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Thermally-induced structural change in polyacrylonitrile

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Introduction

In a recent publication[1] it was pointed out that the dielectric relaxation of polyacrylonitile (PAN) in identical temperature and frequency ranges reported from four different laboratories[1–4], showed some differences, implying differences in the structure of the PAN samples used. Results on the samples used by Hayakawa *et al.*[2] were found to be markedly different from those of the other authors[1,3,4]. Hayakawa *et al.*[2] used a solution-grown PAN film which had undergone heat treatment for 30 h at 130°C, whereas other authors[1,3,4] used powder samples which had not been heat treated. Thus the previous comparative study[1] of the various reports on dielectric relaxation of PAN revealed that the prolonged heat treatment might possibly be responsible for the observed discrepancies in the results. This contention could not be confirmed in the previous investigation[1] because the data on heat treated and untreated PAN were originating from different laboratories and other conditions of sample preparation were not identical.

We have thus attempted a systematic investigation of the effect of heat treatment on the dielectric relaxation of PAN. The heat treated and untreated samples used in this study were identical in all other respects except the heat treatment.

Experimental

PAN used in this work was prepared by free radical polymerization using α,α'-azobisisobutyronitrile as initiator by the method described in detail elsewhere[5].

PAN powder was subjected to heat treatment at 120°C for 24 h under an air atmosphere by keeping the specimen in a closed flask in a constant temperature oven, followed by slow cooling to room temperature. The specimen turned yellow after heat treatment.

For dielectric measurements, discs of about 1 mm thickness and 1 cm diameter were prepared by compressing the pre-dried (vacuum oven at 40°C) PAN powder in a pellet-forming press. The disc surfaces were silver-coated for achieving better electrode contact.

Dielectric measurements at constant frequency (100 Hz) and temperatures varying in the range 30° to 160°C were carried out on a General Radio Bridge (GR 716 CS). Specimens were enclosed in a thermostatically-controlled chamber maintained to within ±0.1°C. A thermocouple placed close to the specimen was used for measurement of specimen temperature.

Results and discussion

Results of dielectric measurements for the untreated PAN and the PAN heat treated at 120°C for 24 h are shown as variations of dielectric constant (ε') *versus* temperature in *Figure 1*, and dissipation factor ($\tan\delta$) *versus* temperature in *Figure 2*.

The insignificant rise in dielectric constant with temperature up to about 90°C observed in both these samples (*Figure 1*) may be attributed to the glassy state of the polymer. The glass transition temperature (T_g) of PAN has

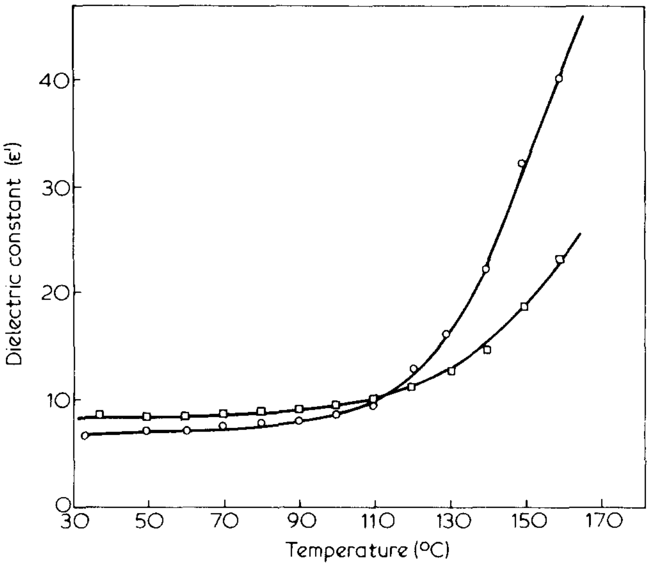

Figure 1 Variation of dielectric constant with temperature for untreated PAN (○) and PAN heat-treated at 120°C for 24 h (□)

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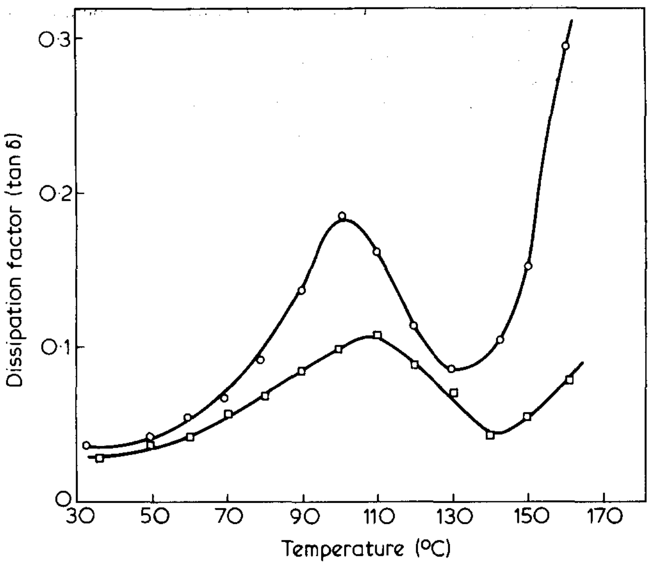

Figure 2 Variation of dissipation factor with temperature for untreated PAN (○) and PAN heat-treated at 120°C for 24 h (□)

been reported to lie in the range 80–104°C by various authors[6]. Above T_g the segmental mobility starts, and hence the dielectric constant rises rapidly with temperature owing to the polarization produced by the alignment of nitrile group dipoles attached to the polymer chain. The increase in dielectric constant over the studied range of temperatures is considerably lower in the case of the heat treated PAN than for the untreated PAN, which implies that a lower number of nitrile group dipoles contribute to the polarization produced in the heat treated PAN.

The loss peak in dissipation (tan δ) which occurs at around 103°C for untreated PAN shifts to about 110°C and becomes broader for the heat treated PAN (*Figure 2*). This relaxation peak has been attributed[1,7] to segmental mobility, characteristic of the glass transition. Occurrence of loss peaks at higher temperatures implies greater restriction on the chain mobility and a broad peak indicates a wider distribution of relaxation times in the heat treated PAN.

Furthermore, since tan δ depends on the dipole moments of relaxing units, the lower values of tan δ imply a lower value of dipole moment of relaxing polymer segments or, in other words, a lower number of orientable nitrile group dipoles in the relaxing segments of the heat-treated PAN.

These observations thus suggest that the heat treatment at 120°C of PAN results in the formation of a larger number of bound nitrile group pairs through their dipole–dipole interaction. During heat treatment at temperatures above T_g the segmental mobility provides the free nitrile groups with an opportunity to approach closely and hence to form bound pairs. The untreated PAN possesses a large number of free nitrile groups, whereas in the heat treated PAN their number is considerably lower. Hence the values of ε' and tan δ might be expected to be lower than those for untreated PAN. The presence of bound nitrile groups would restrict the segment mobility, which is shown by the increase of loss peak temperature in the case of heat treated PAN. Furthermore, since during the heat treatment the bound nitrile groups are more likely to occur at random positions, the lengths of polymer segments between any two successive bound nitrile group pairs may be unequal. Such a distribution of segment lengths could be the cause of the observed wider distribution of relaxation times (broad peak) in the heat treated PAN.

The thermally-induced structural change of PAN seems interesting from the point of view of further improvement of structure for obtaining desired properties for various applications. A more detailed investigation of this thermally-induced structural change, such as the effects of conditions of heat treatment and other parameters would be necessary for a better understanding of this phenomenon and might lead to more useful information.

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