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Creep and glass transition behaviour of fractionated petroleum pitches: the influence of molecular weight and its distribution

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The dependence of viscoelastic properties on the molecular weight of fractionated and and blended petroleum pitches was examined in relation to the creep and glass transition behaviour. The steady-state viscosity, η, as a measure of energy dissipation, and the steady-state creep compliance, J_e^0, as a measure of elastic stored energy, were empirically related to the glass transition point, T_g. The values of η showed a steep dependence on the number average molecular weight, $\bar{M}_n$ ($\eta \propto \bar{M}_n^{42}$). It was proved that the molecular weight dependence of η and J_e^0 manifest through the dependence of T_g on $\bar{M}_n$ ($T_g \propto 1/\bar{M}_n$). Discussion of the blending laws to elucidate the effect of molecular weight distribution has revealed that $\ln \eta$, J_e^0, and T_g are expressed additively by using the mole fraction of each pitch component with different molecular weights.

1. Introduction

Recent developments in the engineering processes of carbon industries, especially the extruding process of pitch fibre, increasingly demand the systematic establishment of isotropic and mesophase pitch rheology. As is well-known, however, the heavy-end materials, such as coal-tar and petroleum pitches, are mixtures of organic condensed-ring compounds with high molecular weights and have such complicated chemical structures that many of the problems in pitch rheology and chemistry remain unsolved. The high molecular weight and the wider molecular weight distribution of pitch molecules could be a crucial reason in making the problems complex and ambiguous.

In general, a number of viscoelastic parameters, such as viscosity, creep function and relaxation modulus, are intimately related to the molecular weight and its distribution of constituent molecules, the relation of which have been intensively studied in polymer rheology and science [1, 2]. The molecular rheology of polymers has revealed the importance of molecular weight and its distribution in polymer technology. One of the current problems in the polymer industry is the control and modification of the molecular parameters to prepare polymers having excellent qualities. In contrast with polymer rheology, the importance of molecule, molecular weight, molecular weight distribution and intermolecular interaction in pitch rheology has hardly been acknowledged. The establishment of a method for molecular weight fractionation and thereby the extensive viscoelastic studies of fractionated pitches with different molecular weights, would be the first step in overcoming this undesirable situation in pitch rheology, as conducted in the earlier works of polymer rheology and science [1, 2].

Pitches are typical glass-forming materials and it has been noticed that the crystalline phase does not appear even if cooled as slowly as possible. Instead of a melting point, such non-crystalline materials have a glass transition point, T_g, below which the molecular motion of the constituents is largely depressed [1, 3]. The tem-

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perature dependence of viscoelastic properties such as relaxation time, viscosity and creep compliance, of glass-forming materials is closely related to their glass transition points, and no precise discussion on the viscoelastic behaviour can be developed without a comprehension of the glass transition phenomenon of those materials. Nevertheless, only little attention has been paid to the glass transition point of pitches [4, 5].

The torsional creep behaviour of fractionated pitches with different molecular weight was investigated in the present work along with dilatometric studies of the glass transition point. The main objective of the work was to elucidate the interrelations of viscoelastic and glass transition parameters of fractionated pitches with molecular weight. The effects of molecular weight distribution on these parameters were also examined.

2. Experimental procedure

2.1. Samples

A petroleum pitch with a softening point (ring and ball method) of 118.0° C was fractionated into six fractions, five benzene-soluble fractions (F1 to F5) and an insoluble fraction, by using benzene as a good solvent and n-hexane as a poor solvent. The elemental analysis of the original pitch showed 90.1% C, 5.3% H, 0.0% N and 4.4% S. The scheme of molecular weight fractionation is depicted in Fig. 1, where use has been made of the fact that a high concentration in benzene of benzene/n-hexane mixture is required to dissolve the pitch components with high molecular weight, and vice versa. The detailed procedure for molecular weight fractionation was worked out in our previous paper [6].

TABLE I The number average molecular weight, $\bar{M}_n$, and blending ratio, f, for fractionated and blended pitches

	$\bar{M}_n$	f*
F1	380	
F2	450	
F3	590	
F4	750	
F5	910	
BS	510	
B1	425	7/3
B2	460	5/5
B3	510	3/7
B4	545	1.5/8.5

*Blending ratio f = (weight of F1/weight of F3).

Blended pitches (B1 to B4), made up from F1 and F3, were also used to elucidate the importance of molecular weight distribution on viscoelastic properties. The blending ratio and the molecular weight for each blended pitch are listed in Table I together with the molecular weight of fractionated pitches (F1 to F5). The measurement of number average molecular weight, $\bar{M}_n$, for each sample was conducted in benzene solution at 45° C using a vapour pressure osometer (Corona

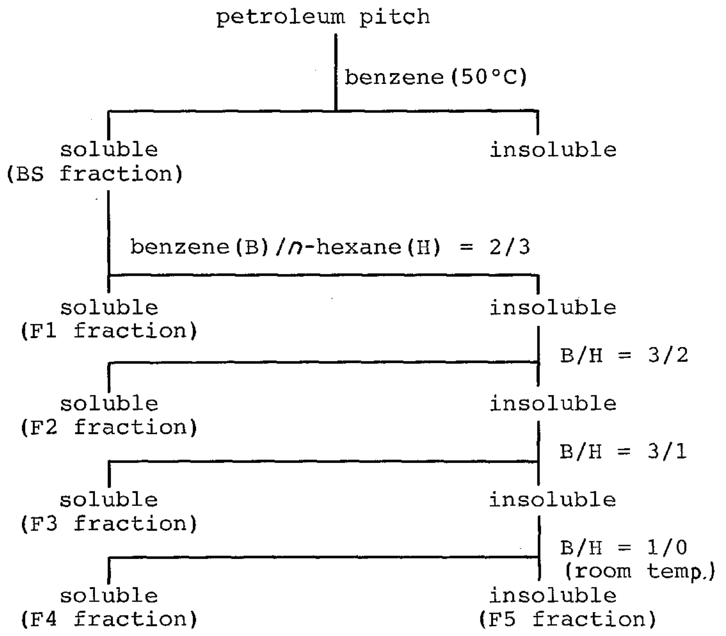

Figure 1 Flow chart for molecular weight fractionation.

Electric Co. Ltd., Type 117). The precision of $\bar{M}_n$ values measured was confirmed to be within ± 3% using benzil as a standard.

