

α -RELAXATION OF AN ISOTROPIC PETROLEUM PITCH: CONTROLLED STRESS AND STRAIN OSCILLATORY RHEOMETRY STUDY

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Introduction

Few recent papers concerned with transient rheological experiments on pitches [1-3] have shown that time-temperature superposition and WLF procedure, widely used for polymer [4], were efficient for data analysis of such material. In this paper, the authors present the first experimental evidence and analysis of the α -relaxation phenomenon and its consequences on the applicability of the WLF procedure.

Experimental

The experimental investigation was performed using a Physica-Rheolab MC100 rheometer under both controlled stress or controlled strain test procedures. Measurements were made at T and ω in the ranges of 95 to 160 °C and of 1 to 101 rad.s⁻¹ respectively, using a standard cone/plate geometry ($D=2.5 \times 10^{-2}$ m, angle: 1°).

Results and Discussion

Data obtained under controlled stress and controlled strain superposed fairly well one on the other. This confirms that those two experimental procedures can be considered as equivalent. An original result appears in the particular G' behaviour at $T > 120^\circ\text{C}$: the isotherms tend to stack together while G'' isotherms still present significant difference. This behaviour is typical of the α -relaxation for which the molecular mobility becomes generalized as a result of the glass-transition. Nowadays, it is well established that this relaxation shows the following universal features [5,6]: (a) a $G''(\omega)$ non-Debye behaviour and (b) a non-Arrhenius T -dependence of the characteristic relaxation time τ_α . The α -relaxation can be illustrated by isochronal plots of G' , G'' and $\tan(\delta)$ (Fig. 1-2). For amorphous polymers, $\tan(\delta)$ peak amplitude is within the 6 to 30 units range and the G' step within a 3 decades amplitude [8]. The A240 obtained amplitudes are strictly in the same order of magnitude: G' step presents a 3 decades amplitude within a 20°C temperature range and the $\tan(\delta)$ a 11 units amplitude peak. The inflexion point temperature of the

G' step has been estimated at $T_\alpha=114^\circ\text{C}$. Anyway, the α -relaxation phenomenon proceeds through a temperature range as glass transition does. The corresponding peak of $\tan(\delta)$ is observed at $T_\delta=124^\circ\text{C}$ which corresponds to the end of the G' step. For $T > 130^\circ\text{C}$, the flow of material is observed (Fig. 2) as it is for amorphous polymers [7]. The shape of G'' isotherms near the α peak is commonly characterized by the two following parameters m and n ($0 < m, n \leq 1$),

$$\begin{aligned} d\log(G'')/d\omega &\sim m & \omega \ll \tau_\alpha^{-1} \\ d\log(G'')/d\omega &\sim -n & \omega \gg \tau_\alpha^{-1} \end{aligned} \quad (1)$$

A simple Debye relaxation is given for $m=n=1$ while usual values observed for polymers are $m \sim 1$ and $0 < n \leq 0.5$. The A240 obtained values are $m=1$ and $n=0.43$ which fall within polymers range. Therefore, the above (a) criterion is well satisfied. τ_α and τ_{mol} values are of the same order of magnitude and the former can be estimated from the oscillatory rheometry results: the low temperature G'' isotherms maximum corresponds to $\omega \cdot \tau_\alpha = 1$ [8]. For the curves without maximum, the shift factors a_T are used to estimate τ_α . The T -dependence of τ_α is usually well parametrized by means of the following TVF equation:

$$\tau_\alpha = \tau_{\alpha 0} \exp(\Delta\alpha_v^{-1}/(T-T_0)) \quad (2)$$

T_0 has been fitted in order to optimise the correlation coefficient ($r=0.992$). A similar analysis using the Arrhenius equation has been tested and was clearly non-linear. Therefore, the (b) criterion mentioned above is well satisfied. Obtained values of T_0 , T_δ , $\Delta\alpha_v$ and $\tau_{\alpha 0}$ are compared (Table 1) to those usually obtained for amorphous polymers and to those published for PH (poly(2-hydroxypropyl ether bisphenol A)) and PVAc (poly(vinyl acetate)) [5]. Those results show that, except for $\tau_{\alpha 0}$, the A240 characteristics fall within the usual values of amorphous polymers and especially within those of the PH and PVAc. Concerning the τ_0 parameter, the A240 value is found to be 10^2 time higher than that for PVAc and 10^3 time higher than the usual amorphous polymers value. This could be explained by the characteristic molecular scale of those species. The G' shift factor presents an asymptotic value for all $T > T_\alpha$. This effect is due to the fact that as the pitch has proceeded through the α -relaxation, its G' behaviour becomes T -independent.

