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Low-frequency dielectric relaxation in rubber

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A rubber sample is investigated by dielectric spectroscopy in the frequency range from $10^{-2} \leqslant \nu \leqslant 10^{7}$ Hz. Measurements are performed under both isothermal (at ambient pressure) and isobaric conditions. The spectral shape of the loss peaks is symmetric and temperature and pressure independent. Hence the temperature-pressure-frequency superposition principle is fulfilled in a cross-linked rubber sample. The Vogel-Fulcher-Tammann temperature law and its pressure counterpart well describe the respective temperature and pressure dependences of relaxation times. In addition we determined the activation volume from isothermal relaxation data.

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INTRODUCTION

The classic Debye dispersion relation with a single relaxation time τ is described as a function of angular frequency ω in the following form:

$$\varepsilon^*(\omega)=\varepsilon_\infty+\frac{\varepsilon_0-\varepsilon_\infty}{1+i\omega\tau}, \tag{1}$$

where ε^* is the complex dielectric permittivity of the material. From the experimental point of view, the dielectric responses of materials, except for dilute solutions, do not exhibit the Debye response characteristics. Hence they are usually modeled by a modified Debye response owing to the distribution of relaxation times:

$$\varepsilon^*(\omega)\propto\frac{1}{[1+(i\omega\tau)^{\alpha}]^{\gamma}}, \tag{2}$$

where α and γ are parameters ranging from 0 to 1. The empirical relation given above was introduced by Havriliak and Negami (HN) [1]. It should be noted that the shape parameters α and $\alpha\gamma$ are related to the low- and high-frequency wings of the relaxation peak, respectively. This relation can be expressed in analytical form:

$$\varepsilon''\approx\omega^{\alpha} \quad \text{for} \quad \omega\ll\omega_0, \tag{2a}$$

$$\varepsilon''\approx\omega^{-\alpha\gamma} \quad \text{for} \quad \omega\gg\omega_0. \tag{2b}$$

The above expressions are commonly known as power-law relationships. Thus α and $\alpha\gamma$ determine the slopes of low- and high-frequency parts of $\varepsilon''(\omega)$ as the dielectric loss curve is plotted in double-logarithmic scale, i.e., $\ln\varepsilon''(\omega)$ versus $\ln\omega$.

The dynamics of glass-forming materials in the glass-transition range is manifest as the main relaxation process, which is commonly referred to as α relaxation. This relaxation shows a series of universal features, which are observed in most glass-forming liquids and polymers regardless of their different particularities at the microscopic level. The most characteristic feature of α relaxation is a nonexponential behavior of the relaxation function. In the time domain, nonexponential decay of the relaxation function is usually fitted by the Kohlrausch-Williams-Watts (KWW) equation [2]

$$\phi(t)=\exp[-(t/\tau)^{\beta}_{\mathrm{KWW}}], \tag{3}$$

where β_{KWW} is the nonexponentiality parameter. On the other hand, taking into account the data obtained in frequency domain, significant broadening of absorption peak in relation to simple Debye process is commonly observed. These peaks usually have an asymmetric shape. As discussed above, they can be well described by the HN function.

Another universal property of glass-forming liquids is related to the temperature dependence of the relaxation rate. It is found that the α-relaxation time systematically deviates from the Arrhenius form upon approaching the glass-transition temperature. This dependence is often analyzed by means of the empirical Vogel-Fulcher-Tammann (VFT) equation [3]

$$\tau=\tau_0\exp\left(\frac{D_T T_0}{T-T_0}\right), \tag{4}$$

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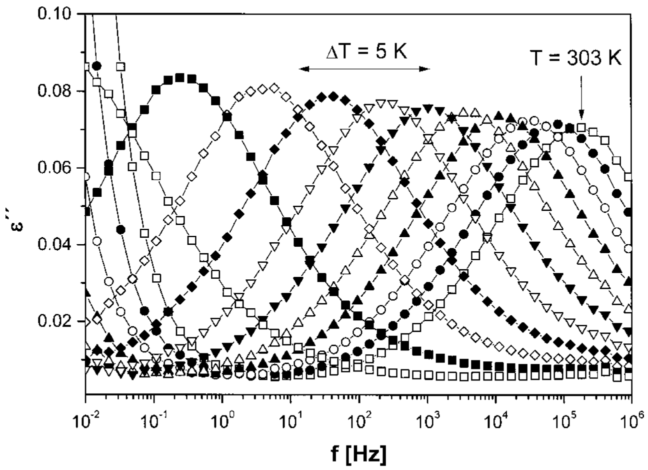

FIG. 1. The frequency dependence of dielectric loss for rubber sample at atmospheric pressure.

where T_0 is the temperature at which the relaxation time seems to diverge and D_T is the strength parameter related to the fragility of material.

