응고 방법에 따른 천연고무의 동적특성

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Characterization of the Dynamic Properties of Natural Rubbers Coagulated Using Different Methods

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초록: 천연고무 라텍스를 아세트산을 사용한 응고(A-NR), 자연 응고(N-NR) 및 미생물을 사용한 응고(M-NR) 등 다른 방법들로 응고하였고, 이들의 가교도, 가교특성, 동적특성 및 열축적 특성 등을 조사하였다. 결과에 따르면 M-NR의 경우 가장 높은 가교도와 가장 빠른 경화속도를 나타냈으며, A-NR은 정 반대인 가장 낮은 가교도와 가장 느린 경화속도를 나타내었다. 이들 고무의 동적특성은 rubber process analyzer(RPA), dynamic mechanical analyzer(DMA) 및 압축 열축적 분석방법 등을 이용하여 측정하였다. 동적특성은 고무의 가교도와 매우 밀접한 관계가 있었음을 알 수 있었고, 손실계수는 M-NR이 가장 낮았으며 A-NR의 경우는 가장 높은 값을 나타내었다.

Abstract: Natural rubber (NR) was coagulated using different methods, i.e., acid coagulation with acetic acid (A-NR), natural coagulation (N-NR), and microorganism coagulation (M-NR). The crosslink density, vulcanization properties, dynamic properties, and heat build-up were investigated. The results showed that M-NR had the highest crosslink density and fastest cure rate, and A-NR had the lowest crosslink density and slowest cure rate. The dynamic properties were measured using a rubber process analyzer, dynamic thermomechanical analysis and compression heat build-up tester; the results showed that the dynamic properties had a close relationship with the crosslink density. The loss factor was lowest for M-NR and highest for A-NR.

Keywords: natural rubber, crosslink density, dynamic properties, coagulation method.

Introduction

Natural rubber (NR) is an important industrial material and is widely used in various fields because of its superior elasticity, flexibility, and resilience. NR is harvested from *Hevea brasiliensis* and is a colloidal system of *cis*-1,4-polyisoprene particles dispersed in an aqueous serum. NR latex (NRL) con-

sists of 20-40% rubber fraction and 5% non-rubber fraction, the remainder is water. The 5% non-rubber fraction contains proteins, lipids, and other components.[1,2] There is a protective layer on the rubber particle surface which is composed of proteins and lipids. The protective layer maintains the stability of the NRL colloidal system.[3,4]

Coagulation is one of most important procedures in NR processing; it destroys the stable colloidal NRL system. In general, NR is coagulated naturally at room temperature.

For technological simplicity and to save time, NRL has been preserved with ammonia and coagulated with organic acid.

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However, this has led to issues regarding costs and its effects on the environment; for example, equipment corrosion by acetic acid increases the maintenance costs. When used for coagulation and protection of NRL, acetic acid and ammonia damage the environment. The mechanical properties of NR coagulated with acetic acid (A-NR) are inferior to naturally coagulated NR (N-NR).[5] There are, therefore, a number of problems with organic acid coagulation.

Microorganisms can degrade the non-rubber components of NRL, such as proteins and carbohydrates, as well as destroy the surface layer on the NR particles and produce organic acids that coagulate the latex.[6] In general, microorganisms destroy the stability of latex, and accelerate the coagulation of latex. Researchers[7-10] first investigated microbial-accelerated coagulation of NR nearly 50 years ago. The results showed that microbially coagulated NR (M-NR) has a faster vulcanization rate and better mechanical properties, gel content, and initial plasticity (P_0) than A-NR, but the aging resistance of M-NR was worse than that of A-NR. In addition, the wet-skid and rolling resistances of M-NR were both higher than those of A-NR.[11] Zhang *et al*. measured the effective storage times of N-NR, M-NR, and A-NR, using thermogravimetry and differential thermal analysis. The results showed that the effective storage times of N-NR and M-NR were longer than that of A-NR, but there was no obvious difference between those of N-NR and M-NR.[12] However, there are no studies about the dynamic mechanical properties of M-NR. In this work, a rubber process analyzer (RPA) and dynamic thermomechanical analysis (DMA) were used to examine the dynamic properties of various rubber materials. The dynamic properties of NR coagulated using different methods were compared, and the relationship between the dynamic properties and the crosslink density was clarified.

