Effect of Concentration on Properties of Vacuum Coagulated Natural Rubber Latex

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Abstract. Vacuum treatment was used to coagulate natural latex, the effects of latex concentration on physical and chemical properties, mechanical properties, molecular weight and crosslink density of vacuum coagulated natural rubber latex (NRL) were investigated. Studies have shown that with the increase of latex coagulated concentration, the nitrogen content of natural rubber (NR) increases and the ash content decreased. In the range of coagulated concentration studied, the plasticity initial value ($P_0$) and plastic retention rate (PRI) ratio of low concentration solidified raw rubber were higher than high concentration of NR. The tensile strength of NR decreased with the increase of solidification concentration. The molecular weight have shown a bimodal distribution, and the number average molecular weight ($M_n$), weight average molecular weight ($M_w$), and $z$ average molecular weight ($M_z$) increased with the solidification concentration of latex, and the dispersion coefficient decreased. With the increase of solidification concentration, the crosslink density of NR decreased first and then increased. The relative molecular mass ($M_c$) of the rubber cross-linking point increased first and then decreased with the increase of solidification concentration.

1. Introduction

Natural rubber latex (NRL) is a kind of polymer emulsion biosynthesized by Hevea brasiliensis. It can be processed to produce raw rubber and concentrated latex. Because of its excellent comprehensive properties, it is widely used in industry, agriculture, national defense, transportation, machinery manufacturing, medical and health fields in our daily life[1-2].

The processing of NRL mainly includes: short-term preservation of fresh latex[3-4], mechanical cleaning, solidification, granulation, dehydration, drying, inspection and so on. The coagulation of NRL is an important part of NR production. The coagulated process not only affects the subsequent work such as mechanical dehydration and drying, but also affects the performance of NR. We commonly used coagulated methods including acid coagulation[5], microbial coagulation[6-7], natural coagulation[8], salt coagulation[9], etc. The factors affecting latex coagulation are coagulant type, coagulant dosage, coagulation concentration, coagulation time, temperature, etc. This article has adopted vacuum[10] to solidify the latex and discussed the effect of solidification concentration on the properties of NR. These
studies should provide novel information affecting the quality of NRL by vacuum coagulated, and providing theoretical guidance.

2. Materials and methods

2.1 Materials

2.1.1 Raw materials
Natural rubber latex, Haijiao Group Jinfu Rubber Processing Branch, ammonia content is 0.26%; acetic acid, chemically pure reagent, zinc oxide, sulfur, stearic acid, accelerator M, etc., are commonly used additives in the rubber industry.

2.1.2 Instruments and equipment
Vacuum drying oven, Shanghai Yiheng Scientific Instrument Co., Ltd.; K9860 automatic Kjeldahl nitrogen analyzer, Haineng Instrument Co., Ltd.; XUF thickness gauge, Shanghai Liuling Instrument Factory; X(S)K-160 open rubber compound Machine, Wuxi Houzhai Zhenxin Machinery Co., Ltd.; British Wallace Rapid Plasticity Meter; Mooney Viscometer, UK Prescott Company; MDR-2000E Rotorless Vulcanizer, Wuxi Yiyuan Electronic Chemical Equipment Co., Ltd.; QLB-25T Flat vulcanizing machine, Jiangdu Zhongyi Experimental Machinery Factory; AI-3000 electronic tensile machine, high-speed rail testing instrument Co., Ltd.; LX-A Shore hardness tester, Jiangdu Mingzhu Experimental Machinery Factory.

2.2 Methods

2.2.1 Preparation of samples
Taking 5 equal amounts of NRL, diluting the latex to corresponding concentration, adding appropriate amount of acetic acid (mass fraction 5%), putting it into vacuum drying oven, vacuum degree to -0.95MPa, taking out pressure for 2h, then granulation, dehydration, drying, Sample is labeled as LC24%, LC26%, LC28%, LC30%, and LC35%.

2.2.2 Preparation of vulcanizate
Basic formula (parts by mass): natural rubber, 100; zinc oxide, 6; stearic acid, 0.5; accelerator M, 0.5; sulfur, 3.5.

The obtained natural rubber raw rubber is masticated on an open type rubber mixer, and the order of addition is: natural rubber→stearic acid→zinc oxide, accelerator M→sulfur. After the rubber mixture was parked for 2 hours, it was vulcanized with a flat vulcanizer, and the vulcanization condition was $145^\circ C \times 90$.

