed in Table 2. This formulation was applied for studying the effect of mixing parameters.

Due to the difference in CTAB specific surface area among the 5 silica grades (see Table 1), the quantities of TESPT as calculated with respect to the CTAB values are therefore different. In this study, the amount of total sulfur was corrected by an addition of elemental sulfur to ensure that every compound contained equal sulfur levels.

Mixing procedures.– The mixing was performed using an internal mixer with a mixing chamber of 500 cm^3 (Chareon Tut Co. Ltd., Thailand). The mixer was operated at a fill factor of 70% and a rotor speed of 60 rpm. For the mixing conditions study, the initial setting mixer temperatures were adjusted from 50-140°C in order to reach final dump temperatures in the

range of 100-170°C. The silica-silane-rubber mixing intervals were varied at 5, 10, 15 and 20 mins. For the other investigations, the initial temperature setting of the mixer was set at 100°C and the mixing interval was chosen at 10 mins in order to obtain dump temperatures of approximately 140 – 145°C.

NR was initially masticated for 2 mins. Then, half of the silica and silane were added and mixed for half of the silica-silane-rubber mixing interval, prior to adding the second half of silica and silane together with TDAE oil. The mixing was continued to the full intervals. Subsequently, ZnO, stearic acid, TMQ and DPG, were added and mixed for 3 mins. The compounds were then dumped, sheeted out on a two-roll mill, and kept overnight prior to the incorporation of CBS and sulfur on a two-roll mill.

Characterization of rubber compounds

Flocculation rate constant.– Silica flocculation can be experimentally described as a first order reaction for which the kinetics can be described by a simple model equation.[11] In order to calculate the flocculation kinetics of silica, the storage modulus at 0.56% strain amplitude of uncured compounds (without curatives) can be monitored during heating at 100°C for 12 mins by using a Moving Die Processability Tester (MDPt, TechPro, USA), or Rubber Process Analyzer (RPA, Alpha Technologies, USA), according to Mihara *et al*.[13] The degree of flocculation (x) can be expressed by the ratio of the storage modulus at time *t* and at infinite time *f*:

$$x = \frac{G'(t) - G'(i)}{G'(f) - G'(i)} \qquad (3)$$

where G′(t) is the storage modulus at 0.56% strain amplitude after heating time t; G′(i) is the storage modulus after preheating for 1 minute; G′(f) is the storage modulus at infinite time, taken as 12 mins. to reduce measuring time.

Then following equation can be applied to calculate the flocculation rate constant (k_a):

$$k_a = \frac{\ln(1 - x_1) - \ln(1 - x_2)}{t_2 - t_1} \qquad [\text{s}^{-1}] \qquad (4)$$

where k_a is the rate constant; t is the heating time; x is the degree of flocculation; 1 and 2 refer to different heating times t.

Reinforcement parameter.− According to Wolff,[17] the reinforcement parameter, α_F, is a filler specific feature, independent of the cure system, and closely related to the

morphology of the filler in the compound. The reinforcement parameter (α_F) was calculated by using the data from the cure characteristics according to Equation (5)[17]:

$$\frac{S'_{max} - S'_{min}}{S'^0_{max} - S'^0_{min}} - 1 = \alpha_F \left(\frac{m_F}{m_P} \right) \qquad (5)$$

where $S'_{max} - S'_{min}$ = torque difference of the silica filled rubber; $S'^0_{max} - S'^0_{min}$ = torque difference of the corresponding gum or unfilled compound; m_F/m_P = filler loading, where m_F and m_P correspond to the mass fractions of filler and polymer, respectively.

For this analysis, the increase in torque (S') was measured using the MDPt at a temperature of 150°C, a frequency of 0.833 Hz and 2.79% strain for 30 mins.

Payne effect.− Storage shear moduli (G') of compounds cured to their t_{95} at 150°C were measured under shear deformation using the RPA. A strain sweep test was done in the range of 0.56 - 100 % strain at 0.50 Hz and 100°C.

