

Time-temperature Superposition and Dynamic Mechanical Properties of Metallocene Polyethylenes

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ABSTRACT

This paper is devoted to the study of dynamic mechanical behaviour of two metallocene polyethylenes (m-PE). For this purpose two metallocene linear low density polyethylene (m-LLDPE) and very low density polyethylene (m-VLDPE) were used consisting of 3.3 mol% butyl and 6 mol% ethyl branches, respectively. The m-LLDPE showed three transitions at 31, -8 and -115°C attributed to the α , β and γ -transitions, respectively. The β -relaxation was observed as a shoulder on the α -relaxation peak. Studies on the m-VLDPE revealed no appreciable α -relaxation but an increased β -relaxation than that of the m-LLDPE. The effects of cooling rate and annealing were also investigated for the m-LLDPE. Slow cooled sample showed a higher α -relaxation temperature and was appreciably greater in breadth and area than that of the sample cooled in water. No appreciable shift in either the α or β -relaxation temperature were found by comparing loss modulus of quenched and annealed sample of the m-LLDPE. The time-temperature superposition principle was also found to be applicable to the α -relaxation process of the m-LLDPE and master curve was obtained at 80°C.

Key Words:

metallocene polyethylene;
enthalpy of relaxation;
DMTA;
superposition principle;
master curve.

INTRODUCTION

When a sinusoidal stress is applied to an elastic solid, the material stores the mechanical energy without dissipation and the strain is in phase with the applied stress. When the stress is applied to a liquid, on the other hand, in a non-hydrostatic

stress state it dissipates all the energy and deformation lags 90° out of phase with the applied stress. Polymers are viscoelastic materials, which show both elastic and liquid behaviour. If a sinusoidal stress is applied to this class of materials nei-

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ther perfectly elastic nor totally liquid behaviour is observed. The strain lags behind the stress by an angle, δ , where $\delta < 90^\circ$. Phase lag results from the time necessary for molecular rearrangements and is related to molecular relaxation phenomena. The complex modulus for a viscoelastic material is defined as [1-4]:

$$E^* = E' + iE'' \quad (1)$$

where, E' is the storage modulus relating to the energy stored by the sample in one cycle as potential energy and E'' is the loss modulus which represents the energy dissipated in one cycle as heat during deformation. The ratio of the energy lost to the energy stored per cycle is defined as $\tan \delta$.

In general, linear and branched PEs exhibit three transitions prior to melting. These have been designated α , β and γ in order of decreasing temperature. However, there are some controversies regarding the assignment and the molecular interpretation of the observed transitions.

α -Relaxation

The α -relaxation is usually observed in the temperature range 20-100°C, depending on the grade of PE. The intensity of the α -relaxation increases with increasing density of PE but levels off at high density. It has been reported [5-6] that the α -peak is due to molecular motions within the crystalline phase and originates from some types of torsional motion within the crystals. It has also been interpreted as being associated with chain mobility within the crystal (e.g., segmental rotation, translation and twist). However, experiment on the linear hydrocarbon alone, $C_{94}H_{190}$, did not show the presence of an α -relaxation and it was concluded that a fold surface was necessary for the presence of the α -process [7]. Sinnott [8] by working on the dynamic mechanical properties of single crystals of linear PE demonstrated that the α -relaxation was due to the motion of chain folds at the crystal surfaces. The α -relaxation was attributed by Boyd [9-10] to the deformation of amorphous regions that occurs as a consequence of reorientation within the crystallites. He stated that the chain stem mobility can lead to redistribution of folds, cilia and intercrystalline links present in the amorphous layer. In other words, the α -relaxation occurred in the amorphous phase but required chain

mobility within the crystals. Khanna et al. [5] also attributed the α -relaxation to the deformation of interfacial regions (chains folds, loops and tie molecules) rather than chain mobility within the bulk amorphous phase, since the latter would not be affected by the crystal chain mobility.

