Letters

Relaxation time and molar free energy of activation of polyacrylonitrile

Two schools of though exist on the structure of polyacrylanitrile (PAN). One group of investigators [1–8] believe in a two-phase structure for PAN and phenomena such as the glass transition, characteristic of the amorphous phase are frequently quoted for this polymer [2, 4, 9]. On the other hand, Bohn, Schaefgen and Statton [10] have suggested a one-phase paracrystalline structure for PAN. In previous papers, Chand and co-workers [11, 12], through a dielectric and X-ray study of PAN, have made efforts to establish the structure of PAN, and have indicated that a two-phase structure is appropriate.

In another study [13] the transition behaviour of the dielectric relaxations of PAN has been confirmed by the Williams, Landel and Ferry (WLF) theory and by a recently-proposed theory of Phillips [14]. Here, the relaxation times and the molar free energy of activation have been calculated from the experimental data as well as from the different studies reported in the literature, Ishida *et al.* [1], Saito and Nakajima [2] and Hayakawa *et al.* [4]. In this communication, a study of the relaxation time and molar free energy of activation for dipole relaxation in PAN, and a comparison with the results of other workers, has been carried out.

PAN, prepared by free radical polymerization in dimethyl formamide at 60° C in an inert atmosphere with α, α'-azobisisobutyronitrile initiator was used in this work. The powdered PAN obtained was dried in vacuum in an oven at 50° C was compressed (at pressure of 155 kg cm^2) to produce the sample disc (of 0.5 mm thickness and 1.3 cm diameter). Dielectric measurements were made on a G. R. Capacitance Bridge Type 716 CS using a two-terminal connection cell in the frequency range 10^2 to 10^5 Hz and temperature range 30 to 150° C.

Fig. 1 shows the variation of ϵ'' with temperature of PAN at different frequencies. The relaxation times $\tau = (1/2f_{\max})$, where $f_{\max}$ is the frequency for which ϵ'' is a maximum, were calculated from the experimental curves and from the literature [1, 2, 15]. The molar free energy of activation, ΔG, for dipole relaxation at a particular temperature was determined by using the relation given in [16–18].

In Fig. 2 the variation of relaxation time, τ, with temperature is shown for our experimental data and for the data reported in [1, 2, 15]. The relaxation time is seen to decrease with increasing temperature. The data from [1] shows results closest to our experimental data. At approximately 127° C both sets of values are in agreement. The relaxation times from [2] and [15] are very much lower than our data at all temperatures.

It should be remarked here that data from [1] and [2] have been attributed to result from a glass transition whereas the data from [15] has been explained on the basis of motion in the paracrystalline phase in PAN.

Fig. 3 shows the variation of molar free energy of activation, ΔG, with temperature. The molar free energy of activation varies with temperature in the same manner as the relaxation time.

A comparison of all four sets of data leads to the following conclusions. Our data and the data from [1] show similar values, while the data from [15] shows quite different values. Data from [2] shows values intermediate between ours and that from [15]. The state (impurity and moisture contents etc.) and the structure of the specimens were not similar.

Even in the study by Thomson [19] two separate peaks in the loss tangent at 100° C and 130° C were observed. After heat treatment at 125° C for 30 h the peaks became flattened, and the higher temperature peak completely disappeared after heat treatment at 160° C for 24 h. The observations of Thomson, however, do show that the heat treatment may produce changes in the structure. Prolonged heat treatment results in a modification of the structure probably through a rearrangement of molecular chains so as to form a larger number of bound nitrile groups (due to dipole–dipole interactions between them). Owing to the larger number of nitrile groups the stability of this rearranged structure appears to be higher. Furthermore, there seems to be critical temperature, above which the destruction or modification of this structure may occur. The study by Hayakawa *et al.* [15] seems to suggest that during the

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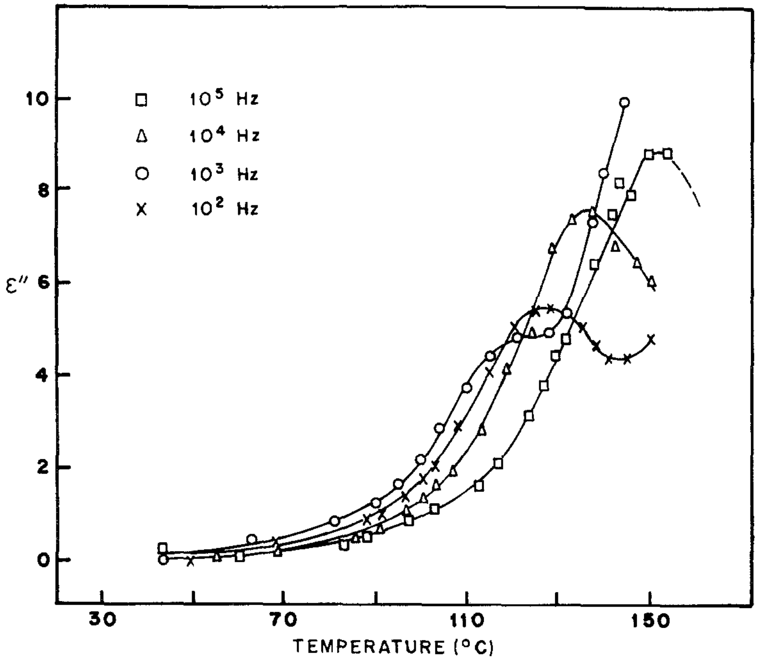

