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DYNAMIC PROPERTIES OF EPOXIDISED NATURAL RUBBER

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The aim of this work is to study the dynamic properties of Epoxidised Natural Rubber (ENR) over a wide range of frequencies and temperatures. Three types of natural rubber with epoxidation levels of 0, 25 and 50 mol % were investigated. The dynamic properties of these materials were measured using a Metravib DMA+1000 in simple shear at different temperatures and frequencies. The glass transition temperature (T_g) was found to increase with increasing epoxidation level. The measured dynamic properties results were superposed to form master curves using time temperature superposition equivalence, allowing the dynamic properties for each ENR vulcanizate to be seen for a broader frequency and temperature range. These data are essential for modelling the vibro-acoustic behaviour of ENR in a range of noise control applications.

Keywords: Epoxidised natural rubber, damping, vibro-acoustic, dynamic mechanical analyser, time-temperature superposition.

1. Introduction

Rubbers are used widely in vibration and noise control applications. The dynamic mechanical properties of rubber, such as dynamic modulus and loss factor, vary with both temperature and frequency. Therefore, it is necessary to test rubber compounds used in vibration and noise control applications over a range of temperatures and frequencies.

In this work, Epoxidized Natural Rubber (ENR) was investigated. ENR is produced by epoxidation process of natural rubber with peracetic acid at the latex stage. A known percentage of its double bonds form epoxide groups. As the epoxide groups are introduced, ENR shows a higher glass transition temperature (T_g) as compared to natural rubber by approximately 1°C for every mol% epoxidation. This will strongly affect the dynamic mechanical properties of ENR [1].

Although ENR has been studied in blends with other polymers such as polychloroprene [2] and ethylene propylene diene monomer rubber [3], there is a relatively small amount of research on the dynamic properties of unblended ENR. This study investigates the effect of the epoxidation level in the rubber on the dynamic properties. From these results the effect on the T_g can be inferred. An important part of this study is to measure the dynamic mechanical properties of ENR as a single matrix across a range of temperatures and frequencies. This work will aid the choice of a suitable ENR for use in noise and vibration control applications. Some methods by which ENR can be used for sound and vibration applications have been considered previously [4].

2. Methodology

2.1 Materials and Sample Preparation

Three types of rubber with different epoxidation levels were supplied by the Malaysian Rubber Board: a natural rubber, SMR-CV60 (0 mol%), ENR-25 (25 mol%) and ENR-50 (50 mol%). All other ingredients such as the crosslinking agent (sulfur), the activators (zinc oxide and stearic acid), the antioxidant (Wingstay L), the accelerator (CBS; N-Cyclohexyl-2-benzothiazole sulfonamide) and the pre-vulcanization inhibitor (PVI) were provided by the Tun Abdul Razak Research Centre (TARRC), United Kingdom. All of the materials were commercial grade. The formulations used are given in Table 1. The formulations are denoted by R0, R25 and R50, where the numbers stand for the epoxidation level of the rubber.

Table 1: Formulations in parts per hundred of rubber (phr).

Ingredient	R0	R25	R50
SMR-CV60	100	-	-
ENR-25	-	100	-
ENR-50	-	-	100
Sulfur	2.5	2.5	2.5
Zinc Oxide	4	4	4
Stearic Acid	4	4	4
Wingstay L	1	1	1
CBS	1	1	1
PVI	0.3	0.3	0.3

The materials were compounded on a laboratory two-roll mill machine maintained below 40°C. The natural rubber was loaded at the beginning of the compounding process. The other ingredients were mixed together and then loaded gradually onto the two-roll-mill. Finally, a smooth and uniform sheet was obtained at the end of the compounding process. The compounding time was kept below 20 mins. The compounded natural rubber was left for 24 hours before being compression moulded for 20 minutes using an electrically heated hydraulic press at 150°C.

2.2 Dynamic Mechanical Characterization

The dynamic mechanical properties of the natural rubber vulcanizates were measured using double bonded shear test pieces on TARRC's Metravib DMA+1000 dynamic mechanical analyser. The nominal sample dimensions and the test conditions are given in Table 2.

Table 2. The nominal dimensions of the rubber specimens and test conditions used in the Metravib DMA+1000 experiment.