Of the fractionated pitches, F1 to F3 and B1 to B4 were used for creep measurement, and F1 to F4 and B1 to B4 for the measurement of glass transition parameters. Because of high values of T_g for F4 and F5, the creep measurement for those samples was not conducted in the present work. For reference purposes, the measurements of creep and glass transition point were also carried out for the benzene-soluble fraction (BS-fraction denoted in Fig. 1).

2.2. Measurement of creep deformation

The apparatus used for creep measurement, which was similar to those of Plazek *et al.* [7], Osaki *et al.* [8], Isono *et al.* [9] and Sakai and Inagaki [10], is shown in Fig. 2, and is of a torsional type and is capable of obtaining creep compliance $J(t)$ under simple shear deformation. Simple shear creep compliance is always required to evaluate quantitative linear viscoleastic parameters because simple shear deformation holds the volume of the specimen constant during creep measurement.

The apparatus comprises the following three units.

1. Torque generating unit: a constant torque, $k\theta$, was produced by rotating the protractor by an angle θ and twisting a torsion wire (0.5 mm diameter and 1500 mm long) which had a torsional modulus $k = 2.87 \times 10^{-3}$ Nm.

2. Torque transmission unit: the constant torque is transmitted to the specimen through a coupling rod suspended from the torsion wire, the coupling rod being centred by a frictionless air bearing. In order to prevent loss of heat from the specimen, the rod was made of Micalex (Tokyo Shibaura Electric Co. Ltd.), which is an excellent insulator of heat and a hard solid with a tensile strength of 40 to 45 MN m^{-2} and a thermal resistance up to 500° C.

3. Specimen holder and chamber: the disc-shaped specimen was sandwiched between two stainless steel plates and fixed on to the specimen holder placed in a Pyrex glass chamber which was immersed in a water bath thermocontrolled to ± 0.05° C. The specimen disc was glued onto the stainless steel plates using α-cyanoacrylate adhesive.

The disc-shaped specimens for creep measurement were prepared as follows: after premoulding each pitch sample by pouring the molten pitch into Teflon moulds with diameters of about 9, 14 and 20 mm, the samples were placed in stainless steel moulds of different diameters, heated in an oven to a temperature about 10° C below the softening point of the samples, kept for about 1 h under a pressure of 6 kN m^{-2}, followed by a gradual cooling down to the glass transition point of the specimens. The sizes of the moulded specimens were 10.0, 15.0 and 22.0 mm diameter and about 5 mm thick. These specimens were kept at temperatures below T_g until creep measurement.

The simple shear creep compliance, $J(t)$, was calculated from the following equation ([1], p. 111),

$$J(t) = \frac{\pi R^4}{2hk\theta}\alpha(t) \qquad (1)$$

where $\alpha(t)$ is the angle of torsional deformation of the specimen, which was measured using a 1.8 m laser beam lever through a mirror attached to the coupling rod (see Fig. 2). R and h are the radius and thickness of the specimen, respectively.

2.3. Measurement of glass transition point

The glass transition point, T_g, for each pitch sample was measured dilatometrically. The dilatometers and techniques employed resemble those proposed by Bekkedahl [11]. The specimen (4 to 5 g) was degassed (10^{-3} mm Hg) in a Pyrex glass dilatometer bulb prior to the addition of pure dry mercury which was used as the indicator liquid. The dilatometer stem consisted of a 1 mm diameter capillary tube. From the change in volume of the contents of the dilatometer, the specific volume, $\bar{v}$ (ml g^{-1}), of the specimen at each temperature was calculated by the usual procedures [11].

The conventional glass transition point, T_g, for each pitch sample was obtained dilatometrically at a cooling rate of 1° C/3 min. In the plots of specific volume $\bar{v}$ against temperature T, T_g was obtained as the temperature at the intersection of the extrapolated lines of the supercooled liquid in the high temperature region and the glassy state in the low temperature region [11].

3. Results

3.1. Creep curve

The creep compliance curves, log $J(t)$ against log

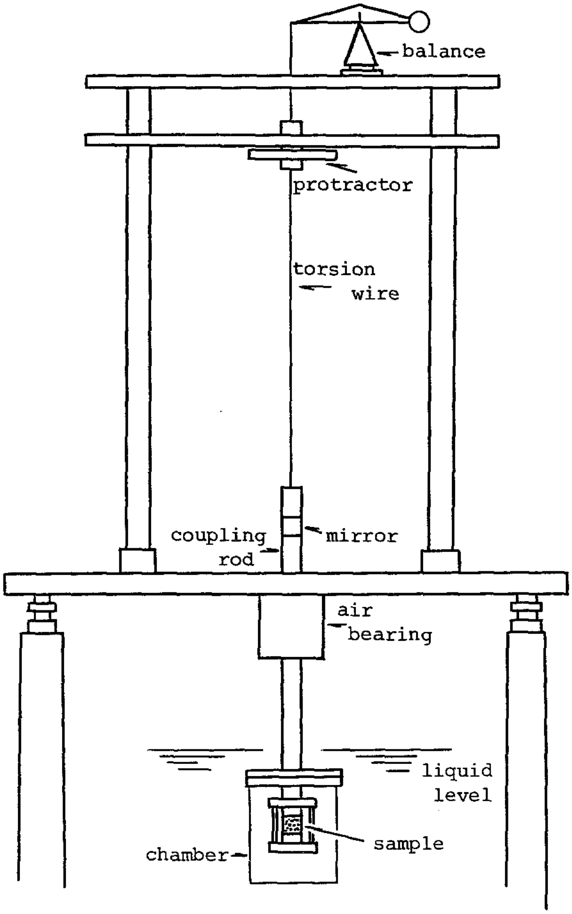

Figure 2 Schematic drawing of the torsional creep apparatus.

