



The influence of non-rubber constituents on performance of silica reinforced natural rubber compounds



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ABSTRACT

An in-rubber study of the interaction of silica with proteins present in natural rubber show that the latter compete with the silane coupling agent during the silanisation reaction; the presence of proteins makes the silane less efficient for improving dispersion and filler–polymer coupling, and thus influences the final properties of the rubber negatively. Furthermore, the protein content influences the rheological properties as well as filler–filler and filler–polymer interactions. Stress strain properties also vary with protein content, as do dynamic properties. With high amounts of proteins present in natural rubber, the interactions between proteins and silica are able to disrupt the silica–silica network and improve silica dispersion. High amounts of proteins reduce the thermal sensitivity of the filler–polymer network formation. The effect of proteins is most pronounced when no silane is used, but they are not able to replace a coupling agent.

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1. Introduction

In recent years, the increasing demand for low-energy consuming and low rolling resistance tyres has lead to growing use of silica in tread compounds. Four essential elements in silica–rubber technology: the rubber polymer, a special type of silica, an effective coupling agent and the appropriate mixing technology are interconnected in expanding the magic triangle of tyre technology: the compromise between rolling resistance (wet), traction and wear. Compared to carbon black, mixing silica compounds involves many difficulties due to the large polarity difference between silica and rubber. A bifunctional organosilane such as bis(triethoxysilylpropyl) tetrasulphide (TESPT) or its disulphide equivalent is commonly used as coupling agent in enhancing the compatibility of silica and rubber, by chemically modifying silica surfaces and eventually creating a chemical link between silica aggre-

gates and the rubber chains [1] as illustrated in Fig. 1. Complications arise during mixing silica compounds as several chemical reactions need to take place, all at their appropriate time slots during rubber processing, namely the silica and silane reaction or silanisation, silane–rubber coupling and crosslinking between the rubber chains [2].

The high-dispersion silica technology, as it is used today, employs mainly solution-polymerised synthetic rubber, and is still not commercially feasible with natural rubber [3]. It was postulated that non-rubber constituents contained in natural rubber such as proteins compete with the coupling agent for reaction with the silica during mixing, so disturbing its reinforcement action [3]. However, no supporting evidence is available on this subject.

Commercial Natural Rubber (NR) comes from the milky sap or latex that exudes from the rubber tree, *Hevea Brasiliensis*, which coagulates on exposure to air. *Hevea* latex consists of rubber hydrocarbon for about 30–45 wt% non-rubber constituents for about 3–5 wt%, and the rest is water. The non-rubber constituents comprise of proteins, amino acids, carbohydrates, lipids, amines, nucleic acids, as well as other inorganic and mineral components [4].

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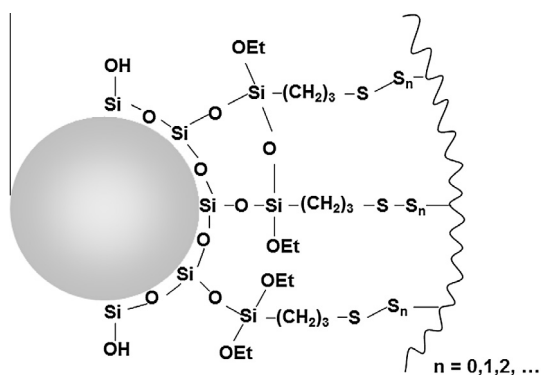


Fig. 1. Silica-silane-rubber coupling.

The work by Tanaka and coworkers has revealed that the fundamental structure of a linear NR chain consists of a long sequence of 1000–3000 *cis*-1, 4 isoprene units, with at the α - and ω -chain ends specific other groups [5,6]. The α -terminal is composed of mono- and diphosphate groups linked with phospholipids by hydrogen or ionic bonds [7]. The ω -terminal entails two *trans*-1, 4 isoprene units [8] and a modified dimethylallyl unit linked with functional groups, which is associated with proteins to form crosslinks via hydrogen bonding [9,10]. Both non-rubber constituents, i.e. proteins and phospholipids are presumed to be the origin of branching and gel formation in NR [11]. These secondary structures play a significant role in the strain-induced crystallization of unvulcanised and vulcanised natural rubber [12,13].

