THE INFLUENCE OF MIXING TEMPERATURE ON SILICA REINFORCED NATURAL RUBBER

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Abstract

Silica-rubber technology encompasses four important elements; the rubber polymer, silica, coupling agent and mixing technology. Since silica is highly polar and hydrophilic, it is not compatible with a-polar rubbers such as natural rubber. A bi-functional silane coupling agent is needed to enhance interaction on nano-scale by the creation of chemical links between the silica particles and the rubber molecules. Processing silica compounds is complicated because several chemical reactions need to take place: between the silica and silane or silanization, silane-rubber coupling and crosslinking between the rubber chains. The present investigation on the influence of mixing temperature on the properties of silica-filled natural rubber compounds using a silane coupling agent, demonstrates that the temperature development during the first mixing stage is of paramount importance as it affects the final properties. The rheological properties, Payne effect and rubber to filler interaction as well as physical properties of silica reinforced natural rubber at varying dump temperatures are discussed.

Keywords: *Natural rubber, silica, silane, reinforcement, tire*

Introduction

Mixing silica compounds involves many difficulties due to the large polarity difference between silica and rubber. In enhancing the compatibility of a-polar rubbers and silica, a bifunctional organosilane such as bis(triethoxysilylpropyl) tetrasulfide (TESPT) is commonly used as coupling agent. The formation of a hydrophobic shell around the silica particle by the silica-silane reaction prevents the formation of filler-filler networks by reducing the silica specific surface energy [1]. During vulcanization, coupling of TESPT with the rubber takes place forming silica-TESPT-rubber bonds. The chemical linkage between silica and rubber is thus the key for its reinforcement in the rubber compound.

The dump temperature is of paramount importance while mixing silica and rubber in presence of TESPT as coupling agent. Wolff has found that temperature has a more dominant effect than time in the silica-TESPT reaction [4]. In order to achieve a sufficient degree of silanization, the temperature during mixing should be above 130°C. However, above 160°C either the coupling agent starts to prematurely react with the rubber matrix or the TESPT starts to donate sulfur; both result in pre-scorch of the compound. Reuvekamp et al. demonstrated that a mixing time of at least 10 minutes at 150°C is necessary to ensure complete coupling of the silica and the silane, and that the reaction between the silica and the silane takes place primarily during the first mixing step [2]. In the present study, the effect of mixing dump temperature on the properties of TESPT-modified silica-reinforced natural rubber is investigated. The rheological properties, Payne effect and rubber to filler interaction as well as physical properties of silica-filled natural rubber at varying dump temperatures of the first mixing stage are discussed.

Materials and methods

Standard Malaysian Natural Rubber (SMR 20) was provided by the Malaysian Rubber Board. Silica Ultrasil 7005 and bis-(triethoxysilylpropyl) tetrasulphide (TESPT) were supplied by

Evonik/Degussa GmbH. The compound recipe was based on a truck tire tread composition: SMR20 (100 phr), Ultrasil 7005 (55 phr), TESPT (5 phr), TDAE oil (8 phr), zinc oxide (2.5 phr), stearic acid (1 phr), antioxidant TMQ (2 phr), sulphur (1.4 phr), N-cyclohexyl-2-benzothiazyl sulphenamide or CBS (1.7 phr) and Diphenyl guanidine or DPG (2 phr).

The compounds were mixed in two stages. The first step mixing was done using a laboratory internal mixer Brabender Plasticoder 350S lab station with 70% fill factor, 60 rpm rotor speed and 14 minutes mixing time. The starting temperature of the mixing chamber and rotor was varied from 70 to 120°C in order to obtain variable dump temperatures. Second step mixing was carried out after 24 hours rest, wherein the curatives were added on a two-roll mill.