Experimental

Materials. Fresh NRL was obtained in Guangdong Province, P. R. China. The microorganism used was *Trichosporon fermentans*; it was grown in our laboratory. ZnO, sulfur, stearic acid, 2-mercaptobenzothiazole (2-MBT), and the other chemicals used were all commercial grade.

Sample Preparation. N-NR: Natural rubber latex was harvested from *Hevea brasiliensis* and self-coagulated, i.e., through natural coagulation; the sample is denoted by N-NR.

A-NR: After being harvested from the *Hevea brasiliensis*, the NRL was preserved by the addition of 0.3 wt% ammonia.

For the acetic-acid-coagulated NR, denoted by A-NR, 3 wt% (300 g) acetic acid was added to the preserved NRL (1 kg), and the mixture was stirred for 5 min at room temperature.

M-NR: For the microorganism coagulated NR, denoted by M-NR, 10 wt% *Trichosporon fermentans* solution was prepared using distilled water, supplemented with saccharose. After culturing for 48 h at 37 ºC, a 10 wt% *Trichosporon fermentans* solution was added to NRL and stirred for 5 min at room temperature; the ratio of mixed solution to NRL was 1:9.

After coagulation, the samples prepared using different coagulation methods were sheeted, granulated, and dried.

Compounding. The dry rubber was compounded according to Chinese Standard GB/T15340-94. The compounded samples contained NR, ZnO, sulfur, stearic acid, and 2-MBT in ratios of 100:6:3.5:0.5:0.5.

Characterization. Crosslink Density Measurements: NR vulcanizate samples had been cut from rubber sheets of about 2 mm thickness and placed into a glass tube. Sample dimensions were 8 mm in length at a diameter of approximately 5 mm. Crosslink density (XLD), molecular weight between crosslinks (M_c), $A(M_c)$ (the proportion of the polymer in the elastomer network), and $A(T_2)$ (the proportion of free end segments and small molecules remaining) were tested using the IIC XLDS-15 nuclear magnetic resonance (NMR) crosslink density spectrometer (Innovation Imaging Co., Germany). The measurement temperature was 60.0±0.1 ºC for natural rubber samples. The 90º and 180º pulse angle were 2 and 4 μs, respectively. The time domain signal has been used for data analysis. Each signal decay covered 512 data points at an acquisition time of 10.24 ms. For determination of the relaxation times, 64 measurements at different tau-values (T_2, XLD) or variation delays (T_1) were carried out. Data analysis was performed with the IIC Analysis software package using a non-linear Marquardt-Levenberg Algorithm. Typical measurement times are between 3 and 8 min. Data analysis of signal decay is analyzed according to a Gaussian-exponential function (1).

$$M(t) = A_0 + A_{M_c} \cdot \exp[-t/T_2 - (qM_2 t^2)/2] + A_{T_2} \cdot \exp(-t/T_2)$$

(1)

$A(M_c)$ and $A(T_2)$ are respective amplitudes of the crosslinked and highly mobile fractions of the polymer in [%] of the total signal, respectively. The data was treated according to equation (1) using the non-linear fitting method, and obtained qM_2, $A(M_c)$, $A(T_2)$ and T_2.

According to the eq. (2), M_c was calculated.

$$M_c = 3CM_{ru}/5n \cdot (qM_2)^{1/2} \qquad (2)$$

C and M_{ru}/n are parameters and their values are 7.2 and 68/4, respectively.[13,14]

Determination of Vulcanization Characteristics: The vulcanization characteristics of the compounds were determined using an MDR-2000 rheometer (Alpha Technological, OH, USA). The samples had been cut from compounds of about 6 g and placed into the moulding chamber. The measurement temperature was 150 °C. The frequency was 1.5 Hz, and strain was 0.5°. M_H, M_L were the highest elastic torque (S') and lowest S' during the measurement, respectively. The t_{90} (optimum cure time), t_{10} were the time when S' reached 90%, 10% of M_H. Cure rate index (CRI) was obtained from eq. (3).

$$CRI = 100/(t_{90} - t_{10}) \qquad (3)$$

The compounds were vulcanized in an XLB-U press molding machine (Zhanjiang Machinery Factory, China), under the conditions 150 °C for the optimum cure time (t_{90}, min).

