

Research Article

Prediction Formula Describing Viscoelasticity of Unvulcanized Rubber Compound Based on Time-Temperature Equivalent Superposition Principle

Yong Li,¹ Xunhua Sun,² Yanan Miao,³ Shuang Zhang,¹ Fangkai Guo,¹ and Long Chen ⁴

¹College of Mechanical and Electronic Engineering, Shandong University of Science and Technology, Qingdao 266590, China

²Qingdao CCS Electric Corporation, Qingdao 266400, China

³College of Safety and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266590, China

⁴College of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, China

Correspondence should be addressed to Long Chen; chenlongc414@126.com

Received 15 April 2022; Revised 3 January 2023; Accepted 18 January 2023; Published 21 February 2023

Academic Editor: Qinglin Wu

Copyright © 2023 Yong Li et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Fitting unvulcanized rubber compound's (URC) dynamic viscoelasticity prediction formula and then constructing its mechanical constitutive model are of great significance for studying defect mechanisms in rubber products. However, it is difficult to measure the dynamic viscoelasticity of unvulcanized rubber at high and low frequencies due to its rapid relaxation property. This paper presents a convenient method to measure the dynamic viscoelasticity of unvulcanized rubber. The data of different temperatures at a fixed frequency are measured by dynamic thermomechanical analysis, and the master curve of unvulcanized rubber is obtained by using the time-temperature equivalent superposition principle, which is used to predict the modulus and stress at different temperatures as a function of frequency. The predicted moduli are in good agreement with experimental data when the strain is less than 10% and the applicable temperature range of the Williams-Landel-Ferry (WLF) equation, which indicates that the proposed method is a feasible way to study the dynamic viscoelasticity of unvulcanized rubber at different temperatures.

1. Introduction

Different rubbers are made into different products because of their flexibility, strength, aging resistance, oil resistance, wear resistance, and other different characteristics, which are widely used in life, industry, agriculture, aerospace, automotive, and other fields [1]. The final performance of its products is not only related to the formula of the rubber material but also the defects produced in the preforming process of the unvulcanized mixed rubber components directly determine its final performance [2]. Taking tire cord as an example, the tire rope turns from developable surface to metasurface in the tire forming process [3]. Because the unvulcanized rubber matrix has extremely low strength and bears large strain, the cord is subjected to transverse tensile stress or normal compressive stress, which is prone to occur such defects as the delamination of rope and rubber

and the crossing of different rubber compounds [4], which makes the modulus matching of rubber compounds unbalanced and affects the final use performance. The establishment of room temperature mechanical constitutive model (stress-strain-strength-time relationship) for unvulcanized rubber can provide important theoretical guidance for the mechanism of defects in the preforming process and further improvement. Among them, the fitting of the wide-frequency dynamic viscoelasticity curve formula of unvulcanized rubber is the necessary prerequisite for constructing the constitutive model.

However, in dynamic thermomechanical analysis (DMA), ultra-low frequency (less than 0.01 Hz) testing takes a long time to complete (e.g., several days or even weeks), and frequencies higher than 30 Hz need to be specially considered or reach the analytical instrument's performance measurable limit [5]. Therefore, it is difficult to obtain effective and reliable