In some samples of PE, a second transition α' has also been observed as a shoulder on the main α -relaxation [11]. This may be due to an interlamellar grain boundary slip process or motions resulting from crystallites of different thickness from those giving rise to the α -relaxation. Zhou [12] reported that only annealed samples, which showed segregation during melting displayed a significant α' relaxation, whereas samples with a single melting peak had no measurable α' relaxation. Therefore, α and α' relaxations have similar origins and the development of more than one α -relaxation can be related to the distribution of lamellae thickness in that the thinner lamellae show a transition at lower temperature.

β -Relaxation

The β -relaxation usually occurs between -30 and 20°C depending upon the grade of PE. The molecular origin of the β -relaxation is still unresolved but is commonly attributed to amorphous phase [13]. Single crystals of linear PE do not exhibit a β -relaxation [8,13]. Khanna et al. [5] proposed that the enhanced intensity of the β -peak in LDPE is due to an increased amorphous volume as a consequence of branching rather than the branches themselves. Mandelkern et al. [11] consider that it results from the motion of disordered chain units associated with the interfacial regions of semicrystalline polymers and copolymers.

γ -Relaxation

The γ -relaxation of linear and branched PE occurs between -120 and -90°C. The intensity of the γ -peak tends to decrease with increasing density indicating that it is mostly associated with the amorphous phase. Illers [5] has shown that the γ -peak is due to the amorphous fraction while Sinnott [8] and Hoffman [13] attribute it to defects in the crystalline phase. They attribute the γ -transition to the association of chain end defects in the polymer crystal. Khanna et al. [5] proposed, however, that the best model for the transition involves a crankshaft motion of short polymer chain

segments involving a minimum of three to four CH₂ units in addition to the reorientation of loose chain ends within the crystalline and amorphous fractions. The temperature at which γ -relaxation occurs is usually associated with the T_g of PE [6,14].

In the past few years a new class of catalysts has been commercialized for the production of polyolefines. These are catalysts based on metallocenes, which are organometallic compounds based on metal π -bonding to the cyclopentadiene rings. Metallocene catalysts generally consist of a transition element from Group 4b sandwiched between two cyclopentadienyl ring structures. They open up new areas for production of high quality polyalkenes with controlled molecular weights, molecular weight distribution, comonomer displacements and variable densities (i.e., crystallinities). Unlike conventional Ziegler-Natta (Z-N) catalysts, which have several active sites with different reactivity, metallocene catalysts provide only a single site for reaction [15-17]. This makes them interesting materials for the study of the effect of molecular structure on their morphology, thermal and mechanical properties.

The present paper compares the dynamic mechanical properties of two metallocene polyethylenes (m-PE). The effects of annealing and cooling rate on the dynamic mechanical response as well as the frequency response of the relaxation spectra have been investigated.

EXPERIMENTAL

The m-PEs used were supplied by Exxon Chemical and BASF with the trade names of Exact 3009 (m-LLDPE) and Luflexen 0332 H (m-VLDPE), respectively. Exact is a copolymer of ethylene and hexene-1 and Luflexen is a copolymer of ethylene and butene-1. The melt flow indices of the m-LLDPE and m-VLDPE as measured by Davenport MFI apparatus at 190°C and 2.160 kg

load are 0.15 and 0.16 g.min⁻¹, respectively. Table 1 shows the other specifications of the two polymers.

Square sheets of the two m-PEs (1.6 mm thick) were prepared using a thermostatically controlled hydraulic press by pressing the granules between two PTFE sheets at 160°C for 5 min. The sheets then were quenched in two different ways. A slow cooling rate was achieved by cooling the sample in the press, i.e. the hot press heaters were switched off and allowed to cool to room temperature (slow cooled sample). In other method the sheets were quenched in water. Annealing of the quenched m-LLDPE samples was carried out in an oven for 24 h at 80°C and 100°C and subsequently reannealed in water.

The degree of crystallinity was measured using a Perkin-Elmer differential scanning calorimeter (model DSC-2) interfaced to a PC. The thermal response was calibrated from the enthalpy of indium.