In this Brief Report we studied the effects of temperature and pressure on the relaxation properties of a cross-linked material (rubber sample). The main result we found was that the temperature-pressure-frequency superposition principle is fulfilled.

EXPERIMENT

Rubber samples were mixed using an internal mixer (Haake Rheocord 90) according to the ASTM D3191 standard formulation. Tin-coupled solution styrene-butadiene rubber (Sn-SSBR) was used as polymer. This polymer contains 21% styrene and 63% vinyl. The percentage of tin coupling is estimated at about 70%. The differential scanning calorimetry (DSC) glass-transition temperature is $-24\,°\mathrm{C}$. The samples were cured at $160\,°\mathrm{C}$ using constant cross-linking density $(t90+\mathrm{mold\,lag})$. The optimum curing time was estimated using the Monsato ODR rheometer.

The temperature-dependent dielectric measurements were carried out using the experimental setup designed by Novo-Control GmbH working in the frequency range between 10^{-2} and 10^{7} Hz. For the high-pressure studies, we used a pressure system constructed by UNIPRESS described in Refs. [4,5]. The capacitor with tested material was placed in the high-pressure chamber. Pressure was exerted on the chamber from a pressure source (special chamber with a piston placed under hydraulic press) through silicone oil. The sample capacitor was sealed with Teflon to separate the sample from the silicon oil. Pressure was measured by the Nova Swiss tensometric pressure meter with a resolution 0.1 MPa.

RESULTS AND DISCUSSION

Figure 1 shows $\varepsilon''(\nu)$ measurements of rubber for various temperatures at atmospheric pressure. Dielectric spectra were also measured at constant temperature and various pressures.

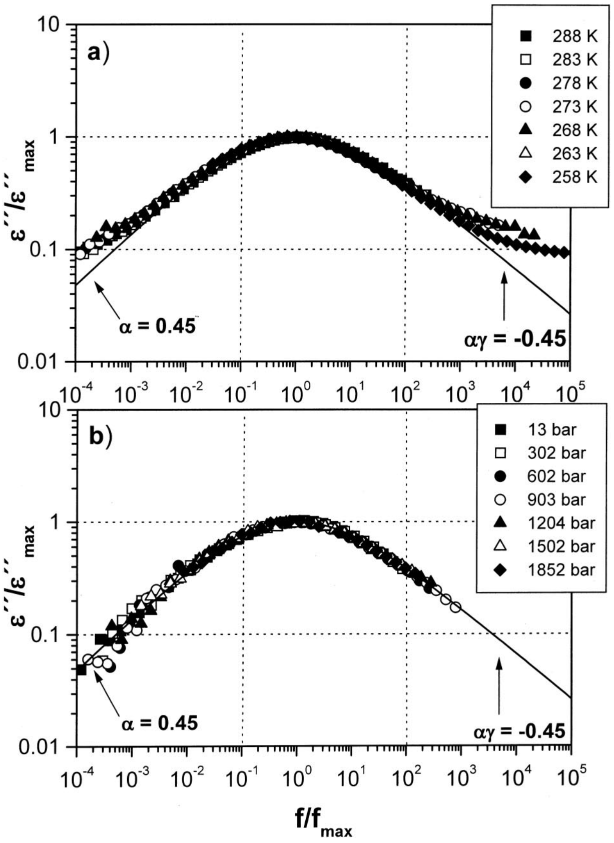

FIG. 2. Top panel: the master curve of the frequency dependence of $\epsilon''(\omega)$ determined at various temperatures. Bottom panel: the master curve of the frequency dependence of $\epsilon''(\omega)$ determined at various pressures. The solid lines are fits to the HN relaxation function.