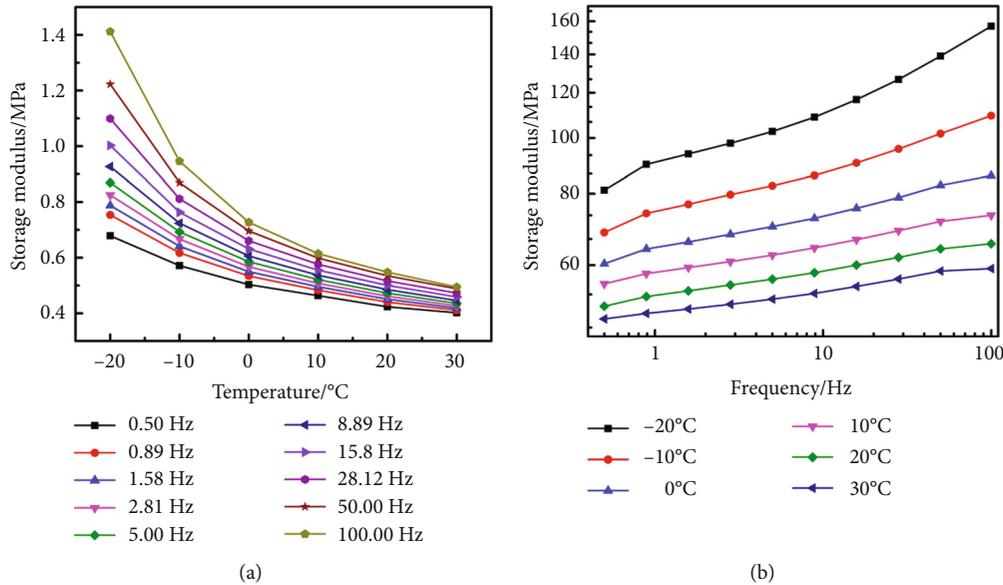


FIGURE 1: (a) The temperature curves of the storage modulus at different frequencies are closer and closer as the temperature increases. (b) Frequency curve of storage modulus at different temperatures. The lower the temperature, the greater the change with frequency.

experimental results by using the DMA characterization technology to scan the unvulcanized rubber, which limits the fitting of the wide-frequency dynamic viscoelasticity curve equation of the unvulcanized rubber. The time-temperature equivalent superposition principle can expand the frequency range of viscoelasticity at a certain temperature through mechanical performance data at the same frequency range at different temperatures [6]. Xue et al. [7] studied natural rubber (NR) by using the time-temperature equivalent superposition principle, which greatly expanded the time-frequency range of viscoelasticity of NR. Krauklis et al. [8] used the time-temperature-plasticization superposition principle (TTPSP) to predict the long-term creep behavior of epoxy compounds [9] and used the short-term creep experimental data to predict the long-term viscoelastic behavior of amorphous polymers below the glass transition temperature. Therefore, applying the time-temperature equivalent superposition principle can not only realize the temperature transformation of dynamic test results of unvulcanized rubber but also expand the research frequency range of unvulcanized rubber at a certain temperature.

Based on the above content, the goal of this paper is to use the time-temperature equivalent superposition principle to establish the master curve of the dynamic viscoelasticity of unvulcanized rubber, in order to obtain more wide-frequency mechanical data. And obtain the master curve to study the performance of the unvulcanized rubber under dynamic loading conditions, as well as obtain the master curve prediction formula to predict the master curve at different reference temperatures. The prediction formula of the properties of unvulcanized rubber was obtained, and it was used to guide the setting of technological parameters in the process of processing and vulcanization, so as to improve the quality of finished rubber.

2. Materials and Methods

Sample components used in this test include NR 90 phr was purchased from Tianjin Wenhua International Trade Co., Ltd, cis-1, 4-polybutadiene rubber (BR) 10 phr was purchased from Heng Shuiyuan Rubber Chemical Co. Ltd, carbon black N234 38 phr and carbon black N115 10 phr were purchased from Shanghai Cabot Chemical Co., Ltd, silica 10 phr (Qingdao Jinzetai Chemical Co., LTD), and anti-aging agent Rubber Antioxidant (RD) 2, 2, 4-trimethyl-1, 2-dihydroquinoline polymerization 2 phr (Shanghai Chengjin Chemical Co., Ltd). The mixer used in the experiment is 1 L mixer (Zhendelong Machinery (Kunshan) Co., Ltd). At the same time, the equipment used in the experiment is also the torque rheometer 300 ml (Harbin Hapu Electric Technology Co., Ltd) In order to obtain stable and reliable samples, the uncured rubber compound was needed to be treated in two steps before the experiment. Three-stage mixing was performed in a mixer. Then, the sample sheet was pressed through the gap of the rollers, and the sample cuboid shape was cut to be 6.00 mm wide, 1.80 mm thick, and 50 mm long.

