

Effects of Coagulation Processes on Properties of Epoxidized Natural Rubber

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ABSTRACT: The epoxidized natural rubber (ENR) with epoxy group contents of 48.4% were coagulated with ethanol and steam and the structures, processing performances, antioxidative behaviors, cure characteristics, and dynamic mechanical properties were analyzed using infrared spectroscopy, rubber processing analyzer, thermogravimetric analyzer, rheometer, and dynamic thermomechanical analyzer, respectively. The results indicate that the ENR coagulated with ethanol (ENR-e) exhibits a compact structure and the contents of residual low-molecular-weight matters are higher than those of unconsolidated

ENR coagulated with steam (ENR-s). Therefore, the processing performance and antioxidative behavior as well as the curing characteristics of ENR-e compound are poorer than those of ENR-s. Although the mechanical properties and wet skid resistance of ENR-s vulcanizate are poorer than those of ENR-e, the heat build-up or rolling resistance of ENR-s is better than that of ENR-e. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1944–1949, 2008

Key words: mechanical properties; rheology; rubber; thermal properties; vulcanization

INTRODUCTION

Epoxidized natural rubber (ENR) is a kind of chemically modified natural rubber prepared by converting a part of carbon–carbon double bonds of natural rubber latex into epoxy groups with performic or peracetic acid.^{1–4} Therefore, the ENR still maintains the molecular configuration similar to that of natural rubber. At the same time, with the polar epoxy groups leading onto the molecular chains, the polarity of ENR increases obviously. In addition to bearing the excellent bulk properties of natural rubber, ENR exhibits excellent oil resistance and low air permeability. Therefore, in the rubber industry, the ENR can be used as the substitutes of acrylonitrile butadiene and butyl rubber to produce the oil-resistant articles such as oil seals, or the airtight products such as pharmaceutical bottle stopper and bike inner tube. It was reported that the wet skid resistance of automotive tire can be improved significantly by adding 5% of ENR with 25 mol % of epoxy groups into tire compound. In addition, through the epoxy groups, other functional groups can also be grafted onto the molecular chains of ENR to meet some special requirements of applications.^{4–9}

At present, the commercial-grade of ENRs with epoxy group contents of 25 mol % or 50 mol % are available as latex or dried rubber gum. To process ENR latex into dried rubber gum, the ENR latex has to be coagulated, followed by the washing and drying processes of wet coagulum. As the natural rubber latex has to be stabilized with nonionic surfactant to prevent acid-induced coagulation of latex during the epoxidation reaction, it is very difficult to coagulate the ENR latex with acetic acid which is commonly used to coagulate the natural rubber latex in natural rubber plantation. In the laboratory, the ethanol is a main coagulant for the coagulation of ENR latex, whereas in the manufacturing scale, the steam was usually adopted to coagulate the ENR latex. In addition, the ENR which is actually a half oxidation product of natural rubber is susceptible to the attacking of heat and oxidation, so the wet ENR coagulum should not be dried under the conditions currently-adopted in the standard natural rubber process. Therefore, the coagulation of ENR latex and the drying process of wet coagulum are the important steps governing the application performance of raw ENR gum. Up till present, the research works are mainly focused on the preparation, structure and properties, vulcanization of ENR, and blending ENR with other polymers,^{4–11} there are no systematic studies on the effects of coagulation methods on the properties of ENR. The main objective of this work is to investigate the effects of coagulation processes on the properties and processing performance of dried ENR gum.

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EXPERIMENTAL

Material and reagents

The high ammonia natural rubber latex concentrate with a dry rubber content of 60% was obtained from Hainan province, P. R. China. The formic acid (Fluka) and hydrogen peroxide (Shanghai chemical reagents, China) were chemically pure reagents and were standardized before use. The ethanol, sulfur, stearic acid, zinc oxide, sodium carbonate, Pregel O (fatty alcohol/ethylene oxide condensate), *N*-phenyl- β -naphthylamine, dibenzothiazole disulfide, *N,N'*-diisopropyl-2-benzothiazole sulfonamide, and 2,2'-methylene bis(4-methyl-6-*tert*-butyl phenol) were commercial products and used as-received.