Figure 1 Variation of ϵ'' with temperature.

heat treatment of their specimens the structure became modified to a different type, probably due to the rearrangement of strongly interacting nitrile groups. The larger the number of such interacting groups so formed, the higher will be the stability of the structure.

The comparative study of the relaxation time and the molar free energy of activation in polyacrylonitrile suggests that the relaxation time and molar free energy of activation calculated from the dielectric relaxations in the same frequency and temperature range are influenced by the structure of PAN. Prolonged heat treatment results in a modification of the structure which may account for the discrepancy in the relaxation time and molar free energy of activation values obtained by different workers.

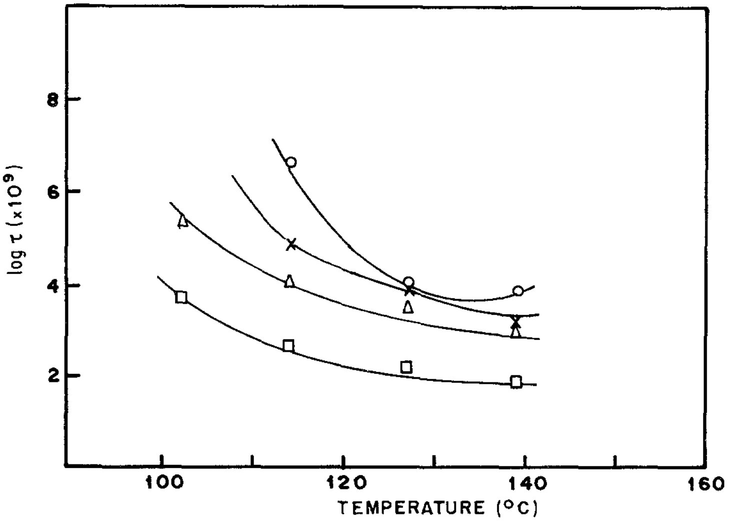

Figure 2 Variation of relaxation time, τ, with temperature for PAN. (○) our experimental values, (X) data from [1], (Δ) data from [2], and (□) data from [15].

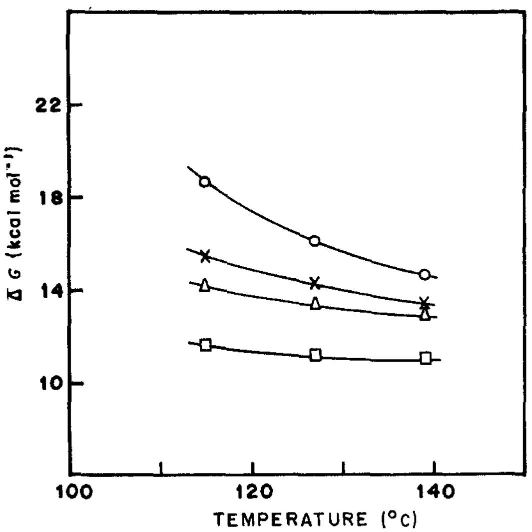

Figure 3 Variation of molar free energy of activation ΔG with temperature for PAN. (○) our experimental values, (×) data from [1], (△) data from [2] and (□) data from [15].

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On the use of small specimens in the measurement of the fracture toughness for brittle materials

The fracture toughness, K_{Ic}, has become a well-established parameter for the assessment of the fracture behaviour of brittle materials. Several methods of measuring this quantity have been advanced. The bend test, the double-cantilever beam test and the double torsion test are the best known of these methods. The bend test in 3-point or 4-point set-up is an especially popular method. The specimen length for this test ranges usually from 30 to 50 mm. Although this size is generally much smaller than the size necessary for other tests, it is nevertheless important that smaller specimens can be used. In order to see whether really small specimens give the same results as larger ones, some experiments using the 3-point bend method were carried out.

Large specimens (dimensions 3 mm × 9 mm × 45 mm) and small specimens (dimensions 1 mm × 3 mm × 15 mm) were machined of several brittle ceramics (see Table I). In each sample a notch

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