It was found that data obtained from isothermal and isobaric measurements look qualitatively the same. For this sample we observe a single, broad, and symmetrical relaxation process with a maximum that moves towards lower frequencies with decreasing temperature or increasing pressure. The shape of the relaxation curves is temperature and pressure independent: therefore, the dielectric absorption peaks can be collapsed onto one master plot. Using a simple scaling procedure (see axis description in Fig. 2), we constructed such a master plot, which is shown separately for isobaric and isothermal data in the top and bottom panels of Fig. 2, respectively. Hence one can conclude that the temperature-pressure-frequency superposition principle is fulfilled in the studied martial.

Analysis of dielectric spectra using the HN relaxation function provides valuable information concerning the relaxation time and shape parameters. As a measure of the relaxation rate, we chose the inverse of frequency at which the absorption peak shows a maximum: $\tau=1/2\pi\nu_{\max}$. The temperature dependence of $\log_{10}\tau$ (solid squares) is plotted in Fig. 3. Additionally, we determined the relaxation times (open circles) based on shift factors, which were used previously to construct the master plot. This procedure provides a broad range of values for $\log_{10}\tau$. However, it is important to note that the above method can be successfully applied only

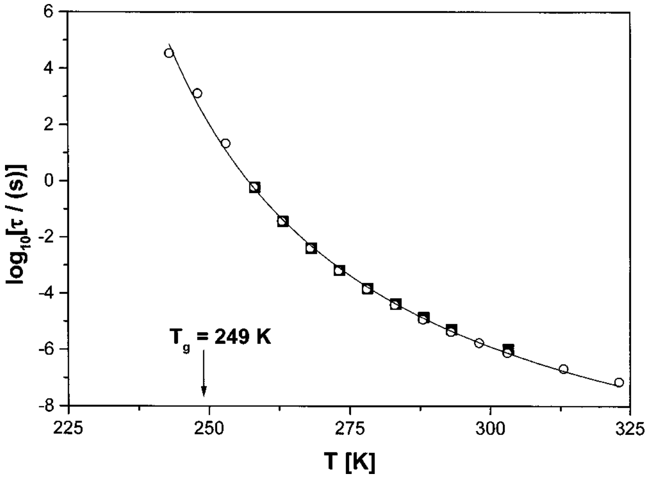

FIG. 3. The temperature dependence of relaxation time in the cross-linking rubber sample. The meaning of the symbols used is explained in the text. The solid line shows the fit using the temperature VFT law.

if the dielectric spectra obey the temperature-frequency superposition principle [6]. As can be seen in Fig. 3, the relaxation times determined in a different way have practically the same temperature dependence which can be well parameterized using the VFT law [Eq. (4)] with the following set of parameters: $\log_{10}\tau_0 = 12.9 \pm 0.4$, $D = 7.4 \pm 0.6$, and $T_0 = 205 \pm 2$. From these parameters one can easily calculate the value of the steepness index [7]:

$$m = \left.\frac{d\log_{10}\tau}{d^{T_g}/T}\right|_{T=T_g} = 2 - \log_{10}\tau + \frac{(2-\log_{10}\tau_0)^2}{D\log_{10}e}, \quad (5)$$

which is commonly used as a measure of fragility of glass formers. It was found that the value of m is equal to $m = 85$ for the studied material. Note that the glass-transition temperature T_g in Eq. (5) is defined as $T_g = T(\log_{10}\tau = 2)$. For most glass formers, the steepness index (or fragility) correlates with the nonexponential parameter β_{KWW} in Eq. (3). According to this phenomenological correlation [7], fragile systems (large m) have a small value of β_{KWW}, whereas strong systems (with small value of m) have a large value of β_{KWW} close to unity. To determine the value of the nonexponential exponent for a rubber sample, we calculated the Fourier transform of $\varepsilon''(\omega)$. Transformed to the time domain, the data have been fitted to a KWW function [Eq. (3)]. The value of β_{KWW} is estimated to be 0.3. Thus our sample can be placed in the group of fragile glass-former materials. We also compared the values of the steepness index and nonexponential exponent obtained for rubber samples with m and β_{KWW} values for other materials that are reported in Ref. [7] (see Fig. 4 in cited reference). It was noted that the fragility of rubber is a little bit smaller than that of other materials that have nearly the same broad relaxation process as studied here. An analogous situation can be also found in orientationally disordered crystals.