Item	Parameter	Value
Nominal Dimensions of Rubber	Thickness	2 mm
	Diameter	10 mm
Test Conditions	Dynamic Strain	0.1 %
	Frequency Range	0.1 Hz to 175 Hz (7 measurements per decade)
	Temperature Range	-40°C to 50°C at 5°C intervals

3. Results and Discussion

3.1 Effect of Temperature

Figure 1(a) illustrates the dependence of the storage modulus (G') as a function of temperature in the range of -40°C to 50°C for the rubbers with different epoxidation levels. These data were taken at an excitation frequency of 10 Hz. It can be seen that all the materials exhibit a relatively high storage modulus in the low temperature region. The storage modulus decreases with the increasing temperature. In this region the mobility of the polymer chains increases so that a reduction in the material stiffness is expected [5]. The storage modulus eventually converges for all three materials at around 40°C.

Figure 1(b) shows the loss factor (tan δ) curves under the same conditions. Above 0°C, tan δ increases with the increasing epoxidation level. The results show, as expected, that the natural rubber with epoxide groups has high damping properties when the temperature approaches the T_g. The T_g for these materials moves towards the higher temperature as the epoxidation level increases. The results suggest that the epoxide groups restrict the movement of the polymer chains by increasing the natural rubber backbone rigidity and their chain interactions. As a result, a higher temperature is needed to overcome the chain rigidity and interactions and allow rubbery behaviour.

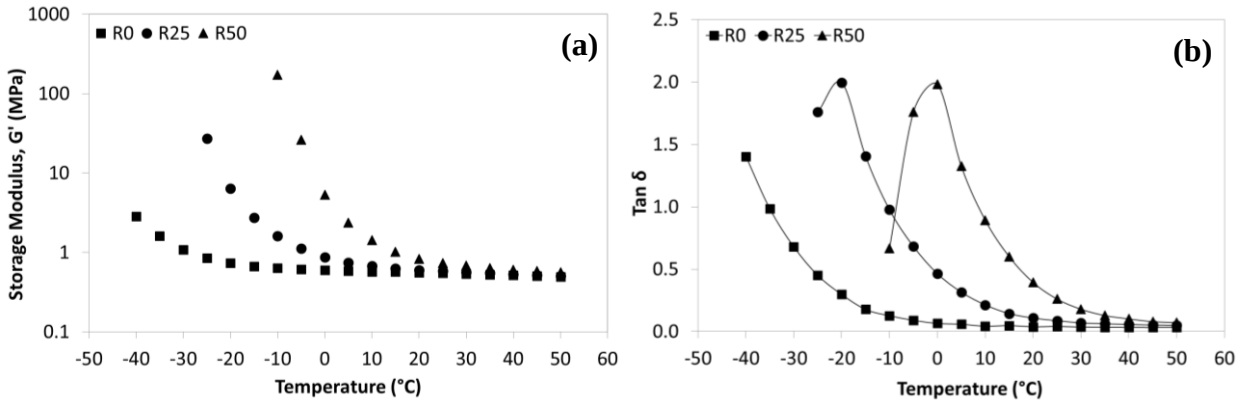

Figure 1: The dependence of (a) G' and (b) tan δ on temperature for R0, R25, and R50 at 10Hz.

3.2 Effect of Frequency

The storage modulus, G' and the loss modulus, G'' of natural rubber with different epoxidation levels as a function of frequency and temperature is plotted in Fig. 2 and Fig. 3 respectively. The storage modulus and the loss modulus are frequency dependent with its value increasing with frequency at all temperatures. However, at higher temperatures the storage modulus is relatively frequency independent. It becomes progressively more dependent on frequency as the temperature decreases. This observation is influenced by the stiffness of the natural rubber, which is effected by the molecular arrangement in the natural rubber matrix. The frequency dependence should be relatively weak at temperatures which are well above the T_g of natural rubber. The molecules in this region are free to move and exhibit relatively little resistance to move, so that a relatively low stiffness of the rubber can be observed. As a result, similar storage modulus values are obtained at high temperatures for all three compounds. However, around the T_g, the frequency dependence should be strong. In this region, the molecules start to move and the resistance to this motion changes rapidly with temperature.

