Effect of the gaseous environment on mechanical relaxations in polymers

P. J. Barham and R. G. C. Arridge
H. H. Wills Physics Laboratory, Royal Fort, Tyndall Avenue, Bristol BS8 1TL, UK

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Differences in the overall level of tan δ are reported for measurements on high density polyethylene in tension under various gaseous environments. The differences do not appear in torsion. The tentative explanation is offered that the effect is due to thermoelastic relaxations of magnitude dependent upon the thermal properties of the environment.

In addition a loss peak in tension is reported occurring at 220K in air but not in nitrogen, argon or helium.

INTRODUCTION

Dynamic mechanical testing has become an established method of studying polymeric materials. A variety of methods exist (see e.g. Ferry[1]) whereby a cyclic strain may be applied to a specimen and the corresponding stress measured. The commonest methods are (a) torsion of a strip of rectangular or circular cross-section, (b) bending (either three or four point), (c) unidirectional tensile testing.

In 'driven' systems the phase difference between stress, and strain is recorded whereas in 'free' systems (damped oscillation) the decay of the oscillations is analysed to give the loss factor. Using linear viscoelasticity there are well-known relations between the quantities obtained in either sort of test.

In most investigations one of either frequency or temperature is varied while the other is kept constant (except that in *resonance* methods both are varied).

Interpretation of the modulus and loss factor variation as temperature and/or frequency are changed is generally in terms of relaxation processes assumed to occur in the bulk polymer and in some cases these have been identified (usually by means of chemical modifications) to be structural rearrangements in the molecular conformation.

While it is usual in the literature to specify the temperatures and frequencies used in a relaxation study there seems to be little mention of the environment of the test specimen, whether gaseous or vacuum.

We show in the work to be described that in some cases the gas used to blanket the specimen is important and different gases give different levels of loss factor.

EXPERIMENTAL

Tensile measurements were made using a device applying a sinusoidal displacement of frequency 0.1 Hz through a load cell (consisting of a linear variable differential transformer (LVDT) in parallel with a linear compression spring of similar stiffness to that of the specimen) and then through a second LVDT connected by a steel rod (of stiffness very large compared to the specimen) to the specimen.

The specimen was mounted inside a chamber the temperature of which could be varied within the range 77 to 380K and controlled to ±2K at any level. The gaseous environment could be changed at will. The general layout of this device was described in a previous publication[9]. The maximum displacement was adjusted by means of an eccentrically mounted roller so that the maximum strain was 0.1%.

Specimens of both isotropic and highly drawn and annealed (draw ratio ~28) polymer were used. Their dimensions were, for the drawn specimen, 109 x 1.82 x 0.12 mm and for the isotropic specimen 112 x 15 x 2 mm. The larger cross-section isotropic specimen was used so as to ensure the two specimens had a similar tensile stiffness.

The outputs of the two LVDT were connected to an X–Y recorder so as to produce an elliptical trace. Assuming linear viscoelasticity the loss factor tan δ and modulus $|E|$ may be determined from these traces.

Several measurements were made of each trace and the maximum and minimum of tan δ obtained from these are plotted on the resulting graphs. We found that we could in general consistently measure values of tan δ in the range 0.001 to 0.1 with an accuracy of ±5%.

Measurements in *torsion* were made using a free oscillation inverted torsion pendulum with a counter balance system to minimize end loading of the specimen. The specimen was again placed in a chamber that could be maintained under any desired atmosphere in the temperature range 77 to 380K. The inertia of the system was adjusted so that the frequency was again ~0.1 Hz and the initial strain 0.1%. An optical recording system (Sefram Graphispot) was used for the measurement of the decay of oscillations.

Measurements of tan δ were made by measuring the decay in amplitude over 30 or 40 oscillations, the maximum and minimum values of several such measurements being plotted on the graphs. We could consistently measure tan δ in the range 0.0005 to 0.05 with an accuracy of ±2.5%).

RESULTS

In *Figure 1* we have plotted tan δ in tension as a function of temperature for the drawn and annealed high density polyethylene specimen (Rigidex 50) on the same scale for four

