Effect of water on relaxations in the glassy and liquid states of poly(propylene oxide) of molecular weight 4000

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The complex relative permittivity of poly(propylene oxide) (PPO) of molecular weight 4000 containing 1.23 wt% water has been measured in the temperature range 77 to 325 K and frequency range 12 Hz to 500 kHz, and the results are compared with the corresponding study of pure PPO-4000. On the addition of water, all the three processes, namely the β-process (at $T<T_g$) and the α- and α'-processes (at $T>T_g$), are shifted to higher temperatures. The strength of the β-process remained unchanged but that of the α and α'-processes increased. The halfwidths of the three processes remained unchanged on dilution with water. The decrease in the relaxation rate of the β-process is suggested to be due to hydrogen bonding of the $-CH(CH_3)-O-CH_2-$ group with water molecules. Water antiplasticizes PPO-4000 and this is interpreted as due to the increased chain length when the chain ends become linked via hydrogen bonds. The static permittivity is increased by $\sim 30\%$ on addition of 1.23 wt% water.

(Keywords: poly(propylene oxide); permittivity; relaxation)

INTRODUCTION

In a detailed study of the effect of water on the dynamic mechanical properties of poly(propylene oxide) of molecular weight 4000 (PPO-4000), Cochrane *et al.*[1] found that the equilibrium shear compliance of the polymer increased by up to 4 decades when 1% water was added to the dried polymer melt, but the solution viscosity was only 5% less than the pure melt viscosity. They deduced that the equilibrium shear compliance is more sensitive to the long-time properties of the first moment of relaxation spectrum and can be influenced by mechanisms too weak to produce differences in the viscosity. Thus the change in the properties could be associated with the polymer molecules being linked extensively by H-bonded water.

PPO-4000 also exhibits a secondary relaxation[2] at temperatures near T_g, which is associated with the localized motions of the chain and contributes to the short-time dynamic shear and dielectric properties of the polymer, as well as a relaxation at $T \gg T_g$, which is associated with the normal modes of the polymer chain and contributes to its very-long-time properties. Both relaxations are likely to be affected by the hydrogen bonding between the end groups of the polymer chain. It, therefore, is important to study the effect of water on the dielectric properties of PPO-4000 in the entire range of its liquid and glassy states.

There are two purposes of this study, namely (i) to investigate whether the addition of water alters the dielectric properties of the polymer melt in a manner similar to that reported for mechanical properties[1] and (ii) to determine how the contribution from secondary relaxation is altered as a result of hydrogen bonding between the chain ends. Pure PPO-4000 has been studied several times before (for a review of this work see ref. 2), but mostly at temperatures above T_g. Since the samples, which the various workers measured, differ in both their respective constitutions and molecular weight distributions and are also likely to be different from our sample, it was necessary to measure the dielectric properties of our pure sample again so that a justifiable comparison with its water mixtures could be made. This too was done and the results are included.

EXPERIMENTAL

The dielectric permittivity ε' and loss ε'' and the loss factor $\tan\delta$ of the melt and glass samples were measured over the frequency range 12 Hz to 1 kHz by means of a General Radio 1689 impedance bridge and above 1 kHz by a General Radio 1615A capacitance bridge. The latter assembly has been described earlier[3].

The three-terminal dielectric cell was constructed of stainless steel. Mycalex discs were used to separate the low and the high electrodes from the ground shields. In all respects the cell was similar to the one described earlier. The capacitance of the cell in air was nominally 11 pF.

The thermostat assembly was constructed of a cylindrical aluminium block which had a heater wire wound around it. The dielectric cell contained in a hermetically sealed glass tube was snuggly fitted inside a ~ 27 mm diameter concentric cavity in the block. The

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entire assembly was kept in a dewar containing liquid nitrogen.

Poly(propylene oxide) was obtained from Aldrich Chemical Company. The mixture with distilled deionized water was prepared by weighing.