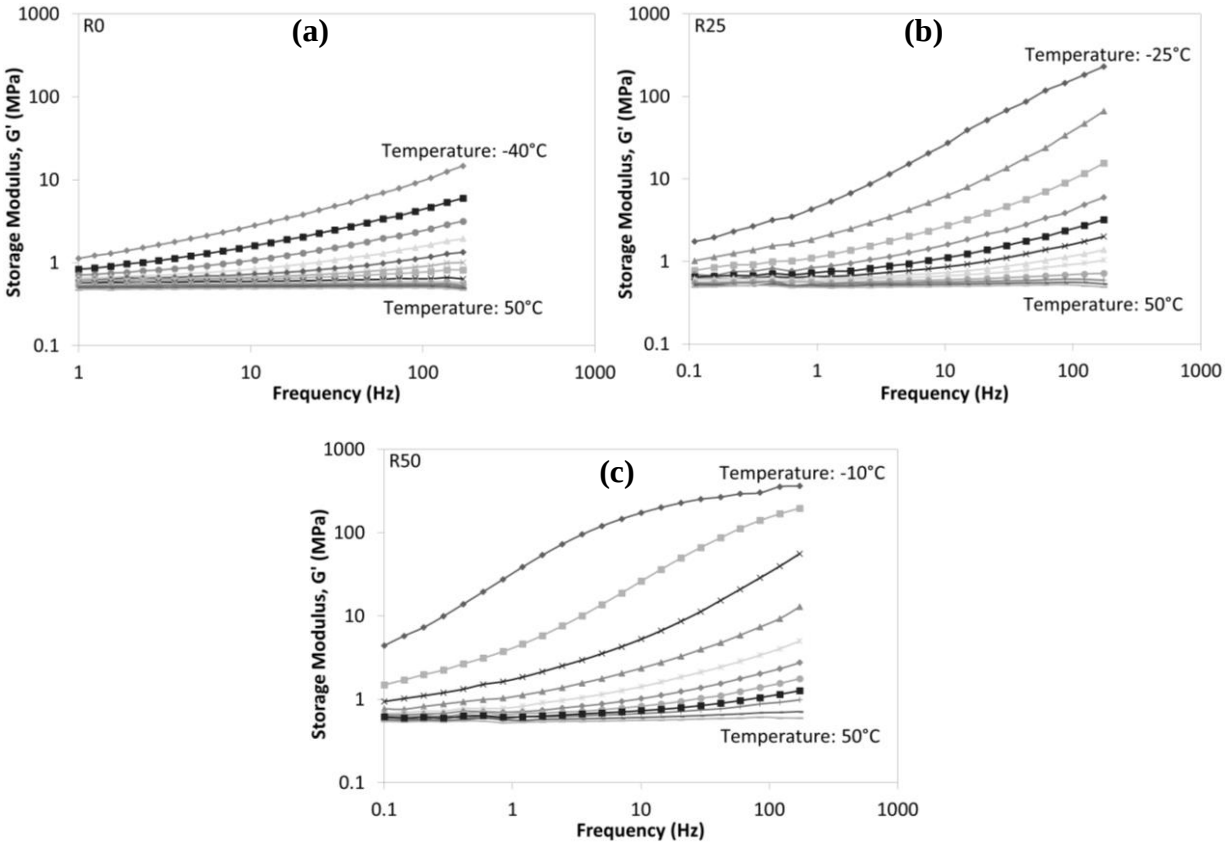

Figure 2: The frequency dependence of the storage modulus of; (a) R0 rubber, (b) R25 rubber and (c) R50 rubber.