Dynamic mechanical analysis was carried out using a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) controlled by an IBM PS-2 computer. Rectangular samples with the sizes 12.7 mm × 1.6 mm × 40 mm were clamped in the measuring head of the DMTA on a steel frame supported by ceramic pillars. The sample was flexed in a dual cantilever mode by a central clamp driven sinusoidally by an electromagnetic vibrator by means of a ceramic drive shaft. The temperature was controlled using a Polymer Laboratories temperature programmer. A double skinned furnace was used to achieve the desired temperatures. Sub-ambient temperatures were achieved by filling a cooling jacket with liquid nitrogen. A temperature range of -150 to 120°C, heating rate of 1°C.min⁻¹ and frequency range from 0.01 to 20 Hz were used. Sample dimensions, geometry and predetermined calibration constants were entered into the DMTA analyzer, which allowed the computer to calculate the storage, loss modulus and tan δ as a function of frequency and temperature.

Table 1. Specifications of the materials.

| Polymer | Grade No. | \bar{M}_w (kg/mol) | \bar{M}_n (kg/mol) | PDI | Density (g/mL) | Comonomer content (mol%) |
|---------|----------------|-------------------------|-------------------------|-----|-------------------|-----------------------------|
| m-LLDPE | Exact 3009 | 102 | 40.7 | 2.5 | 0.923 | 3.3 |
| m-VLDPE | Luflexen 0332H | 97.3 | 50 | 2.0 | 0.908 | 6 |

RESULTS AND DISCUSSION

The degree of crystallinity of water cooled m-LLDPE and m-VLDPE as measured by differential scanning calorimeter (DSC) were $40\pm 2\%$ and $33\pm 3\%$, respectively. Figure 1 shows the variation in loss modulus of the water cooled m-LLDPE with temperature at 1 Hz. Three distinct transitions, corresponding to maxima in the loss modulus can be seen. These were attributed to the α , β and γ -relaxations [18].

Figures 2-4 show plots of $\log E'$, $\tan \delta$ and $\log E''$ against temperature for the water cooled m-LLDPE and m-VLDPE. There is no substantial difference between the $\log E'$ of the two m-PEs at low temperature. However, as the temperature increases to the onset of the β -relaxation and beyond the storage modulus of the m-VLDPE becomes more temperature dependent and drops more than that of the m-LLDPE. $\log E''$ shows that the α and β -relaxations of the m-LLDPE take place with a maximum in $\log E''$ at 31 and -8°C , respectively. The β -relaxation is barely discernable as a shoulder on the α -transition. The β -relaxation is strongly dependent on PE's density [19-20] and as the density increases, the transition is reduced in intensity and shifted to higher temperature. Above 0.92 g.mL^{-1} the β -relaxation merges into the α -relaxation. On the other hand, the m-VLDPE because of its lower density and higher branch content showed an appreciably larger transition with a maximum at -21°C . There are no other transitions at higher temperature, which is in agreement with the results reported for a conventional PE with 6 mol% butene-1 as a comonomer [21]. The activation enthalpy for relaxation was calculated using the

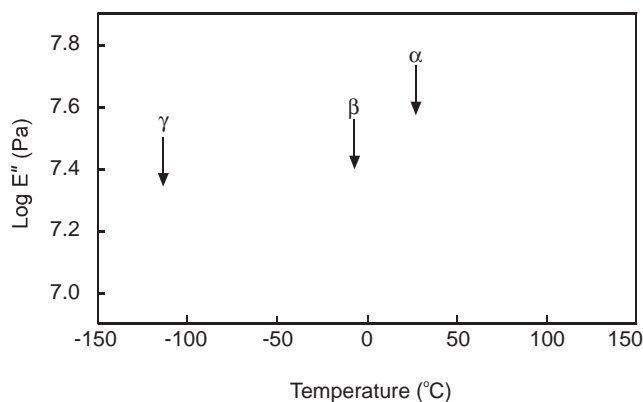


Figure 1. Variation of $\log E''$ for the m-LLDPE with temperature at 1 Hz.