RESULTS

In *Figure 1* are shown the plots of the dielectric loss factor tan δ, measured at 1 kHz at different temperatures from 77 to 325 K, of PPO-4000 and its 1.23 wt% water-containing mixture. The plot for pure PPO-4000 shows three relaxation peaks, β at 167 K, α at 215 K and α' at 244 K, as observed before by several workers[4–7] (who used notation 'A' for the α- and 'B' for the α'-process in the melt) and their temperatures agree with those reported in the literature. In 1.23 wt% water mixture, the β-relaxation peak is completely removed and only a change in slope of the tan δ *versus* temperature plot remains near 175 K; the height of the main or α-relaxation peak is increased by 14%; the minimum at $T \sim 230$ K becomes deeper and is shifted to a higher temperature by ~ 4 K; the height of the α'-relaxation peak is decreased by 5% and shifted to a higher temperature by ~ 2 K; the subsequent minimum at 280 K becomes much shallower, its temperature decreased by 18 K and the dielectric loss factor raised by nearly a factor of 10 at $T > 280$ K.

Beginning from the low-temperature end, the isothermal spectrum of β-relaxation observed below T_g merges with the spectrum of α-relaxation as seen in *Figure 1*, and a separate β-peak could be discerned only at temperatures below 165 K, as evident in *Figure 2*. The dielectric loss tangent at the β-peak at these temperatures is substantially lower than that in the pure polymer melt,

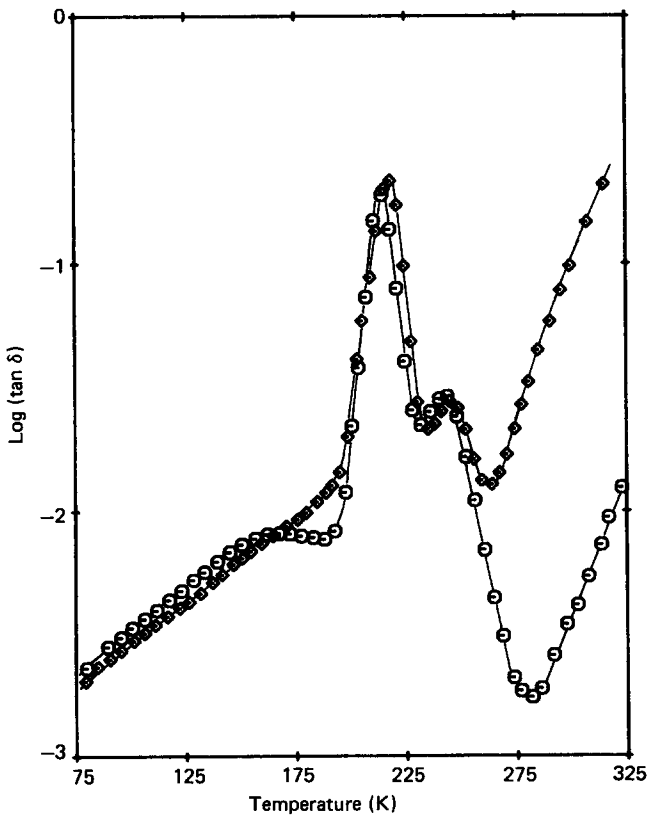

Figure 1 The dielectric loss tangent tan δ at 1 kHz plotted against temperature: ○, pure PPO-4000; ◇, 1.23 wt% water–PPO mixture