RPA Analysis: The dynamic storage moduli (G') and loss factors (tanδ) of the compounds and vulcanizates were measured using an RPA (RPA2000, Alpha Technological, OH, USA). The strain sweep was performed from 0° to 40° at 60 °C and 0.5 Hz. Temperature sweeps from 60 to 150 °C were conducted at 0.5 Hz and 1° strain.

Tanδ Measurements Using Dynamic Thermomechanical Analysis (DMA): DMA measurements were performed using a dynamic mechanical thermal analyzer (Netzsch group, Germany), in rectangular tension mode, at 1, 5, 10, and 20 Hz, with a temperature increase of 5 °C/min and a strain amplitude of 0.005%. The temperature range was 0 to 80 °C and the samples were 2 mm thick and 6 mm wide.

Heat Build-up Measurements Using Compression Tests: The heat build-ups of the vulcanizates were measured using a Gabometer 4000 instrument (GABO QUALIMETER Testanlagen GmbH, Germany), with a force range of 240 N and frequency amplitude of 50 Hz. The chamber temperature was 30 °C. The sample diameter was 17.8 mm and the height was 25 mm.

Results and Discussion

Crosslink Density and Vulcanized Characterization. The crosslink density is an important parameter for evaluating the mechanical and thermal properties of NR. Several methods can be used to measure the crosslink density, such as swelling, mechanical methods, and NMR spectroscopy. NMR spectroscopy has been shown to be an effective method for investigating XLD and network structures.[14-17] The XLD and related parameters were, therefore, determined using NMR spectroscopy in this work; the results are shown in Table 1. The XLD of the M-NR vulcanizate was the highest, at 11.70×10^{-5} mol/cm^3, and had the lowest molecular weight between crosslinks (M_c). $A(M_c)$ is the proportion of the polymer in the elastomer network, and $A(T_2)$ is the proportion of free end segments and small molecules remaining.[14] A higher $A(M_c)$ indicates that more molecules were joined together, and a lower $A(T_2)$ indicates that fewer free ends remained. The M-NR vulcanizate had the highest crosslink density and the A-NR vulcanizate had the lowest crosslink density.

The vulcanization characterization is very important in NR processing.[18] Table 2 shows the cure characteristics at 150 °C of NRs coagulated using the different methods. The scorch

Table 1. Crosslink Density Parameters of NR Vulcanizates Prepared Using Different Coagulation Methods

Samples	XLD (10^{-5} mol/cm^3)	M_c (kg/mol)	$A(M_c)$ (%)	$A(T_2)$ (%)
A-NR	10.0	9.5	88.7	10.3
N-NR	11.2	8.5	90.1	8.5
M-NR	11.7	8.1	93.5	5.9

Table 2. Vulcanization Parameters of NR Samples Prepared Using Different Coagulation Methods

