THERMO-RHEOLOGICAL SIMPLICITY OF CARBON BLACK FILLED RUBBER

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Summary The dynamic moduli of carbon black filled rubber were measured by temperature sweeps and frequency sweeps. The data are overlapped into master curves by horizontally shifts alone and establish the dynamic properties over a frequency range of 21 decades at reference temperature, demonstrating the applicability of the frequency-temperature superposition and the thermo-rheological simplicity. Such simplicity is also confirmed by the van Gurp-Palmen plot and the Cole-Cole plot.

INTRODUCTION

Dynamic viscoelasticity over a wide range of frequency is crucial for rubber component design in the case that the components are loaded oscillately, however, dynamic mechanical analysis (DMA) measurements usually provides only the experimental data below 100 Hz. Thus an extrapolation technique is needed for predicting the properties over 100 Hz. Frequency-temperature superposition (fTS) has been proved to be such a tool, which extends the frequency spectrum by measurements at various temperatures and mastering the curves according to the Williams-Landel-Ferry or Arrhenius transformation. In the present study, carbon black (CB) filled rubber strip specimens were loaded with harmonic deformations at various temperatures and the steady state stress responses for frequency sweeps were evaluated in terms of the storage and the loss moduli. The test data were then discussed and modeled.

DYNAMIC VISCOELASTIC PROPERTIES

Material

Thin rectangular strips with length of 35 mm and width of 7 mm were cut from a 2 mm thick vulcanized rubber sheet, which was provided by the Zhuzhou Times New Material Technology Co., Ltd. in China. The formulation of the rubber compounds was as follows: 100 phr NR(Thailand RRS3), 20 phr CB (N550), 10 phr ZnO, 5 phr antioxidant, 2.5 phr sulfur, 2 phr stearic acid, 2 phr micro crystal wax, 2 phr solid Coumarone resin and 1.4 phr vulcanization activator.

DMA test modes

Dynamic mechanical tests were carried out with a Gabo Eplexor 500N. Temperature sweep tests and isothermal frequency sweep tests were performed under a prestrain of 0.4% and superimposed dynamic strain amplitude of 0.1% respectively.

The temperature sweep tests were planed to explore the frequency dependent T_g of the material. Such tests were carried out from −80 °C to 0°C, using a ramp rate of 2 °C /min and repeated at 1, 2, 3, 5,10, 15, 20, 30 and 50 Hz. The test data are shown in Fig.1.

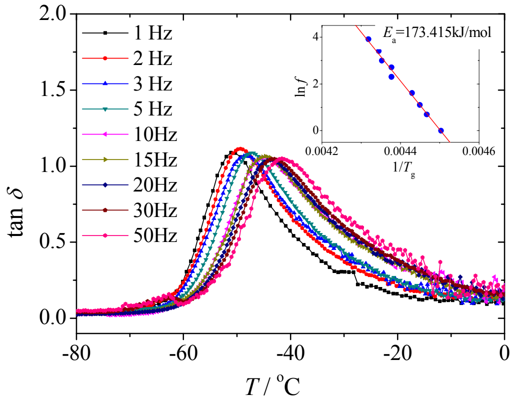

Fig.1. DMA loss factor in temperature sweeps at various frequencies

The isothermal frequency sweep measurements were conducted in a frequency range from 0.01-100Hz and repeated at various temperatures ranging from -70°C to 50 °C. The test data are shown in Fig.2.

