Accelerated natural rubber ageing: an effect of storage temperature on molecular structure and properties

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Abstract. The effect of storage temperature on the storage hardening of natural rubber (NR) and the evolution of molecular structure of natural rubber was investigated. Accelerated storage hardening number (ΔP) increased linearly and plasticity intention index (PRI) increased exponentially with the increment in storage temperature. Ester content and protein content results indicated that variation trend of ΔP is neither identical to the changing of α termini nor to that of ω termini. The gel content changing is related the changing of accelerated storage hardening number. NMR showed that with the increase of storage temperature from 40 °C to 80 °C, the crosslinking density would slightly increase firstly and then decrease. GPC measurement indicated that when the storage temperature rose, the molecular weight began to decrease and the corresponding molecular weight distribution also became wider. when the storage temperature beyond the 50 °C the molecular weight of the raw material rubber increased until the storage temperature reached the 70 °C and the corresponding molecular weight distribution generally became wider.

1. Introduction

Natural rubber is an important biomass resources and is widely applied in many life and industrial purpose due to its comprehensive properties such as the excellent elasticity, outstanding flexing resistance, self-enhancement, etc [1]. However, compared with the synthetic rubber, there is a unique phenomenon that natural rubber will become more vicious and gradually harder during the storage process [2]. This special process occurred in the NR system already become a serious issue to restrict the utilize of NR due to the more energy consumption, frequent follow-up processing recipe adjustment originated from unstable batch-to-batch uniformity. It is well known that storage hardening process depends on the special structure of the natural rubber.

Despite of extensive research for many years, the actual mechanism of storage hardening has not been fully clarified. Some researchers believe that the crosslinking chemical reaction occurred on the so-called abnormal groups such as epoxide [3-5], aldehyde [6], lactone [7], etc. Recently some research also reported that phospholipids and proteins bonded with chain end exist in NR was assumed to dominate the crosslinking point formation and prompt the storage hardening [8]. So far, the detailed rule of storage hardening is still not be predicted and exact mechanism of hardening is a controversial issue. On the other hand, many external environment’s factors exert an important influence on the storage hardening. Among the environmental storage factors, temperature is a key factor which is quietly related to the practical process and storage factory circumstances. Therefore, in this work, the
The effect of storage temperature on the stored characters and evolution of molecular structure of natural rubber were mainly investigated and the relationship between the accelerated storage hardening number and storage temperature was analyzed and fitted by the quantitative equation.

2. Experimental

2.1. Materials and reagent
SCR 5 was provided by Hainan Jinlong Rubber Branch. Phosphorus pentoxide (A. R.) was purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran (A. R.) was from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Chloroform (A. R.), boric acid (A. R.), toluene (A. R.), hydrochloric acid (A. R.), concentrated sulfuric acid (A. R.), potassium bromide (A. R.), sodium hydroxide (A. R.) were all bought from Guangzhou Chemical Reagent Factory.

2.2. Samples preparation
200 g raw natural rubber (SCR 5) were set into the mill and passed through the rolls for eight times to get the sample sheet of 3.2 ~ 3.6 cm. Then button sample (diameter = 1 cm) were cut from the sheet. For each storage temperature, five button samples with close thickness and flat surface were adopted and the median value was as the plasticity value.

2.3. Characterization
Accelerated storage hardening number (ΔP) was calculated by differentials between the plasticity value stored at certain storage temperature and the plasticity before storage. Plasticity retention index (PRI) was the percentage between the plasticity by hot air aging at 140 °C × 30 min and the corresponding plasticity of the sample storage at certain storage temperature. Plasticity value was determined by Wallace Rapid Plastimeter (Wallace Test Equipment); Ester content was measured by FTIR (Spectrum One, Perkin Elmer Instruments) measurement based on the intensity ratio of peaks of carbonyl group at 1739 cm⁻¹ (C=O) to unsaturated carbon (C=C) absorbance at 1664 cm⁻¹. Protein content Nitrogen content of the sample was analyzed by an Automatic Kieldahl apparatus (K9860, Hanon Instruments, China) according to 8088-2008 GB/T. The molecular weight and its distribution of NR samples were determined by GPC (Waters 1515, Waters Corporation). Gel content was determined by following procedure: 0.15 g sample rubber cut into little flecks and put into 50 mL toluene for 5 d to get the (0.3 % (W/V) sample solution and the sample solution was filtered by pre-dried filter gauze (45 μm). At last, the gel was dried constantly at 40 °C in the vacuum. The gel content was calculated by percentage of dried gel weight against the sample weight. Crosslinking density was determined by NMR Crosslink Density Analyzer (VTMR20-010V-T, Suzhou Niumag Analytical Instrument Corporation).