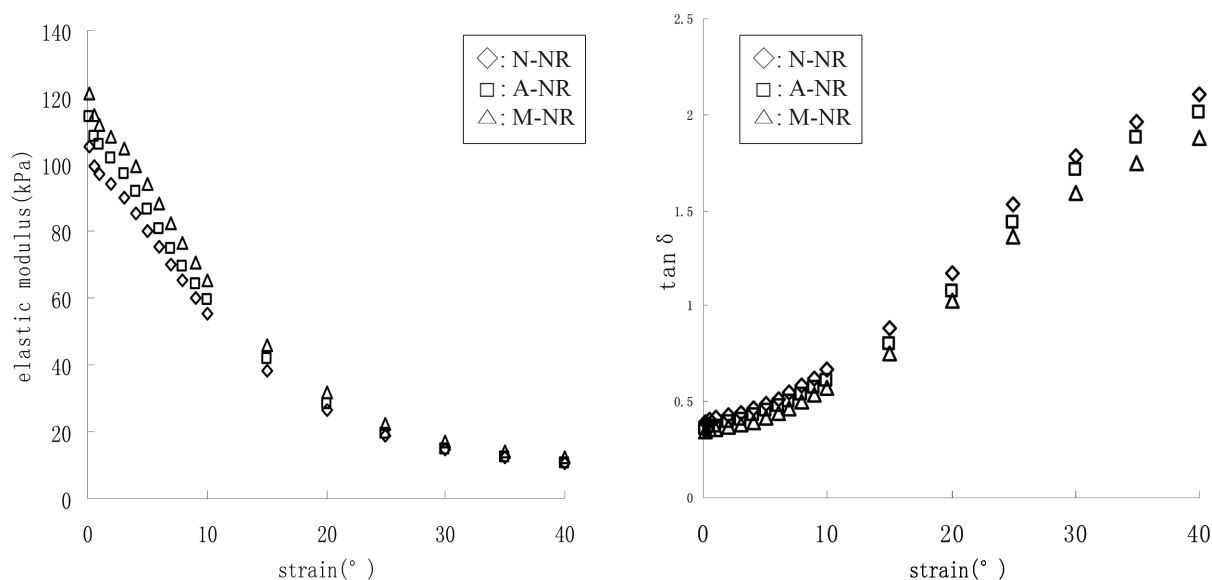|	S_{max} (dNm)	S_{min} (dNm)	t_{10} (min)	t_{90} (min)	CRI (cure rate index)
A-NR	5.76	0.99	1.07	12.54	8.72
N-NR	5.92	0.80	1.00	9.10	12.35
M-NR	6.65	1.02	0.47	8.36	12.67

Figure 1. Relationships between (a) G'; (b) tanδ and strain amplitude for compound samples.

time (t_{10}) and optimum cure time (t_{90}) of M-NR were 0.47 and 8.36 s, both shorter than those of N-NR and A-NR. M-NR had the maximum elastic torque (S_{max}), because it had the highest crosslink density (Table 1). The cure rate index (CRI) showed that M-NR had the fastest cure rate. M-NR, therefore, had both the fastest cure rate and highest crosslink density. We suggest that this is because the proteins on the particle surfaces were degraded in the natural rubber latex prior to coagulation, which accelerated vulcanization and improved the molecular cross-linking in the NR coagulated by microorganisms.[19]

Compound Rubber RPA Analysis. Dynamic functions, such as the dynamic modulus of elasticity and viscosity, can be measured over a wide range of strain amplitudes, frequencies, and temperatures using an RPA.[20] The dynamic properties of the compounds and vulcanizates of the three types of coagulated NR were investigated through strain sweeps and temperature sweeps using an RPA2000.

Strain Sweep: Figure 1 shows the dependences of the elastic modulus (G') and loss factor (tanδ) on the strains of the compound samples at 60 °C and a shear frequency of 0.5 Hz. M-NR had the highest G', and N-NR had the lowest. The G' results in the low-strain region were only slightly different, and were even closer in the high-strain region. The opposite results were obtained for tanδ, and N-NR had the highest tanδ.

Temperature Sweep. Figure 2 shows the dependence of the loss factor (tanδ) on the temperature of the compound samples at 1 and 0.5 Hz. The tanδ of M-NR was the lowest at all temperatures. Below 100 °C, tanδ of M-NR increased, and

then it decreased up to 150 °C, the maximum temperature used. The tanδ values of N-NR and A-NR were maximum at 110 °C, crossed each other, then decreased at 140 °C. Above 140 °C, the tanδ of N-NR decreased more rapidly and was lower than that of A-NR.