Preparation of ENR latex

The concentrated NR latex (1.00 mol, calculated as repeating unit isoprene) was stabilized with the nonionic surfactant Pregel O and diluted with a predetermined amount of distilled water. Formic acid (0.25 mol) and H₂O₂ (0.75 mol) solutions were added slowly to the latex with stirring. The reaction was carried out for 24 h at 50°C. The temperature of the reaction system was reduced to room temperature using water bath, and then the aqueous ammonia was added to adjust the pH up to 9. The ENR latex could be ready for further analysis. The mole contents of epoxy groups determined with FTIR method are 48.4 mol %.

The ENR latex was then coagulated by ethanol or steam, respectively. After the coagulum was washed repeatedly and dried thoroughly, dried ENR gum sample ENR-e (coagulated by ethanol) or ENR-s (coagulated by steam) was obtained.

Infrared analysis

The samples were swollen with a drop of toluene and pressed into disk with KBr and then scanned on a GX-1 Fourier transform infrared spectrometer (FTIR) (Perkin-Elmer, Shelton, USA) with spectral resolution of 4 cm⁻¹ and scanning frequency of 5 and the spectra ranging from 4000 to 400 cm⁻¹ were recorded. The relative absorbencies of carbon-carbon double bonds (at 835 cm⁻¹), epoxy groups (at 870 cm⁻¹), methyl groups (at 1375 cm⁻¹), and hydroxyl groups (at 3460 cm⁻¹) were determined to calculate the molar percentage of epoxy groups. The equations to calculate the molar percentage of epoxy groups of ENR, deduced from Lambert-Beer law, are as follows.

$$C_e = \frac{100k_1A_2}{A_1 + k_1A_2 + k_2A_3}$$

$$C_d = \frac{C_2A_1}{k_1A_2}$$

$$C_o = 100 - C_d - C_e$$

$$A_1 = A_{835}$$

$$A_2 = A_{870} - 0.14A_{835}$$

$$A_3 = A_{3460} - 0.019A_{1375}$$

where the C_e , C_d , and C_o are the molar percentages of epoxy groups, carbon-carbon double bonds and ring opening products. A_{835} , A_{870} , A_{1375} , and A_{3460} are the absorbencies corresponding to 835 cm⁻¹, 870 cm⁻¹, 1375 cm⁻¹, and 3460 cm⁻¹. The values of k_1 and k_2 , calculated from the C_e and C_d values determined using NMR method, are 0.77 and 0.34, respectively.

Processing performance analyses

The dynamic mechanical rheological properties of raw ENR samples were performed on a RPA 2000 Rubber Processing Analyzer (Alpha, Akron, USA) with temperature (50–140°C), oscillation frequency (2–2000 cycles per min), and strain (0–90) sweeping, respectively.^{12,13}

Determinations of vulcanization characteristics and mechanical properties

ENR was mixed in a laboratory Banbury according to ISO 2393 Rubber Test mixes-preparation, mixing and vulcanization-equipment and procedures. The ingredients of formulation in dry weight parts are as follows: ENR (100), sulfur (1.5), stearic acid (2.0), zinc oxide (5.0), *N,N'*-diisopropyl-2-benzothiazole sulfenamide (1.0), dibenzothiazole disulfide (1.0), *N*-phenyl- β -naphthylamine (1.0), 2,2'-methylene bis(4-methyl-6-*tert*-butyl phenol) (1.0), and Na₂CO₃ (0.3).

The vulcanization characteristics of compounds were determined by use of a MDR-2000 rheometer (Alpha, Akron, USA). The compounds were vulcanized in a XLB-U type press molding machine (Zhanjiang machinery factory, China) at the condition of 145°C \times t_{90} min and the mechanical properties of vulcanizates were determined using a Instron-3365 Universal Material Tester (Instron, Norwood, USA).

Dynamic mechanical property analyses

The dynamic mechanical property analyses of vulcanizates were performed on a DMA-242 dynamical mechanical analyzer (Netsch, Sabell, Germany) with sweeping frequency of 5 Hz, sweeping temperature of -120°C to 100°C and heating rate of 5°C min⁻¹.