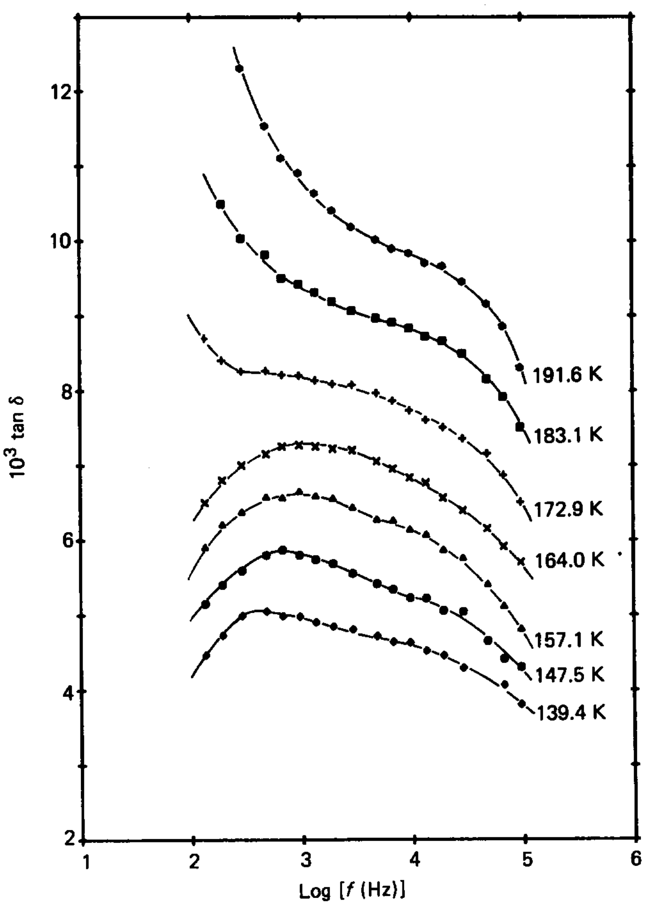

Figure 2 The isothermal spectra of tan δ in the β-relaxation region of 1.23 wt% water–PPO mixture at different temperatures

and the large contribution to tan δ from the α-relaxation made determination of the frequency of the β-relaxation peak less ambiguous.

The dielectric loss spectra in the α-relaxation range of pure PPO-4000 and its 1.23 wt% water mixture are shown in *Figure 3*. Clearly, the height of the α-relaxation peak observed is increased on addition of water by ~ 48% and shifted to a lower frequency for the same temperature of measurement.

The corresponding dielectric loss spectra in the α'-relaxation range are shown in *Figure 4*. Similar to the effect on the α-relaxation, the height of the α'-peak is increased and its frequency lowered by the addition of 1.23 wt% water.

In order to investigate whether or not the shape of the spectrum of α- and α'-processes is altered by the addition of water, normalized plots of $(\varepsilon''/\varepsilon''_{max})$ against $\log(f/f_{max})$ were constructed. These are shown in *Figures 5* and *6*, respectively. It is seen that the halfwidth (2 decades) of the α-relaxation remains unaltered on the addition of water. The spectrum correspond to a $\beta = 0.39$ in the Cole–Davidson equation and $\beta = 0.51$ in the Williams–Watts equation. However, neither of the two empirical equations fit the data satisfactorily in the entire frequency range, partly due to the contributions from the α'-process at the low-frequency end of the spectrum and from the β-process at the high-frequency end, seen in *Figures 1, 5* and *6* and partly because of the intrinsic deviation of the behaviour from these equations in poly(propylene oxide)s, as noted by Alper *et al.*[5]

On addition of water, the shape of the α'-relaxation spectrum also remains unaltered, at least in the