DMA has the advantages of high precision, excellent repeatability, extensive sample holders, auxiliary sample size, direct output of stress in measurement, and analysis of solid, paste as well as liquid [10]. DMA strain scanning method was utilized in this experiment.

Firstly, in order to ensure the stability of Unvulcanized Rubber Compound (URC) samples, clamp the samples at -30°C and then apply 1 N contact force as well as 10% pre-strain. Secondly, using strain loading method, 0.3% pre-pressure is applied at the temperatures of -20°C , -10°C , 0°C , 10°C , 20°C , and 30°C , respectively, and the frequency starts from 0.5 Hz and increases to 100 Hz according to the frequency increment of 4.00 Hz/dec, and apply the stress required to maintain different strains. Finally, the DMA data obtained

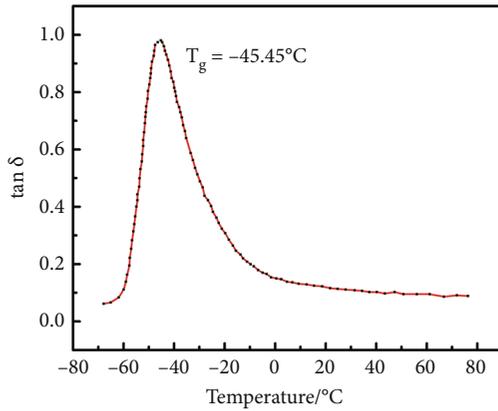


FIGURE 2: Curve of tangent of loss angle changing with temperature.

from the experiment were processed to obtain the required master curve, which is necessary to move the measured modulus curve with the logarithm of frequency at different temperatures horizontally or vertically along the logarithm time axis towards the reference temperature, so that the different curves can be superimposed together.

In this process, using the Williams–Landel–Ferry equation (WLF equation), which was shown in Equation (1), to solve the shift-factors [11]. According to the definition of the glass transition temperature, the temperature corresponding to the peak of the loss tangent $\tan \delta$ curve is the glass transition temperature, so the glass transition temperature can be obtained accordingly. Then, due to the application of the WLF equation has a certain temperature range, that if the temperature is too low, the chain movement of URC is frozen, and only the movement of smaller units than the chain movement occurs; if the temperature is too high, the whole mass center of the chain segment will move, that is, the flow will occur, and the Arrhenius equation will be regressed, so the applicable range of WLF equation reference temperature is $T_g < T_r < T_g + 100^\circ\text{C}$, which can select the reference temperature in this range [12].

Finally, a large number of experiments proved that it is more accurate to use the drawing method to solve the values of C_1 and C_2 of the WLF equation [13]. Firstly, the modulus curves measured on both sides adjacent to the reference temperature are moved to the modulus curves measured at the reference temperature until the three curves are superimposed together. Then, the horizontal shift-factors of the two modulus curves can be measured, and C_1 and C_2 can be obtained by bringing them into the WLF Equation (1). Then, different temperatures are put into the formula to solve the shift-factor α_T , and the curve under the corresponding temperature is moved according to the obtained data, and the required master curve can be obtained.

$$\lg \alpha_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)}, \quad (1)$$

where α_T is the horizontal shift-factors of the curve, C_1 , C_2 is the constant of the WLF equation, T is the measured temperature, and T_r is the reference temperature.

