Role of Divalent Metal Ions on the Basic Properties and Molecular Chains of Natural Rubber

Fuchun Zhao*, Jie Guan*, Wanna Bai†, Tingting Gu*, Huan Liu‡ and Shuangquan Liao§

Key Laboratory of Advanced Materials of Tropical Island Resources (Hainan University), Ministry of Education, School of Materials and Chemical Engineering, Hainan University, Haikou, China

*Corresponding author e-mail: zhaofuchun2005@163.com, †1043386642@qq.com, ‡993245560@qq.com, §2249838279@qq.com, ‡1150030167@qq.com, §Shqliao@263.net

Abstract. Metal ions are a kind of components that cannot be completely removed in natural latex, which have an important influence on the basic quality of natural rubber, such as ash, impurities, Wallace plasticity value, plasticity retention index, etc. The six kinds of common divalent metal ions in natural rubber including calcium ion, magnesium ion, copper ion, manganese ion, iron ion and zinc ion are targeted to explore their influence on the storage characteristics of natural rubber. The fresh latex was added the designed divalent ions, then became the raw natural rubber via some procedures such as solidification, drying. Based on divalent metal ion and their content, the storage characteristics of natural rubber and the microstructure of corresponding natural rubber sample were examined. Wallace plasticity value (P₀), Plasticity retention index (PRI), accelerated storage-hardening number (ΔP) of the resultant samples were tested. The tensile strength, and rubber molecular weight were also determined to explore the effects of different divalent metals on the structural changes of natural rubber. In the experiment, the blank control group was designed. Through the contrast analysis with the blank control group, it was found that the storage stability of the raw rubber depends on not only the type but also the content of divalent metal ions.

1. Introduction

Raw natural rubber usually can be obtained from fresh natural rubber latex by several processing procedures such as coagulation, lavation, drying and the properties of raw natural rubber are related to not only the main rubber molecular structure but also the non-rubber component. The presence of metal ions may change the existence of rubber molecular chain and therefore has a direct effect on molecular weight, branching and gel content, especially on storage characteristics of natural rubber.

Gan [1] found that monovalent cations have no effect on the crosslinking reaction, some divalent cations are able to reduce the storage hardening. Certain transition metal ions catalyzed the degradation of natural rubber. Ratnayake [2] found that the remaining iron ions in the crepe rubber catalyzed the thermo-oxidative degradation and thereby significantly affect the oxidative stability of the rubber. A
reduction of storage hardening by the presence of divalent cations such as magnesium ion was also observed [3].

However, the introduction a certain amount of metal ion into polymers which contain ionic groups may exert an important role on their mechanical properties [4]. Metal ions are considered to react with the \( \omega \)-terminal with hydrogen bonds and link with the \( \alpha \)-terminal through fatty acids [5]. Hence, the presence of metal ion may enhance the cross-linking and promote the storage hardening. At the same time, the loss of some proteins and metal ions should not greatly influence the storage hardening of NR is also reported [6].

From the above, effect of metal ion on natural rubber’s basic quality and storage stability is needed to further exploration. To our knowledge, so far there is hardly seen the report to give the divalent metal ion to the storage characteristics of the NR molecules. So, this work mainly concentrates on the effect of divalent metal ion on difference of molecular chain structure and storage characteristics. A series of experiments were conducted to the influence of adding of different kind of divalent metal ion into NR latex on storage properties, green tensile strength and corresponding molecular weight were elucidated.

2. Experimental

2.1. Materials and reagent
Fresh natural latex (36% dry rubber content) was obtained from Xida Farm, Hainan Province, China. Anhydrous calcium chloride (A. R.) was purchased from Tianjin Da Mao Chemical Reagent Factory, China. Magnesium chloride hexahydrate, Copper sulfate pentahydrate, Manganese chloride and Toluene were purchased from Guangzhou Chemical Reagent Factory, China. Iron dichloride tetrahydrate and Zinc chloride were purchased from Sino-pharm Chemical Reagent Co., Ltd, China. Acetic acid was bought from Xilong Chemical Co., Ltd, China, tetrahydrofuran and came from Thermo Fisher Scientific Co., Ltd.