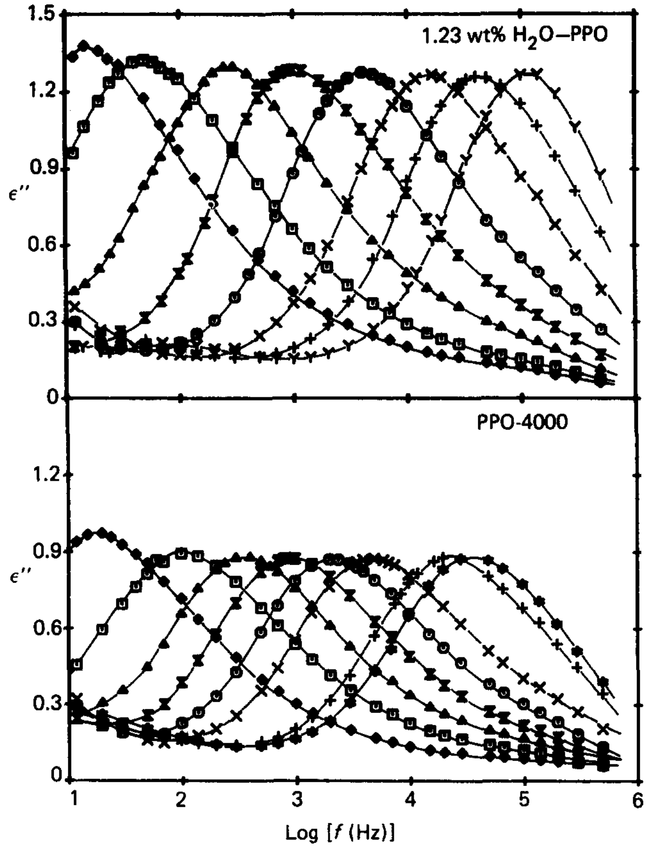

Figure 3 The isothermal spectra of ε'' in the α-relaxation region of pure PPO-4000 (bottom) and its 1.23 wt% water mixture (top). For pure PPO: ◆, 209.1 K; □, 211.0 K; ▲, 214.0 K; ⧗, 215.9 K; ○, 217.8 K; ×, 220.6 K; +, 224.2 K; and ★, 227.0 K. For 1.23 wt% water mixture, the corresponding temperatures are: 210.7 K, 212.8 K, 216.2 K, 219.5 K, 223.3 K, 227.2 K, 231,2 K and Y, 234.6 K

uppermost 25% of the peak. Because of the relatively large contributions both from the d.c. conductivity at the low-frequency end and from the relatively stronger α-process at the high-frequency end, the complete spectrum of the α'-relaxation could not be obtained.

The frequency f_{max} of the maximum loss, which is a measure of the average rate of a relaxation process, for the β-, α- and α'-processes is plotted against reciprocal temperature in *Figure 7*. The rate of the three processes is seen to decrease on the addition of water. The rates of the α- and α'-processes were fitted to the Vogel–Fulcher–Tamman equation:

$$f_{max} = A \exp[-B/(T-T_0)]$$

For the pure polymer, $A = 18.8$ GHz, $B = 640.0$ K and $T_0 = 177.9$ K for the α-process and 367.0 MHz, 946.6 K and 169.1 K, respectively, for the α'-process. For 1.23 wt% water polymer mixture, the corresponding values are 839.9 GHz, 1051.6 K and 168.2 K, respectively, for the α-process and 1.0 GHz, 1089.5 K and 168.2 K, respectively, for the α'-process. The values for the α'-process differ from those of ref. 2, largely because of the difference of molecular weight and molecular weight distribution of the two samples of PPO. These values should be used only for obtaining the data in the frequency range 12 Hz to 200 kHz. The rate of β-relaxation was not fitted to the Arrhenius equation because the uncertainty associated with their determination is large. The results of pure PPO-4000 agree reasonably well with those observed by others[2,4–7], and the interpretation of these results is the same as already given by them[2,4–7]. Therefore, we are main concerned with a discussion of the effect of water on the behaviour of PPO-4000.

DISCUSSION

Addition of water to an amorphous polymer usually lowers its T_g or plasticizes it. This implies that the relaxation rate near T_g is increased by the addition of