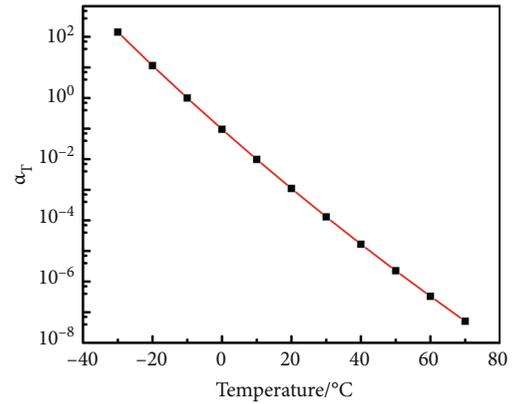


FIGURE 3: Curve of horizontal shift-factors α_T changing with temperature.

3. Results and Discussion

Not all polymers perfectly follow the time–temperature equivalent superposition principle [14], so the feasibility of time–temperature equivalence needs to be verified. It can be seen from Figure 1 that the storage modulus decreases with the increase of temperature. The storage modulus increases with the increase of frequency, and the lower the temperature is, the more sensitive the storage modulus is to the change of frequency, which is in line with the general law of polymer performance change [15]. At the same time, it shows that the data measured by DMA strain scan is more accurate and can be used to study the time–temperature equivalence.

It can be seen from Figure 1(b) that the storage modulus and frequency curves at different temperatures have roughly similar changing trends and shapes, and the higher the temperature, the more obvious it is. This indicates that the curves move towards a certain reference temperature in the horizontal direction and can be superimposed eventually, and it is feasible to obtain the time temperature equivalent master curve.

3.1. WLF Master Curve. The values of C_1 , C_2 change with the change of reference temperature. It can be obtained from Figure 2 that the glass transition temperature of unvulcanized rubber is -45°C , so in this experiment, -10°C is selected as the reference temperature, and the WLF equation constant $C_1 = 59.38$, $C_2 = 571.27$ at -10°C can be preliminaries obtained by fitting the translation data of adjacent temperature curves. The shift-factors of unvulcanized rubber at -20°C , -10°C , 0°C , 10°C , 20°C , and 30°C are calculated by the WLF equation. The relationship between shift-factors α_T and temperature is shown in Figure 3.

According to the definition of shift-factors α_T , is the ratio between stress relaxation time τ at temperature T and stress relaxation time τ_r at the reference temperature T_r , i.e.

$$\alpha_T = \frac{\tau}{\tau_r} = \frac{\rho_r T_r \eta}{\rho T \eta_r}. \quad (2)$$

Since the density changes very little, the temperature is Kelvin, and the density decreases as the temperature increases

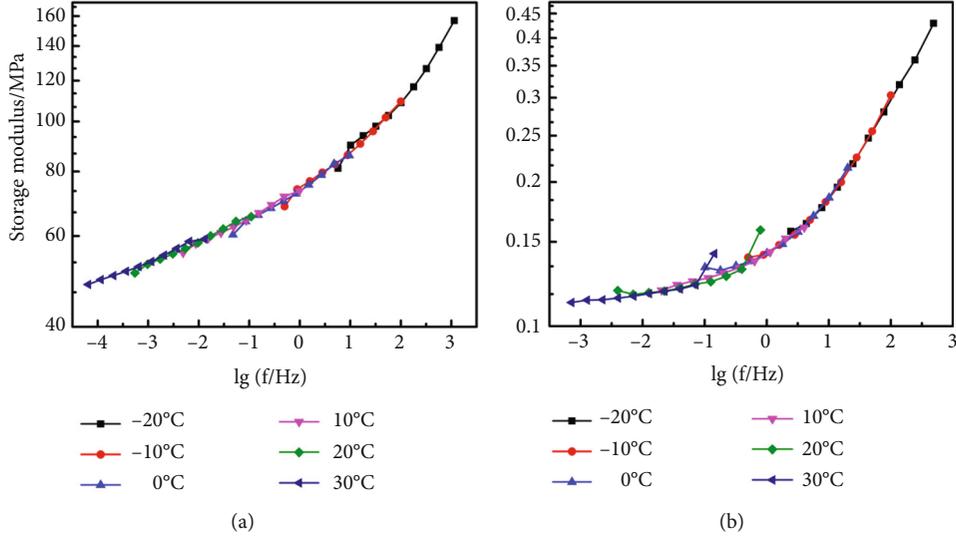


FIGURE 4: (a) Master curve of storage modulus changing with logarithm of frequency at -10°C . (b) Master curve of loss tangent changing with logarithm of frequency at -10°C .