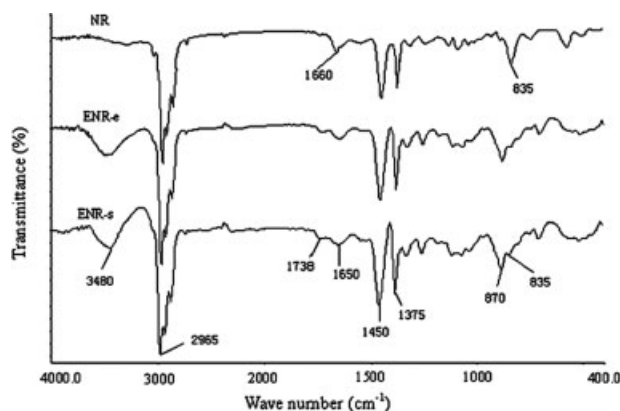


Figure 1 FTIR spectra of ENR samples. Transmittance is expressed on the vertical axis. Wave number is expressed on the horizontal axis in cm^{-1} .

Thermogravimetric analysis

The thermogravimetric analyses of raw ENR samples were carried out using a TG-7 thermal gravimetric analyzer (Perkin-Elmer, USA). The temperature was risen to 650°C from room temperature by a heating rate of $20^\circ\text{C min}^{-1}$ in atmospheres of air with flowing rate of 30 mL min^{-1} .

RESULTS AND DISCUSSION

FTIR analyses

Figure 1 shows the FTIR spectra of ENR-e, ENR-s, and NR. The absorption bands of *cis*-1,4-polyisoprene appear at 2860 cm^{-1} (C—H stretching), 1660 cm^{-1} (C=C stretching), 1450 cm^{-1} (—CH₂— deformation), 1375 cm^{-1} (methyl C—H deformation), and 835 cm^{-1} (=C—H deformation).^{1,10,11} With a part of C=C bonds being converted into epoxy groups, the absorptions at 870 cm^{-1} attributed to the epoxy groups appear on the spectra of ENR-e and ENR-s. During the preparation process of ENR, the formation of hydroxyl groups from the ring-opening reaction of epoxy groups is impossible to be avoided and with the further esterification of some hydroxyl, the ester will be formed, leading to the intensities of the absorptions at 1738 and 3480 cm^{-1} increase. The characteristics seen from the FTIR spectra of ENR-e and ENR-s are similar, indicating that the ENR-e and ENR-s are of similar micro-structures and do not subject to the influences of coagulation methods.

RPA analyses

The ENR samples were swept from 50 to 140°C at the oscillation frequency of 100 cycles per min (cpm) and strain of 1 degree of arc (deg) and the responses of elastic modulus and loss modulus to temperature sweeping are shown in Figure 2. It can be seen that,

with the temperature rising, the elastic moduli of ENR-e and ENR-s decrease gradually, and the elastic modulus of ENR-s decreases more rapidly than that of ENR-e. As a result, the elastic modulus of ENR-s which is higher than that of ENR-e at the low temperature range ($<85^\circ\text{C}$) becomes lower than that of ENR-e from 85°C . The loss moduli of ENR-e and ENR-s increase at low temperature range and then decrease with the temperature rising. The temperatures at which the loss moduli turn to decreasing are 110°C for ENR-s and 120°C for ENR-e, respectively. Therefore, the loss modulus of ENR-s which is higher than that of ENR-e at the low temperature range becomes lower than that of ENR-e from 115°C . The results indicate that the ENR-e flows easily at low temperature, while at high temperature, the ENR-s is easy to be processed.

The responses of elastic modulus and tangents of loss angles ($\tan \delta$) to frequency sweeping were obtained by sweeping the samples from 2 cpm to 2000 cpm at temperature of 60°C and strain of 0.5° (Fig. 3). With the oscillation frequency increasing, the elastic moduli of both ENR-e and ENR-s rise, whereas the $\tan \delta$ values decrease. The rapid rising tendency of elastic modulus and rapid reducing tendency of $\tan \delta$ appear at lower frequency range (<250 cpm). However, when the frequency is larger than 250 cpm, not only the rising tendency of elastic modulus, but also the decreasing tendency of $\tan \delta$ becomes slow gradually. In addition, within the whole range of sweeping frequency, the elastic modulus of ENR-e is higher than that of ENR-s, whereas, the $\tan \delta$ of ENR-e is lower than that of ENR-s.