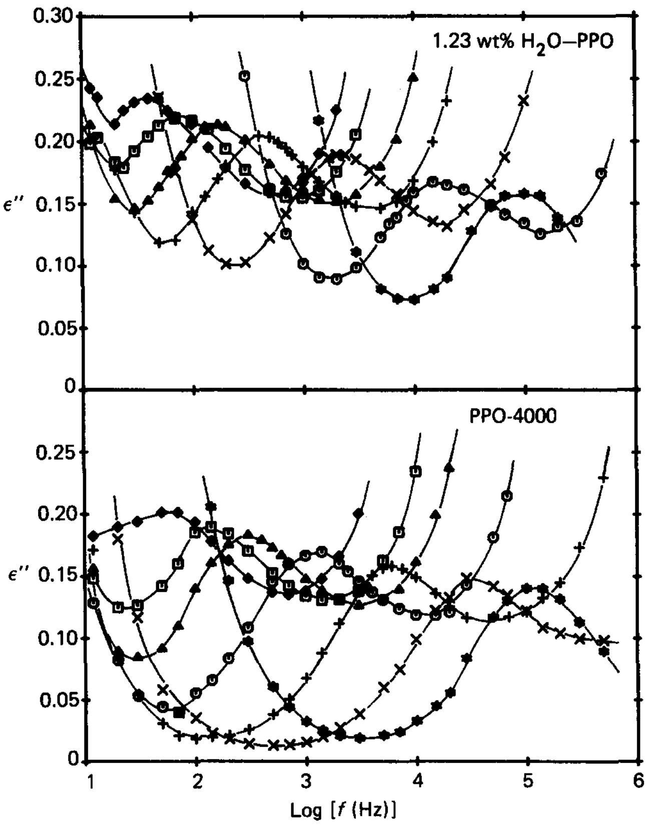

Figure 4 The isothermal spectra of ε'' in the α'-relaxation region of pure PPO-4000 (bottom) and its 1.23 wt% water mixture (top). For pure PPO: ◆, 229.9 K; □, 232.2 K; ▲, 236.6 K; ○, 245.0 K; +, 256.7 K; ×, 270.3 K; and ★, 285.7 K. For 1.23 wt% water mixture: ◆, 232.9 K; □, 234.6 K; ▲, 237.9 K; +, 242.1 K; ×, 251.8 K; ○, 267.1 K and ★, 284.5 K

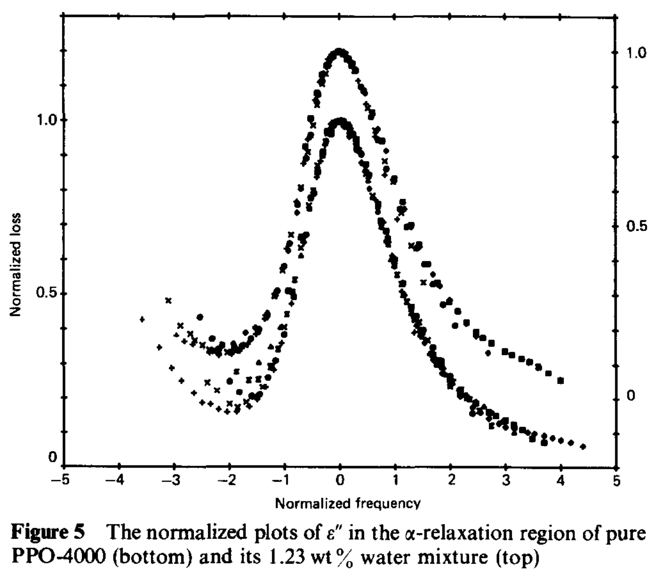

Figure 5 The normalized plots of ε'' in the α-relaxation region of pure PPO-4000 (bottom) and its 1.23 wt% water mixture (top)