t, obtained at different temperature, are shown for F2 and B2, as examples, in Fig. 3. The curves increase monotonically with time and are straight lines with a slope of 1.0 over a long time span at the relatively high measurement temperatures, which are related to the steady-state flow at which all of the retardation mechanisms of the pitch samples are considered to have faded out. The reduced master curves of creep compliance, $J(t)$ against $\log t/a_\mathrm{T}$, superimposed at a standard temperature of $T_0 = (273 + 60.0)\,\mathrm{K}$ are shown in Fig. 4 for all pitch samples using the "time–temperature superposition rule" ([1], Chap. 11), where a_T is the shift factor for the superposition along the time axis in Fig. 4. The shift factor is plotted against $1/T$ semilogarithmically in Fig. 5. The detailed procedure for the superposition of the creep curves of pitch has been described in our previous paper [10]. The data in Fig. 5 are well represented by a straight line, the equation of which is

$$\ln a_\mathrm{T} = \frac{3.62 \times 10^4}{T} - 109 \qquad (2)$$

3.2. Glass transition point, T_g

The specific volume, $\bar{v}$, for F3 and B3, as examples, is plotted against temperature in Fig. 6, where the temperature giving the extrapolated intersection of the two straight lines is the glass transition point, T_g, of the sample pitch. Table II lists the important parameters for the glass transition behaviour, T_g, specific volume, $\bar{v}_\mathrm{g}$, at T_g and volume–temperature coefficient, $(\mathrm{d}v/\mathrm{d}T)_l$ and $(\mathrm{d}v/\mathrm{d}T)_\mathrm{g}$ for the supercooled liquid and glassy state; these parameters are essential in the discussion of the viscoelastic properties and free volume near T_g. It is worth noting that T_g shows a marked increase with increase in molecular weight.

4. Discussion

4.1. Separation of viscous and elastic characteristics

Some portion of the external work applied to the viscoelastic material during creep deformation is stored in the specimen as elastic strain energy, and the rest is converted into heat flow as viscous

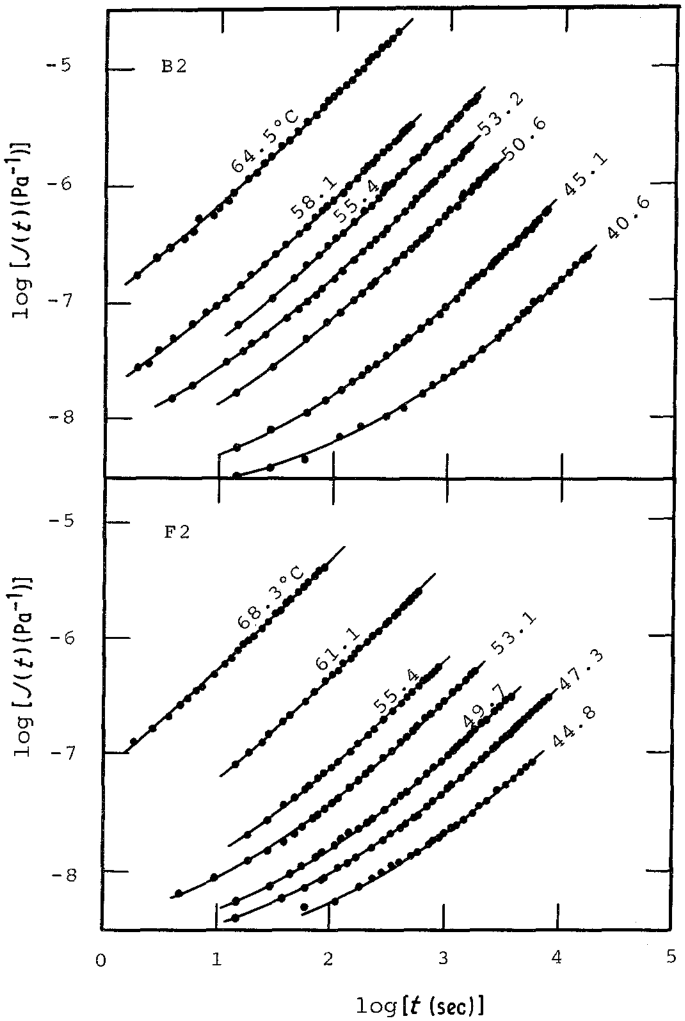

Figure 3 Creep curves for F2 and B2 at different measurement temperatures.

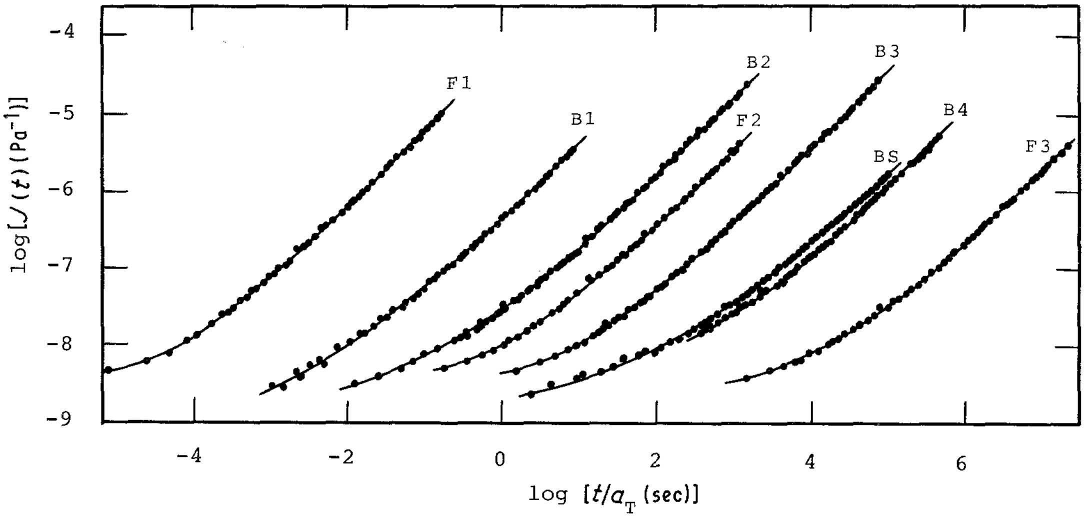

Figure 4 Master curves of shear creep compliance. The standard temperature for superposition is 60.0° C.