2.3 Performance test

2.3.1 Physical and chemical properties
The ash content of NR is determined according to GB/T4498; the nitrogen content of NR is determined according to GB/T8088; the initial plastic value $P_0$ of NR is determined according to GB/T3510, and the plastic retention rate of NR is determined by GB/T3517; Mooney viscosity is measured according to GB/T1233-1992.

2.3.2 Physical and mechanical properties
The tensile properties were in accordance with the national standard GB/T528-92, and the tensile speed was 500 mm/min; the tear strength was measured according to GB/T528-91, and the hardness was measured according to GB/T6031-1998.
2.3.3 Molecular weight and its distribution
The rubber sample was dissolved in tetrahydrofuran by chromatography, and the rubber concentration was 5 mg/ml. The molecular weight and distribution of the rubber were measured by a Waters 1515 gel chromatograph. The standard sample was polystyrene.

2.3.4 Crosslink density
The crosslink density of the samples was tested using a German IIC-XLDS-15HT NMR crosslink density meter. The experimental temperature was 80°C, the frequency was 15 MHz, and the magnetic induction was 315 A/m.

3. Results and Analysis

3.1 Effect of latex concentration on physical and chemical properties of vacuum coagulated NR
The effect of the solidification concentration of latex on the physical and chemical properties of vacuum-solidified NRL is shown in Table 1. It can be seen that the nitrogen content, ash content, plastic initial value $P_0$ and the plastic retention rate PRI of the vacuum solidified NR are in compliance with the requirements of SCR-5 (standard rubber No.5). With the solidified concentration of the latex increasing, the nitrogen content of NR increase and the ash content decrease. $P_0$ did not change much, and the PRI decrease slightly. It is indicated that the latex concentration is slightly lower, and the heat-resistant oxygen aging performance of NR is slightly better in the study. Mooney viscosity reflects the processing properties of raw rubber[11]. It can be seen from Table 1 that the Mooney viscosity increases first and then decreases with the increase of latex concentration. When the latex concentration is 28%, the Mooney viscosity is the largest.

Table 1. The physical and chemical properties of NR coagulated by vacuum

| Sample | Nitrogen content /% | Ash content /% | $P_0$ | PRI/% | Mooney viscosity /ML(1+4)100°C |
|--------|---------------------|----------------|-------|-------|-----------------------------|
| LC24%  | 0.2684              | 0.2005         | 40    | 75    | 62.7                        |
| LC26%  | 0.2840              | 0.1746         | 40    | 75    | 63.0                        |
| LC28%  | 0.2715              | 0.1797         | 40    | 70    | 70.2                        |
| LC30%  | 0.2880              | 0.1706         | 41    | 68    | 62.1                        |
| LC35%  | 0.2989              | 0.1463         | 38    | 76    | 64.9                        |
| SCR-5  | $\leq 0.60$         | $\leq 0.60$    | $\geq 30$ | $\geq 60$ | --                         |

3.2 Effect of latex concentration on mechanical properties of vacuum coagulated NR
Mechanical properties are one of the most important performance indexes of NR. Table 2 shows the effect of latex concentration on the mechanical properties of NR by vacuum solidified. It can be seen that when the latex concentration is increased from 24% to 35%, the tensile strength is reduced from 20.37 MPa to 17.07 MPa, because the mechanical properties of the vulcanizate are closely related to the crosslink density. When the latex concentration is low, it is beneficial to form a crosslinked network structure. With the increase of concentration, the 100% modulus and 300% modulus of NR decrease first and then increase, and the elongation at break increases first and then decreases. The tear strength and the Shore hardness vary little with the change in latex concentration.

Table 2. The mechanical properties of NR coagulated by vacuum

| Sample | Tensile strength/MPa | 100%modulus /MPa | 300%modulus /MPa | Elongation at break/% | Tear strength /(kN/m) | Shore hardness/° |
|--------|----------------------|------------------|------------------|----------------------|----------------------|------------------|
| LC24%  | 20.37                | 0.58             | 1.47             | 731.90               | 29.84                | 36               |
| LC26%  | 18.12                | 0.54             | 1.42             | 713.50               | 28.05                | 36               |
| LC28%  | 19.73                | 0.49             | 1.29             | 784.00               | 29.06                | 36               |
3.3 Effect of latex concentration on molecular weight and distribution of vacuum coagulated NR

The number average molecular weight (Mn), weight average molecular weight (Mw), Z average molecular weight (Mz) and molecular weight distribution width coefficient (Mw/Mn) of NR obtained by vacuum solidified NR of different concentrations are shown in Table 3, Mw and molecular weight distribution are shown in Figure 1. It can be seen from Table 3 that as the solidification concentration of the latex increases, the Mn, Mw, and Mz of NR increase gradually, and the dispersion coefficient gradually decreases. However, when the latex solidification concentration is 35%, Mn, Mw, and Mz are the lowest. Because it is advantageous to form a branched structure and a gel structure, and the molecules are connected to each other to form a spatial network structure, causing the molecular weight of the rubber to become larger and the distribution to be wider [12-13] when the latex concentration is low. It can be seen from Figure 1 that the molecular weight of the vacuum solidified NRL has a bimodal distribution and a relatively broad molecular mass distribution.