The cure characteristics at 150°C were measured using a RPA 2000 rheometer from Alpha Technologies, under the conditions of 0.833 Hz and 2.79% strain. Filler-filler interactions or Payne effect were determined from RPA strain sweep measurements at 100°C and 0.5 Hz. The Payne effect was calculated as the difference between storage modulus, G' at 0.56% and G' at 100.04% strain. The Wolff filler-structure parameter, α_f was determined from the ratio between the increase in rheometer torque of the filled compound and that of the unreinforced gum: [3].

$$\frac{D_{max} - D_{min}}{D^o_{max} - D^o_{min}} - 1 = \alpha_f \frac{m_f}{m_p} \qquad (1)$$

where D_{max}–D_{min} is the change in torque for filled compound, D^o_{max}–D^o_{min} is the change in torque for gum compound, m_f/m_p is the weight ratio of filler to polymer, and α_f is a filler specific constant which is independent of the cure system and closely related to the morphology of the filler.

Bound rubber content (BRC) measurements were performed on masterbatches with toluene at room temperature for seven days. Tensile properties of the vulcanizates cured for their respective t_{95} at 150°C, were measured using a Zwick Z020 tensile tester according to ISO-37. Scanning electron microscopy (SEM) of the fracture surface of vulcanizates was carried out using a JSM-5000 Neoscope Benchtop SEM.

Results and discussion

Cure Characteristics

The effect of dump temperature after the first mixing step can be clearly observed in the cure characteristics of the NR-silica compounds (Figure 1). The compounds with low dump temperature below 150°C exhibit a two step cure curve with high torque as well as long scorch and cure times. The initial torque rise at the beginning of the vulcanization is associated with flocculation of silica in the compound indicating no or little silanization has occurred in the compound. Compounds with dump temperatures above 150°C show no appearance of flocculation and provide progressively lower torque and shorter scorch times. Around 150°C the in situ modification reaction of silica with TESPT occurs sufficiently fast to result in more silica surface covered with TESPT: increased hydrophobation of silica results in better dispersion in the NR. This prevents re-agglomeration of the silica. The compounds with the highest dump temperatures display the lowest maximum torques, no flocculation, the shortest cure time but also reversion of cure. The temperature during mixing will normally rise somewhat higher even than the final dump temperature. At temperature >160°C, TESPT tends to disproportionate into the corresponding disulfide. The released sulfur reacts with reactive double bonds of NR to form crosslinks. Hence, at high mixing temperature TESPT acts as sulfur donor to NR during mixing, which will cause scorch or prevulcanization in the compound.

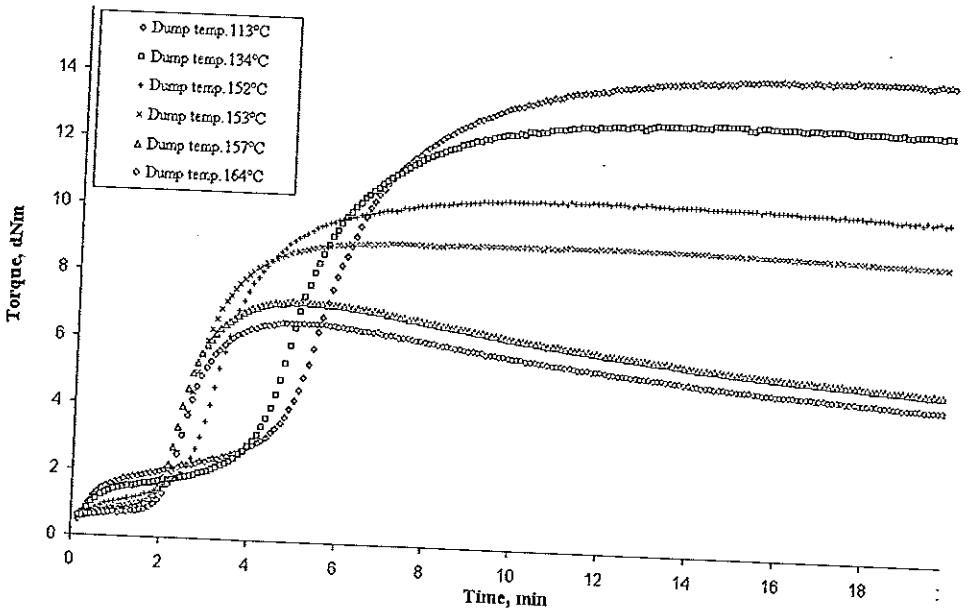


Figure 1: The cure characteristics at 150°C of NR compounds mixed till different dump temperatures in the first mixing stage