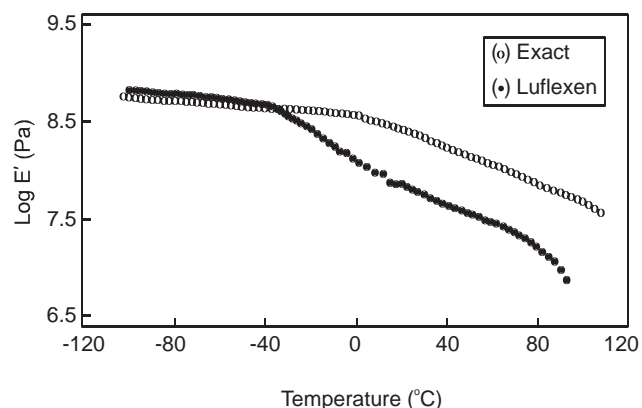


Figure 2. A comparison of $\log E'$ for the m-LLDPE and m-VLDPE at 1 Hz.

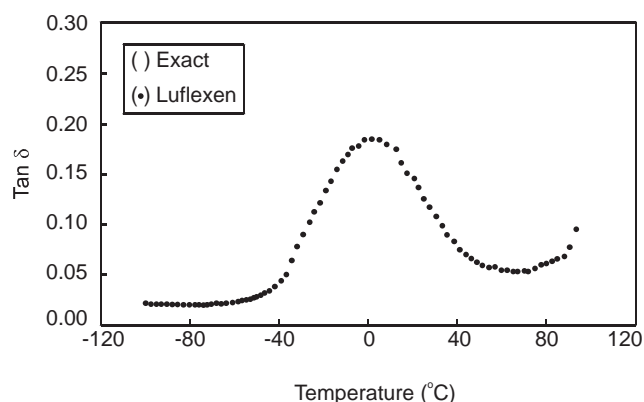


Figure 3. A comparison of $\tan \delta$ for the m-LLDPE and m-VLDPE at 1 Hz.

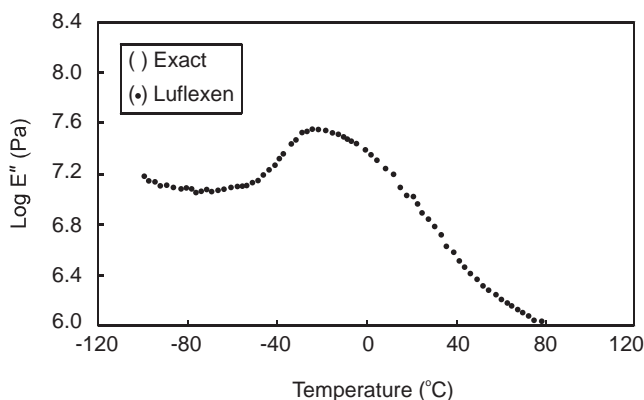


Figure 4. A comparison of $\log E''$ for the m-LLDPE and m-VLDPE at 1 Hz.

Arrhenius equation [22-23], i.e.

$$\ln f = \ln A + \frac{\Delta H}{RT_r} \quad (2)$$

where, f is the frequency, ΔH is the activation enthalpy

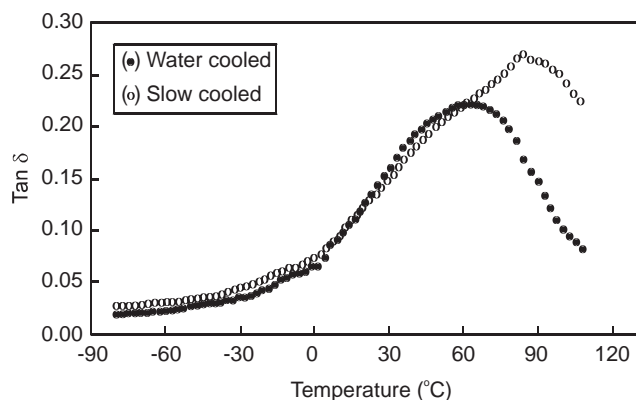


Figure 5. The effect of cooling rate on the value of the loss tangent of the m-LLDPE at 1 Hz.