The responses of $\tan \delta$ and elastic modulus to strain sweeping were obtained by sweeping the samples from 0.50 to 90° at 6 cpm and 60°C (Fig. 4). The elastic torques of both ENR-e and ENR-s increase

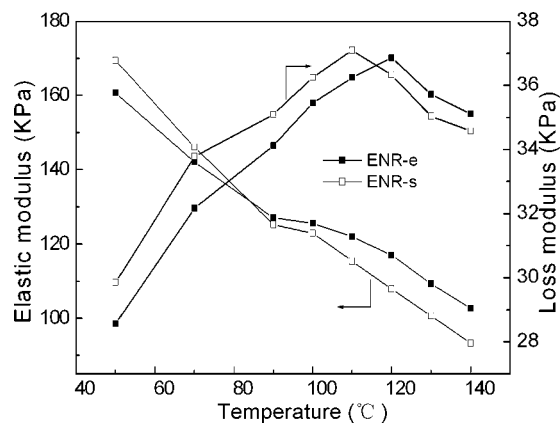


Figure 2 Responses of elastic and loss module of ENR samples to temperature. Elastic modulus is expressed on the left vertical axis in kPa and loss modulus is expressed on the right vertical axis in kPa. Temperature is expressed on the horizontal axis in $^\circ\text{C}$.

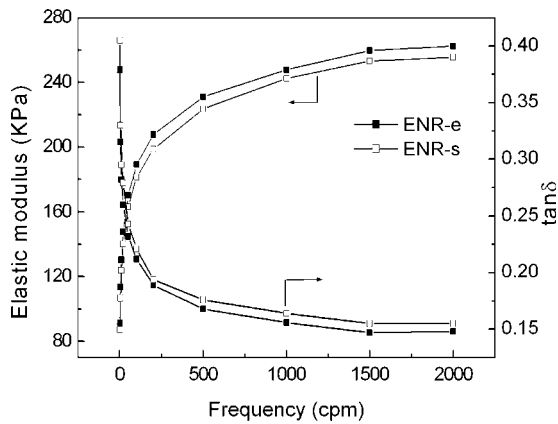


Figure 3 Responses of elastic module and $\tan \delta$ of ENR samples to frequency. Elastic modulus is expressed on the left vertical axis kPa and $\tan \delta$ is expressed on the right vertical axis. Frequency is expressed on the horizontal axis in cpm.

with strain increasing. When the strain is lower than 20° , the rapid increasing tendencies of elastic torque of ENR samples can be observed. However, when the strain is larger than 20° , the elastic torques of ENR samples increase slowly. The $\tan \delta$ values of both ENR-e and ENR-s increase gradually with the strain increasing from 0 to 45° . But when the strain is larger than 45° , the $\tan \delta$ values of ENR samples are basically unchanged. Within the whole experiment strain range, the elastic torque of ENR-e is larger than that of ENR-s, whereas, the $\tan \delta$ of ENR-e is lower than that of ENR-s.

The processing performance of raw rubber can also be characterized by determining the stress-relaxation time using a RPA2000 Rubber Processing Analyzer,¹³ and the raw rubber with a short stress-relaxation time exhibits a good processing performance.

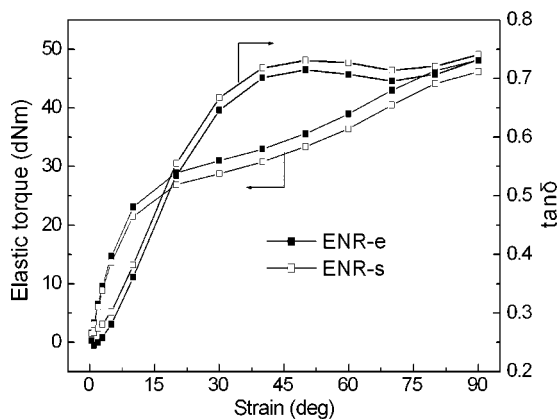


Figure 4 Responses of elastic torques and $\tan \delta$ of ENR samples to strain. Elastic torque is expressed on the left vertical axis in dNm and $\tan \delta$ is expressed on the right vertical axis. Strain is expressed on the horizontal axis in degree.