We suggest that during the temperature sweep, the compounds were cured as the temperature increased. The higher the crosslink density, the lower tanδ is; therefore, when the crosslink densities of the compounds increased beyond a certain degree (the peak point), tanδ began to decrease. The M-NR cure rate was faster than those the other samples, so the
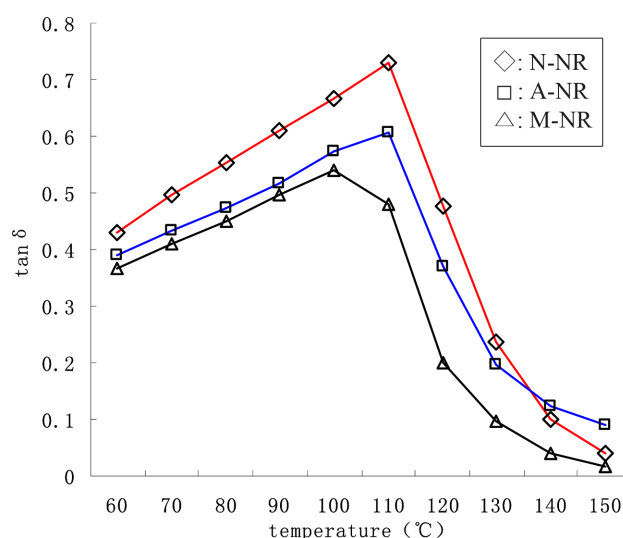

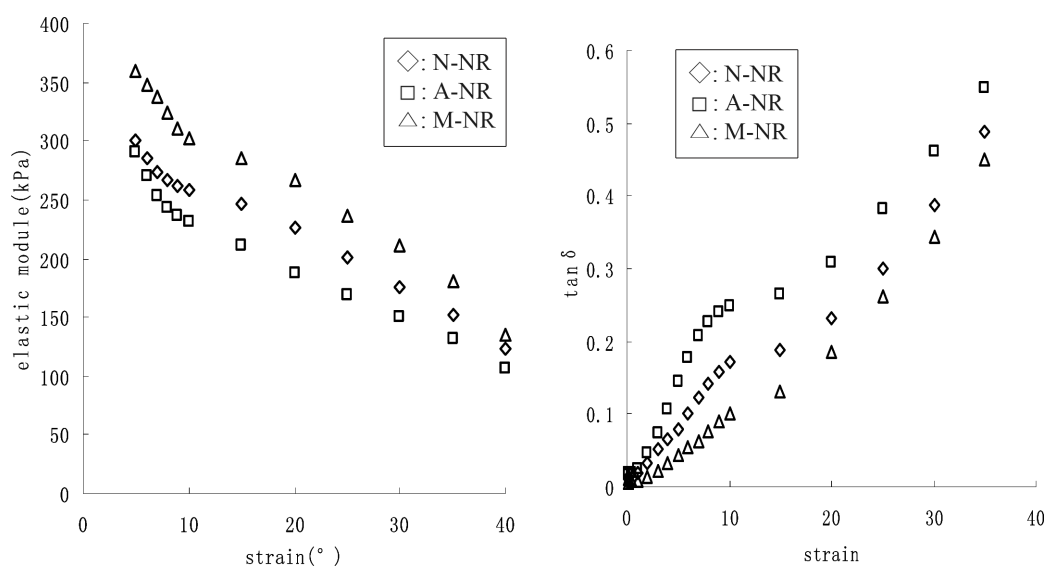**Figure 2.** Tanδ as a function of temperature of compound samples.

Figure 3. Relationships between (a) G'; (b) tanδ and strain amplitude for vulcanized samples.

peak point appeared at a slightly lower temperature. The vul-
canizate of N-NR had a higher crosslink density than that of A-
NR up to 140 °C.

Vulcanizate RPA Analysis (Strain Sweep). Figure 3 shows
the dependences of the elastic modulus (G') and the loss factor
(tanδ) on the strain of the vulcanized sample at 60 °C and a
shear frequency of 0.5 Hz. With increasing strain, G' decreased.
At low strain, the G' of M-NR was higher than those of the
others; this may be attributed to it having the highest crosslink
density. At higher strain, the G' values of the three samples
were close, because the crosslinked structure was destroyed.
The vulcanized NRs had crosslinked structures, therefore their
G' values were higher than that of compound samples in the
strain sweeps (Figure 1). The opposite results were obtained
for tanδ, i.e., the tanδ values of the vulcanizates increased with
increasing strain. This is attributed to higher strain increasing
the internal friction between the molecules.[21] A-NR had the
highest tanδ and M-NR had the lowest. In addition, there was
a plateau in the curve of tanδ, related to the destruction of the
network structure by higher strain.