of relaxation, A is a constant, R is the gas constant and T_r is the relaxation temperature. Defining T_r from the maximum in E'' , an Arrhenius plot of $\ln f$ against $1/T$ was used to determine the activation enthalpy of relaxation of the m-VLDPE. This was found to be 350 ± 60 kJmol^{-1} which is in the range of values for the β -relaxation, 265 ± 64 kJmol^{-1} [21].

The effect of crystallinity and lamellar thickness, on the relaxation temperature was also studied by cooling the m-LLDPE from the melt at different rates, as depicted in Figures 5 and 6. The α -relaxation intensity increased and shifted to higher temperature with the more crystalline slow cooled sample ($45 \pm 2\%$) over that of the quenched sample ($40 \pm 2\%$). $\log E''$ revealed an appreciable increase in the breadth and area under the α -relaxation curve. This can be attributed to an increased heterogeneity of morphology. However, the position and intensity of the β -relaxation did not change significantly.

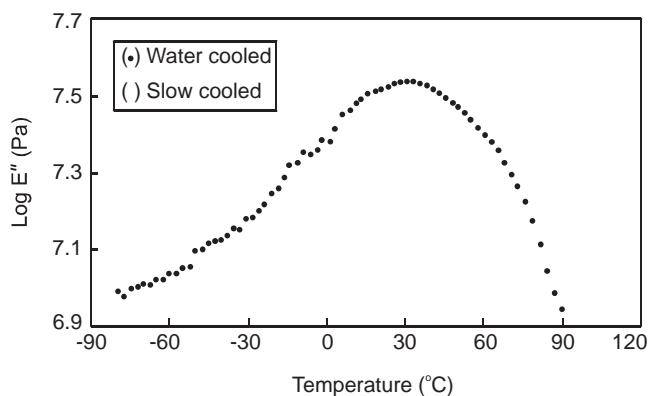
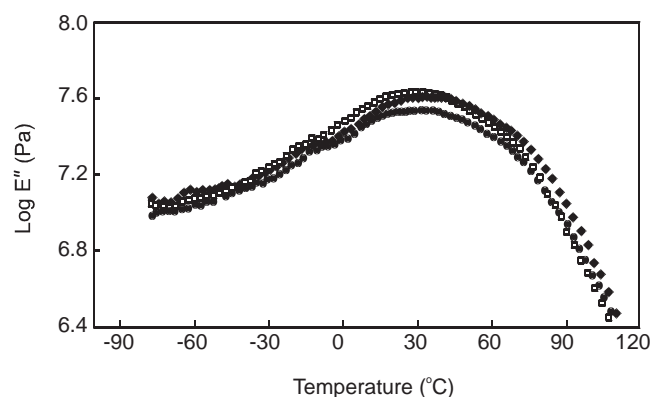


Figure 6. The effect of cooling rate on $\log E''$ of the m-LLDPE at 1 Hz.



(●) water cooled; (□) annealed at 80°C ; (◆) annealed at 100°C .

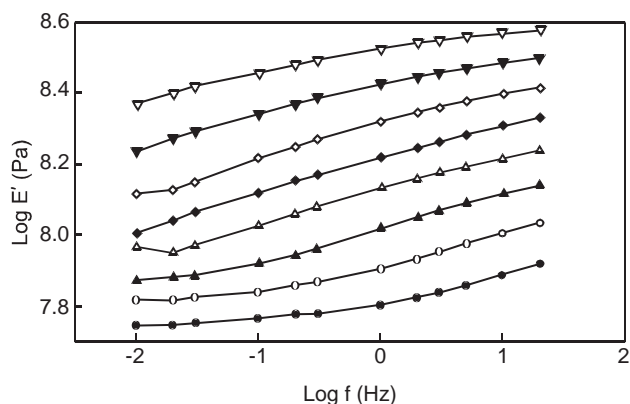
Figure 7. The effect of annealing on $\log E''$ of the m-LLDPE at 1 Hz.