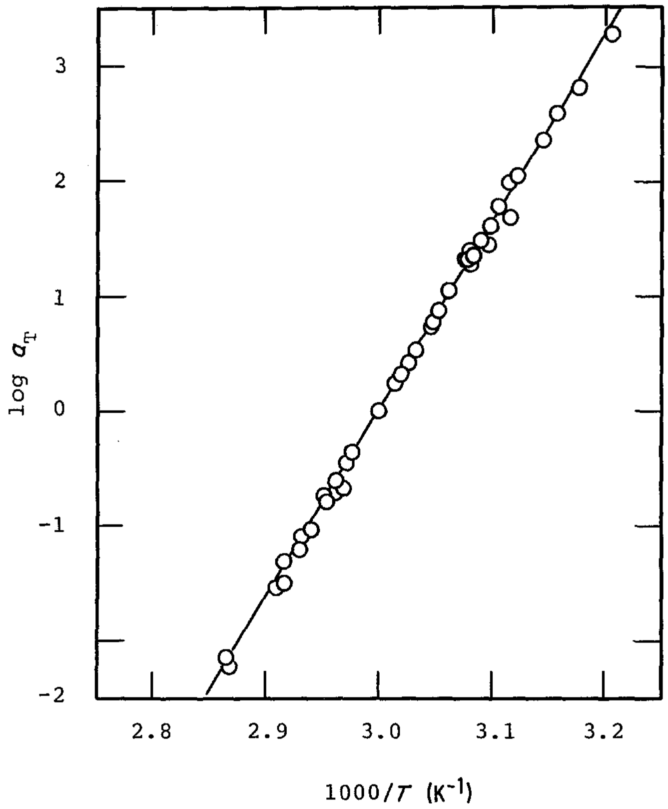

Figure 5 Temperature dependence of shift factor, a_T, employed in Fig. 4. The standard temperature for superposition is 60.0° C.

energy dissipation. Therefore, at least two of the characteristic parameters, viscous and elastic, should be addressed to characterize the viscoelastic material. The steady-flow viscosity, η, as a measure of viscous energy dissipation [1] and the steady-state creep compliance, J_e^0, as a measure of elastic stored energy [1, 22] are suitable characteristics which are easily obtainable from the creep curve. The values of η and J_e^0 are conventionally evaluated using the following extrapolations to infinite time:

$$1/\eta = \lim_{t \to \infty} \mathrm{d}J(t)/\mathrm{d}t$$

and

$$J_e^0 = \lim_{t \to \infty} [J(t) - t/\eta]$$

These conventional extrapolations, however, give erroneous results in cases where the retardation time of the specimen is sufficiently long for the steady-state flow not to be attained. In order to obtain reliable values of η and J_e^0, it is always desirable to perform the experiments over a very long duration to attain steady-state flow. Assistance in estimating η and J_e^0 in long-term creep experiments can be provided by the extrapolation method of Ninomiya:

TABLE II Some parameters for glass transition

	T_g (K)	$\bar{v}_g$ (ml g^{-1})	$(\mathrm{d}\bar{v}/\mathrm{d}T)_l$ (10^4 ml g^{-1} deg^{-1})	$(\mathrm{d}\bar{v}/\mathrm{d}T)_g$ (10^4 ml g^{-1} deg^{-1})
F1	290.8	0.8369	4.25	1.90
F2	312.8	0.8286	4.08	1.95
F3	337.0	0.8265	3.70	1.60
F4	357.8	–	–	–
BS	325.8	0.7358	3.60	1.50
B1	299.2	0.8293	4.25	1.70
B2	311.3	0.8291	4.04	1.72
B3	316.1	0.8264	3.75	1.60
B4	326.4	0.8268	3.75	1.45

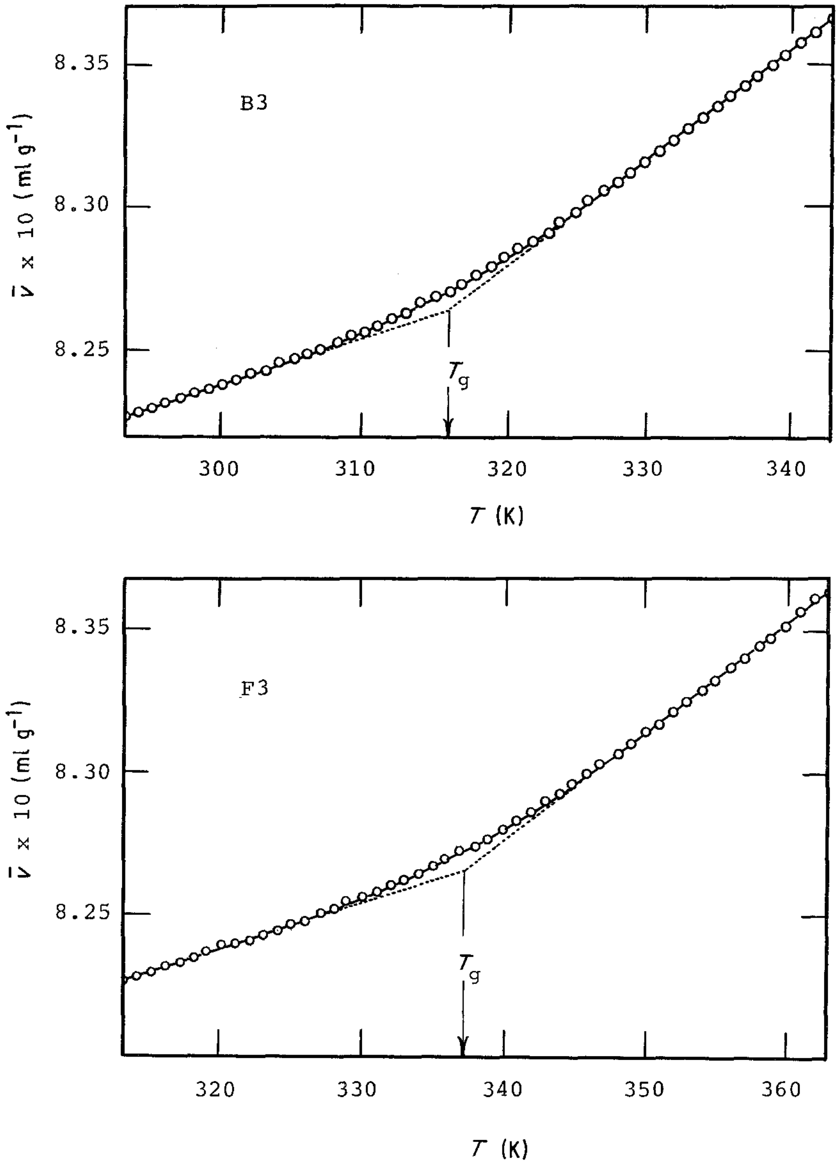

Figure 6 Plots of specific volume, $\bar{v}$, against temperature, T, for F3 and B3 to evaluate the glass transition point, T_g.

$$1/\eta = \lim_{1/t \to 0} J(t)/t = \lim_{1/t \to 0} mJ(t)/t \quad (3)$$

and

$$J_e^0 = \lim_{1/t \to 0} \frac{d}{d(1/t)} \left[\frac{J(t)}{t}\right] \quad (4)$$

where

$$m = \frac{d \log J(t)}{d \log t} \quad (5)$$

Further details of the extrapolation method are covered by Nimomiya ([12], [1] p. 117). The Nimomiya extrapolation is employed in the present work.