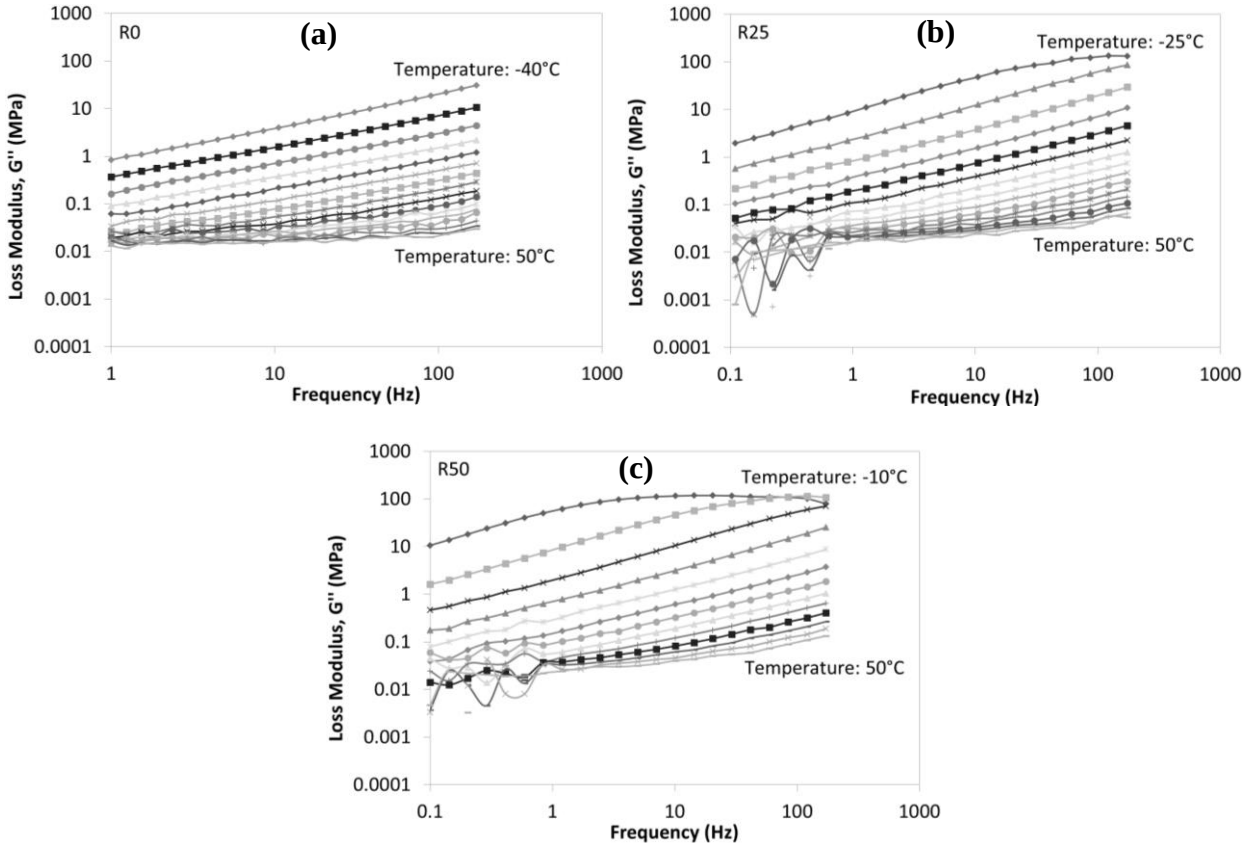

Figure 3: The frequency dependence of the loss modulus of; (a) R0 rubber, (b) R25 rubber and (c) R50 rubber.

3.3 Time-Temperature Superposition

In practice, the dynamic properties of the rubber materials can be tested in a limited frequency range. However, it is possible to extrapolate the dynamic properties of rubber to a wider frequency range using the time-temperature superposition principle [6]. The principle is also known as the method of reduced variables [7]. The method is able to describe the extrapolated dynamic properties in a reduced frequency range. This principle is expressed in the following equation [7, 8]:

$$G_{T_0}\left(a_T \omega\right) = \frac{\rho_0 T_0}{\rho T} G_T\left(\omega\right). \tag{1}$$

where G_{T_0} and G_T are the shear modulus at the reference temperature, T_0 and at a given temperature, T, respectively. a_T is the horizontal shift coefficient, ω is the frequency, while ρ_0 and ρ are the density of the material at T_0 and T, respectively, and:

$$\frac{\rho_0 T_0}{\rho T} = b_T. \tag{2}$$

b_T being the vertical shift coefficient. The horizontal shift coefficient, a_T, is used to adjust the horizontal position of the isothermal curve along the frequency axis, whereas the vertical shift coefficient, b_T, is used to adjust the vertical position of the isothermal curve. In this study, the horizontal shift coefficients, a_T, are determined empirically with respect to the reference temperature of 20°C. The vertical shift coefficients, b_T, for all isothermal curves are determined using Eq. (2). It is assumed that the material density did not change significantly with temperature, so that the density value is constant. Finally, a single master curve can be obtained through this process so that the storage and loss moduli are determined as a function of the reduced frequency (a simplified range of frequency in the master curve plot). Figure 4 shows the three storage modulus master curves as a function of the reduced frequency covering the range from 0.0001 Hz to 10,000,000 Hz for R0, R25 and R50 vulcanizates using the data shown in Fig 2.