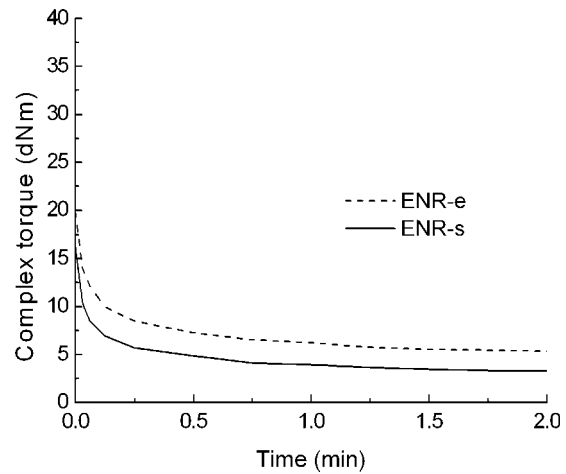


Figure 5 Response curves of ENR samples to stress relaxation. Complex torque is expressed on the vertical axis in dNm. Time is expressed on the horizontal axis in min.

In this experiment, 80% of given stress was applied to the samples at 60°C , and the variation of complex torque with time was recorded (Fig. 5). The times that the complex torques reduce to 80% of the original values are 0.74 min for ENR-e and 0.34 min for ENR-s, respectively. It is obvious that the stress-relaxation time of ENR-s is shorter than that of ENR-e. Therefore, the steam-coagulated ENR-s exhibits better processing performance than that of ENR-e.

The RPA analyses clearly indicate that the coagulation method exhibits effect on the processing performance of ENR gum, and the processing performance of steam-coagulated ENR-s is better than that of ENR-e. When the ENR latex is coagulated with ethanol, the coagulation process which is actually performed at room temperature is very slow and the compact wet coagulum can be obtained. When being coagulated with steam, the ENR latex can be coagulated instantly once the temperature of latex is above the cloud temperature of nonionic surfactant. However, with the steam escaping from preliminarily-formed coagulum, the coagulum obtained actually is much unconsolidated. Obviously, the ENR-s with unconsolidated structure should be easily processed.

By determining the difference of tangents of loss angles of raw rubber before and after ageing (expressed as the $\Delta \tan \delta$) using RPA, the antioxidative behavior of raw rubber can be characterized, and the raw rubber with high $\Delta \tan \delta$ value exhibits

TABLE I
Tan δ Values of ENR Samples

| | ENR-e | ENR-s |
|----------------------|-------|-------|
| $\tan \delta_1$ | 1.308 | 1.291 |
| $\tan \delta_2$ | 0.600 | 0.631 |
| $\Delta \tan \delta$ | 0.708 | 0.660 |

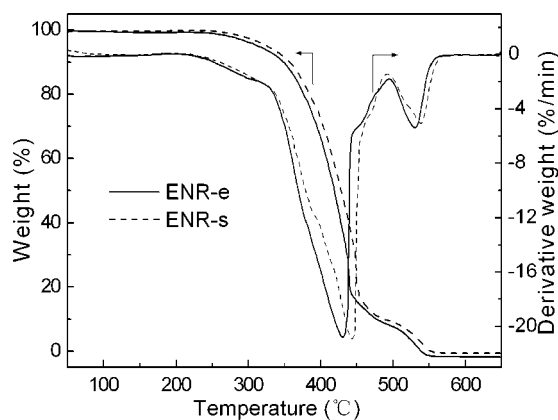


Figure 6 TG-DTG curves of ENR samples. Weight is expressed on the left vertical axis in percent and the derivative weight is expressed on right vertical axis in $\% \text{ min}^{-1}$. The temperature is expressed on the horizontal axis in $^{\circ}\text{C}$.

a poor antioxidative behavior.⁸ In this experiment, the $\tan \delta_1$ values of ENR samples were determined at 100°C with a frequency of 6 cpm and strain of 1200%. After the samples were aged for 15 min at 200°C with frequency of 6 cpm and strain of 420%, then the $\tan \delta_2$ were determined at 100°C with frequency of 6 cpm and strain of 1200%. As the $\Delta \tan \delta$ value of ENR-e is higher than that of ENR-s (see Table I), it seems that the antioxidative behavior of ENR-e is poorer than that of ENR-s.