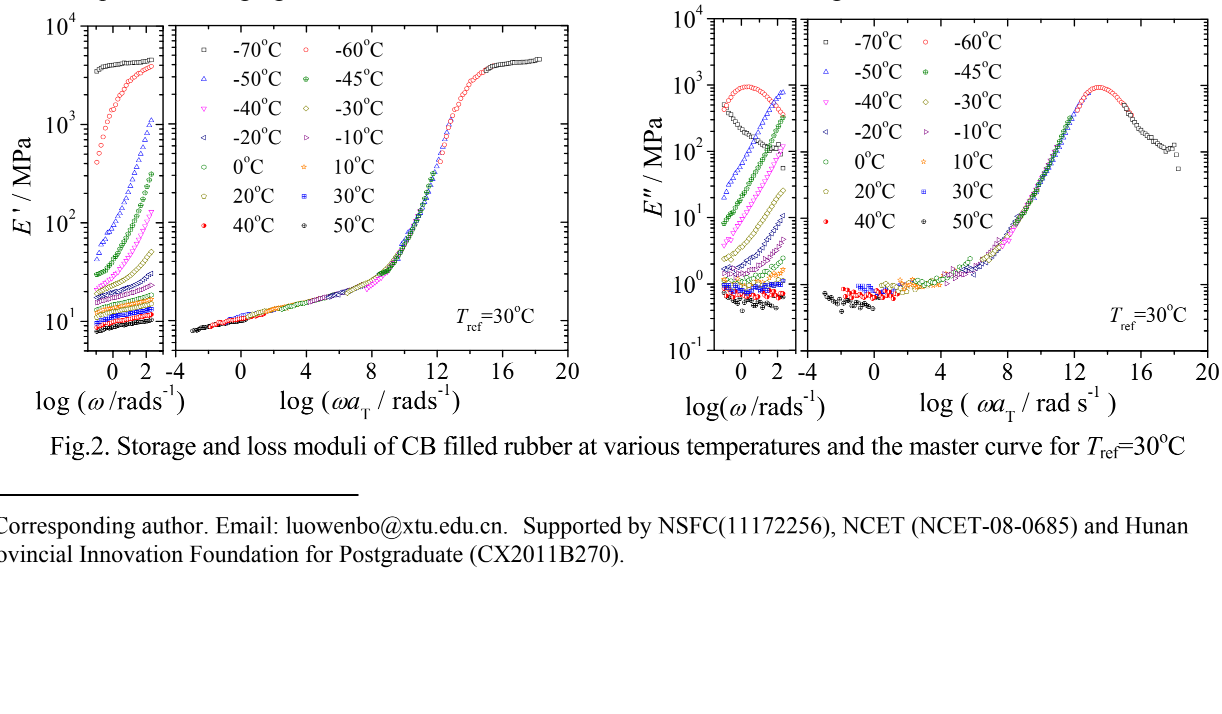

Fig.2. Storage and loss moduli of CB filled rubber at various temperatures and the master curve for T_{ref}=30°C

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Results and discussions

Temperature-sweeping DMA is often used to characterize the glass transition temperature(T_g) of a material. A prominent peak in tanδ appears at T_g of the polymer. It is shown from Fig.1 that increasing test frequency causes a shift of T_g to higher temperatures. The E_a value for glass transition can be obtained by an Arrhenius type relationship $f = f_0 \exp\left(-E_a / RT_g\right)$, where f_0 is a frequency constant. The inset of Fig. 1 shows the Arrhenius plot between $\ln f$ and $1/T_g$. The line fits well with the test data, and E_a is thus determined to be 173.415kJ/mol according to the line gradient.

Fig.2 show the isothermal frequency sweep test results, where the storage and loss moduli are shown as a function of the test temperature and frequency. These results reveal that higher frequency results in higher storage and loss moduli except for very low temperatures.

According to fTS, the frequency function of dynamic properties (E', E'' and tanδ) at one temperature can be horizontally shifted along the logarithmic frequency axis and overlapped on the curves at neighboring temperatures to form a master curve. Materials whose rheological properties obey fTS are termed thermo-rheologically simple materials.