Bound rubber content.− Bound rubber measurements were carried out both with and without ammonia treatment. The ammonia treatment was done in order to cleave the physical linkages between rubber and silica, so that the true chemically bound rubber could be determined.[17] 0.2 g of uncured masterbatch (without curatives) was put into a metal cage and immersed in 20 ml of toluene for 72 h at room temperature. The toluene was renewed every 24 h. The sample was removed from the toluene, dried at 105°C for 24 h. The sample was immersed again in 20 ml of toluene for 72 h at room temperature in either a normal or an ammonia atmosphere. Again, toluene was renewed every 24 h. The sample was finally dried at 105°C for 24 h and weighed.

The bound rubber content was calculated according to Equation (6)[17]:

$$Bound\ rubber\ content\ (\%) = \frac{W_{fg} - W_f}{W_p} \qquad (6)$$

where W_{fg} is the weight of silica with the bound rubber attached; W_f and W_p are the weight of silica and polymer in the specimen, respectively; which are calculated with reference to the compound formulation and initial sample weight.

RESULTS AND DISCUSSION

Effect of mixing conditions

The flocculation rate constant (k_a) indicates how fast the silica particles/aggregates flocculate under thermal treatment at the onset of cure. A lower value of k_a means slower

flocculation development or smaller tendency towards self-association of silica to form agglomerates in the compounds during thermal treatment and compound storage.

The compound dump temperature and silica-silane-rubber mixing interval clearly influence the flocculation phenomenon, as shown in Figure 1. The flocculation rate constant decreases with increasing dump temperature, and becomes constant when the dump temperature reaches approximately $130^{\circ}C$. An extended silica-silane-rubber mixing interval also reduces k_a. The results correspond with the reinforcement parameter (α_F value) which is used to qualitatively indicate the degree of silica dispersion,[17] as shown in Figure 2. A lower α_F indicates better dispersion. So, by increasing dump temperature, a better silica dispersion is achieved. The plateau for the flocculation rate constant and reinforcement parameter above the dump temperature of $135^{\circ}C$ reveals optimal silica dispersion under the mixing conditions studied.

The degrees of silica dispersion in the compounds are confirmed by analyzing the Payne effect or filler-filler interaction, as shown in Figure 3. The Payne effect decreases with increasing dump temperature and levels off when the dump temperature exceeds $130^{\circ}C$. It is clear that increasing dump temperature enhances the degree of dispersion as evidenced by the decrease of flocculation rate constant, reinforcement parameter and Payne effect.

The mixing process of silica, TESPT silane coupling agent and rubber involves chemical reactions, i.e. the reaction between silanol groups of silica and alkoxy groups of silane, the so called silanization reaction.[4-6] In the presence of TESPT at high temperature, a crosslinking reaction by free sulfur released from TESPT inevitably occurs. The silanization reaction is activated by a temperature as low as $120^{\circ}C$[9] already, and premature crosslinking of silica-TESPT filled NR compounds has been reported to start at that temperature of $120^{\circ}C$.[18] Hence, by increasing dump temperature and extending mixing time, a better silanization efficiency is obtained to promote the hydrophobation of the silica surface leading to better silica dispersion (Figure 2) and a lower Payne effect (Figure 3). Furthermore, the formation of a lightly crosslinked network by premature scorch additionally prevents the re-agglomeration of silica aggregates.

The silanization reaction and premature crosslinking induce chemical bonds between silica-silane, silica-silane-rubber and rubber-rubber. To verify the chemically bound rubber contents on the silica surface, an extraction technique was applied according to Wolff's procedure.[17] The bound rubber content as shown in Figure 4 reveals the increase of bound rubber content with increasing dump temperature up to approximately $135^{\circ}C$, and thereafter a

leveling off. An extended silica-silane-rubber mixing interval also leads to a higher bound rubber content.

The increased bound rubber content, i.e. increased filler-rubber interactions, can be correlated with a reduction of the flocculation rate constant (Figure 1) as the mobility of silica particles/aggregates is more restricted by the networks generated during compound mixing. It is clear that the network contributions derived from filler-rubber interaction and rubber-rubber crosslinking play a significant role on silica dispersion stability (i.e. the flocculation process), and consequently influence the silica dispersion and filler-filler interaction.