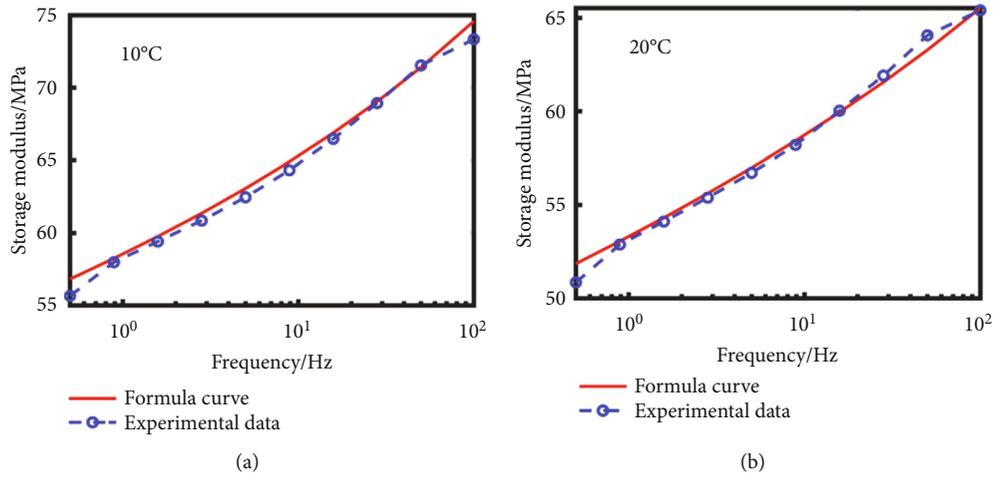


FIGURE 5: (a) The comparison between the formula curve of energy storage modulus at 10°C and the test data shows that $R\text{-square} = 0.9912$. (b) The comparison between the formula curve of energy storage modulus at 20°C and the test data shows that $R\text{-square} = 0.8670$.

so $\rho_r T_r / \rho T \approx 1$ is usually taken [16], so α_T can be regarded as the ratio of viscosity at different temperatures, namely

$$\alpha_T = \frac{\tau}{\tau_r} \approx \frac{\eta}{\eta_r}. \quad (3)$$

Choi et al. [17] have established a new viscosity model, which shows that the viscosity of polymer always decreases with the increase of temperature. According to Equation (3), when the measured temperature exceeds the reference temperature, the displacement factor will become smaller and smaller as the temperature increases, which are consistent with the changing trend of the displacement factor temperature curve in the figure. It is proved that the viscosity change of URC conforms to the free volume theory, which means that the WLF equation is applicable to URC. And the displacement factors obtained are accurate in theory.

By fitting the horizontal shift-factors α_T with the temperature curve, the shift-factors formula of the curve moving towards the reference temperature curve at different temperatures can be obtained

$$\alpha_T = 0.02448 \exp(-0.276T) + 0.07076 \exp(-0.2159T). \quad (4)$$

After the shift-factor α_T is obtained by solving the WLF equation, the storage modulus curve and loss tangent curve at -20°C , 0°C , 10°C , 20°C , and 30°C are, respectively, moved to the reference temperature of -10°C in the Origin software to obtain the master curve as shown in Figure 4.

