

Glass-transition and secondary relaxation in SBR-1502 from dynamic mechanical data

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Received 19 October 1998; received in revised form 12 February 1999; accepted 5 May 1999

Abstract

The dynamic mechanical behavior of a compound styrene-butadiene rubber (SBR-1502) was measured in the frequency range from 10^{-3} to 10 Hz and between 80 and 300 K. The loss tangent data reveal two transitions, α and β , characterized by the temperatures T_α and T_β . Both processes showed an Arrhenius behavior and so the activation energies were calculated. A molecular interpretation on the β relaxation in SBR is also introduced. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Loss tangent; Glass transition; Secondary relaxation

1. Introduction

Several studies of the dynamic mechanical behavior of polymers demonstrate that many polymers show more than one structural relaxation when they are investigated in a wide range of temperatures [1]. However, the main transition normally studied corresponds to the glass transition usually named α -transition. This phenomenon is characterized by a temperature [2], T_g or T_α , in which the material changes from the glassy to the rubbery state.

In addition to the α -transition, other secondary transitions can appear in the glassy region, detected by different loss peaks in the $\tan \delta$ plot [1]. These transitions are usually labeled with Greek letters: β , γ , and so on. The secondary relaxation process has been widely studied by dynamic mechanical, dielectric and NMR techniques in many amorphous polymers, but there is not enough information in the case of elastomers.

These secondary transitions in elastomers have been reported by some authors [3–6]. An earlier report was published by Bartenev [4], who measured natural rubber (NR) and styrene-butadiene rubber (SBR) by mechanical and electrical spectroscopy in the region from 83 to 300 K. Ni et al. [3] investigated 1,2-polybutadiene (BR) by dynamic mechanical and electrical techniques over a temperature range between 93 and 373 K. Some evidence of secondary

transitions in elastomers in that temperature region is summarized by Sircar [5]. As far as we know, there have been no other reports on secondary transitions on styrene-butadiene rubber analyzed using dynamic mechanical spectroscopy.

The dynamic mechanical response of a linear viscoelastic material is usually given by the complex modulus G^* as a function of the circular frequency ω . Here G^* is presented in terms of its real and imaginary parts, i.e., $G^* = G' + iG''$, where G' is the shear storage modulus and G'' the loss modulus. The loss tangent ($\tan \delta$), or internal friction, is defined as the ratio between G'' and G'

$$\tan \delta = \frac{G''}{G'}. \quad (1)$$

In this paper we report a dynamic mechanical study of the main and secondary relaxations of an SBR compound. Measurements of loss tangent were made over a wide range of temperatures and frequencies. Two relaxation processes were detected and designated α and β in order of decreasing temperature. The activation energy associated with both processes is also estimated.

2. Experimental

2.1. Materials

In this work we use a cured compound of SBR-1502 filled with carbon black. SBR-1502 contains 23.5% bound

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Table 1
Compound formulation (in phr)

| | |
|------------------------|-----|
| SBR 1502 | 100 |
| Carbon black HAF N-330 | 40 |
| Zinc oxide | 3 |
| Stearic acid | 2 |
| Aromatic oil | 10 |
| Antioxidant | 1 |
| TBBS | 1 |
| Sulfur | 1.5 |

styrene, i.e. a molecular proportion in the chains of one styrene for every six or seven butadienes. The chemical structure of butadiene in the SBR copolymer consists of 55% *trans*-1,4, 9.5% *cis*-1,4 and 12% 1,2-butadiene.

The molecular weight of the polymer was measured by GPC and a value of $M_n = 176.000$ g/mol was obtained. The compound formulation is given in Table 1.

The gum mix was prepared in a Laboratory mill, and this was later characterized at 433 K by means of torque curves in a Monsanto MDR 2000 rheometer. From this curve the time of maximum torque, t_{100} , was obtained. The density of the compound was $\rho = 1.09$ g/cm³.

Samples as sheets of $150 \times 150 \times 2$ mm were cured at 433 K at a time of t_{100} . The samples were cooled rapidly in ice and water at the end of the curing cycle. In order to the measure the dynamic properties, strip samples of $30 \times 3 \times 2$ mm were cut using a die.

2.2. Dynamic mechanical test

The loss tangent was measured with an automated sub-resonant forced pendulum [7]. The principle of measurement is based on the relationship between stress, σ , and strain, ϵ . Considering a sinusoidal stress applied to the system, the strain will also be sinusoidal though lagging behind the stress by a phase angle, ϕ . The loss tangent is the tangent of this angle, that is

$$\tan \delta = \tan(\phi(\omega)) \quad (2)$$

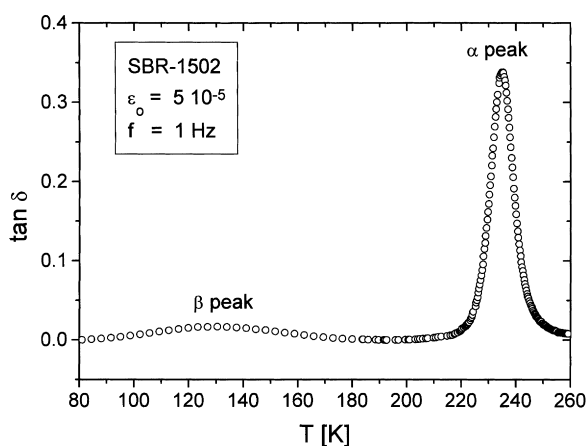


Fig. 1. Plot of $\tan \delta$ vs. temperature for SBR-1502 at 1 Hz.