Effect of silane coupling agents

The plots of flocculation rate constant and Payne effect as functions of silane content are shown in Figure 5. The incorporation of silane coupling agent at 6.0 wt% of silica to the compounds drastically reduces the rate of flocculation, but a further increase of silane loading leads to only a small change in the flocculation kinetics. The use of TESPT can suppress the flocculation process to a greater extent compared to TESPD. This means that TESPT provides better silica dispersion stability than TESPD for filled-NR compounds.

The results of the Payne effect reveal the reduction of filler-filler interaction with increasing silane contents as shown in Figure 5. This can be attributed to the hydrophobation effect of the bifunctional organosilanes. The reduction of Payne effect is more pronounced in the TESPT-based compound compared to the TESPD one. The results of flocculation rate constant and Payne effect are in good agreement, and confirm that a silane coupling agent is required for silica-filled NR compounds to enhance filler-rubber interaction and dispersion stability.

Due to the difference in sulfur contents and thermal stability of TESPT and TESPD which consist of a tetrasulfide and disulfide chain, respectively, these two types of silane provide different levels of chemically bound rubber content (Figure 6). TESPT donates free sulfur into the system, while TESPD does not,[9,10,18,19] so that the reactive sulfur present in the mixes during mixing is different. The bound rubber content, as shown in Figure 6, clearly shows that the compounds with TESPT have noticeable higher bound rubber than those with TESPD. Besides filler-rubber interactions generated by the silanization reaction, the TESPT-based compounds will inevitably contain some rubber-rubber crosslinks. The network contribution caused by the released sulfur from the silane structure is in good agreement with the previous works.[10,18,19] Again, the increase of bound rubber accompanies the decrease of flocculation rate constant. In this case, suppression of re-agglomeration is due to mobility

restriction of silica aggregates by the filler-rubber interaction and the network originating from the silane coupling agents.

Effect of silica types

The flocculation of silica aggregates in the compounds filled with highly dispersible (HD) silicas develops faster than for the compounds with conventional (CV) silicas, as illustrated in Figure 7. Our previous results with regard to mixing conditions and silane coupling agents show that the flocculation rate constant is reduced when the chemically bound rubber is increased, as depicted in Figure 1 and 5, respectively. However, the HD silicas which provide higher filler-rubber interaction, as indicated by a lower Payne effect and higher bound rubber content (see Figure 7 and 8), display a higher flocculation rate constant. Therefore, the faster flocculation process in the HD silica-filled compounds can be accredited to a higher ability of silica aggregates to migrate through the still unvulcanized compound.

It is well known for colloidal systems that the diffusion constant depends on temperature, and inversely relates to viscosity and radius of the particles. This relation has been validated for filled rubber compounds and it has been demonstrated that the carbon black flocculation is governed by matrix viscosity.[20] The increase of flocculation rate constant with increasing chemically bound rubber, and with increasing DBP value which indicates filler structure (Figure 8), is therefore attributed to a smaller size of the silica aggregates. The higher filler structure leads to a greater extent of agglomeration breakdown, resulting in smaller aggregates which can diffuse faster under thermal conditions. A better dispersion also leads to a reduction in the mean distance between filler aggregates which facilitates filler networking. The results suggest that even though HD silica is employed, the flocculation process in the compounds cannot be prevented. However, this feature does not give adverse effect on the Payne effect measured at 100 °C as the HD silicas still display less filler-filler interactions than the CV counterparts.

Effect of epoxide functional groups on NR

Epoxidized natural rubbers (ENRs) with various levels of epoxidation were used to investigate their polar influence on filler-filler and filler-rubber interactions, as well as on the flocculation process of silica-filled compounds. The use of ENR is to enhance the compatibility between silica and NR. Figure 9 and 10 show the improvement of filler-rubber interactions, as demonstrated by the lower Payne effect and higher bound rubber content when ENRs were used as matrix instead of NR. The ENR-based compounds even without

TESPT show significantly lower Payne effects when compared to normal NR, whether without or even with silane. This reflects an improved silica dispersion due to better polarity matching. A small reduction of Payne effect is seen when the epoxide contents are increased from 10 to 25 mol%. However, further increase of epoxide content has an adverse effect on the filler-filler interactions due to the dominant effect of complex polar interactions in the ENR structure itself.