The effect of annealing on $\log E''$ of the m-LLDPE is shown in Figure 7. No measurable shift either in relaxation temperature or breadth of α and β -relaxation was detected. It seems that no appreciable rejection of butyl branch from the crystals happened on annealing of the m-LLDPE at the temperatures studied since this should have increased the interfacial content and broaden the β -relaxation peak [12].

The relaxation temperature as well as the activation enthalpy for the γ -relaxation of the water cooled m-LLDPE were found to be -115°C and 87 ± 15 kJmol^{-1} , respectively. The value of activation enthalpy was very similar to that obtained for the crankshaft motion, i.e. 54 kJmol^{-1} [21] and in agreement with Khanna et al. [5] theory that the γ -relaxation originated from the rotation of small sequences due to conformational changes via a crankshaft motion in conjunction with reorientation of loose chain ends within crystalline and amorphous fractions.

The dependence of the α -relaxation on frequency was investigated for the water cooled m-LLDPE. Figures 8 and 9 show plots of $\log E'$ and $\log E''$ against frequency at several temperatures, respectively. The α -relaxation was identified from the maximum in the loss modulus. It shifted to higher frequencies with increasing temperature.

It would be desirable to have the DMTA response of a polymer over a wider range of frequencies to predict its behaviour but in conventional DMTA the range of frequencies is limited from 10^{-2} to 10^2 Hz. A method to obtain the response of the material over a wider



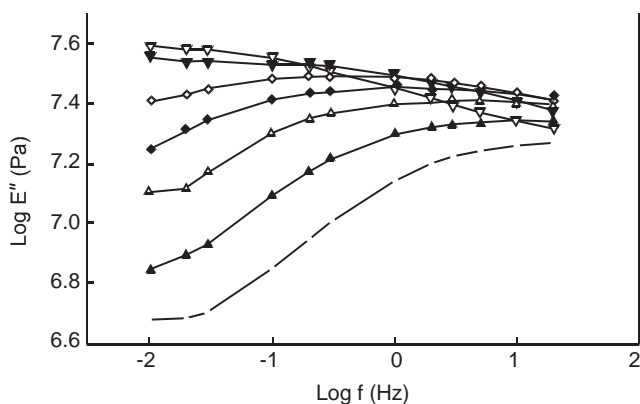
(●) 80°C; (○) 70°C; (▲) 60°C; (△) 50°C; (◆) 40°C; (◇) 30°C; (▼) 20°C; (▽) 10°C.

Figure 8. The dependence of storage modulus on frequency for the water cooled m-LLDPE at various temperatures.

range of frequency is to use the time-temperature superposition principle. This originated from the fact that the effect of time and temperature are similar for most viscoelastic materials.

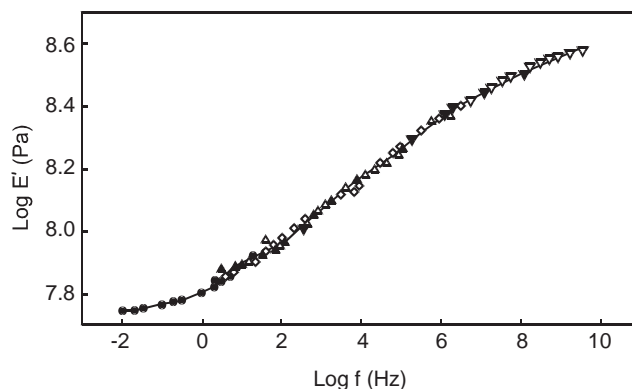
In order to obtain a reliable master curve, Cembrola [24] suggested that both horizontal and vertical shifts should be applied in the case of PE. However, a superficial analysis of the results showed that if each curve was shifted horizontally to the left or right by a shift factor $\log a_T$, coincidence of adjacent curves could be achieved for the m-LLDPE. Figure 10 shows the master curve for $\log E'$ at a reference temperature of 80°C. A reasonable superposition was obtained over the frequency range 10^{-2} to 10^{10} Hz.