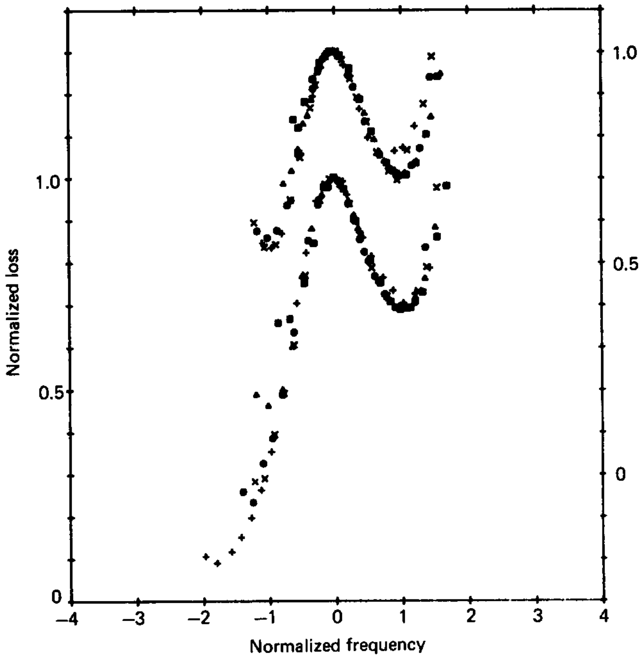

Figure 6 The normalized plots of ε'' in the α'-relaxation region of pure PPO-4000 (bottom) and its 1.23 wt% water mixture (top)

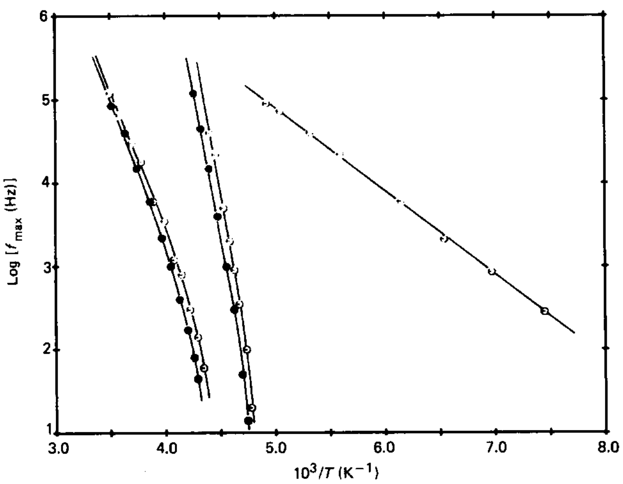

Figure 7 The frequency of maximum loss in the α'-, α- and β-relaxation regions: ○, PPO-4000; and ●, its 1.23 wt% water mixture

water. The decrease in the dielectric relaxation rate, seen in *Figures 1, 3, 4* and *7*, on the addition of water to PPO-4000 is, therefore, unusual and should be regarded as a reflection of hydrogen-bond interactions between water molecules and PPO-4000 chains.

Assuming a molecular weight of 4000, we calculate that a weight fraction of 0.45% water is adequate to achieve a linear combination of polymer chains into one long chain if the bonding occurred via hydrogen bonds at the chain-terminating hydroxyl groups. Therefore, the remaining 0.78 wt% (out of 1.23 wt%) water would hydrogen bond with some of the oxygen groups within the polymer chain and may affect the relaxation characteristics of those segments which are hydrogen bonded to the remaining number of water molecules.

Hydrogen bonding alters both the relaxation rates in the liquid PPO-4000 and in its glassy states, as well as the total polarization or strength of dielectric relaxation. The former is due entirely to a change in the intermolecular interactions between the segments within a chain or segments of different chains. The latter is partly due to the much higher dipole moment of the water molecule and partly due to any dipolar correlations introduced by the hydrogen bonding. The change in the relaxation rates of the various processes on addition of water is of interest because it represents the effects on the friction coefficient of segmental motions. We discuss them in the following.

Relaxations below T_g

Figure 2 shows that the β-relaxation peak in the mixture is not resolved until $T < 173$ K. This is due mainly to an overwhelmingly large contribution to tan δ from the α-process at the low-frequency end of the spectrum. At temperatures where the peak becomes clear, the height of the peak, i.e. tan δ_{max}, is approximately the same as observed in the pure PPO-4000 (see ref. 2). The height of the peak decreases rapidly with temperature and the γ-process begins to become resolved at a higher frequency. The temperature at which the γ-process begins to become resolved and the magnitudes of tan δ associated with it are similar to those observed in the pure PPO-4000 (ref. 2). Thus the broad relaxation observed at 164.8 K further broadens and gives indication of two components, β and γ, as the temperature is decreased—the combined ($\beta + \gamma$) process is transformed continuously with temperature, and gives a partial resolution of the γ-process at 139.4 K. Clearly, the presence of water in PPO-4000 does not affect the height or magnitude of tan δ at temperatures below 164.8 K.