Payne effect and rubber-filler interaction

The Payne effect for the compounds before and after vulcanization is illustrated in Figure 2. With increasing dump temperature, the silica-silica interaction reduces as seen in the drop of the Payne effect. The effect can be seen even more clearly after the compound is vulcanized. The conditions during the initial mixing stage are very important, as they persist into the final properties of the compounds. It also indicates that the reaction between silica and coupling agent may not be complete after the first stage of mixing. The silanization reactions may still continue in the subsequent mixing steps. At higher dump temperature more silanization reactions occur and the silica surface is hydrophobized.

Rubber to filler interaction is improved at higher dump temperature as seen in the bound rubber content of NR-silica compound in Figure 3. Ammonia treatment on the bound rubber of the NR-silica masterbatches separates the physically and chemically bound rubber. The chemically bound rubber content increases with dump temperatures up to 150°C, but above 150°C it stabilizes. The rise in chemically bound rubber and decreasing physically bound rubber up to 150°C can be explained by the higher rate of silanization. At 150°C, there is saturation in the amount of TESPT which has reacted and the surface of silica covered. Additional interactions above 150°C between the non-hydrophobized silica surfaces are physical of nature.

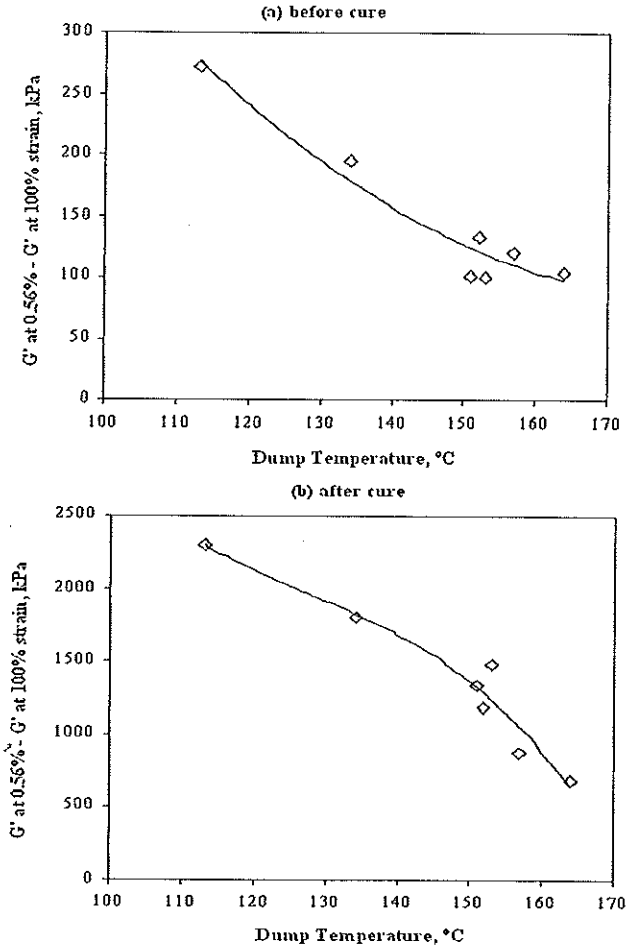


Figure 2: Payne effect of NR-silica compounds versus dump temperature (a) before cure (b) after cure