Figure 11 demonstrates the flocculation rate constant of silica-filled ENR compounds. Among the group of ENRs studied, the ENRs with 15-25 mol% epoxide show the slowest flocculation development, in accordance with the lowest Payne effect (Figure 9). This is attributed to the best possible filler-rubber interaction provided by the modified NR. Even though significant scatter in the k_a-values is observed, it can still be seen that the polar-modified NR exhibits higher flocculation rate constant compared to NR with TESPT.

As previously mentioned, the flocculation process is also influenced by matrix viscosity and size of aggregate. Both silica and ENR possess relatively high polarity in their structure, and so tend to form self-association via hydrogen bonding or polar interaction among either the same or different types of molecules. The epoxide functionalities can produce polar-polar interaction and even self-crosslink due to the opening of oxirane rings, as described earlier.[16] The change of chain conformation and aggregate size certainly affect the migration ability. In addition, the modified NR tends to have lower molecular weight than NR to some extent due to the reagents used for the epoxidation reaction. Therefore, the parameters involved in the ENR system are more complicated when compared to that of the NR compounds.

CONCLUSIONS

Silica-reinforced natural rubber compounds are investigated with emphasis on the flocculation process, described by a flocculation rate constant at 150$^{\mathrm{o}}$C. A higher mixer dump temperature and silica-silane-rubber mixing intervals increase the bound rubber content attributed to network contributions by both filler-rubber interactions and premature crosslinking caused by sulfur in TESPT. Increased bound rubber, decreased Payne effect, lower reinforcement parameter (i.e. better dispersion) and smaller flocculation rate constant are observed when the dump temperature is raised. An increase of silica coupling agent loading increases chemically bound rubber content and suppresses the flocculation process. With respect to these properties, TESPT clearly shows a better performance than TESPD.

The use of highly dispersible (HD) silicas results in higher bound rubber content and smaller Payne effect, compared to the use of conventional silica. The bound rubber content corresponds to the silica structure, as indicated by the DBP adsorption value. The results show that a higher silica structure leads to better dispersion but a faster flocculation process. Furthermore, the presence of epoxide groups in a range of 15-25 mol% epoxide in epoxidized natural rubber (ENR) enhances filler-rubber interaction, but has only a limited effect on flocculation rate.

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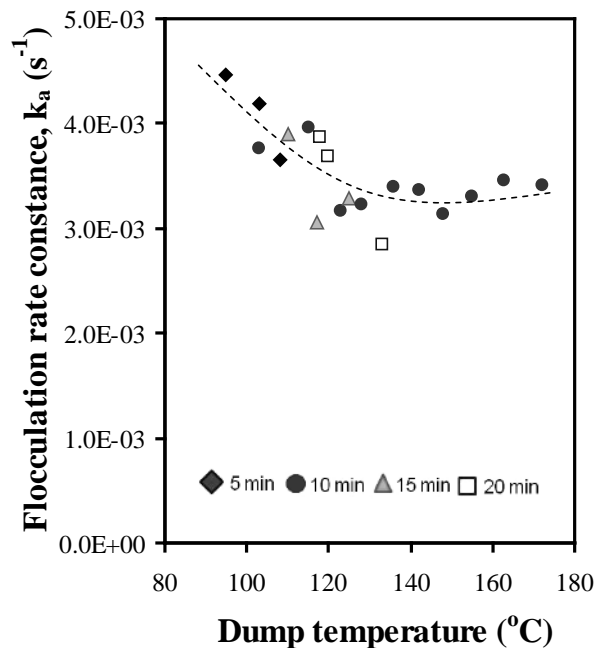[20]   T. Wang, M.-J. Wang, J. Shell, N. Tokita, *Kautsch. Gummi Kunstst.* **53**, 497 (2000).