The β-relaxation peak in *Figure 1* seems to shift to a higher temperature on the addition of water. That this does occur is clearly evident in the relaxation rates or f_m plotted in *Figure 7*, where for a given temperature the rate of β-relaxation at 164 K is 22% lower in 1.23 wt% H_2O solution than in pure PPO-4000. This effect on the rate is quite different from the generally observed effect of plasticizers in polymers where the rate is found to remain unaltered on the addition of small molecules in the polymer matrix.

The features of small-scale motions associated with the β-process are difficult to rationalize in terms of both the free volume[8,9] and configurational entropy theories[10] and the observed decrease in the rate of the β-process on addition of water does suggest that intermolecular barriers play an important role in determining the features of the relaxation. The addition of water to PPO-4000 does not produce a further relaxation which could be attributed to the motion of unbonded water molecules or to the rotation of the O–H group of a water molecule (singly) hydrogen bonded to the segment of the PPO chain.

Relaxation above T_g

The strength $\Delta\varepsilon$ of both the α- and α'-relaxations is increased on addition of water to PPO-4000, as seen by an increased value of ε''_{max} in *Figures 3* and *4* although the height of the tan δ peak of the α'-process in *Figure 1* is seen to decrease. The decrease in the tan δ_{max} when the strength $\Delta\varepsilon_{\alpha'}$ of the α'-process increases is mainly due to the increase in the limiting high-frequency permittivity ε_∞ of the α'-process (which is numerically equal to the limiting low-frequency permittivity of the α-process) according to the equation for a single relaxation process:

$$\tan \delta_{max} = \Delta\varepsilon / 2(\varepsilon_0 \varepsilon_\infty)^{1/2}$$

where $\Delta\varepsilon = (\varepsilon_0 - \varepsilon_\infty)$, and ε_0 is the limiting low-frequency permittivity of a process with a single relaxation time.

The shapes of the spectra of the α- and α'- processes and their halfwidths remain unaltered on the addition of water as seen in *Figures 5* and *6*. The rates of both relaxations are seen to decrease in *Figure 7*.

Since the values of $T_0 (= 168.2\,K)$ are the same for α- and α'-processes, and their values of A and B differ, it follows that for a given temperature the 'activation energy', i.e. $\partial \log f_{max}/\partial(1/T)$, for the α'-process is greater than for the α-process. Cochrane *et al.*[1] have suggested that the α'-process is related to the normal mode contribution observed in the creep and dynamic mechanical studies and that the α-process is related to the viscoelastically faster but weaker process. The evidence in *Figure 7* shows that both processes are affected in a similar way on the addition of 1.23 wt% water to PPO-4000, but their 'activation energies' at a given temperature are affected differently.

In their careful work on the effect of water on the viscosity and equilibrium recoverable compliance $J_e{}^0$, Cochrane *et al.*[1] found that the addition of 1% water raised $J_e{}^0$ of PPO-4000 by as much as 4 decades, and caused the value of J_e^0 to become nonlinear with applied stress, without measurable change in the steady-state viscosity. The increase in J_e^0 and associated τ is equivalent to antiplasticization of PPO-4000 by water. The observed decrease of the dielectric relaxation rate or increase of the relaxation time seen in *Figure 7* confirms Cochrane *et al.*'s[1] interpretation of the dynamic mechanical measurements. While it is clear that the effect on dielectric relaxation time is much less pronounced than that on dynamic shear relaxation time, the qualitative similarity in the dielectric and dynamic shear behaviour does point to a common physical mechanism for the two types of losses in PPO-4000.

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