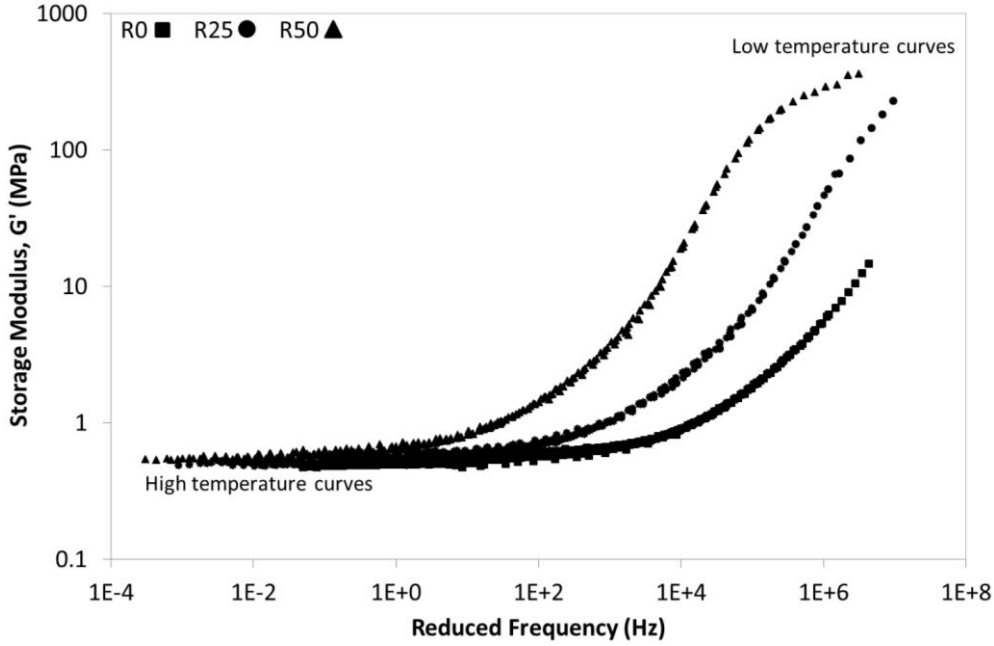

Figure 4: The master curves of the storage modulus of R0, R25 and R50 rubbers as a function of the reduced frequency.

Figure 5 shows the master curves for the loss modulus of R0, R25 and R50 vulcanizates using the data shown in Fig 3. The loss modulus of each rubber is also strongly frequency dependent, with its value increasing with frequency over the examined testing regime.

