The effect of hydroxylamine sulfate on the storage hardening of natural rubber

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Abstract. Natural rubber (NR) consists of rubber and non-rubber components, which is mostly cis-1,4-polyisoprene. The main non-rubber components are proteins and phospholipids which are attached at each end of the NR chains. If we store NR for prolong period, the proteins and phospholipids promote formation of a NR network. This causes the gel formation with increasing the Mooney viscosity of NR, and this is called storage hardening. The objective of this work is to study the effect of hydroxylamine sulfate on the storage hardening of natural rubber. Three types of natural rubber sample were prepared: pure NR, NR with 0.2 phr of hydroxylamine sulfate, and NR with 2.0 phr of hydroxylamine sulfate. Samples were characterized immediately (time 0) and after 12 weeks of storage at room temperature. We found that gel content and Mooney viscosity of NR without hydroxylamine sulfate are increased with the storage hardening for 12 weeks. However, both NR samples with hydroxylamine sulfate represent constant viscosity values because hydroxylamine sulfate inhibits the network and gel formation in NR. This is important as the stabilization of NR properties in the function of time is required by rubber industry.

1. Introduction
Natural rubber (NR) can be obtained from Hevea brasiliensis plant. NR latex has been used in industry for surgical glove, pillow and mattress, elastic band, medical products, and tire industry, plus many more. NR consists of rubber and non-rubber components, the main component is the cis-1,4-polyisoprene. The non-rubber fractions consist of proteins (ω-terminal) and phospholipids (α-terminal) which are not only attached at each end chain of polyisoprene but also included in the serum [1]. When we store the NR for prolonged period of time, proteins and phospholipids at the end chain could promote formation of NR network through protein-protein interactions at the ω-terminal or phospholipid-phospholipid interaction at the α-terminal. The increase of branch chain or network of NR as a function of time can be determined by the Mooney viscosity via the storage hardening [2]. The storage hardening of NR can be inhibited by a stabilizer. Nimpaiboon et al., [3] studied the effect of polar chemicals on the storage hardening of NR. Three types of polar chemicals were used: phenol, diethylene glycol, and hydroxylamine hydrochloride. They found that gel content, Mooney viscosity, and Wallace plasticity values of NR samples with phenol and diethylene glycol are increased with storage hardening. However, NR sample with hydroxylamine hydrochloride represents constant values of those three parameters.
2. Experimental

Four hundred grams of rubber samples from natural latex (supplied by Num rubber and latex. Co. Ltd, Trang, Thailand) were masticated using a two-roll mill (Yong Fong). Three types of NR sample were prepared: pure NR, NR with 0.2 phr of hydroxylamine sulfate (HS from Sigma-Aldrich), and NR with 2.0 phr of hydroxylamine sulfate. Then, samples were characterized part same day after preparation (time 0 or 0 week) and after 12 weeks of storage at room temperature. The gel content was measured by dissolving NR sample in toluene (RCI Labscan). The solution was kept in the dark at room temperature, for one week. Finally, the solution was filtered, weighed, and calculated with respect to the original NR sample [4]. Mooney viscosity analysis was performed using a Mooney viscometer (TECHPRO, viscTECH+) within a sealed, pressurized and heated cavity. The rubber sample was heated at 100°C for 1 min before analysis. After that, the rubber samples were continuously measured for 4 min by the torque required to keep the rotor rotating at a constant rate as a function of time for reading the Mooney viscosity which was recorded as torque in Nm. The functional group in rubber samples was determined by using attenuated total reflection Fourier transform infrared (ATR-FTIR, VERTEX 70 BRUKER). Rubber samples were cut into small pieces and put on Ge crystal probe at 600–4000 cm\(^{-1}\). The processability under strain sweep modes of the rubber samples was investigated by a rubber processing analyser (RPA 2000, Monsanto). The strain sweep mode was in the range of 0.5–100%, the process was carried out at 100°C and 1 Hz.

3. Results and discussion

Mooney viscosity relates to the flow of elastomers like natural rubber, the value depends on the macrostructure of rubber. The results of the Mooney viscosity of samples at various storage times are shown in Table 1. The Mooney viscosity of pure NR increases after 12 weeks, in contrast, Mooney viscosity of NR with hydroxylamine sulfate is stable whatever the concentration of HS.

| Samples          | Mooney viscosity (± 5 a.u.) |
|------------------|-----------------------------|
|                  | 0 week | 12 weeks |
| Pure NR          | 40     | 52       |
| NR with HS 0.2 phr | 45     | 46       |
| NR with HS 2.0 phr | 40     | 38       |

The results of the gel content are shown in Table 2. At time 0, the pure NR has gel content larger than that of NR with hydroxylamine sulfate. After 12 weeks, pure NR has a higher gel content resulting from gel formation during prolonged storage. The gel content depends on proteins and lipids that are responsible for the gel formation. In contrast, the gel content is stable for NR with hydroxylamine sulfate. The effect of proteins and lipids causes a gel network that calls storage hardening in NR. This result is in good agreement with the result of Mooney viscosity.

| Samples          | Gel content (wt.%) |
|------------------|--------------------|
|                  | 0 week | 12 weeks |
| Pure NR          | 57.0 ± 0.4 | 64.9 ± 1.9 |
| NR with HS 0.2 phr | 54.7 ± 3.2 | 54.6 ± 5.6 |
| NR with HS 2.0 phr | 53.3 ± 2.2 | 53.7 ± 0.5 |

The FTIR spectra have been used to determine the composition of samples, especially with respect of the N-H bonds in NR with hydroxylamine sulfate samples at 3600 – 2600 cm\(^{-1}\) (Figure 1), indicating
that at time 0, samples showed peaks of the amine group at 3280 cm\(^{-1}\), the fatty acid ester group at 1740 cm\(^{-1}\), the aldehyde group at 1710 cm\(^{-1}\) and the amide I group at 1660 – 1630 cm\(^{-1}\) (data not shown here). After 12 weeks, NR with hydroxylamine sulfate samples represented rather no change in the FTIR spectra.

Figure 1. FTIR spectra of NR with/without hydroxylamine sulfate samples: (A) 0 week and (B) 12 weeks

In the case of pure NR, the peak of the amine group at 3280 cm\(^{-1}\) and the peak of the amide I group at 1660 – 1630 cm\(^{-1}\) were increased respectively after storage time for 12 weeks. The results of the storage modulus (G’) and the strain of NR with hydroxylamine sulfate samples for 0 and 12 weeks were shown in Figure 2. At time 0, the results showed that all the samples represent the same level of rigidity, this result is in good agreement with the result of Mooney viscosity. After 12 weeks, the results of NR with hydroxylamine sulphate rather decreased compared to those at time 0, except for pure NR where its G’ increased.

Figure 2. Relationship between storage modulus (G’) and the strain of NR with/without hydroxylamine sulfate samples for 0 week (A) and 12 weeks (B)

4. Conclusions
Hydroxylamine sulfate can be used to inhibit storage hardening in NR. The dynamic gel networks and Mooney viscosity of NR with hydroxylamine sulfate are stable compared to the NR without hydroxylamine sulphate. This means that the viscosity stabilizer restrained the intermolecular links between non-rubber components of the rubber chains, resulting in an almost constant Mooney viscosity.
and gel content. The result of processability under strain sweep is in good agreement with that of Mooney viscosity.

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5. References

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