This breakdown of the time-temperature superposition principle is commonly observed for miscible polymers in the glass transition region [6]. Considering the applicability of the WLF procedure, those results lead to the fact that it is only applicable at temperature lower than T_{α} . At last, comparison in Fig. 3 of the G'' shift factors with the results previously published [1] lead to the conclusion that both geometries (plate/plate and cone/plate) are fairly equivalent.

Conclusions

A relaxation is observed at 114°C as a 3 decades G' isochrone step and at 124°C as a 11 units peak of $\tan(\delta)$ isochrone. As this relaxation fulfills both the non-Debye and non-Arrhenius criteria, it is well identified as an α -relaxation. The TVF characteristic parameters of the corresponding τ_{α} are very similar to those published for amorphous polymers. The applicability criteria of the WLF method are well fulfilled at temperature lower than T_{α} . At higher temperature, G' shift factor reaches asymptotic value as the pitch has proceeded through the α -relaxation phenomena toward the pseudo-newtonian viscous liquid state.

References

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	$\tau_{\alpha 0}$ (s)	$\Delta\alpha_v$ (K^{-1})	T_0 ($^{\circ}C$)	$T_g - T_0$
PH	3.2×10^{-13}	10.4×10^{-4}	75	22
PVAc	10^{-12}	7×10^{-4}	-7	49
usual	10^{-13}	5×10^{-4}	-	50
A240	1.3×10^{-10}	6.7×10^{-4}	30	22-44

Table 1. α -relaxation parameters of various amorphous polymers and the A240 isotropic pitch.

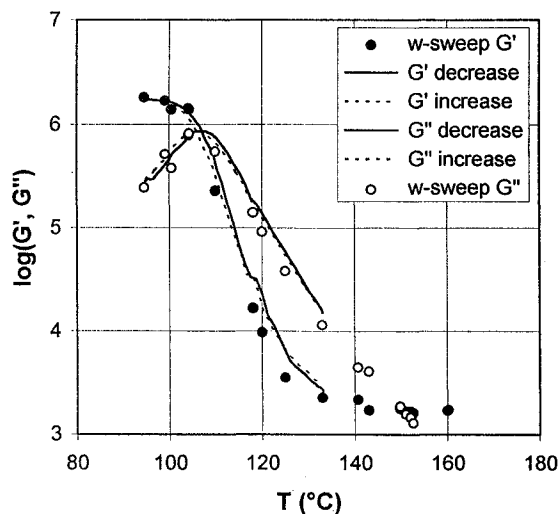


Fig. 1. G'' and G' moduli iso- ω and T scans.

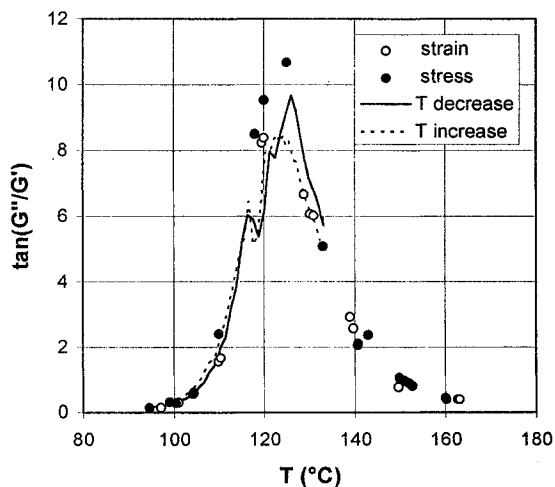


Fig. 2. Controlled stress and strain $\tan(\delta)$ isochrones and T scans at 101 rad.s^{-1} .

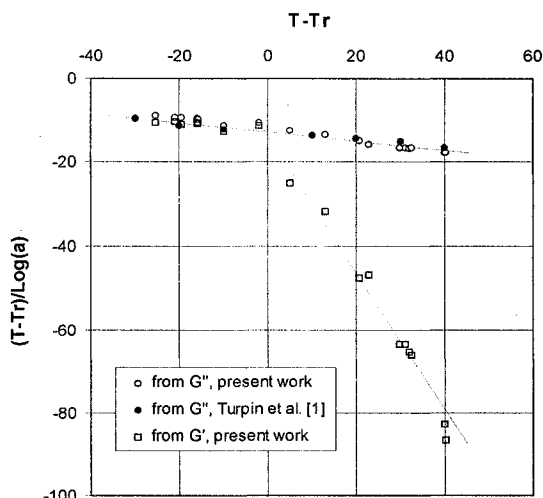


Fig. 3. WLF plot reduced to $120^{\circ}C$.