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A THERMOMECHANICAL TECHNIQUE FOR CHARACTERIZING PITCH

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Abstract

Thermomechanical analysis (TMA) in a tube-compressive mode can be used to characterize pitch in a reproducible and sensitive way. In a single experiment, this technique enables simultaneous determination of the glass transition temperature, the softening temperature and the rheological behaviour of a pitch sample. Results on a typical Australian coal-tar pitch are consistent with Bingham fluid behaviour above its softening temperature with a yield stress of the order of 100 Pa. In a similar test a petroleum pitch sample exhibited no yield stress.

Keywords: glass transition, pitch, rheology, softening temperature, TMA

Introduction

Pitch is an important industrial binder material and has been investigated extensively. Recently, with the development of technologies for manufacturing carbon fibres from pitch precursors, pitch characterization is receiving more and more attention from researchers in the fields of thermal analysis, materials science and polymer processing. Among the various properties of a pitch, the glass transition temperature and the softening temperature, as well as the rheological behaviour of a softened pitch are, of fundamental importance. These properties reflect mesophase formation kinetics of a pitch and other processing conditions which determine the quality of the final products. This paper reports a novel characterization technique for pitches using thermomechanical analysis in a tube-compressive mode.

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Principles of TMA in a tube-compressive mode

TMA is carried out in a tube-compressive mode by placing the test material in a tube and causing a ram to push down on the sample. The pressure on the sample is determined by the weight loaded on the ram. By heating the sample in a programmed manner and recording the displacement of the ram, changes in mechanical properties of the sample are detected as a function of temperature. This mode of TMA has been reported in the determination of the thermal softening behaviour of wood particles [1].

Pitch is a typical amorphous material and has relatively low glass transition and softening temperatures. Below the softening temperature this mode of TMA detects changes in the mechanical properties of a solid sample in the usual way. However, when a pitch changes into a fluid state (above its softening temperature), the sample fluid expected to be displaced and pushed out of the tube by the ram. In this case, the TMA cell turns into a penetrometer in which the displacement of the ram will be dominated by the fluid mechanics and the rheological properties of the fluid sample. The TMA cell used in this study is shown schematically in Fig. 1, where the inner diameter for the tube is b, and

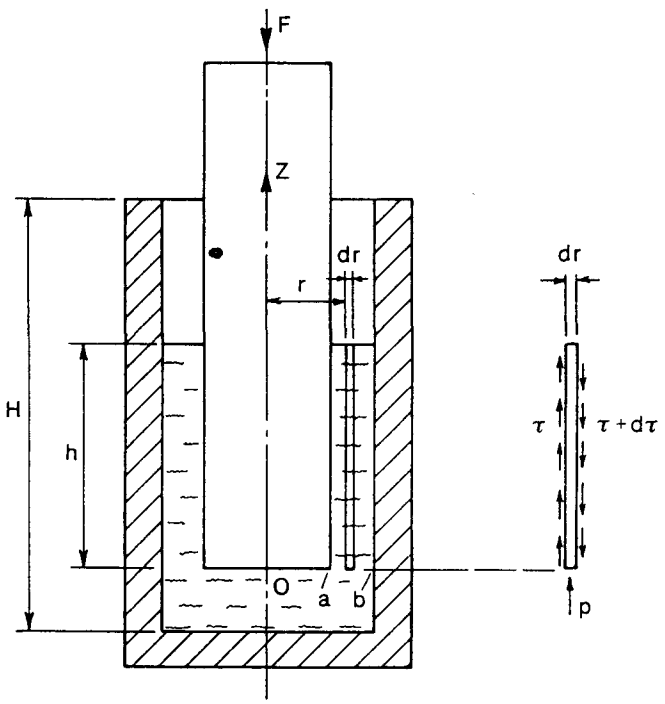

Fig. 1 A schematic diagram of the TMA cell used in this study

the outer diameter of the ram is a. The depth of the tube is assumed to be H and h is the height of the fluid sample.

Bikerman [2] analyzed the velocity distribution of a Newtonian fluid in the annular gap of a penetrometer and derived an expression for the velocity (V) of the ram:

$$V = \frac{1}{\eta h} \frac{p}{4}\left((a^2 + b^2) \ln\left(\frac{b}{a}\right) - (b^2 - a^2)\right) \quad (1)$$

where, η is the viscosity of the fluid and varies with temperature; p is the pressure acting on the bottom end of the annular gap and equals, approximately, the loading F divided by the cross sectional area of the ram.

In Eq. (1), the loading p and the geometric factor in brackets are constant during a particular experiment with the same cell. Thus, the velocity of the ram directly reflects the change in viscosity of the fluid sample.