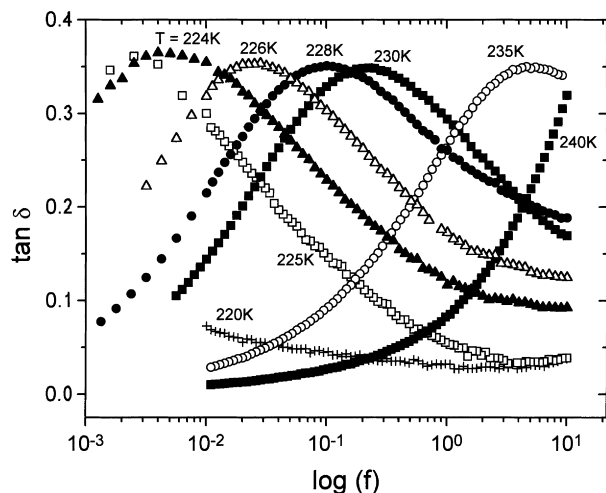


Fig. 2. The $\tan \delta$ of SBR-1502 plotted against the frequency for several temperatures.

Measurements were made in a He atmosphere at 0.2 Torr. The strain amplitude, ϵ_o , was maintained constant at a value of 5×10^{-5} during the test. This low value guarantees the linear viscoelastic behavior.

Three types of evaluations were made. Firstly, $\tan \delta$ was measured at a constant frequency of 1 Hz with a temperature ramp of 0.25 K/min in the range of 80 to 260 K. Secondly, isothermal measurements were made for a frequency range of 10^{-3} to 10 Hz for temperatures between 220 and 240 K. Finally, $\tan \delta$ was evaluated within a temperature range of 80 at 160 K at a frequency between .05 and 10 Hz.

As is usual in a sub-resonant pendulum, the experimental data of $\tan \delta$ vs. temperature were analyzed assuming a background exponential of loss tangent using the following formulae [8]

$$(\tan \delta)_B = a_0 + \frac{a_1}{T} \exp\left(-\frac{H_B}{kT}\right) \quad (3)$$

where a_0 and a_1 are the adjusting constants, H_B is the activation energy of the background, k the Boltzmann constant and T the absolute temperature. This background was subtracted for all data of loss tangent vs. temperature affecting strongly only the beta peak.

3. Results

Fig. 1 shows the plot of $\tan \delta$ for SBR-1502 as a function of the temperature at 1 Hz. In this figure the background was subtracted using the relationship given in Eq. (3) with $H_B = 0.14$ kcal/mol. In this figure it is possible to see a peak at $\tan \delta$ at 235 K associated with the main relaxation (α) related to the glass transition, T_g , of the compound. Another lower transition clearly appears below T_g at around of 125 K. This secondary transition is in correspondence to those reported by Bartenev et al. [4] in SBR-1502.

In Fig. 2 the $\tan \delta$ experimental curves are given as a

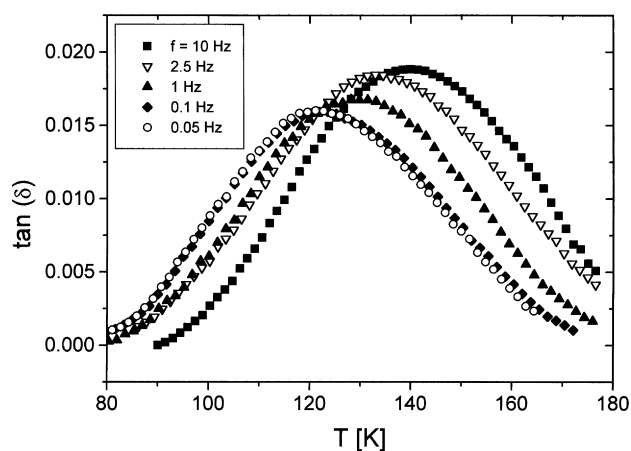


Fig. 3. Plot of $\tan \delta$ vs. temperature for SBR-1502 at various frequencies.

function of the test frequency at constant temperature. The temperatures selected to make isothermal tests were chosen around the maximum of the α peak, between 220 and 240 K as shown Fig. 1. The plots, made on a semi-logarithmic scale, show a broad peak of $\tan \delta$ for each temperature.

Finally, in Fig. 3 the results of $\tan \delta$ vs. temperature are shown for several frequencies in the temperature range from 80 to 180 K. In this figure it can be observed that an increase in frequency produces a shift in the location of a peak which agrees with that expected in the theory of linear viscoelasticity. For all data the background was subtracted, and H_B was independent of frequency tests.