4.2. Temperature dependence of shear viscosity

The viscosity, η, for each pitch sample is plotted semilogarithmically against the inverse temperature, $1/T$, in Fig. 7. Log η is seen to increase linearly with $1/T$ and this linear relation seems to hold even near or at the glass transition point. i.e. the temperature dependence of viscosity for our pitch samples can be well described in the

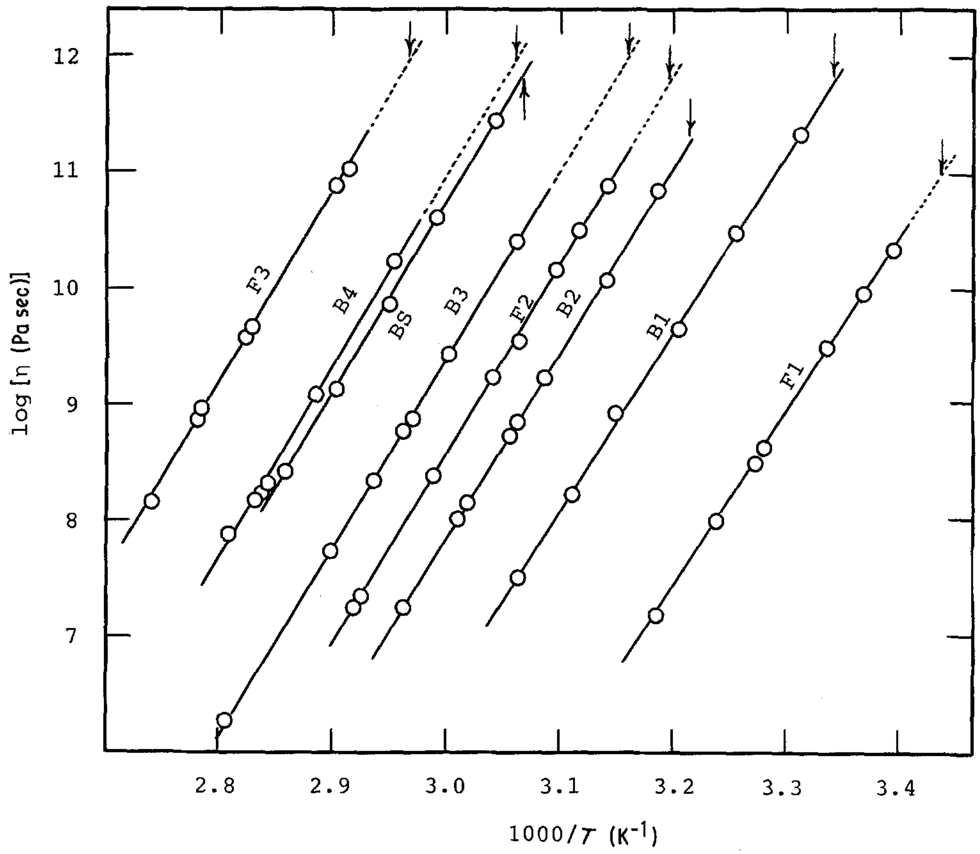

Figure 7 Temperature dependence of steady-state shear viscosity η. The arrows denote the glass transition point, T_g, for each pitch sample.

present temperature range by the Andrade equation [13]:

$$\eta = \eta_0 \exp\left(\frac{\Delta H_\eta}{RT}\right) \tag{6a}$$

in which η_0 is a constant, ΔH_η the activation energy for shear flow, and R the gas constant. The values of ΔH_η for the fractionated and blended pitches are ~ $72 \pm 3\,\text{kcal mol}^{-1}$ ($= 3.0 \times 10^5\,\text{J mol}^{-1}$), being slightly higher than that reported previously [10]. Taking account of the experimental fact that Equation (6a) would be satisfied even at T_g (see Fig. 7), Equation 6a can be rewritten as:

$$\ln \frac{\eta}{\eta_g} = \frac{\Delta H_\eta}{R}\left(\frac{1}{T} - \frac{1}{T_g}\right) \tag{6b}$$

where η_g is the shear viscosity at T_g. The importance of Equation 6b will be shown in Fig. 8, if the reduced viscosity η/η_g is plotted against $(1/T - 1/T_g)$. All the viscosity data for all pitch samples at different measurement temperatures fall beautifully on a straight line, where $\Delta H_\eta/R = 3.62 \times 10^4$ K, i.e. Equation 6b expresses universally the temperature dependence of reduced viscosity for pitches with various values of T_g, if ΔH_η is insensitive to T_g, as in the present case. The universal expression of Equation 6b will play a significant role in explaining the molecular weight dependence of η as seen in the following section.

Many of the properties of liquids, whether organic or inorganic, and polymeric or not, demonstrate the presence of a substantial portion of free volume, which may be presented as holes or voids associated with packing irregularities [3]. Although the free volume is poorly defined, it is a useful semi-quantitative concept for the understanding of material properties at temperatures near T_g. The various types of free volume theory have been successfully applied to the temperature dependence of viscoelastic parameters of glass-forming materials. The Doolittle expression [14], Vogel's equation [15] and the WLF equation [16], those expressions being