Figure 1 Effect of dump temperature on flocculation rate constant of silica-filled NR compounds prepared with various silica-silane-rubber mixing intervals.
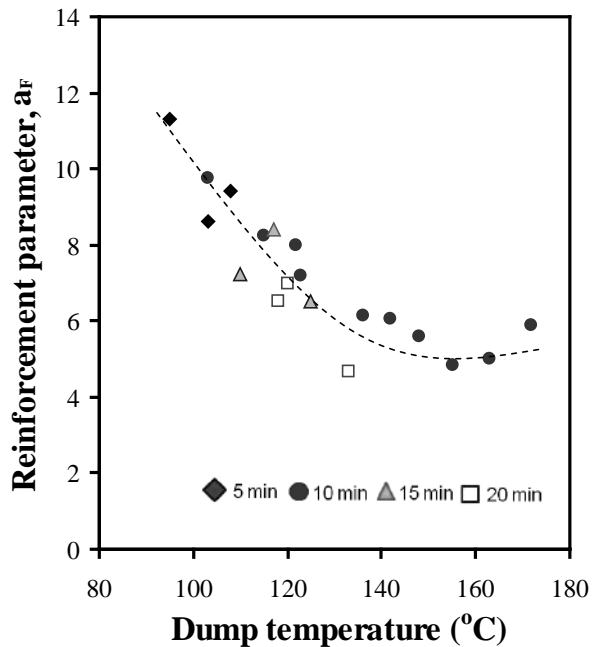