2.2. Preparation of natural samples including divalent metal ions
210 g Fresh natural latex (36%) was diluted to 20%, then was added metal ion salt and was agitated slowly by magnetic stirrer for 20 min. afterwards, the resultant latex was coagulated by acetic acid solution (2%). The raw natural rubber was obtained from the wet solid rubber by the subsequent procedure such as washing, drying in the oven at 60 oC until completely transparent. The mass of salt was calculated by the corresponding cation content and four samples containing 0.32 mmol, 1.6 mmol, 8 mmol, 40 mmol, respectively were prepare for each kind of divalent metal ion.

2.3. Characterization
Plasticity of natural rubber sample was determined by a Wallace rapid lactometer according to GB/T 3520-1992. Plasticity retention index (PRI) was calculated using equation PRI (%) = \( P_{30}/P_{0} \) ×100. Storage hardening value number (\( \Delta P \)) was different value that plasticity after accelerated storage subtracts plasticity before accelerated storage. The molecular weight and its distribution of NR samples were determined by GPC (Waters 1515, Waters Corporation).

3. Results and discussion

3.1. Wallace plasticity value and Plasticity retention index
Fig. 1 showed the effect of different metal ions on Wallace plasticity value (\( P_{0} \)). As can be seen from Fig. 1, with the increment of metal ions concentration, \( P_{0} \) first increased and then decreased with to the calcium ion and manganese ion. Unlike the calcium ion and manganese ion, the other metal ions always reduced \( P_{0} \) when their content increased and manganese ion reduced \( P_{0} \) at the largest degree.
Plasticity retention index (PRI) is an important raw rubber property measuring the resistance to thermo-oxidation of natural rubber [2]. Fig. 2 gives the effect of different metal ions on Plasticity retention index (PRI). It can be clearly found that PRI has went down when these three kinds of metal ions content ranged from 0.32 mmol to 40 mmol for 75g NR. Manganese ion is some special and the corresponding PRI decreased and then increased when its content increased.

3.2. Accelerated storage hardening number

Accelerated storage hardening number (ΔP) is an important parameter to evaluate the storage stability of the raw natural rubber. Fig. 3 showed the effect of different metal ions on ΔP. As can been seen, the accelerated storage hardening number of natural rubber sample containing any kind of manganese ion, iron ion and zinc ion reduced remarkably with the content of metal ion ranging from 0.32/75 g mmol to
40 mmol/75 g. However, the accelerated storage hardening number of natural rubber sample containing calcium ion or magnesium increased.

![Figure 3](image.png)

**Figure 3.** Effect of different metal ions on accelerated storage hardening number.

Then decreased. When the content of these two kinds was the 1.6 mmol/75 g, ΔP reached the maximum value. Among the metal ions in the experiment, copper had an important influence on ΔP, which can be indicated that ΔP was -10 when copper ion content was only 0.32/75 g.

### 3.3. Tensile strength

The tensile strength of un-vulcanized natural rubber can reflect the tangled degree of rubber molecular chains and the interaction of rubber molecular chains in the matrix which mainly depends on the length of molecular chains. Fig. 4 showed the effect of different divalent metal ions on green strength of raw natural rubber. In the whole range of metal ions content, the green strength of samples containing magnesium ion and zinc ion had the similar tendency of first increasing and then decreasing. This means that magnesium ion and zinc ion at lower content may play a role in crosslinking points between rubber molecular chains and enhancing the interaction of molecular chains. However, when these two types of metal ions at higher content, the green strength reduced. When the content of calcium ion was low, the green strength was high. With the further increased content of calcium ion, the green strength almost kept the same level. To contrast, the other three metal ions including manganese ion, iron ion and copper ion reduced remarkably the green strength even at low ion content.
3.4. Molecular weight