4. Discussion

4.1. α -Relaxation

The glass transition temperature was obtained from the maximum of a Gaussian curve that fitted the data of Fig. 1 in the α -peak. A value of $T_g = 235$ K at 1 Hz was obtained.

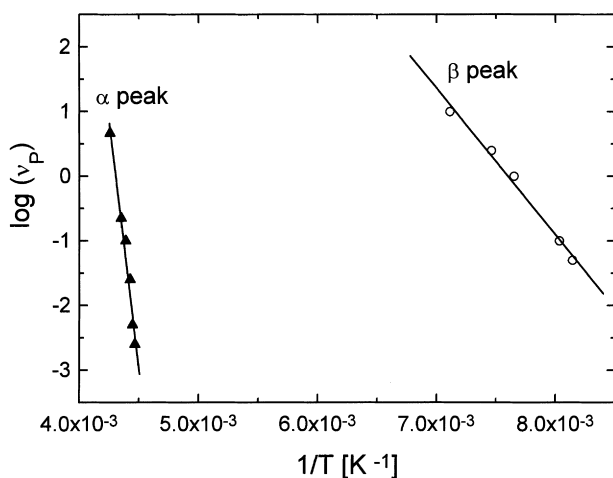


Fig. 4. The Arrhenius plot. The slope gives the activation energy of the α - and β -peak.

This result is similar to those published in the literature by other authors [9,10]. It is known that the presence of carbon black in the compound would affect only lightly the location in temperature of the peak [11].

The curves in Fig. 2 indicate that $\tan \delta$ is dependent on frequency. The main effect of the increase in frequency is the shift of the curve to the right (i.e. to higher temperatures). If an Arrhenius-type relationship [2] for the frequency of the peaks (ν_p) is assumed, then

$$\log(\nu_p) = \log(\nu_0) - 0.4343 \frac{\Delta H}{kT} \quad (4)$$

where ΔH is the apparent activation energy of the process, k the Boltzmann constant, T the absolute temperature and ν_0 a pre-exponential factor. The values of $\log(\nu_p)$ are plotted against the $1/T$ in Fig. 4. Using Eq. (4) for fitting the data, the activation energy ΔH results from the slope of the straight line. Consequently a value of $\Delta H = 70.18$ kcal/mol is obtained for the α process. This value is in the range of those published for the α -transition for rigid polymers, such as PMMA and PS [12–14].

4.2. β -Relaxation

As has already been mentioned, we found a secondary transition for SBR-1502 at 125 K measured at 1 Hz. In order to calculate the activation energy, we carried out measurements of $\tan \delta$ versus temperature at constant frequency (Fig. 3).

With the increase of the test frequency, the maximum of β -peak is shifted toward higher temperatures. Since the plot of $\log(\nu_p)$ against reciprocal absolute temperature ($1/T$) is linearly accurate (Fig. 4), we may express the temperature dependence of ν_p in the Arrhenius form. Therefore for the β -process, the activation energy obtained from the slope of the line in Fig. 4 is $\Delta H = 10.3$ kcal/mol.

In styrene butadiene rubber, both the phenyl group (from styrene) and the 1,2-vinyl structures (from butadiene) would offer resistance to rotational motion [15]. Ni et al. [3] studied the secondary relaxations of polybutadiene. They showed that the β -relaxation is not observed when the amount of 1,2-vinyl units in BR is smaller than 57%. Moreover, they did not observe the γ -relaxation of the butadiene when the amount of 1,2-vinyl units was smaller than 45%. We should notice that in the SBR, 1,2-vinyl units are the minority. Thus, we can be sure that the observed relaxation at 125 K is not due to the presence of butadiene units in SBR. Therefore, it could be attributed that the β -relaxation observed in the SBR, has its origin in the rotation of the phenyl group.

On the other hand, the γ -peak in polystyrene (PS) has been found in dynamic-mechanical measurements at low frequencies (1 Hz) by Illers and Jenckel [16] at 132 K. Although the discussion is open, several authors [13,16,17] assigned the phenyl group rotation as the origin of γ -peak of PS. Reich and Eisenberg [17] and Yano and

Wada [13] found that the activation energy necessary to produce the γ -relaxation in PS lies between 8–10 kcal/mol. Tonelli [18], calculated that the barrier to complete rotation of phenyl groups is about 9–10 kcal/mol. These results are in good agreement with the activation energies obtained for the β -peak in SBR measured in this work. Thus, this research would strengthen our hypothesis that the β -peak is due to phenyl group rotation.

5. Conclusion

The loss tangent of SBR 1502 compound show data two transitions between 80 and 260 K. The α -transition associated with the glass transition temperature is related to a single process of activation energy of $\Delta H = 70.18$ kcal/mol. The second relaxation in the glassy region of the SBR compound can be modeled by a single mechanism with an activation energy of $\Delta H = 10.3$ kcal/mol. On the basis of the intensity and activation energy analysis of the β -peak, we believe that this transition is associated with the rotation of the phenyl group in the styrene butadiene copolymer.

Acknowledgements

This work was supported by the University of Buenos Aires, Argentina (TY05), Comisión Nacional de Energía

Atómica and Consejo Nac. de Investigaciones Científicas y Técnicas.

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