Experimental

Pitch samples

Commercial grade samples of Ashland 240 petroleum pitch and a typical Australian coal-tar pitch were used as test materials in this study. The glass transition temperature for the pitches was measured by DSC.

TMA experiments

A suitable TMA cell consisting of a tube and a ram was designed and fabricated in our laboratory [3]. Pitch particles were crushed in a mortar to 250 μm and dried under vacuum at room temperature for more than 6 h. Pitch (about 15 mg) was placed in the tube and packing voids removed by gentle vibration under a slight load. The ram was placed is position and the whole assembly placed in the TMA oven with the required compression mass on the ram. All the experiments used a Rigaku Thermoflex TMA Series module interfaced with a NEC microcomputer for data storage and processing (Rigaku Thermal Analysis Station TAS 100, software modified by the authors). A slow heating rate 1 deg·min^{-1} (in N_2, flow rate 100 ml·min^{-1}) was used so as to eliminate any possible effect due to thermal gradients within the TMA cell. The accuracy of TMA sample height changes was confirmed periodically by direct micrometer measurements of the height (±1 μm) of holder plus sample, both before and after a heating sequence.

Glass transition measurements by differential scanning calorimeter (DSC)

Pitch particles pulverized to 250 μm were dried under vacuum at room temperature for 6 h. About 15 mg of pitch was then packed into an aluminium DSC cell. After annealing at 140°C for 5 min, the sample was rapidly cooled to − 40°C. The DSC curve was then recorded as the sample was heated at a rate of 20 deg·min^{-1}. All the measurements were performed using a Perkin-Elmer II differential scanning calorimeter equipped with a refrigerator and interfaced with a microcomputer for data storage and processing. Instrumental calibration for temperature was made using distilled water as a standard.

Results and discussion

Figure 2 presents the DSC curves for the two pitches. Glass transition temperatures, determined by reading the temperature of maximum gradient of the curves (T_{g_2}), were found to be 62°C for the petroleum pitch and 50°C for the coal-tar pitch. Above the glass transition points, no changes in the DSC curves were observed as the samples pass through their softening temperatures. This is because the softening point of an amorphous material is only a change in the mechanical deformability of the sample but not a thermodynamic transition.

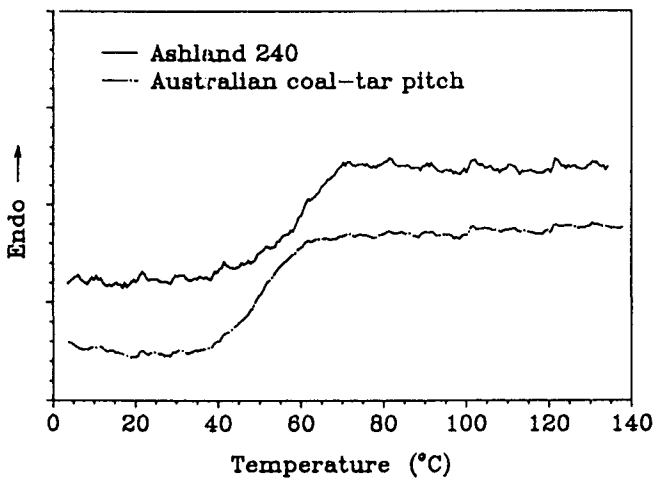

Fig. 2 DSC curves for the petroleum pitch and coal-tar pitch

Figure 3 shows a TMA curve for the petroleum pitch with 1.960 N (200 g) of loading. The left *Y* axis denotes the sample height expressed as a percentage, and the right *Y* axis indicates the derivative of the sample height with respect to time, which is proportional to the velocity of the ram dropping down. At 62°C,

an initial height decrease was detected, and this decrease continues to about 30% of the original sample height. This behaviour reflects a change in the mechanical strength (and/or plasticity) of the pitch during its glass transition, in which the frozen molecular segments recover their mobilities, resulting in a much higher deformation ability than that below the glass transition. With the deformation of pitch particles increasing, the contacting area of pitch particles increases and the inter-particle voids are gradually eliminated. Descent of the TMA ram ceases with the removal of these voids. This can be seen from the plateau in the approximate range 90–106°C. However, as the temperature increases, the state of the pitch changes from a solid to a fluid allowing the ram to descend again. The softening temperature, therefore, can be determined as the point, at which the derivative begins to deviate from the zero line. From Fig. 3, it is read as 106°C. The sample height becomes zero at a temperature of 183°C, indicating that the ram has touched the bottom of the tube of the TMA cell.

