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Rheological Behavior of Raw Natural Rubber Coagulated by Microorganisms

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Abstract: Tests of the strain sweep, frequency sweep and stress relaxation for raw natural rubber coagulated by microorganisms (NR-m) and raw natural rubber coagulated by acid (NR-a) were carried out with the use of a rubber process analyzer (RPA). The results showed that the storage torque, complex viscosity of NR-m were higher than those of NR-a while the loss factor was lower. The effect of temperature on viscosity of raw NR was studied following the Arrhenious-Frenkel-Eyring model. The viscous flow behavior of NR-m was poorer than those of NR-a. Furthermore, stress relaxation measurements of raw NR showed a longer period of relaxation for NR-m.

Keywords: *Microorganisms coagulation, natural rubber, rheological properties.*

Introduction

Natural rubber (NR) latex from *Hevea Brasiliensis* is a renewable biosynthesis polymer with excellent outstanding resilience, high strength and good processability, etc^[1-3]. It is composed of about 30-40% rubber hydrocarbon as rubber latex particles and about 6-8% minor non-rubber components such as proteins, mineral salts, carbohydrates, organic acids and lipids dispersed in water^[4,5]. These non-rubber substances are presumed to important role in controlling the structural change of rubber molecules during coagulation^[6] and storage^[7] processes, as well as affecting the properties of NR.

NR structure is presumed to be consist of two trans-1, 4 isoprene units, a long chain of cis-1, 4-polyisoprene repeating units, two kinds of functional groups at both initiating- and terminating-ends, i.e., the ω - and α -terminal, in which the former is bonded with proteins by hydrogen bonding, whereas the latter is presumed to be linked with mono- and diphosphate groups to form branching points via hydrogen bonding^[8]. NR usually contains the linear chains so-called the soluble sol phase and the cross-linked chains so-called the insoluble gel phase as show in Figure 1, respectively^[9,10]. In the production of raw natural rubber, the coagulation of fresh latex is an important process step of the effects on quality of NR. The microbial-coagulation of latex not only can improve quality of NR products but also to reduce environmental pollution due to highly acidic rubber effluent^[6,11].

We also know that NR is a linear high molecular weight elastomer with a wide molecular distribution. Studies showed that NR contains elasticity and viscosity behaviors during rheological behavior measurements using Mooney viscometer, Wallace plastimeter and

rubber process analyzer (RPA)^[9]. Rheological behavior of polymers is presumed to important role in affecting processability and properties of final products^[12]. Several researchers have reported the influence factors of rheological behavior of raw rubber. The rheological properties of the liquid rubbers consist of linear chains of low molecular weight depend mainly on the composition of the main chain were investigated by G. N. Petrov et al.^[13]. Mitra et al.^[14,15] observed that the influence of quasi-nanosized gels on the rheological and mechanical properties of raw NR and styrene-butadiene rubber (SBR) was investigated. It has been found that the rheological properties of these cross-linked gel-filled polymers depend on several factors such as gel concentration, size, distribution, and crosslink density. Dimier et al.^[16] reported the effect of the degree of mastication during processing on the viscosity of NR. E. Ehabe, et al.^[17] studied the influence of the maturation and storage before processing on the rheological behavior of the processed raw rubber. However, there are few reports about the study of the effects of coagulation processes of latex on the rheological behavior of NR. This paper explores the rheological properties of raw microbial-coagulated NR by frequency sweep, strain sweep and stress relaxation using a RPA (MFR, Prescott UK).

Experimental

Materials

The NR latex with a dry rubber content of 33% was obtained from the rubber processing factory of experimental farm which belongs to Chinese Tropical Agriculture Academy (Hainan, P. R. China).

Preparation of samples

Natural rubber coagulated by acid (NR-a): The 300 mL NR latex was coagulated with 20 mL 5% acetic acid in 500 mL conical flask. After the coagulum was washed repeatedly and dried thoroughly in an oven of 70 °C, dried NR-a sample was obtained.