From isothermal data we determined the effect of compression on the relaxation rate. Figure 4 shows the pressure dependence of relaxation times at constant temperature $T = 299$ K. Like our previous high-pressure results on other glass formers, it turns out that this dependence can be well described by means of the pressure counterpart of the temperature VFT law [8,9]:

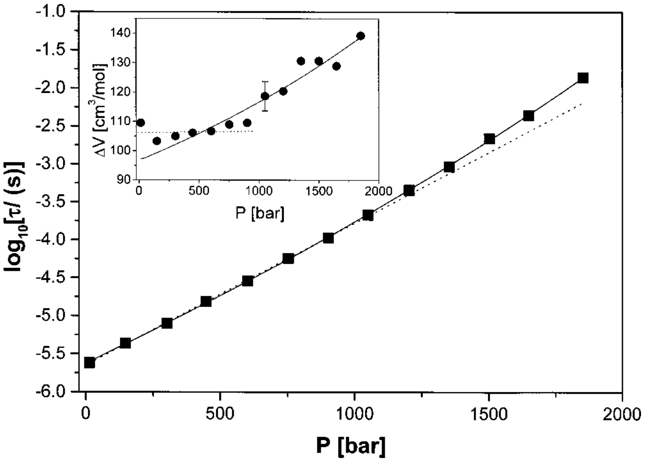

FIG. 4. The pressure dependence of relaxation times at $T = 299$ K. The experimental data were fitted to the pressure counterpart of the temperature VFT law. The inset shows the activation volume plotted as a function of pressure. The solid and dashed lines were obtained combining Eq. (6) with Eqs. (8) and (7) with Eq. (8), respectively.

$$\tau = \tau_0 \exp\left(\frac{D_P P}{P_0 - P}\right), \quad (6)$$

where P_0 is the pressure where the relaxation time seems to diverge and D_P is the strength parameter. We also noted that the $\tau(P)$ dependence could be well described in the pressure range from 1 bar to 1 kbar using the activation form [10]

$$\tau = \tau_0 \exp\left(\frac{P\,\Delta V}{RT}\right), \quad (7)$$

where ΔV is activation volume and R is a gas constant. Obtained from a fitting procedure, the value of activation volume is equal to 107 cm^3/mol. However, above 1 kbar the relaxation times systematically deviate from Eq. (7) on approaching the glass transition. This behavior can be related to the change of activation volume on pressure. The inset in Fig. 4 shows the effect of compression on ΔV determined from [10]

$$\Delta V = 2.303RT\left(\frac{\partial\log_{10}\tau}{\partial P}\right)_T. \quad (8)$$

It is evident that the change of activation volume with increasing pressure is more pronounced above 1 kbar.

As discussed earlier with respect to Figs. 1 and 2, the observed relaxation process has a symmetric shape with $\alpha = \alpha\gamma = 0.45$. The symmetric shape may suggest that the differences between the short- and long-range correlations disappear for cross-linked samples. The above conclusions have been based on the model proposed by Schönhals and

Schlosser that provides interpretation for shape parameters in polymeric systems [11]. According to this model, the parameter α describes the local chain dynamics of amorphous polymers, whereas the other parameter $\alpha\gamma$ is related to the intermolecular correlation of segments of different chains.

The dielectric studies of rubber sample were also performed at temperatures below T_g up to $T=T_g-100$ K. It was noted that there is no indication of the presence of the β process in the investigated frequency range, which is again similar to the situation found in plastic crystals [12]. Our measurements may lead to the conclusion that β relaxation is a property of supercooled liquids only.

CONCLUSIONS

The dielectric relaxation properties of a cross-linked rubber sample under isothermal and isobaric conditions are investigated. As a result, we found that dielectric absorption curves conserve the temperature-pressure-frequency superposition principle, making possible the construction of a master curve by applying simple scaling procedures.

The temperature and pressure dependences of relaxation times are well reproduced by the temperature VFT law and its pressure counterpart, respectively. Concerning isothermal relaxation data, we determined the value of activation volume which is related to the volume required for relaxation.

The relaxation dynamics of the studied system can be characterized by means of two quantities: (1) the fragility parameter (or steepness index) and (2) the nonexponential exponent. The values of both parameters suggest that our sample can be classified as a fragile system. However, this material does not strictly obey the phenomenological correlation between the steepness index and the nonexponential parameter established for most glass-forming liquids and polymers.

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