Table 3. Molecular weight and molecular weight distribution of NR coagulated by vacuum

| Sample | Mn×10^4 | Mw×10^4 | Mz×10^4 | Dispersion coefficient (Mw/Mn) |
|--------|--------|--------|--------|-----------------------------|
| LC24%  | 22.09  | 152.74 | 335.02 | 6.91                        |
| LC26%  | 33.49  | 166.34 | 338.41 | 4.97                        |
| LC28%  | 34.42  | 162.99 | 343.63 | 4.74                        |
| LC30%  | 51.70  | 179.17 | 350.43 | 3.47                        |
| LC35%  | 21.82  | 139.63 | 317.78 | 6.40                        |

Figure 1. Average relative molecular weight and molecular weight distribution of NR coagulated by vacuum

3.4 Effect of latex concentration on crosslink density of vacuum coagulated NR

The 1H-NMR relaxation related parameters of NR vulcanizates of different solidification concentrations is shown in Table 4. As we can be seen from Table 4, the relative molecular mass (Mc) between adjacent cross-linking points is inversely proportional to the nuclear magnetic resonance cross-linking density (XLD), because the number of cross-linking points on the rubber molecular chain is much and the rubber molecular chain between adjacent cross-linking points is short when the XLD is large.

Figure 2 is a graph showing the relationship between the crosslink density (XLD) of different vulcanize samples and the relative molecular mass (Mc) between cross-linking points. It can be seen
from the figure that as the coagulation concentration of the latex increasing, the crosslink density decreases first and then increases. The specific values are $14.3 \times 10^{-5}$ mol/mL, $13.6 \times 10^{-5}$ mol/mL, $13.3 \times 10^{-5}$ mol/mL, $13.4 \times 10^{-5}$ mol/mL, and $13.7 \times 10^{-5}$ mol/mL respectively. And $M_c$ increased slightly as the latex solidification concentration increased first.

Table 4. The crosslinked structure of NR coagulated by vacuum

| Sample   | Crosslinking density $\times E^{-5}$ (mol/mL) | $M_c$ (kg/mol) | A (Cross-linking proportion %) | B (Suspension chain weight %) | Relaxation time $T_2$(ms) |
|----------|-----------------------------------------------|----------------|--------------------------------|--------------------------------|--------------------------|
| LC24%    | 14.30                                         | 6.98           | 72.48                          | 27.52                          | 24.77                    |
| LC26%    | 13.60                                         | 7.35           | 72.96                          | 27.04                          | 23.40                    |
| LC28%    | 13.30                                         | 7.49           | 72.18                          | 27.82                          | 23.51                    |
| LC30%    | 13.40                                         | 7.45           | 69.36                          | 30.64                          | 25.28                    |
| LC35%    | 13.70                                         | 7.29           | 70.50                          | 29.50                          | 23.65                    |

Figure 2. The crosslinked structure of NR coagulated by vacuum

4. Conclusion

(1) The nitrogen content and the ash content of NR decreases with the latex concentration increasing, and the plasticity initial value $P_0$ and the plastic retention rate PRI of the slightly lower concentration NR are slightly higher.

(2) Within the range of coagulated concentrations studied, the tensile strength of vacuum solidified NR is slightly reduced with latex concentration increasing, and vacuum solidification can be carried out with a lower concentration of latex.

(3) The molecular weight of the vacuum solidified rubber has a bimodal distribution, the number average molecular weight ($M_n$), the weight average molecular weight ($M_w$), and the $z$ average molecular weight ($M_z$) gradually increase and the dispersion coefficient decreases with the solidification concentration of the latex increasing. When the solidification concentration exceeds 30%, the indicators change in the opposite direction.

(4) As the latex concentration increases, the crosslink density of NR decreases first and then increases, and $M_c$ change in the opposite direction.

Acknowledgments

Found project: Hainan province natural science foundation project (517073), Key laboratory of tropical Island resources advanced materials ministry of education foundation project (AM2017-15); Hainan province major science and technology project (ZDKJ2016020-2); Public welfare industry (Agriculture)
scientific research special foundation project (201403066).

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