Natural rubber coagulated by microorganisms (NR-m): The 300 mL NR latex was coagulated by the microorganisms existing in the natural latex in 500 mL conical flask at the temperature of 30 °C for 48 h. After the coagulum was washed repeatedly and dried thoroughly in an oven of 70 °C, dried NR-m sample was obtained.

Measurement of rheological properties

The strain sweep was carried out at an oscillation frequency of 6cpm, and the frequency sweep was carried out at a fixed strain of 7%. Test temperatures were 60 °C, 100°C and 150 °C, respectively. The stress relaxation experiments were conducted at 100 °C, with the step strain of 70%, and a test time of 2 min.

Interpretation data

The rheological property of the raw NR sample is relation to viscosity of rubber at a fixed shear rate, viscosity decreases rapidly with shear rate increases. This is strongly non-Newtonian dependent on viscoelastic, thixotropic and temperature, which these aspects are important in practical rubber processes^[18]. The apparent viscosity of rubber is normally defined as:

$$\eta^a = \sigma / \dot{\gamma} \quad (1)$$

where σ and $\dot{\gamma}$ are the shear stress and shear rate, respectively. This corresponds to the power law equation proposed by Ostwald^[19] as follows:

$$\sigma = k \dot{\gamma}^n \quad (2)$$

where k and n are constants of rubber, which are the consistency index and flow behavior index, respectively. Equations 1 and 2 may be combined to give:

$$\eta^a = k \dot{\gamma}^{n-1} \quad (3)$$

The relationship between temperature and apparent viscosity is expressed following the Arrhenius-Frenkel-Eyring equation^[20], which is valid for power-law fluids:

$$\eta^a = A e^{(E/RT)} \quad (4)$$

where E is the activation energy of the flow, R is the universal gas constant (8.314 J·mol⁻¹·K⁻¹), T is the absolute temperature (K), A is the pre-exponential component. The logarithmic form for Equation 4 can be written as follows:

$$\log \eta^a = \log A + \frac{E}{2.303RT} \quad (5)$$

The activation energy is calculated from the slope of a linear plot of logarithmic of apparent viscosity ($\log \eta^a$) versus the reciprocal of the absolute temperature ($1/T$). The complex viscosity, η^* , is used as η^a in our work because η^* corresponds well to the η^a value obtained from a capillary rheometer^[21].

Results and Discussion

Responses of samples to frequency sweeping

NR-a and NR-m samples were swept at temperature 60 °C and a strain of 7%. The results are shown in Figures 2 and 3, respectively. It can be seen from Figure 2 that the variation features of storage torques (S') of NR-m are similar to those of NR-a. The S' of both NR-a and NR-m increase with rising the oscillation frequency. It is obvious that S' increases sharply at lower frequency range (lower than 100 cpm). However, when the frequency is larger than 100 cpm, the rising tendency of S' becomes slow gradually. Figure 3 shows that the loss factors ($\tan \delta$) decrease with increasing frequency. Furthermore, the S' of NR-m is higher than that of NR-a, whereas, the $\tan \delta$ of NR-m is lower than that of NR-a within the whole

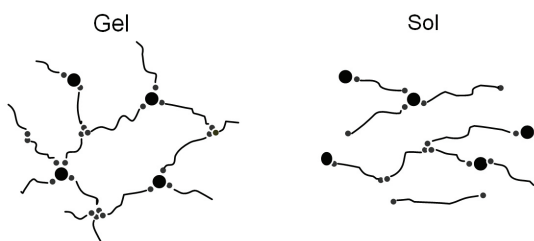


Figure 1. The structure of gel and sol phases in NR.