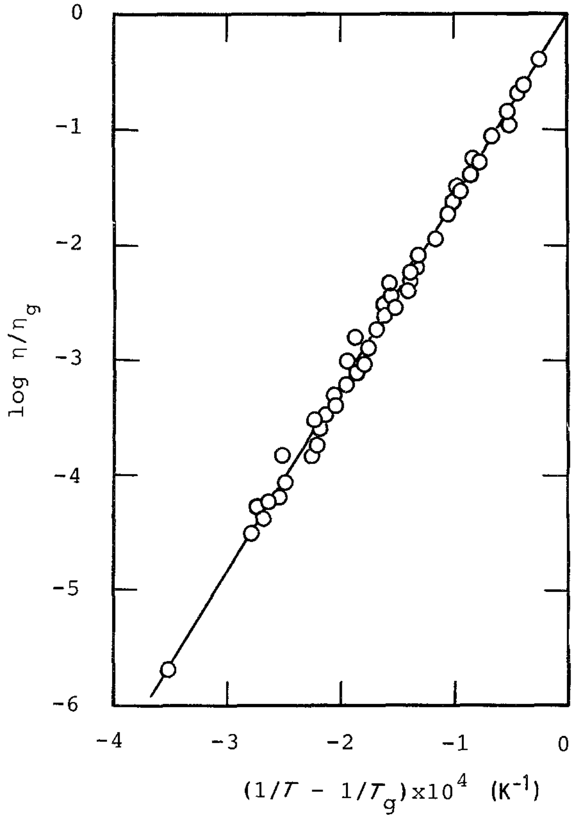

Figure 8 Universal relation between reduced viscosity, η/η_g, and temperature $(1/T - 1/T_g)$ expressed by Equation 6b.

equivalent to each other under some assumptions [17], claim that Andrade's equation, which does not take the free volume effect into account, is not suitable for expressing the temperature dependence of η and a_T near T_g, and that ΔH_η depends on temperature. Taking account of the temperature dependence of free volume, the WLF equation [16] can beautifully explain the temperature dependence of ΔH_η. In the present experimental results, on the other hand, the steady-state viscosity seems to be successfully described by the Andrade equation even near T_g, and ΔH_η = constant (= 72 kcal mol^{-1}) in this temperature range. It must be noted, however, that the value of ΔH_η for the usual pitches at sufficiently high temperatures, for example 100 to 150° C above T_g, ranges from 30 to 40 kcal mol^{-1} [18–20], suggesting that ΔH_η is not a constant, but has a functional form depending on temperature. Therefore, the linearity in Fig. 7 and the empirical expression of Equation 6b seem to be the only fact restricted to a relatively narrow temperature range. Further studies would be required over a wider temperature range in order to elucidate the applicability of the free volume theory to pitch rheology.

4.3. Interrelations between molecular weight and shear viscosity and glass transition point

The logarithmic plot of log η against log $\bar{M}_n$ is shown in Fig. 9 for the fractionated and blended pitches. The dependence of η on molecular weight, $\bar{M}_n$, as proposed, is very remarkable; the slope of the approximate linear relation is as large as 42, in other words, a variation of only 5% in $\bar{M}_n$ induces a 200% change in η. This means that control of molecular weight is very significant in the practical uses of pitches in engineering processes. Such a strong dependence of η on $\bar{M}_n$, however, would tend to decrease with increasing temperature, as pointed out by Fox and Flory for a low molecular weight polystyrene [21].

The glass transition point, T_g, is plotted against the inverse of molecular weight, $1/\bar{M}_n$, in Fig. 10. T_g is a linear function of $1/\bar{M}_n$ and is successfully expressed by

$$T_g = T_{g\infty} - \frac{B}{\bar{M}_n} \qquad (7)$$

where $T_{g\infty}$ and B are experimental constants having values of 423 K and 5.1×10^4 K, respectively. Some deviation from Equation 7, however,

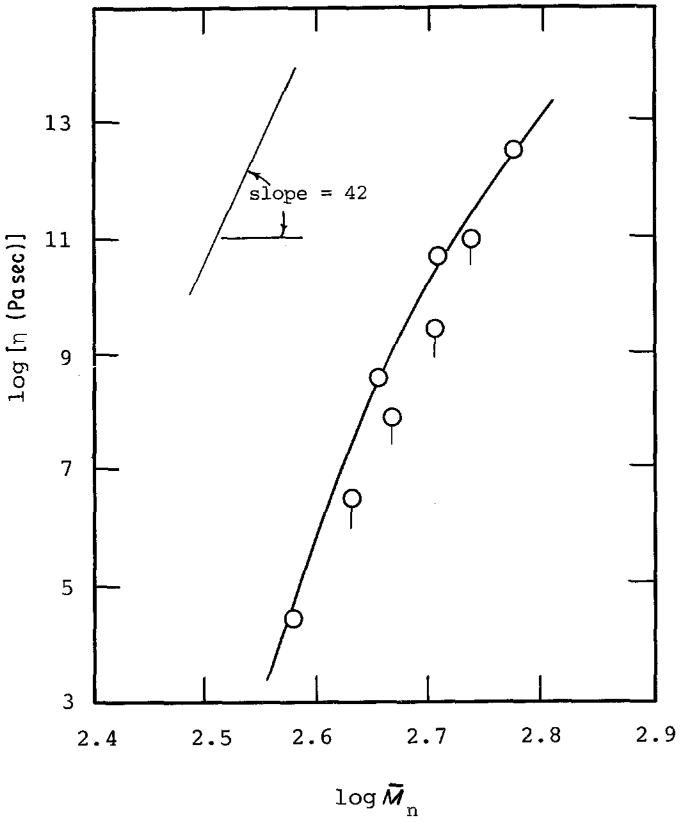

Figure 9 Molecular weight dependence of steady-state shear viscosity η at 60.0° C. The plots for blended pitches are denoted by ♀.

is observed for blended pitches. The reason for this is not clear at present, but the value of T_g for the blended pitches is also approximately proportional to $1/\bar{M}_n$. This inverse proportionality is similar to the experimental results reported by Fox and Flory for low molecular weight polystyrene [21].

Substituting the empirical relation of Equation 7 into Equation 6b, the dependence of reduced viscosity, η/η_g, on $\bar{M}_n$ and T is expressed as