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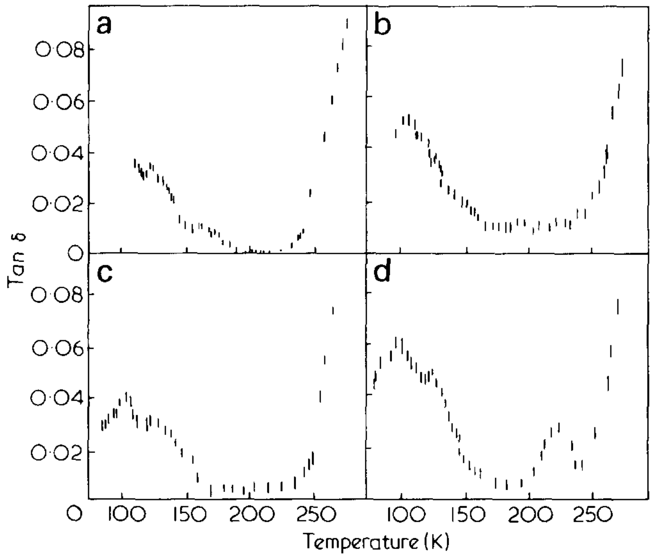

Figure 1 Loss factor tan δ in tension for four different atmospheres (Drawn specimen, error bars represent extreme values). a, nitrogen; b, helium; c, argon; d, air

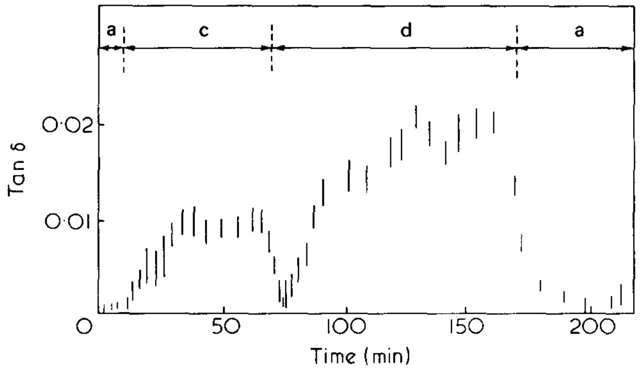

Figure 2 Loss factor tan δ at 220K as a function of time during changes of environmental gases. (Drawn specimen, error bars represent extreme values) a, nitrogen; c, argon; d, air

different atmospheres. It is clear that there are systematic variations of tan δ as between the different gases, particularly at 220K. We therefore performed another experiment in which we held the specimen at 220K and changed the gases. The resulting changes in tan δ as a function of time are plotted in *Figure 2*. It is also worth noting at this point that we retested the specimen in all these environments several times without detecting any significant changes in tan δ from those shown in *Figure 1*.

Figure 3 shows the variation of tan δ, measured in torsion, with temperature for different atmospheres for the same specimen. No significant variations between the different environments are apparent here, within the accuracy of our experimental technique). *Figures 4a* and *4b* show tan δ in tension as a function of temperature for the isotropic sheet in argon and in air, again showing a significant variation. *Figure 4c* is tan δ in torsion in air, showing no significant effect at 220K. (We ensured that torsional stiffnesses of the drawn and the isotropic specimens were similar. This meant that due to the high anisotropy of the drawn specimen, the dimensions of the isotropic specimen for torsion were different from the isotropic tensile test piece – they were in fact 112 x 0.9 x 0.1 mm).

The general features of all these curves may be summed up as follows. In the tensile tests there is a peak in the tan δ – temperature curve at 220K when the specimen is tested in air; this peak is absent when the environment is helium, argon or nitrogen. In the plateau region of tan δ from 170K to 230K the lowest loss is seen for a nitrogen environment and the highest for one of helium.

In the torsion tests however none of these features is seen and the value of tan δ appears more or less independent of the environment with, in particular, no indication of a peak at 220K.

Preliminary work on polypropylene indicates that the effect at 220K, though present, is of much smaller magnitude.

DISCUSSION

Although mechanical relaxation tests are commonly carried out below room temperature they are usually made in torsion, not in tension, and it is perhaps for this reason that we have found few references to the presence of a loss peak at 220K in air in high density polyethylene. A relaxation observed by a variety of techniques (including mechanical methods) and sometimes attributed to a glass transition, has been reported in this temperature region. See, for example, reference 2 and references 1–50 therein. On examination of the literature, however, most of the mechanical relaxation studies reported in this region have been in low density