Figure 2 Effect of dump temperature on reinforcement parameter of silica-filled NR compounds prepared with various silica-silane-rubber mixing intervals.
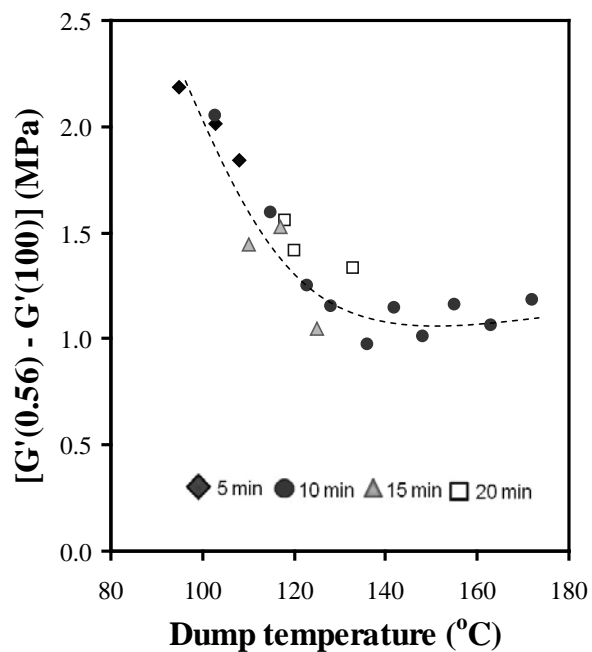
Figure 3 Effect of dump temperature on Payne effect of silica-filled NR compounds prepared with various silica-silane-rubber mixing intervals.
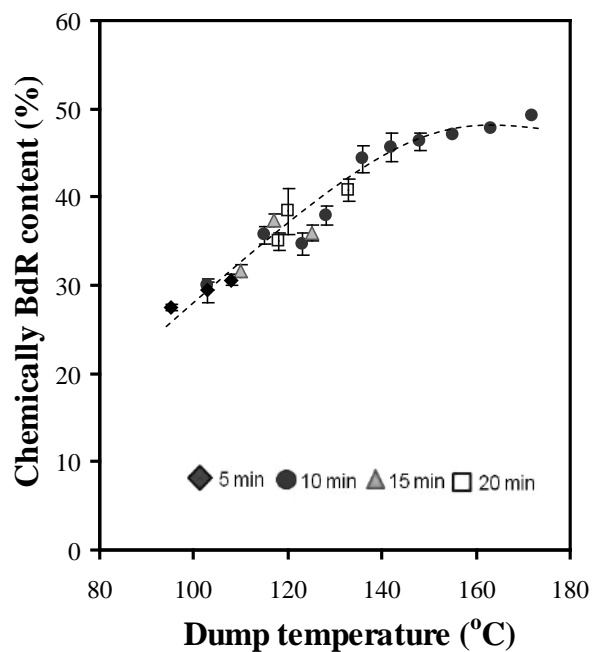
Figure 4 Effect of dump temperature on chemically bound rubber (BdR) content of silica-filled NR compounds prepared with various silica-silane-rubber mixing intervals.
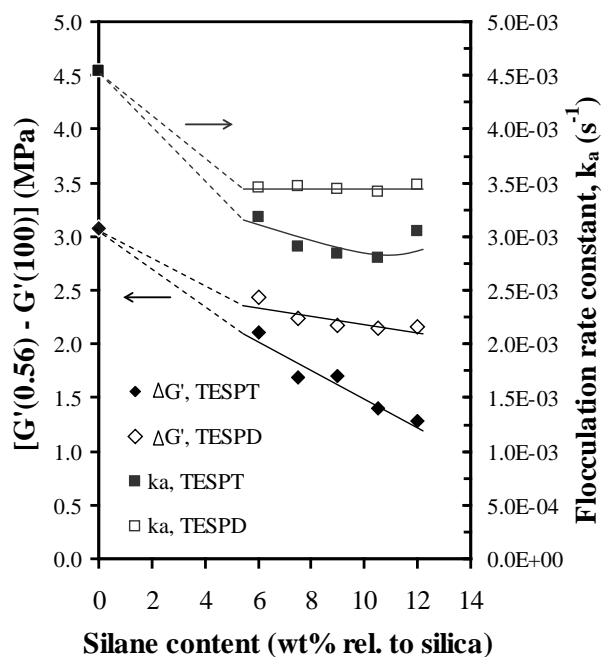
Figure 5 Effect of silane content on Payne effect and flocculation rate constant of silica-filled NR compounds.
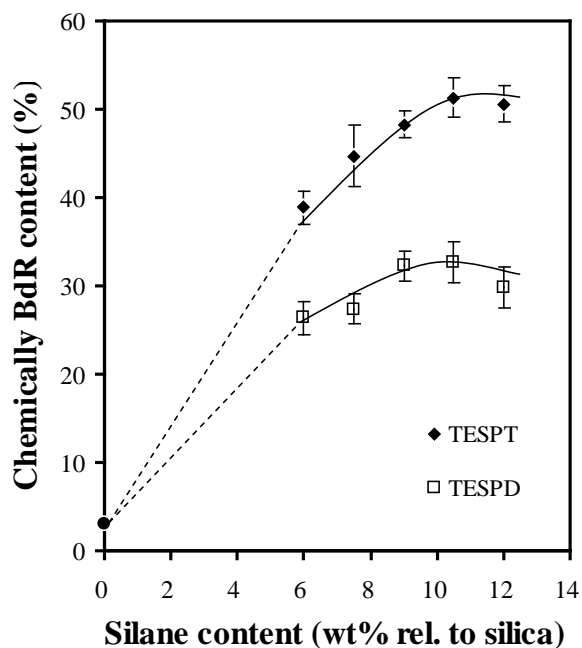