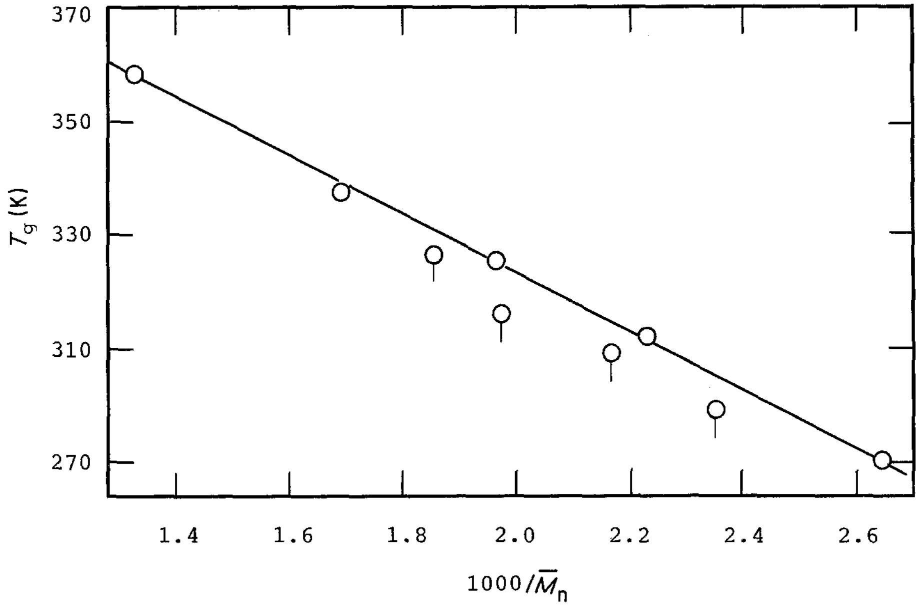

Figure 10 Molecular weight dependence of glass transition point, T_g. The straight line is given by Equation 7. The plots for blended pitches are denoted by ♀.

follows,

$$\ln\frac{\eta}{\eta_g} = \frac{\Delta H_\eta}{R}\left[\frac{1}{T} - \frac{1}{T_{g\infty} - (B/\bar{M}_n)}\right] \tag{8}$$

Using the experimental values of η_g for each sample (about 10^{12} Pa sec for all samples) and introducing the values of the experimental constants, $\Delta H_\eta/R = 3.62 \times 10^4$ K, $T_{g\infty} = 423$ K, $B = 5.1 \times 10^4$ K, and $T = (60.0 + 273.2)$ K, the calculated relationship between η and $\bar{M}_n$ is drawn in Fig. 9 as a solid curve, and is in good accordance with the experimental values. This leads to the conclusion that the strong dependence of η on $\bar{M}_n$ in Fig. 9 ensues directly from the molecular weight dependence of T_g (Equation 7).

4.4. Steady state shear creep compliance, J_e^0

The temperature dependence of J_e^0 for all our pitches is shown in Fig. 11. The empirical relation of J_e^0 against T is expressed by the same equation as in our previous work [10]:

$$J_e^0 = J_g + A(T - T_g) \tag{9}$$

The temperatures at the intercept on the abscissa in Fig. 11 give T_g for the pitches, the values of which are in good agreement with the dilatometric values (see Table II). Slope A seems to be approximately the same for all samples ($A \approx 4.0 \times 10^{-9}$ Pa^{-1} K^{-1}). The monotonic increase in J_e^0 with temperature suggests an elastic mechanism of pitch materials is enthalpic, not entropic as for organic polymers.

In the same manner as viscosity, J_e^0 may be related to molecular weight through the molecular weight dependence of T_g as follows:

$$J_e^0 = J_g + A\left(T - T_{g\infty} + \frac{B}{\bar{M}_n}\right)$$

$$= \text{const.} + AT + \frac{A \cdot B}{\bar{M}_n} \tag{10}$$

This equation means that J_e^0 decreases with increasing molecular weight, i.e. pitch materials at a constant temperature become stiffer with increase in molecular weight.

4.5. Blending law

For the purpose of elucidating the influence of molecular weight distribution on rheological parameters, the blending effect on η, T_g and J_e^0 is discussed here, using blended pitches B1 to B4 (see Table I). Prior to the rheological discussion, it is noted that the empirical values of $\bar{M}_n$ for

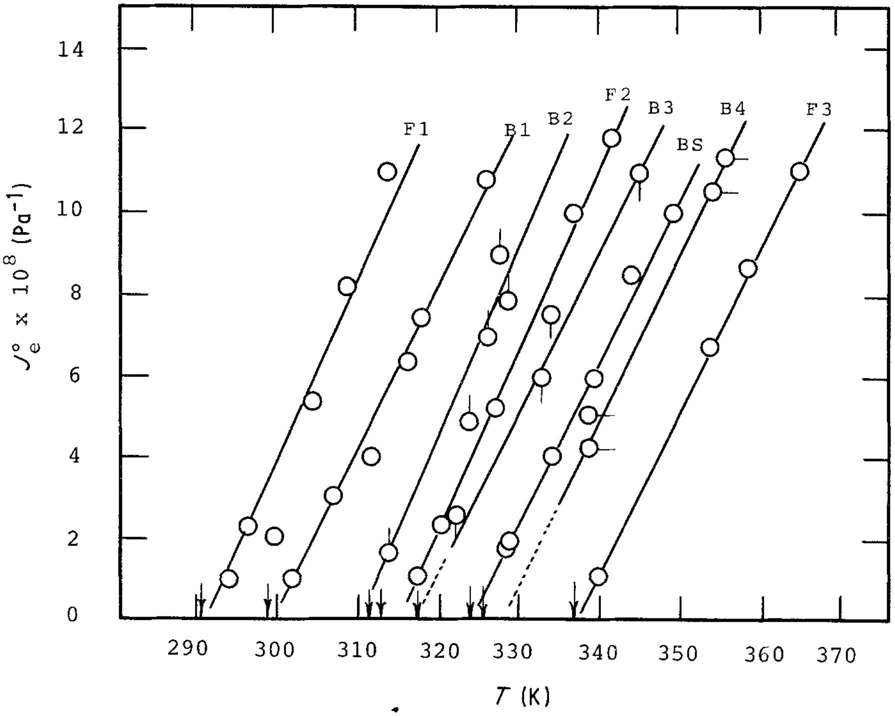

Figure 11 Temperature dependence of steady-state shear creep compliance J_e^0. The arrows show the glass transition point evaluated using the dilatometric method.

B1 to B4 measured by VPO (see Table I) are in good agreement with those calculated by the following number-average expression,

$$\bar{M}_{\mathrm{nb}} = \bar{M}_{\mathrm{n1}}f_1 + \bar{M}_{\mathrm{n3}}f_3 = 1\Bigg/\left(\frac{w_1}{\bar{M}_{\mathrm{n1}}} + \frac{w_3}{\bar{M}_{\mathrm{n3}}}\right) \qquad (11)$$

where f_1 and f_3 are the mole fractions of F1 and F3 pitches, and $\bar{M}_{\mathrm{nb}}$, $\bar{M}_{\mathrm{n1}}$ and $\bar{M}_{\mathrm{n3}}$ are the number average molecular weights of blended, F1 and F3 pitches, respectively. w_1 and w_3 are the weight fractions of F1 and F3 pitches.