It can be seen from the figure that the various curves are superimposed well. The master curve obtained greatly expands the study range of the unvulcanized rubber storage

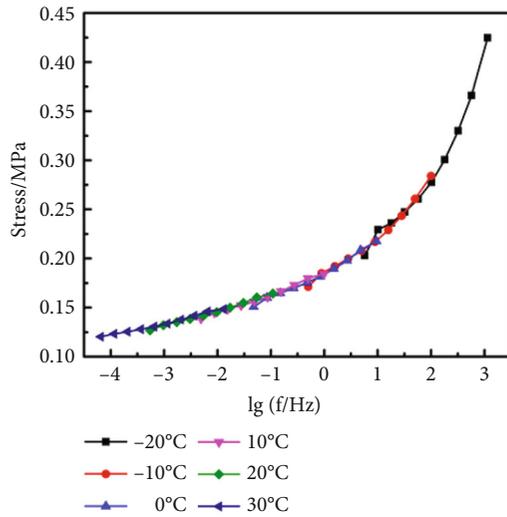


FIGURE 6: The curves at different temperatures in the master curve of stress logarithmic change with frequency are well superimposed.

modulus and loss tangent with frequency. Even the viscoelastic change of unvulcanized rubber at 0.0001 Hz frequency can be obtained in the figure. In fact, this is an extremely difficult task for ordinary measurement methods. The master curve method can be used to express the performance of unvulcanized rubber under dynamic loading conditions.

Matlab software was used to fit the principal curve, and the relationship between the memory modulus and the frequency at -10°C was obtained.

$$E' = 67.54 \exp(0.08364 \log_{10} f) + 7.184 \exp(0.7868 \log_{10} f), \quad (5)$$

where E' is the storage modulus, which refers to the amount of energy stored by elastic deformation during material deformation, reflecting the elastic value of material, and f is the frequency.

In order to obtain the master curves of the viscoelasticity of unvulcanized rubber changing with frequency at different temperatures, it is necessary to repeatedly calculate the master curves, and the data at multiple temperatures need to be measured, which requires a lot of work, and the measurable temperature range is limited due to the influence of WLF applicable temperature. Therefore, we propose to deduce the prediction formula of storage modulus changing with temperature according to the obtained master curve formula and shift-factors formula to solve this problem preliminarily. The prediction formula obtained is as follows

$$E'_T = 67.54 \exp(0.08364 (\log_{10} f \alpha_T)) + 7.184 \exp(0.7868 (\log_{10} f \alpha_T)). \quad (6)$$

Substituting 10°C and 20°C into the prediction formula, the formula curve and experimental data obtained are shown in Figure 5.

Matlab software was used to calculate the R -square between the prediction formula curve of storage modulus with temperature and the fitting curve of test data at 10°C and 20°C . The obtained values were 0.9912 and 0.8670, respectively. Consistency between the formula curve and the test data curve was good. The prediction formula can be used to reflect the change of storage modulus of unvulcanized rubber with temperature.

The prediction formula of application expanded the unvulcanized rubber viscoelastic temperature frequency range, with good effect, consider to be used in the study of the mechanical behavior of unvulcanized rubber, according to the above steps, unvulcanized rubber's stress master curve under -10°C is obtained (Figure 6), and get the corresponding master curve fitting formula and forecast formula.

The fitting formula of stress principal curve and the stress prediction formula are as follows

$$\sigma = 0.17 \exp(0.09 \log_{10} f) + 0.01 \exp(0.90 \log_{10} f), \quad (7)$$

$$\sigma_T = 0.17 \exp(0.09 (\log_{10} f \alpha_T)) + 0.01 \exp(0.90 (\log_{10} f \alpha_T)). \quad (8)$$

The obtained prediction formula curve is compared with the experimental data obtained at 10°C and 20°C and processed in Matlab. The obtained comparison curve and the determinable coefficient are shown in Figure 7.

It can be seen from Figure 7 that the curves obtained by the prediction formula at different temperatures are in good agreement with the experimental data curves, and the determination coefficients are all above 0.8. Therefore, it is a feasible way to express the dynamic viscoelasticity of unvulcanized rubber at different frequencies and temperatures by using the prediction formula. This method can be used to monitor the change of the properties of unvulcanized rubber in the process of vulcanization, which can control the technological parameters in the process of processing by it and can improve the quality of rubber products, which has great significance to promote the development of rubber products.