To compare the antioxidative behaviors further, the ENR-e and ENR-s were analyzed using a thermogravimetric analyzer and the thermogravimetric and derivative thermogravimetric (TG-DTG) curves were shown in Figure 6. It is obvious that the characteristics seen from the TG-DTG curves of ENR-e and ENR-s are similar. However, the TG-DTG curves

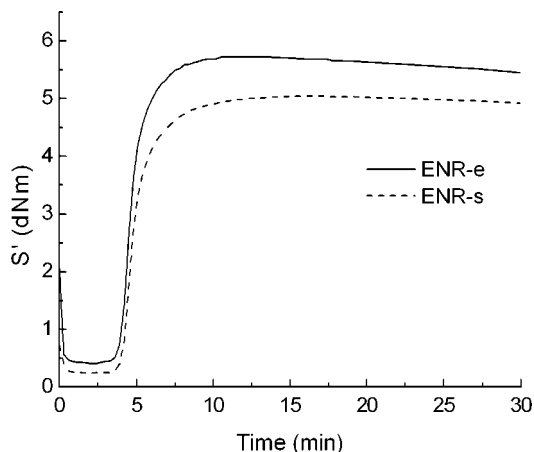


Figure 7 Cure graphs of ENR compounds. Torque (S') is expressed on the vertical axis in dNm. Time is expressed on the horizontal axis in min.

TABLE II
Parameters of Cure Graphs of ENR Compounds

| | M_L | M_H | t_{s1} | t_{s2} | t_{10} | t_{90} |
|-------|-------|-------|----------|----------|----------|----------|
| ENR-e | 0.40 | 5.74 | 4.10 | 4.25 | 4.31 | 6.26 |
| ENR-s | 0.21 | 4.96 | 4.20 | 4.38 | 4.45 | 6.24 |

of ENR-e shifts towards low temperature and the onset temperatures calculated by bi-tangent method are 376°C for ENR-e and 381°C for ENR-s, respectively. After the coagulation of ENR latex, the wet coagulum has to be soaked and washed repeatedly in water to remove the residual low-molecular-weight matters such as formic acid, hydrogen peroxide, surfactant, and the nonrubber components originally existing in natural rubber latex. It is obvious that the residual low-molecular-weight matters are not easy to be removed from the compact ENR-e and the contents of these matters in ENR-e are higher than those in ENR-s. When the analyses of ENR samples were performed on a thermogravimetric analyzer, the releases of low-molecular-weight matters from the sample as well as the effects of some residual matters such as formic acid and hydrogen peroxide on the thermal degradation of ENR sample lead the TG-DTG curves of ENR-e shift towards low temperature.

Vulcanization characteristics and mechanical properties

The curing characteristics of the mixed compounds of ENR samples were determined using a MDR-2000 type rheometer and the corresponding parameters read from the graphs (Fig. 7) are shown in Table II. It can be seen from Table II that both the minimum and maximum torques (M_L and M_H) of ENR-e are larger than those of ENR-s, while the scorch time (t_{10}) of ENR-s is slightly longer than that of ENR-e. It is obvious that the ENR-e with high elastic modulus and low loss modulus exhibits the high M_L and M_H values. The difference of short scorch time should be attributed to the effects of residual acids in ENR samples. As mentioned above, the contents of residual matters, especially the formic acid, in ENR-e are higher than those in ENR-s. Under the acceleration of residual acid, the scorch time of

TABLE III
Mechanical Properties of ENR Vulcanizates

| | 300% Modulus | 500% Modulus | Tensile Strength (MPa) | Elongation at Break |
|-------|--------------|--------------|------------------------|---------------------|
| ENR-e | 1.76 | 3.93 | 15.30 | 629 |
| ENR-s | 1.48 | 3.34 | 15.01 | 649 |

ENR-e compound is shortened. Therefore, the ENR-s coagulated with steam exhibits good cure characteristics. Table III shows that the moduli at 300 and 500% strain and the tensile strength of ENR-e are slightly higher than those of ENR-s, whereas the elongation at break for ENR-e is lower than that of ENR-s. The results are in agreement with those from cure graphs. The ENR-e with higher torque values exhibits larger tensile strength and lower elongation at break.