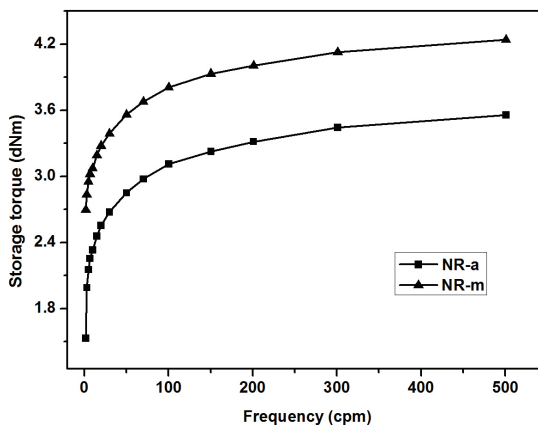


Figure 2. Responses of storage torques of samples to frequency.

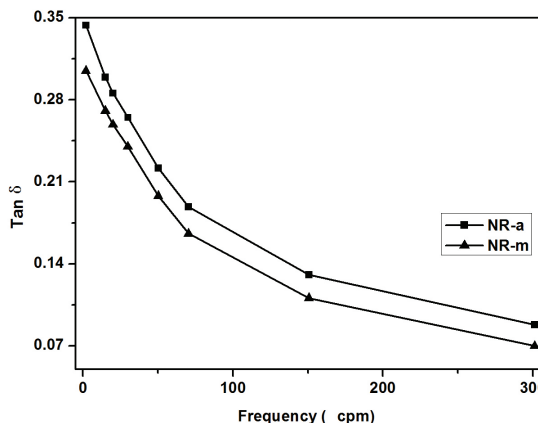


Figure 3. Responses of $\tan \delta$ of samples to frequency.

range of frequencies. The results indicate that the NR-m exhibits a higher elasticity and a lower internal friction compared with NR-a.

Responses of samples to strain sweeping

The results of the responses of both NR-a and NR-m to strain sweeping at 60 °C and an oscillation frequency of 6cpm are shown in Figures 4 and 5, respectively. Figure 4 demonstrates the relationship between S' and strain. The response of S' from the strain sweep is sensitive to rheological differences among coagulation processes. It can be seen that S' of the samples increase with rising strain. When the strain is lower than 100%, the rapid increasing tendencies of S' is observed. However, when the strain is larger than 100%, the increment tendency of S' becomes slowly because of the irreversible movement of the molecular chains. After passing the plateau, with the increment of strain, S' increases again due to the strain-induced crystallization^[22]. The value of S' of NR-m is higher than that of NR-a. The reason is likely to that microorganisms digest some proteins and other non-rubber substances by metabolism to form the consolidated structure during the process of microbial coagulation, which the greater shear stress is required to break down the entwist structure of rubber molecular chains^[23]. It can be seen from Figure 5 that the $\tan\delta$ of

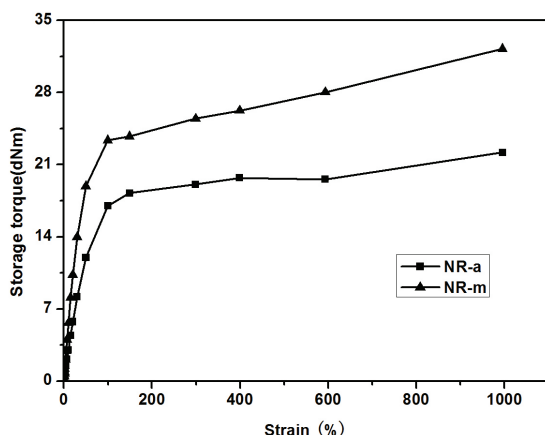


Figure 4. Responses of storage torques of samples to strain.

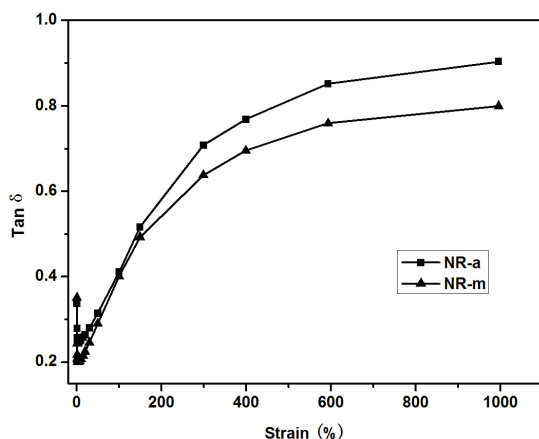


Figure 5. Responses of $\tan\delta$ of samples to strain.

both NR-a and NR-m exist a similar variation feature, which the increment is a nonlinearly with increasing strain. The $\tan\delta$ of NR-m is lower than that of NR-a over the whole range of strains.

