Acoustic properties of poly(phenylene sulphide)

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The acoustic properties of amorphous and crystalline poly(phenylene sulphide) samples were studied as a function of temperature above 105 K. The loss tangent and the velocity of sound were measured. Information on the β-relaxation process and on the glass transition were obtained.

(Keywords: poly(phenylene sulphide); acoustic properties; viscoelastic properties; transition temperatures; segmental mobility; relaxation processes)

Introduction

Few investigations have been carried out on the viscoelastic properties of poly(phenylene sulphide) (PPS)[1–3]. Analysis of these results shows the necessity of further systematic studies in this field to achieve a more detailed understanding of the properties of PPS, particularly in the high temperature region.

For such investigations of amorphous and crystalline PPS films we chose the acoustic method[4–6]. This method allows the measurement of polymer parameters, such as the velocity of sound (c), the dynamic elasticity modulus (E) and the mechanical losses.

There is a strict correlation between the chemical and physical structure as well as the thermodynamic state and the molecular mobility of polymers. Segmental and chain mobility may be described by parameters such as c, the sound absorption coefficient and the components of the complex E values. The magnitude and the nature of the changes in c and E with frequency or temperature provides information on the mechanical and deformation properties of polymers. The loss modulus and the loss tangent ($\tan\delta$), sometimes referred to as internal friction or damping, are mainly determined by the type and intensity of molecular motion. The study of acoustic properties reveals information about relaxation processes peculiar to a given polymer. Different kinds of polymer chain mobility can be analysed by the acoustic method.

Experimental

The PPS samples studied were from commercial material (TEDUR 9500, Bayer AG, Germany; $M_w = 55\,000$ g mol^{-1}). PPS was used as practically amorphous and semicrystalline material. The amorphous material was obtained by quenching from the melt. A mass related degree of crystallinity $X_{cw} = 5\%$ was calculated from heat of melting measurements according to literature data[7]. Crystalline samples were annealed at 150°C for 1 h in air ($X_{cw} = 32\%$).

For our investigation of acoustic properties the method of forced resonance flexural oscillations, also referred to as the vibrating reed technique, was used. This method is based on the measurement of the amplitude of the oscillations at the free end of a polymer reed while changing the frequency of the inducing force applied to the clamped end of the reed. Details of the equipment and calculation can be found elsewhere[6,8].

The measurements of c and $\tan\delta$ were conducted within a frequency range of 20–2000 Hz and a temperature range of 110–423 K. The errors in determining c and $\tan\delta$ are ~1% and 5%, respectively. Measurements were made at two frequencies allowing the activation energy of the relaxation processes to be calculated.

Results and discussion

The results of experimental investigations of acoustic parameters in PPS films show that several temperature transitions could be observed while examining the temperature dependence of c and $\tan\delta$ (*Figures 1* and *2*).

For the amorphous sample *Figure 1* shows that below the glass transition temperature (T_g) $\tan\delta$ depends only slightly on temperature. The intensity of the relaxation processes at these temperatures is low, as in the low temperature region the local motion of small kinetic elements of PPS chains is limited. However, the β-relaxation manifests itself in the temperature dependence of $\tan\delta$ in the temperature interval 193–223 K. From the c *versus* T plot it can be seen that changes in the temperature coefficient of c ($\Delta c/\Delta T$) occur in the low temperature region at 148 K.

This low temperature relaxation was reported earlier[1] from the study of viscoelastic properties of PPS by torsion experiments in the low temperature region. It was interpreted as an unfreezing of the torsional oscillatory motion of the phenylene groups in the backbone of the PPS chains, which is hindered at lower temperatures[1,2,9]. The small magnitude of the activation energy for the β-relaxation of PPS (50–52 kJ mol^{-1}) may be explained by the fact that only a relatively small number of repeating units is participating in this process.

The low intensity of the low temperature relaxation in amorphous PPS may explain the low toughness and fracture resistance of the glassy polymer[10].