4. Conclusions

The glass transition temperature of unvulcanized rubber was determined as -45°C by DMA dynamic measurement method. And it can be proved by experimental data that the WLF equation is suitable for unvulcanized rubber, as well as the shift-factor can obtain a better superposition master curve. The prediction formulas for the storage modulus and stress of unvulcanized rubber with temperature are obtained by using the time-temperature equivalent superposition principle, which show that the obtained prediction formula curve is in good agreement with the experimental data.

A new formula for predicting the change of properties of unvulcanized rubber was obtained, and the difficult problem of measuring properties of unvulcanized rubber was preliminarily solved. Compared with previous studies, the prediction formula obtained in this paper extends the frequency

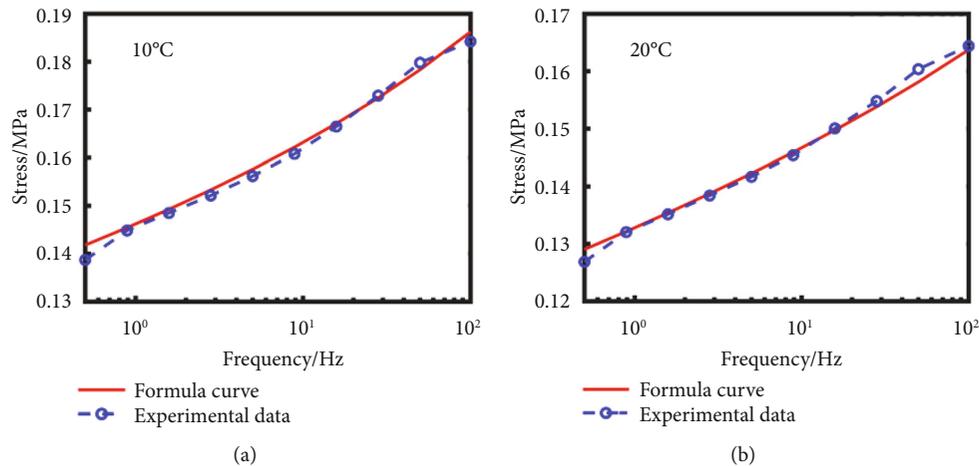


FIGURE 7: (a) By comparing the stress formula curve at 10°C with the test data, R -square = 0.9305. (b) R -square = 0.8564 is obtained by comparing the stress formula curve at 20°C with the test data.

and temperature range of studying the viscoelasticity of unvulcanized rubber, and can predict the performance changes of unvulcanized rubber at different temperatures. It can be used to monitor the properties of unvulcanized rubber in the process of processing and vulcanization, which is of great significance to improve the quality of rubber products.

Data Availability

All data generated or mentioned during this study are included in this published article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Authors' Contributions

Yong Li: conceptualization, methodology, software, validation, formal analysis, investigation, writing—original draft, and visualization. Xunhua Sun: software, resources, data curation, and supervision. Yanan Miao: visualization, validation, and writing—original draft. Shuang Zhang: software, resources, data curation, writing—review and editing, and supervision. Fangkai Guo: software, resources, and data curation. Long Chen: writing—review and editing, supervision, project administration, and funding acquisition.

Acknowledgments

Financial supports from the Mountain and Sea Talents Project of Shandong University of Science and Technology (grant numbers: 01040055230), the National Nature Science Foundation of Shandong Province of China (grant numbers: ZR2018MEE024) were gratefully acknowledged.