Rheological behavior of NR samples

In the dynamic mode of RPA, the relationship between shear strain and shear rate is given by the following equation:

$$\dot{\gamma} = \gamma_0 \omega \sin(\omega t) \quad (6)$$

where γ_0 is the maximum strain, ω is the frequency and t is the time. Equation 6 gives two types of shear rates, involving a strain shear rate, $\dot{\gamma}_s$, and a frequency shear rate, $\dot{\gamma}_f$. The $\dot{\gamma}_s$ is produced by the change in strain at a constant frequency, while the $\dot{\gamma}_f$ is produced by the change in frequency at a fixed strain. The series curves of $\log \eta^*$ versus $\log \dot{\gamma}_f$ and $\log \dot{\gamma}_s$ according to Equation 3 are shown in Figures 6 and 7, respectively.

It can be seen from Figure 6 that the decrease in $\log \eta^*$ with rising $\log \dot{\gamma}_f$ over the whole range of $\dot{\gamma}_f$ values and the decrement of $\log \eta^*$ is linearly; this is a phenomenon called shear thinning, i.e., a feature of non-Newtonian behavior. Figure 7 indicates that the log-log plot of η^* versus $\dot{\gamma}_s$ has two regions. In low $\dot{\gamma}_s$ values, the

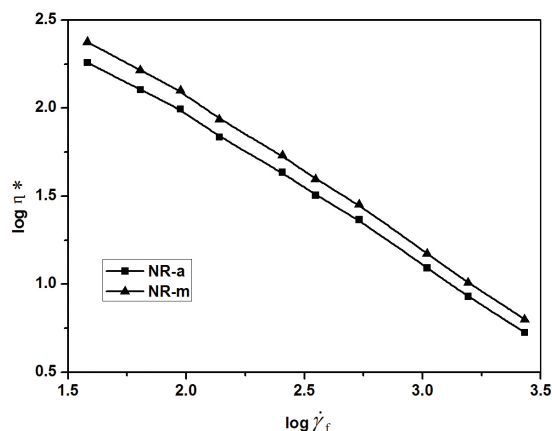


Figure 6. The relationship between $\log \eta^*$ and $\log \dot{\gamma}_f$.

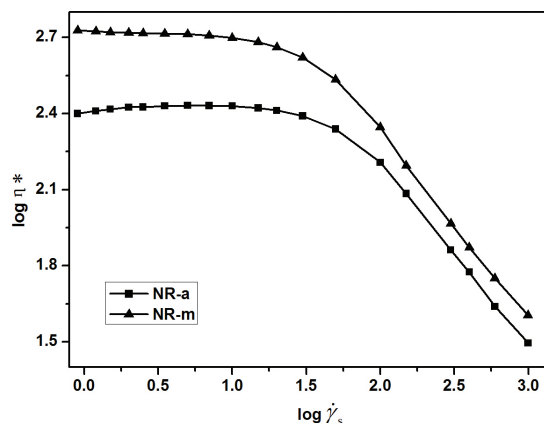


Figure 7. The relationship between $\log \eta^*$ and $\log \dot{\gamma}_s$.