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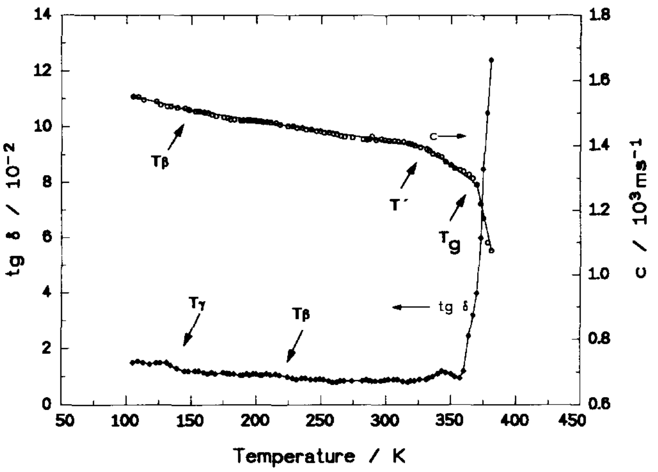

Figure 1 Temperature dependence of loss tangent and velocity of sound for amorphous PPS

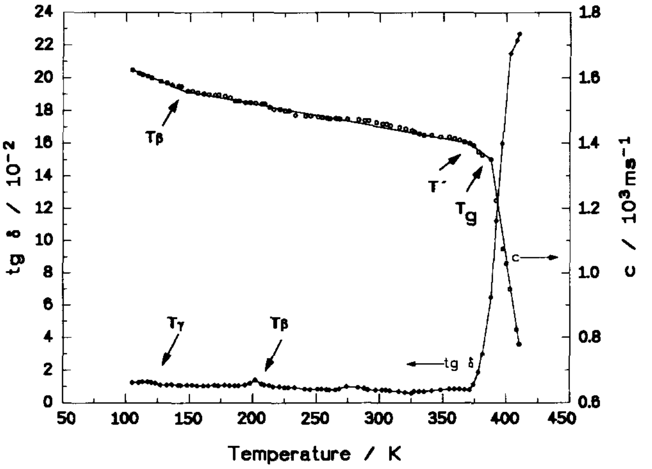

Figure 2 Temperature dependence of loss tangent and velocity of sound for annealed PPS

At 133 K a shoulder in the tan δ curve is evident in the amorphous sample. It must also be noticed that at temperatures below 133 K tan δ increases with decreasing temperature. This is probably due to the γ-relaxation, which is supposed to occur at lower temperatures. However, we consider that it might be due to reorientation of phenylene rings in the backbone chain of PPS, probably coupled with torsional rotational motions of nearby chain units. Such a mechanism has been proposed by Rigby and Dew-Hughes[2] to explain results obtained from dielectric studies on polymers containing phenylene groups in the main chain.

The basic relaxation process manifests itself above 320 K. It is associated with a transition from the glassy to the rubbery state of the polymer. This transition is due to the unfreezing of micro Brownian segmental mobility, resulting in the greatest change in the dynamic modulus and in the appearance of the most intensive peak for the losses.

The plot of *c versus T* shows another transition temperature for PPS in the main relaxation region from 330 to 390 K. Owing to the great attenuation of the oscillation energy in the samples, it was only possible to observe the low temperature branch of the peak in the glass transition region. The two transitions result from the unfreezing of the segmental mobility in two levels of supermolecular organization of the polymer. The change of the coefficient $(\Delta c/\Delta T)$ at the higher temperature of 370 K is due to the glass transition. The preceding relaxation at 331 K is related to the unfreezing of co-operative segmental motion in the random polymer matrix[6,11]. It should be noted that the temperature difference for these two transitions is 39 K for the amorphous sample.

Figure 2 shows the results from acoustic measurements obtained with the annealed sample. It can be easily seen that T_g increases to 398 K. Also the temperature of the preceding process increases to 371 K.

Annealing at comparatively low temperatures above the glass transition leads to the appearance of crystallites formed by sections of the polymer chains. In this case the crystallites act as crosslinks. This increases *c* and dynamic elasticity modulus in the annealed sample and supports the rigidity of the material at temperatures above 398 K.

The difference of the two transition temperatures in the main relaxation region decreases to 27 K. From this result it may be concluded that the amorphous phase becomes more homogeneous.

Conclusions

For PPS the observed relaxations below T_g show a low degree of molecular mobility for small kinetic elements of the chains. The β-relaxation was observed in the temperature interval from 193 to 223 K for the amorphous sample from tan δ or 148 K from the measurement of *c*. The β-relaxation is probably connected to the oscillatory motions of the backbone phenylene groups of PPS[1].

At 133 K a branch of the γ-process is presumably detected, which is ascribed to the reorientation of phenylene rings in the backbone chain of PPS[2].

In the main relaxation region amorphous PPS exhibits two transitions due to the unfreezing of the segmental mobility in two levels of supermolecular organization of the polymer. One of these processes is the glass transition at 370 K, the other at 331 K is connected to the segmental motion in the random matrix of PPS.

Annealing of the polymer leads to increasing transition temperatures in the main relaxation region. Crystallite growth leads to an increase in *c* and dynamic elasticity modulus. In this case the crystallites act as crosslinks and support the rigidity of the material at temperatures above 398 K.

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