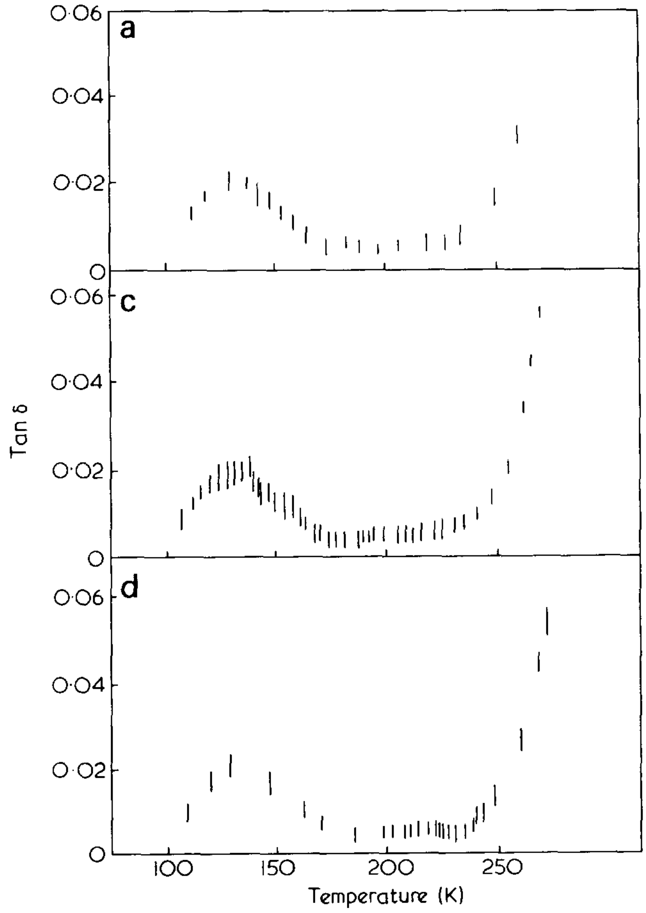

Figure 3 Loss factor tan δ in torsion for three different atmospheres. (Drawn specimen, error bars represent extreme values). a, nitrogen; c, argon; d, air

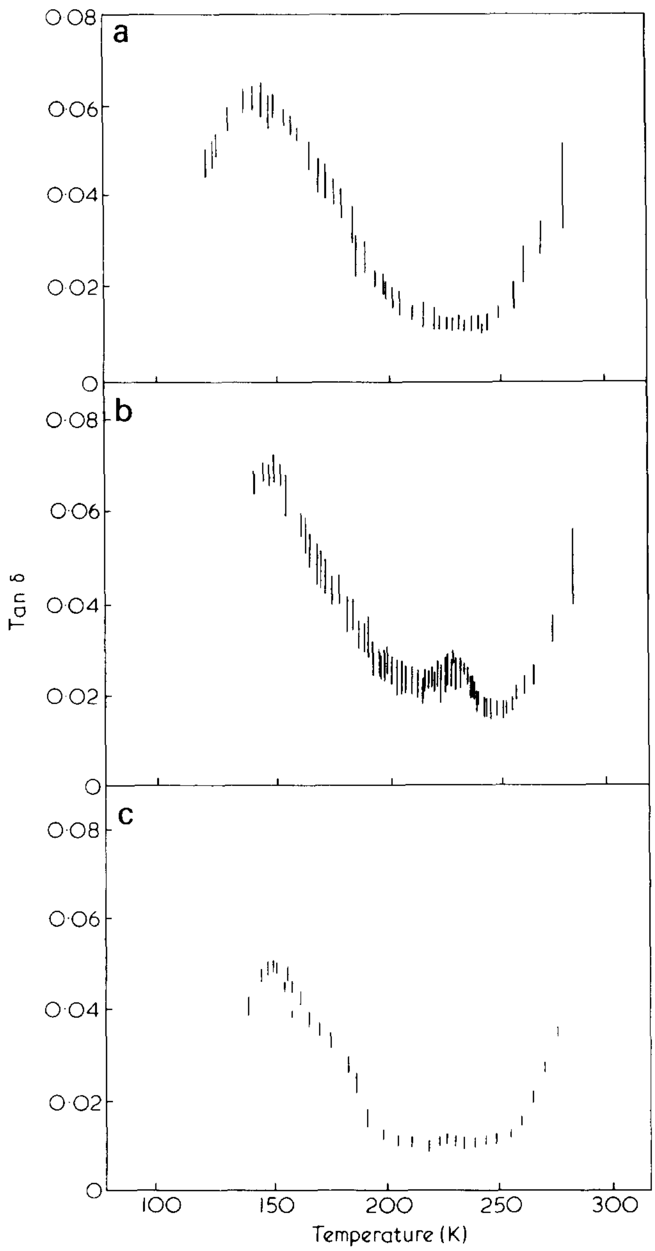

Figure 4 Loss factor tan δ for isotropic specimen, (a) Tension in argon; (b) tension in air; (c) torsion in air. (Error bars represent extreme values)

(branched) polyethylene. The so-called β peak has been observed many times and its relative absence in linear polyethylene demonstrated by Kline, Sauer and Woodward[3], Oakes and Robinson[4], Illers[5] and Reding, Faucher and Whitman[6]. Clark, Turner-Jones and Sandford[7] are doubtful of the peak they reported at 220K in linear polyethylene using the vibrating reed in vacuum at 50–300 Hz.