Since the effect of molecular weight on viscosity is through the molecular weight dependence of T_g, as stated in the previous section, it would be readily anticipated that the blending law of molecular weight will be governed by that for T_g. Experimental values of T_g for F1, B1 to B4, and F3 are plotted against the mole fraction f_3 and the weight fraction w_3 of F3 pitch in Fig. 12. The experimental values of T_g are well expressed additively using f_3 but not w_3, i.e. we can make an important conclusion in general terms that the glass transition point, T_g, for a pitch comprising molecules with molecular weight M_i of mole fraction $f(M_i)$ is expressed by

$$T_g = \sum_{i=1}^{N} f(M_i)T_g(M_i) \qquad (12a)$$

or by an integral form as

$$T_g = \int_0^\infty f(M)T_g(M)\,\mathrm{d}M \fallingdotseq \langle T_g\rangle_n \qquad (12b)$$

Substituting the results of the molecular weight blending law for T_g (Equation 12b) into Equation 6b, the reduced viscosity, η/η_g, can be described as

$$\ln\frac{\eta}{\eta_g} = \frac{\Delta H_\eta}{R}\left(\frac{1}{T} - \frac{1}{\langle T_g\rangle_n}\right) \qquad (13)$$

Equation 13 is probably approximated with a good accuracy by*

$$\ln\frac{\eta}{\eta_g} = \frac{\Delta H_\eta}{R}\left(\frac{1}{T} - \left\langle\frac{1}{T_g}\right\rangle_n\right) \qquad (14)$$

Equation 14 suggests, by taking account the unsusceptibility of ΔH_η and η_g on molecular weight and molecular weight distribution, that the molecular weight dependence of ln η might be given by a number-average expression, i.e. the shear viscosity, η, for a pitch having a molecular weight distribution $f(M)$ can generally be expressed by

$$\ln\eta = \int_0^\infty \ln\eta(M)f(M)\,\mathrm{d}M \qquad (16)$$

A plot of ln η against f_3 for the blended pitches

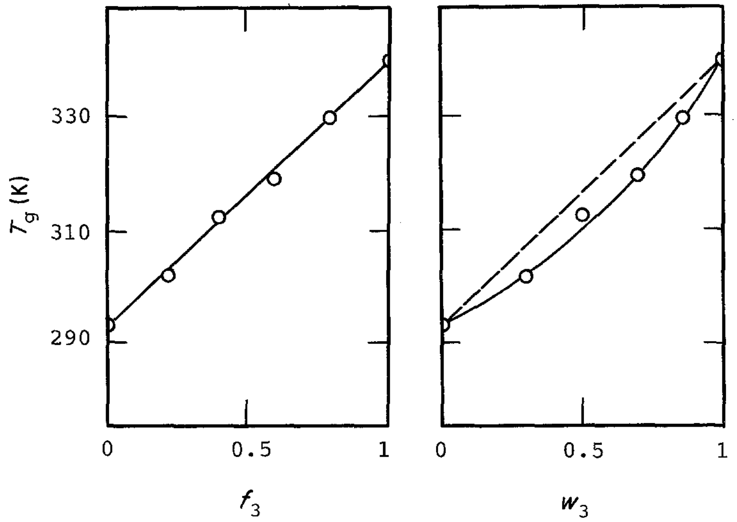

Figure 12 Interrelations of glass transition point, T_g, for F1, B1 to B4, and Fe3, with mole fraction, f_3, and weight fraction, w_3, of F3 pitch.

$$* \quad \left\langle\frac{1}{T_g}\right\rangle_n - \frac{1}{\langle T_g\rangle_n} = \frac{1}{\langle T_g\rangle_n}\left\langle\frac{\langle T_g\rangle_n - T_g}{T_g}\right\rangle_n \qquad (15)$$

Even for a sufficiently large deviation in T_g from its average, say, $|\langle T_g\rangle_n - T_g| \fallingdotseq T_g$, the difference between $\langle 1/T_g\rangle_n$ and $1/\langle T_g\rangle_n$ is of the order of $1/\langle T_g\rangle_n \fallingdotseq 3 \times 10^{-3}$ for $T_g \fallingdotseq 300$ K.

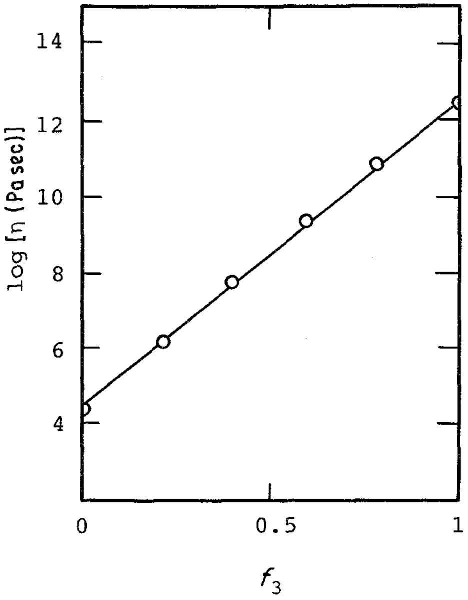

Figure 13 Plots of log η against mole fraction f_3 of F3 pitch at 60° C.

is shown in Fig. 13, ln η varying on a straight line, which supports the validity of the blending law in Equation 16.

5. Conclusions

Based on the measurement of torsional creep and glass transition point for fractionated petroleum pitches with different molecular weights, the following conclusions are drawn.

1. The reduced viscosity, η/η_g, is expressed universally by the following equation within the temperature range of our experiments:

$$\ln\frac{\eta}{\eta_g} = \frac{\Delta H_\eta}{R}\left(\frac{1}{T} - \frac{1}{T_g}\right)$$

2. The glass transition point, T_g, is empirically described as

$$T_g = T_{g\infty} - \frac{B}{\bar{M}_n}$$

The molecular weight dependence of η and J_e^0 manifest themselves through the dependence of T_g on $\bar{M}_n$.

3. The steady state creep compliance, J_e^0, increases with temperature, the empirical equation for which is

$$J_e^0 = J_g + A(T - T_g)$$

4. From the discussion on blending law, ln η, T_g and J_e^0 are well expressed additively using the mole fraction of each pitch component with different molecular weight.

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