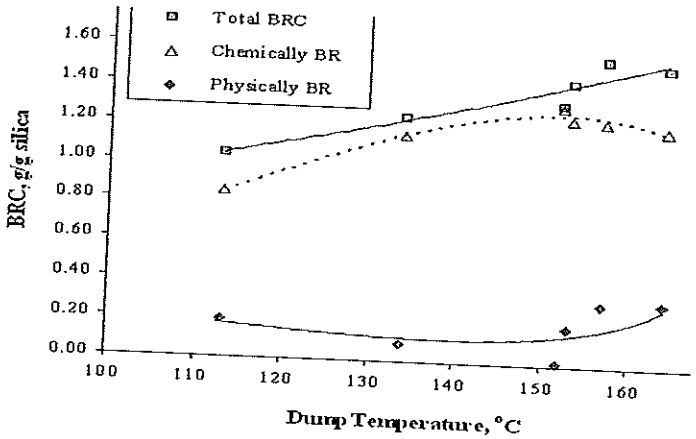


Figure 3: Bound rubber contents (BRC) of silica-filled NR at varying dump temperatures

The Mooney viscosities of the NR-silica compounds at varying dump temperature are depicted in Figure 4 (a). The Mooney viscosity increases with increasing dump temperature up to 150°C. At dump temperature higher than 150°C, the Mooney viscosity tends to become constant. It demonstrates that above 150°C the optimal amount of TESPT is used to cover the surface of silica and this gives maximum silica-TESPT coupling.

The Wolff filler structure, α_f is plotted vs. dump temperature in Figure 4(b). α_f was defined as the structure of the filler as it exists in the vulcanizate after possible breakdown during mixing and vulcanization. With increasing dump temperature, α_f of NR-silica is greatly reduced. The values of α_f at dump temperatures above 150°C are similar to those reported by Wolff for the TESPT-modified silica-filled NR and for reinforcing carbon black [4]. At higher dump temperatures, the hydrophobation of the silica surface led to reduced silica inter-aggregate interaction. It also indicates more filler to-rubber interaction to occur at higher dump temperature.

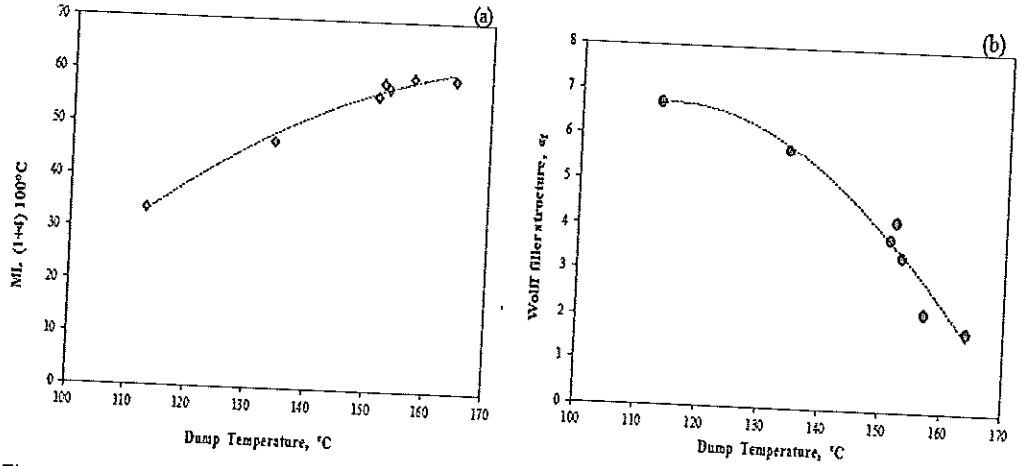


Figure 4: (a) Mooney viscosity and (b) Wolff filler structure parameter, α_f of silica-filled NR as a function of dump temperature

Physical Properties

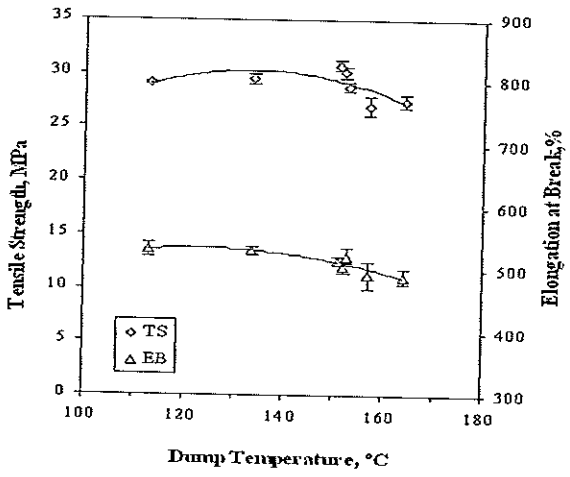
Tensile properties of silica compounds at varying dump temperature are illustrated in Figure 5. They have an optimum at 150°C dump temperature. The tensile strength and elongation at break drop at dump temperatures higher than 150°C. Both moduli at 100% and 300% elongation are also reduced at dump temperatures above 150°C.