Figure 6 Effect of silane content on chemically (BdR) bound rubber content of silica-filled NR compounds.
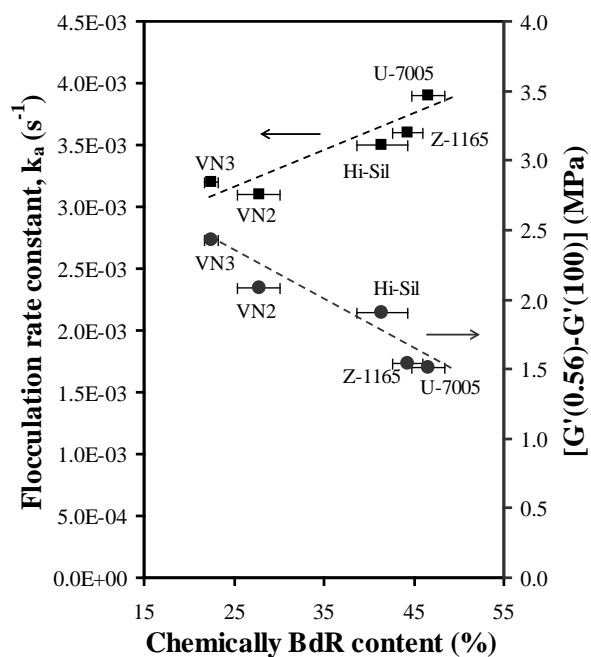
Figure 7 Effect of silica types on flocculation rate constant and Payne effect as function of chemically bound rubber (BdR) content of the silica-filled NR compounds.
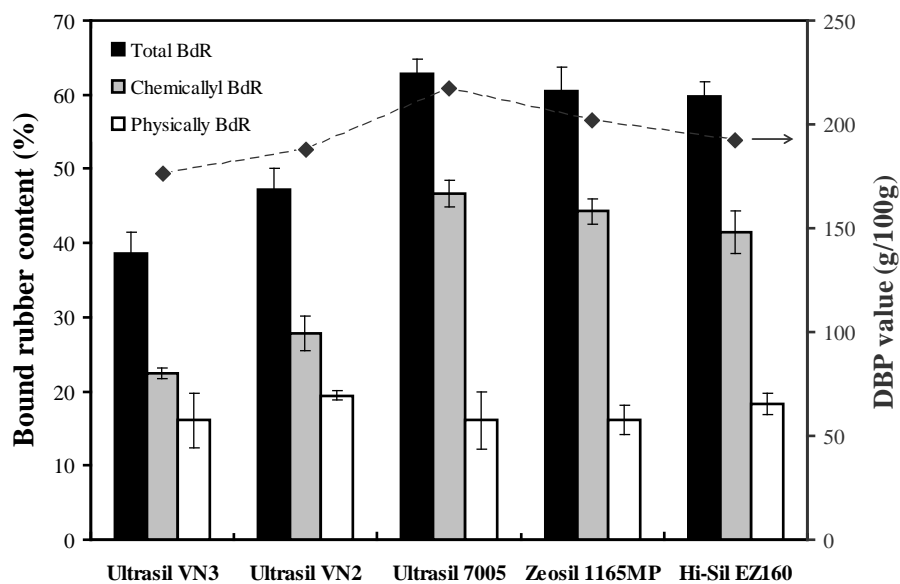

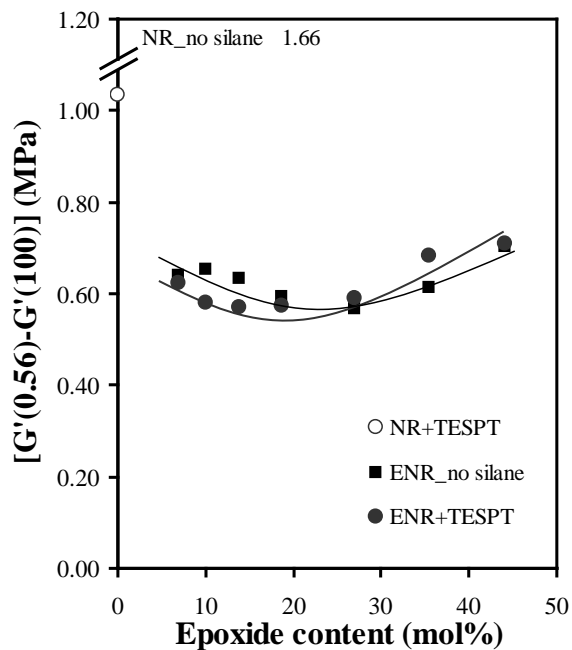**Figure 8** Effect of silica types on bound rubber content in relation to DBP value of the silica-filled NR compounds.