Table 1 showed the effect of different metal ions on number-average molecular weight ($M_n$). Compared with $M_n$ of unincorporated sample, that of the raw natural rubber incorporated into

Table 1. Molecular weight of samples containing different kinds of divalent metal ions.

| Metal ions  | Number-average Molecular Weight at different level of metal ions |
|-------------|---------------------------------------------------------------|
|             | 0.32 mmol | 1.6 mmol | 8 mmol | 40 mmol |
| calcium     | 169345    | 180565   | 180704 | 99280   |
| manganese   | 146513    | 105327   | 71140  | 50272   |
| iron        | 136547    | 108646   | 59288  | 41010   |
| zinc        | 227448    | 212193   | 198403 | 150127  |
| magnesium   | 229314    | 166054   | 119093 | 70380   |
| copper      | 78983     | 37860    | 35562  | 41372   |

Low content of magnesium ion increased, which was corresponding with the previous green strength (Seen from Table 1 and 3.3). Except for the calcium ion, the other metal ions make the $M_n$ with the increased metal ion concentration. At the same time, $M_n$ increased first and then went down with the increment of calcium ion content. Three kinds of metal ions including manganese ion, iron ion and copper ion had a dramatic influence on molecular weight and they all make the $M_n$ go down.

4. Conclusion

Divalent metal ions is a important factor which are related to the basic quality of natural rubber such as wallance plasticity value, plasticity retain index, green strength and molecular weight, etc. It is found that not only the type but also the incorporated content of divalent metal ion affect the storage characteristics of natural rubber. Among the six type of metal ions, calcium ion and zinc ion has the similar effect on properties of raw natural rubber. Natural rubber is more sensitive to manganese ion and iron ion, because they may accelerate the aging process of natural rubber at slightly higher concentration of metal ions. Manganium ion unexpectedly increased the storage stability at low concentration. Copper ion is harmful to the storage property and the effect is largest among the experimental metal ions.
Acknowledgments
This work was financially supported by National Natural Science Foundation of China [no. 51563006], Key Laboratory of Advanced Materials of Tropical Island Resources (Hainan University), Ministry of Education [no. AM2017-04] and Major science and technology projects of Hainan province [no. ZDKJ2016020-2] fund.

References
[1] S. N. Gan and K. F. Ting, Effect of treating latex with some metal ions on storage hardening of natural rubber, Polymer. 34 (1993) 2142 - 2147.
[2] U. N. Ratnayake, P. H. S. Kumara, T. A. S. Siriwadene, A. K. D. W. Prasad and V. C. Rohanadeepa, Effect of iron in processing water on quality of crepe rubber, J. Rubber Res. Inst. Sri Lanka. (2011) 1 - 14.
[3] Nimpaiboon, S. Amnuaypornsri and J. T. Sakdapipanich, Obstruction of storage hardening in NR by using polar chemicals, Rubber Chem. Technol. 89 (2016) 358 - 368.
[4] T. Kurian and N. M. Mathew, Natural Rubber: Production, Properties and Applications, John Wiley & Sons, Inc. (2011) 403 - 436.
[5] M. Salomez, M. Subileau, J. Intapun, F. Bonfils, J. Sainte-Beuve, L. Vaysse and E. Dubreucq, Micro-organisms in latex and natural rubber coagula of Hevea brasiliensis and their impact on rubber composition, structure and properties, J. Appl. Microbiol. 117 (2014) 921.
[6] J. Yunyongwattanakorn, Y. Tanaka, S. Kawahara, W. Klinklai and J. Sakdapipanich, Effect of Non-Rubber Components on Storage Hardening and Gel Formation of Natural Rubber During Accelerated Storage under Various Conditions, Rubber Chem. Technol. 76 (2003) 1228 - 1240.