change in $\log \eta^*$ with $\log \dot{\gamma}_s$ increases and appears as a straight line that is almost parallel to the $\log \dot{\gamma}_s$ axis; the constant n is approximately 1, i.e., a feature of Newtonian behavior. The change in $\log \eta^*$ decreases with increasing $\log \dot{\gamma}_s$ in the range of high $\dot{\gamma}_s$ values; this is so-called a feature of non-Newtonian behavior. It can be found from Figures 6 and 7 that, there are types of rheological behaviors in the conditions of different external forces. The η^* value of NR-m is higher than that of NR-a in the whole range of tests. This result depends on the change of average molecular weight, which the relationship between viscosity and average molecular weight obeys the Mark-Houwink equation: $\eta_0 = KM_w^{\alpha[24]}$, where η_0 is the zero-shear viscosity, K is a constant that depends on temperature, M_w is the weight average molecular weight, α is the power law exponent. The reason might be that the increase in the molecular weight of NR-m and/or the wider molecular weight distribution led to an increase in the value of the zero-shear viscosity, η_0 .

The values of the consistency index (k) and flow behavior index (n) for different samples at different temperatures calculated from the initial linear region observed at a lower frequency shear rate according to the logarithmic form for Equation 3 and listed in Table 1. It can be seen that the variations of n values show the pseudo-plastic behavior ($n < 1$) for NR-a and NR-m systems. The n values of NR-m are lower than that of NR-a at all the temperatures and the k values of NR-m are higher. These clearly confirm the increase in the resistance to flow of NR molecules by microbial-coagulation, indicating NR-m existence as a poor viscous flow behavior. With rising temperature, the k values of all the samples decrease and the n values increase. It is well known that viscosity decreases and pseudo-plasticity increases with an increase in processing temperature. This may be due to higher the temperature, more thermal energy supplied to NR segments that may cause the easy alignment of NR chains in the direction of flow^[25].

Activation energy of the viscous flow

The activation energy (E) of viscous flow is the lowest energy, which overcomes the potential barrier for jumping of molecular-kinetic units of a polymer network into vacancies during flow processing; it is based on the entropy elasticity of a macromolecular network that causes an increase of the material's flow resistance in the course of deformation^[26]. E values of NR-a and NR-m at different shear rates are plotted in Figures 8 and 9, respectively. It can be seen that the values of E of samples decrease with rising shear rate and E of NR-m is higher than that of NR-a for all the tests. The reason could be that the enzymatic activity of microorganisms may catalyze reactions involved in gel formation, such as the oxidation of polyunsaturated fatty acid leading to the formation of aldehyde groups, which enhances the rigidity and polarity

of molecular chain, and the free volume is less and intermolecular slippage between molecules is restricted due to the formation of micro-network results, which promotes higher flow restriction^[23,27,28].

Responses of samples to stress relaxation

Stress relaxation test is often considered as the simplest and fastest way to quantify the viscoelastic response of polymeric materials. The stress relaxation process in rubbers, involves physical and chemical processes which occur in them. The chemical relaxation involves rearrangement of chemical bonds in the chains and lateral chemical bonds occurring in a chemical reaction process, and as a result of the action of stresses. Physical stress relaxation involves rearrangement of different structural elements, which are removed from the equilibrium state by external forces and occur in the field of force of intermolecular forces, its relaxation time is 10^{-6} - 10^{-5} times longer than that of the chemical relaxation at 20 °C^[29].

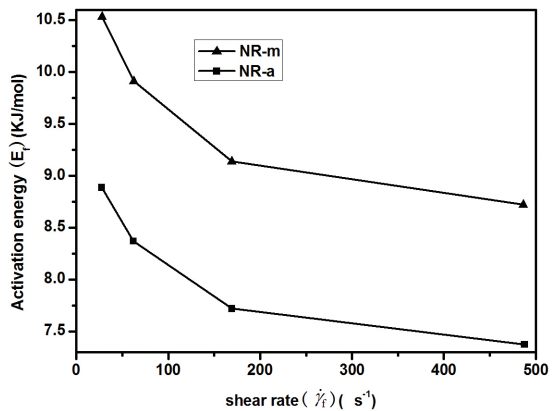


Figure 8. Variation of activation energy with frequency for NR samples.