Our results both in torsion and tension under atmospheres of nitrogen, argon or helium confirm the absence or near-absence of the β peak in linear polyethylene. It seems clear, therefore, that the 220K peak we report in tensile measurements in air is probably not a material effect, but one of different origin. (It is still, of course, of practical relevance in the applications of polymers such as polyethylene for example in refrigeration, where an atmosphere of air or carbon dioxide may exist).

Our apparatus is, we think, more sensitive than that of other workers and we have also used several different environmental gases which is not, as far as we can ascertain, usual practice. We can, in fact, find very few references in the literature to the environmental gas used in tests. Kastelic and Baer[8] investigated the effect of nitrogen and argon on relaxations in polycarbonate and poly(ethylene terephthalate) in torsion, but no significant effects were found. The usual tensile apparatus quoted in most papers on mechanical relaxation is the Rheovibron which is a relatively high frequency device not capable of the accuracy (tan $\delta < 0.001$) which we can attain. This is demonstrated by the detection of a fine structure in the γ-relaxation which may be seen in *Figure 1* and on which we have already commented elsewhere[9].

EXPLANATION OF THE EFFECTS

We have demonstrated that certain effects occur in tension but not in torsion. These are (a) a peak at 220K which appears only when experiments are conducted in air and (b) differences in the level of tan δ over the whole temperature range depending upon the environmental gas.

The fact that these effects occur in tension but not in torsion suggests an origin in the dilatation which accompanies a tensile test. It is not at present possible to put forward a quantitative theory and, in any case, a great deal more experiment needs to be done in order to test any theory. There are, however, several plausible explanations of the observed effects.

(i) Surface adsorption and desorption of gas during cyclic strain.

(ii) The generation, growth and collapse of voids in the material during cycling.

(iii) The pressure-controlled percolation of gas into and out of the material during cycling ('sponge' effect).

(iv) The thermoelastic effect (diffusion of heat produced i.e. absorbed) by straining modified by the diffusivity of the surrounding gas.

220K peak

The 220K peak is observed only in air (note, no special arrangements were made to dry the air).

The main components of air which we have not investigated separately are oxygen, carbon dioxide and water. Since there is a phase transition in CO_2 at 194.6K it is tempting to attribute the presence of the 220K peak to CO_2. We would argue that cyclic straining or thermoelastic effects will cause cyclic changes in the amount of adsorbed CO_2 causing measurable losses.

Assuming the heat of adsorption of CO_2 to be about 7000 calories per mole the maximum loss at 220K then corresponds to the cyclic adsorption of 7×10^{14} CO_2 molecules. This amounts to a monolayer covering an area of about 25 mm^2 which is less than the surface area of the specimens. The maximum loss peak assuming the above mechanism would be expected to occur above the phase transition temperature as observed, since at or below this temperature adsorption should be complete.

Environmental effects

Here we consider the suggested possibilities one at a time:

(i) Surface adsorption and desorption is unlikely to be the cause in this case, since the observed effects exist well above the boiling points of the gases involved and they are not temperature sensitive. In addition a higher loss would be expected from the higher boiling point gases, contrary to observation.

(ii) It is known (Brown[10]) that crazing is initiated at or near liquid nitrogen temperature in polyethylene and other polymers by the plasticizing effect of nitrogen and argon. However, the effect is stated to cease above 150K and in any case involves far higher strains (5%) than those used in our studies (0.1%).

(iii) Calculations following Kambour[11] on the sponge effect lead to a predicted tan δ of about 10^{-6}, unobservable with our techniques.

(iv) The thermoelastic effect has been shown by Zener[12] to explain quantitatively certain observed losses in metals. The intensity of the effect, involving as it does the diffusion to the surroundings of the heat produced or absorbed by *elastic* straining of a solid may be expected to depend upon the diffusivity of the surrounding medium.

In our case the diffusivity of helium is 9 times greater than that of nitrogen, thus we expect the highest loss to occur in helium, as observed. In addition there is a frequency dependence of the thermoelastic effect due to the time taken for heat to diffuse through the specimen. With the frequency and specimen size we were using this time is of the order of the period of oscillation. Again, more experiments over a frequency range using specimens of a variety of sizes and composition are called for.

CONCLUSIONS

We have shown that measured loss in cyclic tensile deformation of high density polyethylene depends markedly upon the environmental gas. (1) A loss peak at 220K occurs in air, we tentatively assign this to cyclic adsorption and desorption of carbon dioxide. (2) The overall level of loss over the range 77K to 250K depends upon the gaseous environment, being highest in helium. We suggest that this is a thermoelastic effect. Neither of these effects occurs in torsion.

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