Scanning Electron Microscopy (SEM) surface morphology

The surface morphology of fractured NR-silica vulcanizates is depicted in Figure 6. The macro dispersion (remaining agglomerates $\geq$ 1 μm) of silica in the NR vulcanizates can be seen in these pictures. Significantly less silica agglomerates are observed in the vulcanizate mixed at high dump temperature, due to the increased breakage of silica-silica interactions with higher efficiency of silanization.

Conclusions

The temperature conditions during the initial mixing stage of silica-NR compounds are of paramount importance as they seriously affect the final properties of the compounds. If insufficient temperature is reached during the initial stage, the silanization reaction between silica and coupling agent still continues in subsequent mixing or vulcanization steps. With increasing dump temperature, filler-filler interaction in a NR-silica compound decreases and silica-rubber interaction improves as evidenced by a drop in the Payne effect and increment in bound rubber content. The optimum temperature for silanization of silica with TESPT in NR is 150°C and this gives a pronounced effect on the physical properties.



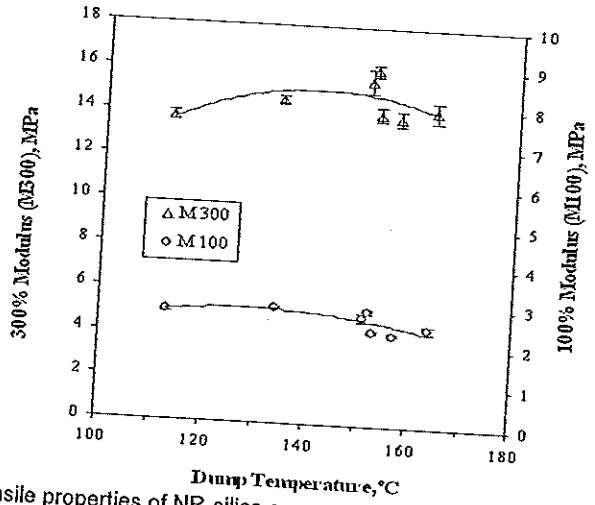
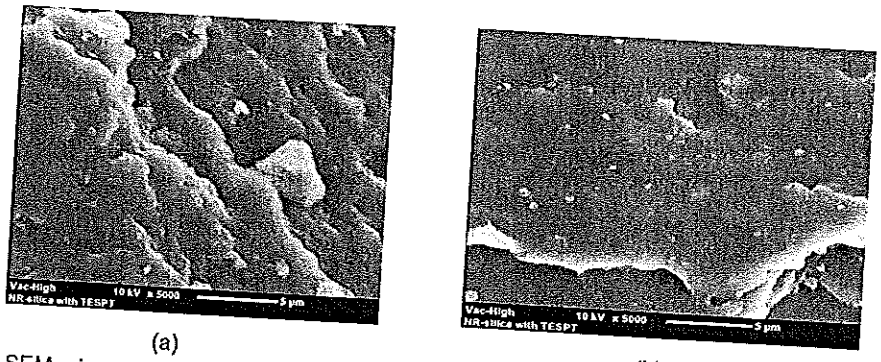


Figure 5: Tensile properties of NR-silica compounds at varying dump temperatures



(a) (b)

Figure 6: SEM micrographs of NR-silica vulcanizates at low (a) and high (b) dump temperature

Acknowledgement

The authors would like to express gratitude for financial support from the Malaysian Rubber Board, Malaysia for this project.

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