

C. C. Lee and P. V. Wright

ture and δl is a small length. The well known examples of polymers which form extended chain crystals, polytetrafluoroethylene and polyethylene crystallized at high pressures, are known to have disordered crystalline lattices at temperatures close to the melting temperature. Bassett has shown that the polyethylene lattice transforms from an orthorhombic to a disordered hexagonal structure under the high pressure conditions at which chain extension occurs.

A study of the morphology of the poly(ethylene oxide) complexes is in progress. In a preliminary inspection¹ by scanning electron microscopy, the

fracture surface of a sample of the sodium iodide complex which had been slowly cooled from the melt was compared with a similarly treated sample of the uncomplexed polymer. This showed that discrete lamellar structures several thousand angstrom units in thickness were present in the complexed polymer which could not be observed in the uncomplexed polymer. Further work is required to establish whether these structures represent individual extended chain lamellae and so to determine whether the cooperative process which gives rise to the order-disorder transformation is involved in a morphological change.

The University of Sheffield, Department of Ceramics, Glasses and Polymers, Elmfield, Northumberland Road, Sheffield S10 2TZ, UK
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Conversion of dielectric to viscoelastic data

In a recent communication¹ it has been shown that it is possible to relate the viscoelastic loss angle with the equilibrium real and imaginary parts of the complex dielectric permittivity in the α -transition zone of some amorphous polymers, by means a formula obtained from a main result of Di-Marzio and Bishop²:

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + KG^*(\omega)} \quad (1a)$$

with

$$K = \frac{4\pi R^3}{kT} \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \quad (1b)$$

where $\epsilon^* = \epsilon' - j\epsilon''$ is the complex dielectric permittivity, G^* the dynamic shear modulus, R the radius of the rotating group, k the Boltzmann constant and T the absolute temperature.

These results have been obtained by generalizing Debye's theory to the case where the friction coefficient, $\zeta(\omega)$, is a function of the frequency.

From equations (1) we can obtain:

$$\tan \delta_{\text{visc}} = - \frac{(\epsilon_0 - \epsilon_\infty)\epsilon''}{(\epsilon_0 - \epsilon')(\epsilon' - \epsilon_\infty) - \epsilon''^2} \quad (2)$$

which depends only on dielectric parameters. The viscoelastic $\tan \delta$

values for some polymers [poly(vinyl acetate)(PVAc) and poly(ethyl methacrylate)(PEMA)] calculated from this equation agree with the direct experimental data, as shown in *Figure 1*.

In some cases it is necessary to apply the time-temperature superposition method and in others (curve C in *Figure 1*) a shoulder appears, possibly due to the fact that at high temperatures two mechanisms of relaxation are superimposed: one is due to the glass-rubber transition (α) and the other is due to the first of the secondary transitions (β) in the glass zone. Finally, in another case (curve B), the value of the $\tan \delta$ peak is not the same in all the cases that we compare, but this is not a critical question because of the difficulties of measuring the $\tan \delta$ exactly at the top of the transition.

We have checked some empirical equation for the α -transition and show how to reduce the dielectric data represented with a Havriliak and Negami arc³ to the viscoelastic data by means of equation (2). This arc equation is:

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{(1 + (j\omega\tau_0)^{1-\alpha})^\beta} \quad (3)$$

When we substitute the real and ima-

inary parts of this equation into equation (2) we obtain, after some rearrangements:

$$\tan \delta_{\text{visc}} = \frac{r^{\beta/2} \sin \beta\theta}{r^{\beta/2} \cos \beta\theta - 1} \quad (4)$$

where

$$r = \left[1 + (\omega\tau_0)^{1-\alpha} \sin \frac{\pi}{2} \alpha \right]^2 + \left[(\omega\tau_0)^{1-\alpha} \cos \frac{\pi}{2} \alpha \right]^2$$

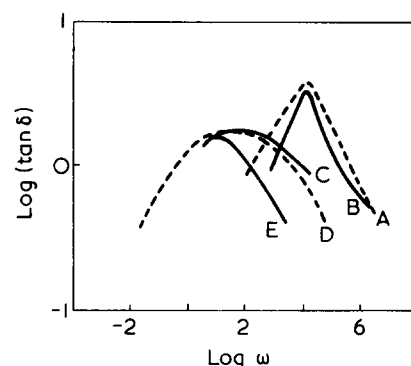


Figure 1 Loss tangent for PVAc and PEMA: A, PVAc (mechanical)⁶ 75°C; B, PVAc (mechanical from dielectric)⁷ 75°C; C, PEMA (mechanical from dielectric)⁸ 100°C; D, PEMA (mechanical)¹¹ 100°C; E, PEMA (mechanical at 1 Hz to eliminate the β peak)⁹ 100°C

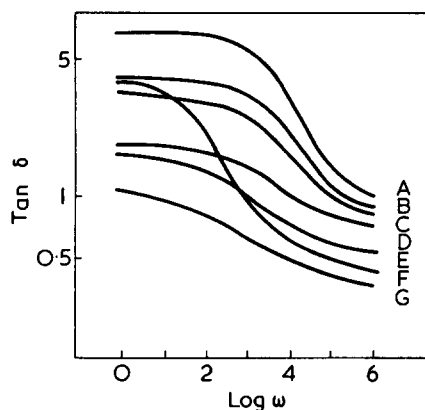


Figure 2 Loss tangent for some polymers from the Havriliak and Negami equation: A, PVAc¹⁰ (76.1°C); B, PnOcMA⁴ (21°C); C, PnHMA⁴ (40°C); D, PnBMA⁴ (59°C); E, PMA⁴ (30°C); F, PChMA⁴ (121°C); G, PMMA isotactic⁴ (63°C)

$$\theta = \arctan \frac{(\omega\tau_0)^{1-\alpha} \cos(\pi/2)\alpha}{1 + (\omega\tau_0)^{1-\alpha} \sin(\pi/2)\alpha}$$

We have chosen polymers for which we know the dielectric data⁴ and have calculated $\tan \delta$ from equation (4). From the comparison it follows that the behaviour at high frequencies

($>10^8$ Hz) is asymptotic to a constant value, and, at low frequencies, $\tan \delta \rightarrow \infty$. We can see these facts in the Figure 2 and we also have:

$$\lim_{\omega \rightarrow \infty} \frac{r^{\beta/2} \sin \beta\theta}{r^{\beta/2} \cos(\beta\theta) - 1} = \tan \left(1 - \alpha\right) \frac{\pi}{2} \beta \quad (5)$$

This behaviour in the low frequency marginal zone has been by Havriliak and Negami⁴, although they attribute it to the possibility of another relaxation in the low frequency range; this conclusion is clearly unjustified. Consider that it is necessary to change the α and β parameters in these zones if we want to adjust the arc to the real behaviour.

Our conclusions closely resemble those of Bordewijk⁵ who claims from the analysis of the asymptotic behaviour of the distribution function that, in the high or low frequency zones, it is necessary to choose carefully others parameters in order to fit the experimental data.

R. Diaz Calleja

Laboratory of Thermodynamics, Department of Chemistry (UPB), ETSIIB Barcelona 14, Spain
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