Dynamic mechanical properties of ENR vulcanizates

The dynamic mechanical properties of ENR vulcanizates were also analyzed and the changes of loss factor ($\tan\delta$), storage Young's moduli (E') and loss Young's moduli (E'') of ENR-e and ENR-s with temperature are shown in Figure 8. It can be seen that during the glass transition stages, the dynamic property variation trends of the vulcanized sheets of both ENR-e and ENR-s are similar. In the glassy state ($\leq -15^\circ\text{C}$), the E' and E'' values of the ENR-s vulcanized sheet are larger than those of ENR-e, whereas the $\tan\delta$ value almost equals to that of ENR-s. In the glass transition stage, the E' value decreases obviously, while the E'' and $\tan\delta$ value increase rapidly. The maximum values of E'' appear at 0°C , whereas the temperatures corresponding to the maximum values of $\tan\delta$ are 10.4°C for ENR-e and 10.8°C for ENR-s, respectively. With the temperature rising up to high elasticity state continuously, the variation curves of E' of ENR-e and ENR-s overlap gradually and the similar variation trend is observed from the curve of E'' . In general, the $\tan\delta$ values at 60°C and 0°C can be used to characterize the heat built-up or rolling loss behavior and the wet skid resistance of vulcanizate, respectively.^{14,15} The $\tan\delta$ values of ENR-e and ENR-s at 0 and 60°C read from Figure 8 are shown in Table IV. As the

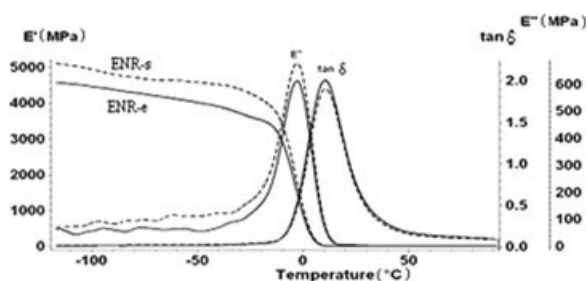


Figure 8 DMA spectra of ENR vulcanizates. Storage Young's modulus (E') is expressed on the left vertical axis in MPa. The $\tan\delta$ is expressed on the right vertical axis (inside) and the loss Young's modulus (E'') is expressed on the right vertical axis (outside) in MPa. Temperature is expressed on the horizontal axis in $^\circ\text{C}$.

TABLE IV
Tan δ Values of ENR Vulcanizates

| Temperature ($^\circ\text{C}$) | 0 | 60 |
|----------------------------------|-------|-------|
| ENR-e | 0.841 | 0.141 |
| ENR-s | 0.768 | 0.124 |

$\tan\delta$ values of ENR-e are slightly higher than those of ENR-s at both 0 and 60°C , the wet skid resistance of ENR-e is better than that of ENR-s, whereas the heat build-up or rolling resistance of ENR-e in the rolling process is higher than that of ENR-s.

CONCLUSIONS

1. The ethanol-coagulated ENR which has consolidated structure and high contents of residual low-molecular-weight matters exhibits higher elastic modulus and elastic torque, longer stress-relaxation time and lower loss modulus and $\tan\delta$ than those of steam-coagulated ENR. In addition, under the effects of residual matters, the antioxidative behavior of ethanol-coagulated ENR decreases and the scorch time of the compound is shortened. Therefore, the processing performance and antioxidative behavior as well as the curing characteristics of compound of ethanol-coagulated ENR are poorer than those of steam-coagulated ENR.
2. Although the mechanical properties and wet skid resistance of steam-coagulated ENR vulcanizate are poorer than those of ENR-e, the heat build-up or rolling resistance is better than that of ENR-e. Therefore, during the process of ENR latex being converted into dried ENR, the ENR latex should be coagulated with steam.

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