DMA Measurements and Heat Build-up. Tanδ and heat
build-up (compression fatigue properties) were used to deter-
mine the NR dynamic properties. The tanδ value is correlated
with molecular mobility in the polymeric material, and is
related to the internal friction of the NR molecules.[22-24]

It is well known that tanδ can be used to determine heat
build-up. The lower the tanδ value is, the lower the heat build-
up. The tanδ was measured by DMA and the results were

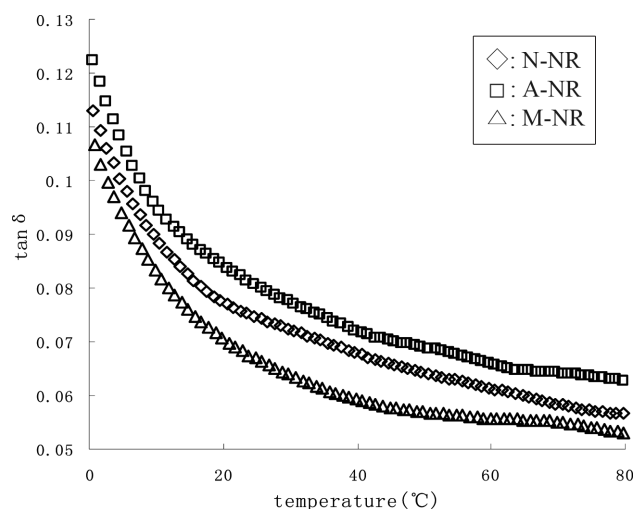**Figure 4.** Tanδ values of three coagulated NRs as function of tem-
perature at 20 Hz.

showed in Figure 4 and Table 3.

Figure 4 shows the temperature dependences of the loss fac-
tors (tanδ) which measured by DMA at 20 Hz of the NR vul-
canizates prepared using the different coagulation methods.
With increasing temperature, tanδ decreased for all the vul-
canizates. The tanδ of M-NR vulcanizates was lower than
those of the other vulcanizates. A-NR had the highest tanδ; a
high tanδ is caused by rapid molecular chain movements.

Table 3 lists the heat build-ups of the vulcanizates at 30 °C
and the tanδ values of the vulcanizates which measured by
DMA at 30 °C for various frequencies. The results showed that

Table 3. Heat Build-ups and Tanδ Values Obtained by Dynamic Mechanical Analysis at 1, 5, 10, and 20 Hz, at 30 °C

	tanδ (1 Hz)	tanδ (5 Hz)	tanδ (10 Hz)	tanδ (20 Hz)	Heat build-up (°C) at 50 Hz
A-NR	0.0513	0.0668	0.0768	0.0769	15.6
N-NR	0.0456	0.0651	0.0744	0.0720	10.5
M-NR	0.0382	0.0558	0.0650	0.0640	5.9

with increasing frequency, the tanδ values of all the samples increased. As in the case of the results of the strain sweep of vulcanizates RPA analysis (Figure 3), tanδ of M-NR was the lowest, and that of A-NR was the highest. The order of the heat build-up changes corresponded to those of the loss factor, 5.9 °C for M-NR, 10.5 °C for N-NR, and 15.6 °C for A-NR. The heat build-up results were in good agreement with the loss factors determined using RPA (Figure 3) and DMA (Figure 4) measurements. The lower compression heat build-up of M-NR is attributed to its higher crosslink density. A dense network structure restricts slippage and friction of the molecular chains of NR.

Conclusions

The vulcanization rate of M-NR was fastest, and that of A-NR was slowest. M-NR had the highest crosslink density of the three types of sample. This was caused by the proteins on the particle surfaces being degraded, which accelerated the vulcanization and improved the molecular crosslinking in the NR coagulated by microorganisms. Molecular chain movements in M-NR were more difficult than in the other coagulated rubbers, because of the high crosslink density. The RPA and DMA results showed that M-NR had the lowest loss factor and heat build-up.

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