3. Results and discussion

3.1. Accelerated storage hardening number and plasticity retention index
Figure 1 shows accelerated storage-hardening number (ΔP) with the elevated storage temperature (ST) and the linear fit of ΔP as function of storage temperature (ST). It is clearly seen that ΔP increased linearly from 3 to 18 when ST was elevated correspondingly from 40 °C to 80 °C. Furthermore, the relationship between ΔP and ST can be linear fitted by the Equation 1, the Adj. R-Square was 0.975 which demonstrated that the fitting equation was significant and credible.

\[
\Delta P = 0.399 \times ST - 13.320
\] (1)
Figure 1. Linear fit of accelerated storage hardening number with the elevated storage temperature.

Figure 2 demonstrates the effect of the storage temperature \( ST \) on plasticity intention index \( PRI \). Compared the \( \Delta P \), the \( PRI \) decreased from 59.8% to 48.2% when the \( ST \) was elevated correspondingly from 40°C to 80°C. The relationship between \( PRI \) and \( ST \) was also fitted and found that the exponential equation can fit the experimental data. The exponential equation was as following equation 2 and the Adj. R-Square was 0.993.

\[
PRI = 47.903 + 649.586 \times \exp(-0.100 \times ST)
\]  

(2)

Figure 2. Exponential Fit of plasticity intention index \( PRI \) with the storage temperature.

3.2. Ester content and protein content

Polyisoprene chains from Hevea brasiliensis contain two type of functional groups at initiating and terminating ends, that are so called \( \alpha \)- and \( \omega \)-termini, bonded with phospholipids and proteins,
respectively [9, 10]. In order to evaluate the changes of chain end in the storage process when the ST was elevated, ester and protein content were determined to indicate the α-termini and ω-termini. From the Figure 3, ester content firstly increased, then reached the maximum value at 60 °C and began to decreased with further improved storage temperature which demonstrated that α termini has higher level at 60 °C. However, as respect to protein contents, it has an approximately opposite trend. Combining the above 3.1, it can be found that changing trend of $\Delta P$ is neither identical to the changing of α termini nor to that of ω termini.

![Figure 3](image.jpg)

**Figure 3.** Effect of storage temperature on ester and nitrogen content.

### 3.3. Gel content and its growth velocity

Gel content is an indicator of interaction of ω-termini and α-termini [11, 12]. Figure 4 shows the effect of the storage temperature on gel content and gel content growth. It can be seen that at lower temperatures, from 40 °C to 50 °C, the gel content increased slowly. However, in the medial temperature region of 50 °C ~ 60 °C the gel content increased sharply and when the temperature shifted to higher zones, the gel content began to increased slowly again. In the Figure 4, differential the function of gel content variation versus temperature was calculated. It can easily be seen that the growth velocity of gel content was maximum at the temperature range from 50 to 60 °C.

![Figure 4](image.jpg)

**Figure 4.** Effect of storage temperature on gel content and gel content growth.
3.4. Crosslinking density and $M_c$

Crosslinking density of raw material rubber is from a weak chain network due to the reaction between protein or to the reaction between protein and phospholipid [13]. It was found that with the increase of storage temperature from 40 °C to 50 °C, the crosslinking density would slightly increase. However, when the storage temperature went on elevating, the crosslinking density began to decreased. $M_c$ is another parameter which is the weight between two adjacent crosslinking point (seen in Figure 5). When $M_c$ is larger, the length of the adjacent crosslinking point is longer. This demonstrates that $M_c$ is inversely proportional to crosslinking density. Therefore, the $M_c$ firstly decreased and then increased in the range of 50 °C ~ 80 °C storage temperature. From above gel content results, we can see that gel content has a similar changing trend with the crosslinking network. The improvement crosslinking density might come from gel formation formed by some molecule chains in natural rubber matrix.

![Figure 5. Effect of storage temperature on crosslinking density and $M_c$.](image)

3.5. Molecular weight

Figure 6 shows the effect of storage temperature on weight average molecular weight and Figure 7 gives out the GPC curves which indicated the molecular weight distributions of NR samples at different storage temperature. It is noted that when the storage temperature rose from 40 °C to 50 °C, the molecular weight began to decrease and the corresponding molecular weight distribution also became wider which may be attributed to the decomposition of hydrogen bond between proteins or phospholipids and resultant part decomposition of branching points. However, when the storage temperature beyond the 50 °C the molecular weight of the raw material rubber increased until the storage temperature reached the 70 °C and the corresponding molecular weight distribution generally became wider. This indicated that the storage temperature became higher, the chemical crosslinking might occur and formed the new crosslinking point again and result in the increment of molecular weight. Nevertheless, when storage temperature was quietly high, there is a competition between chemical crosslinking and decomposition of the molecular chains and the decomposition began to prevail.
4. Conclusions
Accelerated storage-hardening number rises linearly with the elevated storage temperature and can be predicated by a fitting equation. Unlike the accelerated storage-hardening number, plasticity intention index rises exponentially with the increment of storage temperature. The accelerated storage-
hardening number is related to both end groups of natural rubber chain whereas is quietly related to the gel content changing. The process and structural changing are different when the storage temperature ranged from 40°C to 50°C. The lower temperature can result in decomposition of physical interaction of proteins of phospholipids and the higher temperature will promote the chemical interaction of crosslinking or decomposition of molecular chains.

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