To construct a master curve by applying the fTS concept, a reference temperature T_{ref} was be selected to be 30 °C and the rheological data at all the other temperatures shifted manually with respect to frequency until the curves merge into single smooth function. The experimentally determined horizontal shift factors ($\log a_T$) and the predicted values by Arrhenius model are shown in the same Fig.3 for comparison. The constructed master curves of the dynamic moduli are shown in Fig.2. It is shown that the master curves establish the dynamic mechanical behavior over a frequency range of 21 decades. The applicability of the fTS indicates that the dynamic viscoelastic behavior of CB-filled rubber is thermo-rheologically simple. Such simplicity is also confirmed by the Cole-Cole plot and the van Gurp-Palmen plot shown in Fig.4 and Fig.5 respectively.

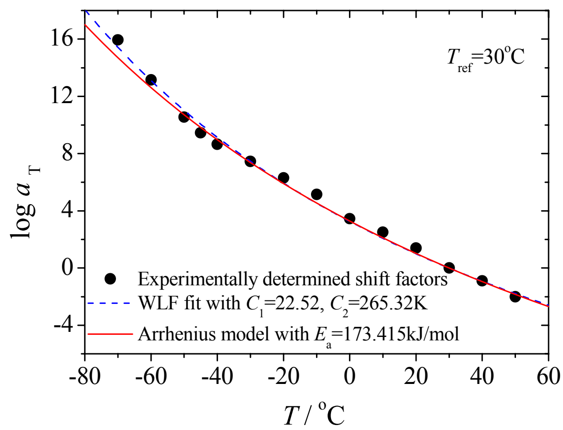

Fig. 3. Temperature shift factors vs. temperature and the predicted values by Arrhenius model

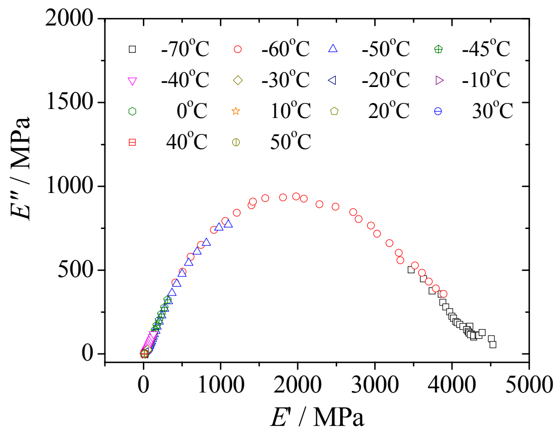

Fig.4. Cole-Cole plot (loss modulus vs. storage modulus)

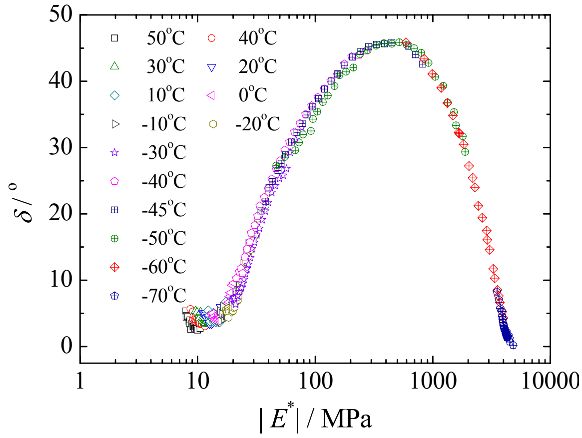

Fig.5 van Gurp-Palmen Plot, showing the phase angle δ as a function of the absolute value of the complex modulus measured at different temperatures

CONCLUSION

In conclusion, the dynamic viscoelsticity of carbon black filled vulcanized natural rubber were investigated by DMA frequency sweep and temperature sweep tests. The frequency-temperature superposition principle is applicable to create master curves from the isothermal frequency sweep measurements at various temperatures. It demonstrates that the carbon black filled rubber behaves thermal rheologically simple and the master curves establish the dynamic mechanical behavior over a frequency range of 21 decades. Such thermo-rheological simplicity of carbon black filled rubber is also confirmed by the Gurp-Palmen plot and the Cole-Cole plot. Furthermore, the shift factors used for creation of master curves of storage modulus, loss modulus and loss factor can follow both the WLF equation and Arrhenius relationship.

References

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