References

- [1] L. Zhu, M. Li, S. Zhao et al., "Ultra-high impact PPR composites at low-temperature through enhanced preferential loading of nanoparticles at polymeric interface induced by properly vulcanized rubber dispersed phase," *Composites Science and Technology*, vol. 227, p. 109593, 2022.
- [2] M. Wen, S. Wang, X. Zhang, and A. He, "Constructions of special network structure in natural rubber composites for improved anti-fatigue resistance," *Composites Science and Technology*, vol. 227, p. 109572, 2022.
- [3] M. Wang, R. Wang, X. Chen et al., "Effect of non-rubber components on the crosslinking structure and thermo-oxidative degradation of natural rubber," *Polymer Degradation and Stability*, vol. 196, p. 109845, 2022.
- [4] X. Tian, K. Wang, T. Shan et al., "Study of waste rubber catalytic pyrolysis in a rotary kiln reactor with spent fluid-catalytic-cracking catalysts," *Journal of Analytical and Applied Pyrolysis*, vol. 167, p. 105686, 2022.
- [5] D. Ionita, M. Cristea, and C. Gaina, "Prediction of polyurethane behaviour via time-temperature superposition: Meanings and limitations," *Polymer Testing*, vol. 83, p. 106340, 2020.
- [6] B. N. V. S. Ganesh Gupta K, B. Sen, M. M. Hiremath, R. K. Prusty, and B. C. Ray, "Enhanced creep resistance of GFRP composites through interpenetrating polymer network," *International Journal of Mechanical Sciences*, vol. 212, p. 106728, 2021.
- [7] C. Xue, H. Gao, Y. Hu, and G. Hu, "Experimental test and curve fitting of creep recovery characteristics of modified graphene oxide natural rubber and its relationship with temperature," *Polymer Testing*, vol. 87, article 106509, 2020.
- [8] A. E. Krauklis, A. G. Akulich, A. I. Gagani, and A. T. Echtermeyer, "Time-temperature-plasticization superposition principle: predicting creep of a plasticized epoxy," *Polymers*, vol. 11, no. 11, p. 1848, 2019.
- [9] A. O. Fulmali, B. A. Nayak, B. N. V. S. G. Gupta K et al., "Effect of 1D carbon nano-tube and fiber reinforcement on the long-term creep performance of glass fiber/epoxy composite using the time-temperature superposition principle," *Materials Today: Proceedings*, vol. 47, no. Part 11, pp. 3263–3268, 2021.
- [10] Y. Li, X. Sun, S. Zhang, Y. Miao, and S. Han, "Experimental investigation and constitutive modeling of the uncured rubber

- compound based on the DMA strain scanning method,” *Polymers*, vol. 12, no. 11, p. 2700, 2020.
- [11] M. Jasso, J. Stastna, G. Polacco, and G. Cuciniello, “Development of internal structure of polymer-modified asphalts via transformations of the reduced frequency,” *Journal of Applied Polymer Science*, vol. 138, p. e50037, 2021.
- [12] J. Dudowicz, J. F. Douglas, and K. F. Freed, “The meaning of the “universal” WLF parameters of glass-forming polymer liquids,” *Journal of Chemical Physics*, vol. 142, p. 3701, 2015.
- [13] Z. Qiang, Y. Yilan, and L. Yu, “Re-discussion on the coefficient solution method of WLF equation,” *Polymer Bulletin*, pp. 111–115, 2010.
- [14] N. B. Olsen, T. Christensen, and J. C. Dyre, “Time-temperature superposition in viscous liquids,” *Physical Review Letters*, vol. 86, no. 7, pp. 1271–1274, 2001.
- [15] L. Cai, B. Guo, C. Zhang, X. U. Jun, and Z. Huang, “Long-term stress relaxation prediction for nylon 1010 using time-temperature superposition method,” *Chemical Journal of Chinese Universities*, vol. 40, no. 4, pp. 832–840, 2019.
- [16] H. Pingshen, *Mechanical Properties of Polymers*, University of Science and Technology of China Press, 2nd edition, 2008.
- [17] B. Choi, M. S. Jeong, and K. S. Lee, “Temperature-dependent viscosity model of HPAM polymer through high-temperature reservoirs,” *Polymer Degradation and Stability*, vol. 110, pp. 225–231, 2014.