Figure 9 Influence of epoxide content on Payne effect of silica-filled ENR with and without
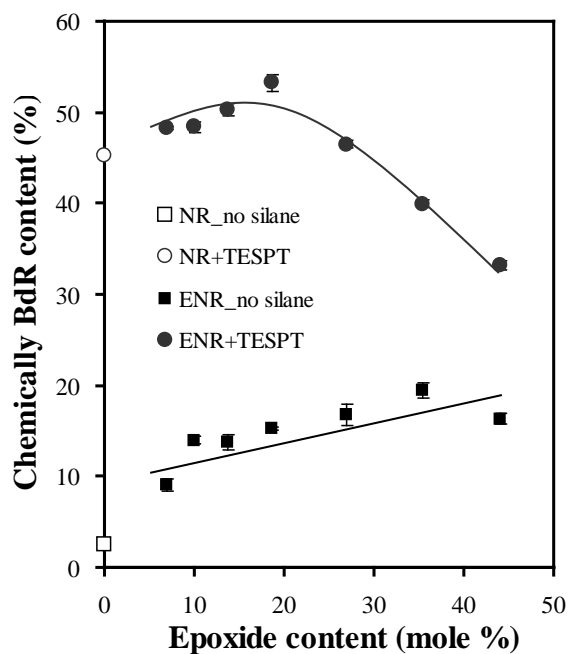
TESPT silane coupling agent.

Figure 10 Influence of epoxide content on bound rubber content of silica-filled ENR with and
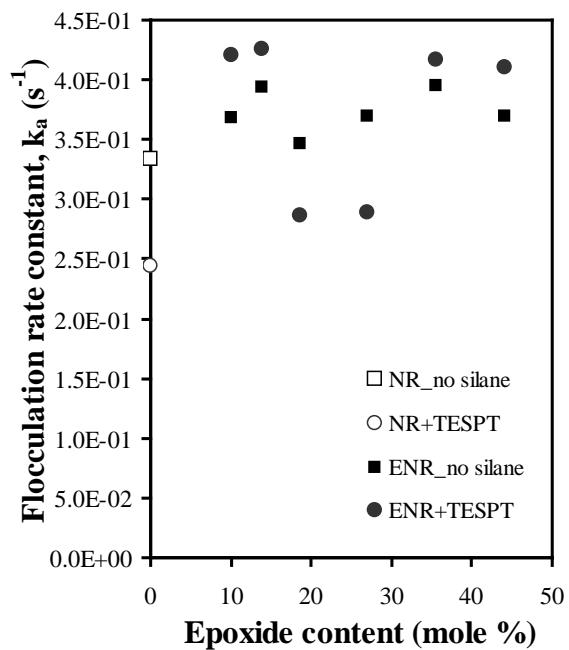
without TESPT silane coupling agent.

Figure 11 Effect of epoxide content on flocculation rate constant of silica-filled ENR with and without TESPT silane coupling agent.

Table 1. Supplier, type and technical data of silicas.

Silica	Supplier	Type	CTAB[a] (m^2/g)	DBP[b] (g/100g)
Ultrasil VN3	Evonik Degussa, Germany	CV[c]	165	176
Ultrasil VN2	Evonik Degussa, Germany	CV	125	185
Ultrasil 7005	Evonik Degussa, Germany	HD[d]	171	217
Zeosil 1165MP	Rhodia Silices, France	HD	150	202
Hi-Sil EZ160	PPG Industries, Netherlands	HD	150	192

[a] CTAB is the cetyl trimethylammonium bromide specific surface area.; [b] DBP the dibutylphthalate adsorption capacity.; [c] CV is conventional precipitated silica.; [d] HD is highly dispersible silica.

Table 2. Compound formulation.

Ingredient	Dosage (phr)
Natural rubber (or ENR)[a]	100.0
ZnO	3.0
Stearic acid	1.0
TMQ	1.0
Ultrasil 7005 (or other)[b]	55.0
TESPT (or TESPD)[c]	5.0 (or variable)[c]
TDAE oil	8.0
DPG	1.1
CBS	1.5
Sulfur	1.5

[a] With regard to the variation of ENRs, ENRs with 7, 10, 14, 19, 27, 36, and 44 mol% epoxide were used instead of NR while Ultrasil 7005 was applied without and with TESPT 5.0 phr.; [b] For the 5 different types of silica (as detailed in Table 1), the TESPT content was fixed at 5.0 phr.; [c] For varying types and quantities of silane, TESPT and TESPD were varied from 0, 6.0, 7.5, 9.0, 10.5 to 12.0 wt% relative to the silica or equal to 0, 3.3, 4.1, 5.0, 5.8 and 6.6 phr, respectively.