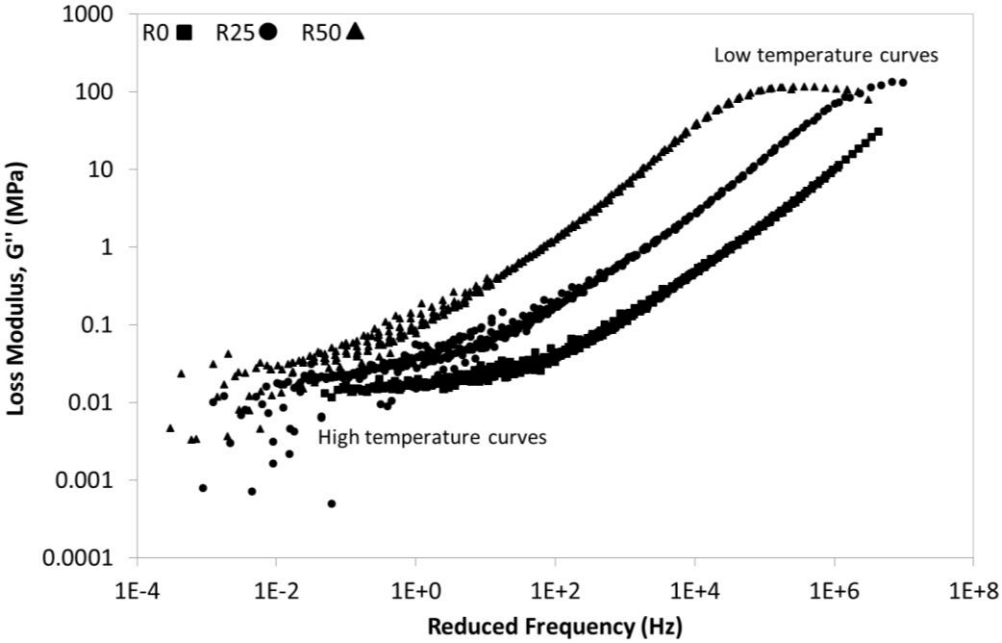

Figure 5: The master curves of the loss modulus of R0, R25 and R50 rubbers as a function of the reduced frequency.

The relationship between the storage modulus, G' and the loss modulus, G'' for natural rubber with different epoxidation levels is shown in Fig. 6. This is known as Cole-Cole plot [9]. The Cole-Cole plot for R0, R25 and R50 rubbers fall on a single curve that is independent of the epoxidation level. The results show that the epoxidation does not influence the relationship between storage modulus and loss modulus.

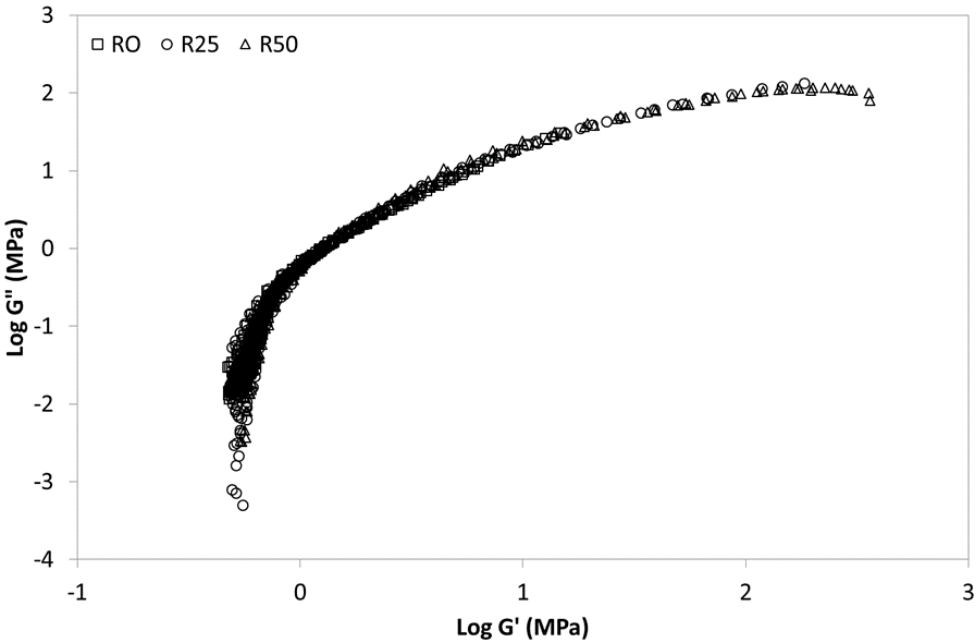

Figure 6: The Cole-Cole plots for R0, R25 and R50 rubbers.

4. Conclusions

Three types of natural rubber-based compounds with different epoxidation levels: SMR-CV60 (0 mol%), ENR-25 (25 mol%), and ENR-50 (50 mol%) have been the focus of this study. The results suggest that the dynamic properties of the rubbers are temperature and frequency dependent. The measured dynamic properties were superposed to form master curves which can be obtained through the time-temperature superposition principle. These curves enable the dynamic properties of rubber with different epoxidation levels to be predicted in a broader frequency and temperature range. The Cole-Cole plots for the rubbers were also plotted. The data fall on a single curve that is independent of the epoxidation levels suggesting that the epoxidation does not influence the relationship between the storage modulus and loss modulus. The results obtained may be used to choose the level of epoxidation in natural rubber to achieve the desired dynamic properties for a particular application.

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