The protein content of NR varies upon its source and methods of production. The nitrogen content of the NR is related to the protein level. It is generally accepted that the conversion factor from nitrogen content to protein content is 6.25 [4,14]. Typical raw NR has a nitrogen content in the range of 0.3–0.6%. Many attempts have been made to purify NR from the non-rubber constituents such as proteins. One of the most successful attempts is the ‘Deproteinised Natural Rubber’ (DPNR) which is characterised by its very low nitrogen, ash and volatile matter contents compared to the equivalent commercial NR. DPNR is produced via treatment of natural rubber latex with bioenzyme (proteinase), which hydrolyses the proteins present into water soluble forms [15]. In addition, deproteinisation of natural rubber is also achieved in the latex stage with urea in the presence of a surfactant, such as sodium dodecyl sulphate [16,17]. On the other hand, during concentrated latex production, the serum phase after centrifugation contains 5–10% of the total rubber, and many of the non-rubbers. This is coagulated with sulphuric acid to produce skim rubber with a low dirt content and light colour and that is relatively cheap. Skim rubber has a high protein content [18], where the nitrogen content has values in the range of 1.5–2.5%.

Gregg and Macey [19] have demonstrated that the insoluble non-rubber constituents in NR account for the differences in properties between compounded NR and compounded synthetic polyisoprene. This non-rubber material is mostly proteins and responsible for the higher

modulus, faster scorch time and higher tear strength of NR. The protein is postulated to act as a reinforcing filler at low concentration (3–4 wt.%) and as a cure activator. Othman and Hepburn [4] have shown that the presence of proteins from B-, C-serum and proteolipids did not significantly affect the elastic modulus of rubber vulcanisate. However, the presence of its hydrolysed constituents, amino acids, gave a marked increase in the modulus of vulcanisates, in particular alanine and arginine, the basic and neutral amino acids, respectively [20].

In the present paper, the influence of non-rubber constituents in NR, particularly proteins, on the properties of silica-filled NR compounds in the presence and absence of coupling agent is illustrated. In order to demonstrate the variation of proteins content in NR, DPNR and skim rubber are selected in comparison with normal NR. The filler–filler and filler-to rubber interactions of silica reinforced NR compounds at varying mixing dump temperatures is highlighted.

2. Experimental

2.1. Materials

Natural rubbers with different protein contents were compared in this study. The rubbers with their protein contents based on nitrogen estimations are summarised in Table 1. The nitrogen contents of the three rubbers were determined by the semi-micro Kjeldahl procedure carried out by the Materials Characterisation Unit, Malaysian Rubber Board (MRB).

The compound formulation used throughout this investigation is shown in Table 2. Highly dispersible silica, Ultrasil 7005 from Evonik with CTAB surface area of 164 m²/g was used. The other compounding ingredients were used as obtained from the respective sources, as indicated in Table 2.

2.2. Compounding

The compounds were mixed in 2 steps. The mixing procedure is described in Table 3. The first step was done using a laboratory internal mixer Brabender Plasticoder 350S lab station with a capacity of 390 ml. The fill factor of the mixer was fixed at 70% and the rotor speed used was 60 rpm. The starting temperature of the mixing chamber and rotor was varied from 70 to 120 °C in order to obtain variable temperature histories and dump temperatures. After mixing for 14 min, the batches were sheeted out on a Schwabenthan Polymix 80T 80 × 300 mm two-roll mill, under a tight nip with 10

Table 1
Protein content of natural rubber's used.

Rubber type	Nitrogen content (wt%)	Protein content (wt%)
NR (SMR 20)	0.21	1.3
DPNR (pureprena)	0.07	0.4
Skim rubber	2.06	12.9

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