The importance of the master curve in practice is



(○) 70°C; (▲) 60°C; (△) 50°C; (◆) 40°C; (◇) 30°C; (▼) 20°C; (▽) 10°C.

Figure 9. The dependence of loss modulus on frequency for the water cooled m-LLDPE at various temperatures.



(●) 80°C; (○) 70°C; (▲) 60°C; (△) 50°C; (◆) 40°C; (◇) 30°C; (▼) 20°C; (▽) 10°C.

Figure 10. A master curve for the water cooled m-LLDPE at 80°C.

obvious. However, since crystal lattices in a crystalline material make some difficulties to chain relaxations, the usefulness of the superposition adopted for glassy materials is not confirmed. In order to determine the physical significance of the applied superposition the amount of activation enthalpy for the transition was obtained using the following equation [25-26]:

$$\Delta H = R \left[\frac{d \ln a_T}{d(1/T)} \right] \quad (3)$$

where, ΔH is activation enthalpy, a_T is shift factor, T is absolute temperature and R is the gas constant. By plotting $\ln a_T$ against $1/T$ a linear relationship was observed (Figure 11) and the activation enthalpy calculated from the slope was found to be 207 ± 50 kJmol $^{-1}$. This is in the range of values that have been reported [21] for the α -relaxation, 185 ± 72 kJmol $^{-1}$. This shows that the

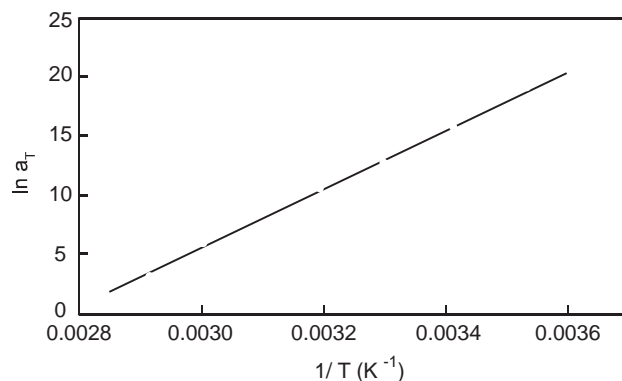


Figure 11. An Arrhenius plot of $\ln a_T$ against $1/T$ for the water cooled m-LLDPE.

relaxation process, which was examined to evaluate the reliability of the principle of time-temperature superposition, was mainly an α -relaxation. Nevertheless, a slightly higher value could be related to contributions from other relaxations such as β -relaxation.

CONCLUSION

The dynamic mechanical relaxation behaviours of two m-PEs have been studied by DMTA. The m-LLDPE showed three transitions in which the β -relaxation appeared as a shoulder on the α -relaxation. While a higher α -relaxation temperature was observed for the slow cooled m-LLDPE compared to that of the quenched sample, no appreciable shift in the β -relaxation was observed. The variation of $\log E''$ with temperature showed that the α -peak became broader than that of the quenched sample. This revealed a greater degree of heterogeneity within the sample. By comparing $\log E''$ of quenched and annealed samples it was found that there was no appreciable shift in either α or β -relaxations. DMTA studies on the m-VLDPE showed no appreciable α -relaxation and the β -relaxation was more significant. It also appeared at lower temperatures than that of the m-LLDPE.

The frequency dependence of the molecular relaxation in the bulk m-LLDPE was also investigated over a limited range of frequencies and the master curve of frequency dependence of $\log E'$ obtained at 80°C.

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