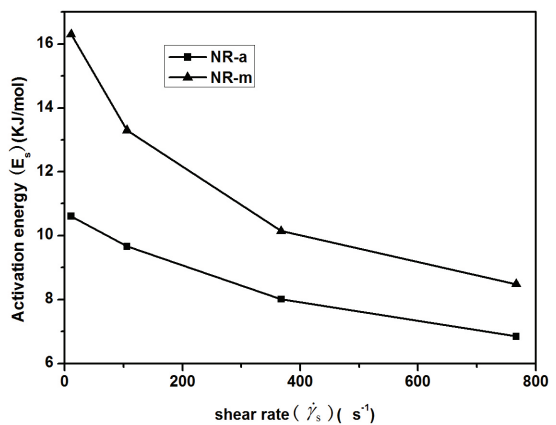


Figure 9. Variation of activation energy with strain for NR samples.

Table 1. Flow behavior index (n) and consistency index (k) of different coagulation systems.

Sample	$k \times 10^{-3} \text{ (kPa} \cdot \text{s}^n)$			n		
	60 °C	100 °C	150 °C	60 °C	100 °C	150 °C
NR-a	1.402	0.661	0.535	0.108	0.181	0.201
NR-m	1.985	0.739	0.619	0.078	0.169	0.190

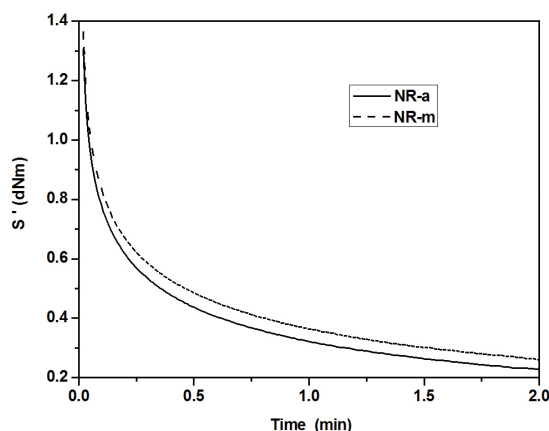


Figure 10. Response curves of NR samples to stress relaxation at 100 °C.

The variation of S' with time is shown in Figure 10. It has seen that the decrement of S' with the prolongation of the test times. The times that S' reduce to 0.4 dNm from the original values for NR-a and NR-m are 0.62 and 0.81 min, respectively. It is obviously observed that the stress relaxation time of NR-m is longer than that of NR-a, indicating NR-m exhibits a higher elasticity and a lower flowability. The result could be due to the formation of higher gel content and higher molecular weight during the microbial-coagulation process resulted in longer relaxation time^[30-32].

Conclusions

The curves of S' and $\tan\delta$ response from frequency and strain showed that S' of NR-m was higher than that of NR-a while the $\tan\delta$ was lower. With rising frequency and strain, the increment of S' for all the tests, but the $\tan\delta$ decreased and increased, respectively. The decrement of η^* was linearly related to the increase in $\dot{\gamma}_f$, which was consistent with the non-Newtonian behavior. The changes in η^* with $\dot{\gamma}_s$ showed that NR behaves like Newtonian flow in the range of low $\dot{\gamma}_s$ values and like non-Newtonian flow (pseudoplastic behavior) in the range of high $\dot{\gamma}_s$ values. The η^* curve of NR-m was higher than that NR-a in the all regions. The effect of temperature on viscosity of raw NR was studied following the Arrhenius-Frenkel-Eyring model. The value of k of NR-m was higher than that of NR-a at all the temperatures, while the variation of n value was lower, which was the pseudo-plastic behavior ($n < 1$) for NR-a and NR-m systems. These clearly confirm the increase in the resistance to flow of NR molecules by microbial-coagulation. E value of NR-m was higher than that of NR-a. The reason could be that the movement of modular chains was restricted due to the formation of micro-network results by microbial-coagulation. The stress relaxation measurements showed that the relaxation time of NR-m was longer than that of NR-a.

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