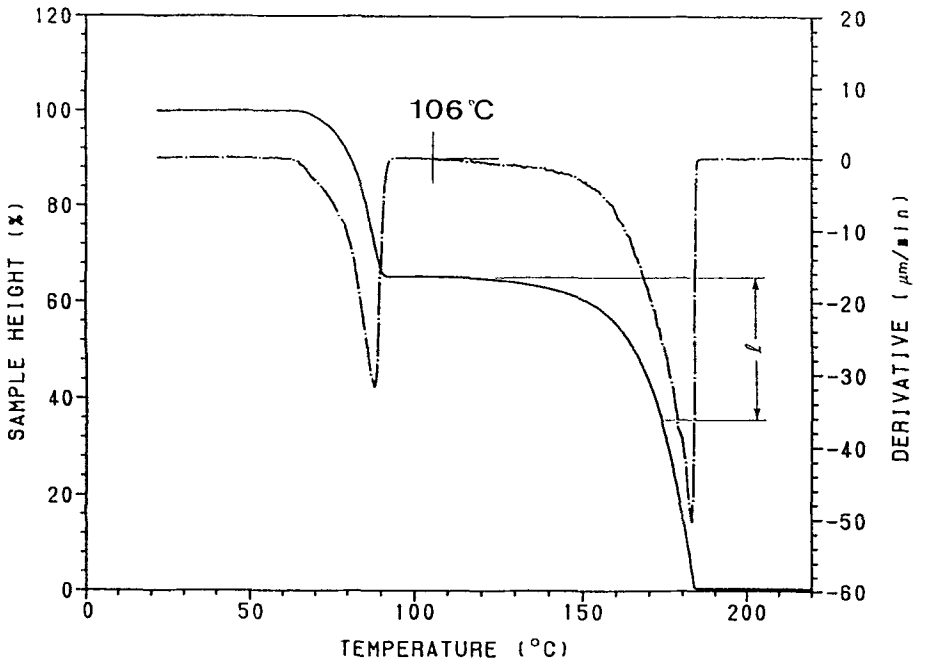

Fig. 3 TMA curves for the petroleum pitch

Assuming the first drop in the TMA curves results entirely from the elimination of inter-particle voids of the packed particles in the TMA cell, one may calculate, from a material balance point of view, the sample height, h, at each temperature, as shown in Figs 1 and 3.

$$h = \frac{b}{2(b-a)} l \tag{2}$$

where the symbol l is the descent height of the ram from the plateau after the glass transition temperature.

Substituting Eq. (2) into Eq. (1) leads to,

$$\eta = \frac{k}{V l} \tag{3}$$

where k is a constant determined by the geometry of the TMA cell and the loading of a TMA experiment. This k can be written as

$$k = \frac{p}{2} \frac{(b-a)}{b} \left((a^2 + b^2) \ln\left(\frac{b}{a}\right) - (b^2 - a^2) \right) \tag{4}$$

Equation (3) indicates that the temperature dependence of viscosity can be obtained from the reciprocal of the product of the sample height variation and its derivative. The TMA data for A240 pitch from 115 to 180°C shown in Fig. 3, were further processed according to Eq. (3). Figure 4 shows the relative change of viscosity. The viscosity of the pitch fluid was found to decrease around 100 times over this temperature range. Furthermore, an almost linear plot was observed, indicating an exponential decrease of the viscosity of the pitch fluid with increasing temperature.

The TMA curves for the coal-tar pitch are shown in Fig. 5. The glass transition and softening temperatures were found to be 50 and 98°C, respectively. However, unlike the petroleum pitch, the softening of the coal-tar pitch did not

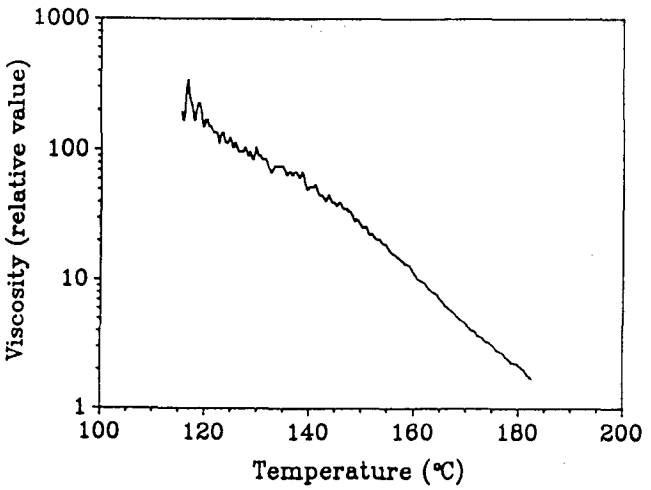

Fig. 4 Viscosity variation with temperature for A240

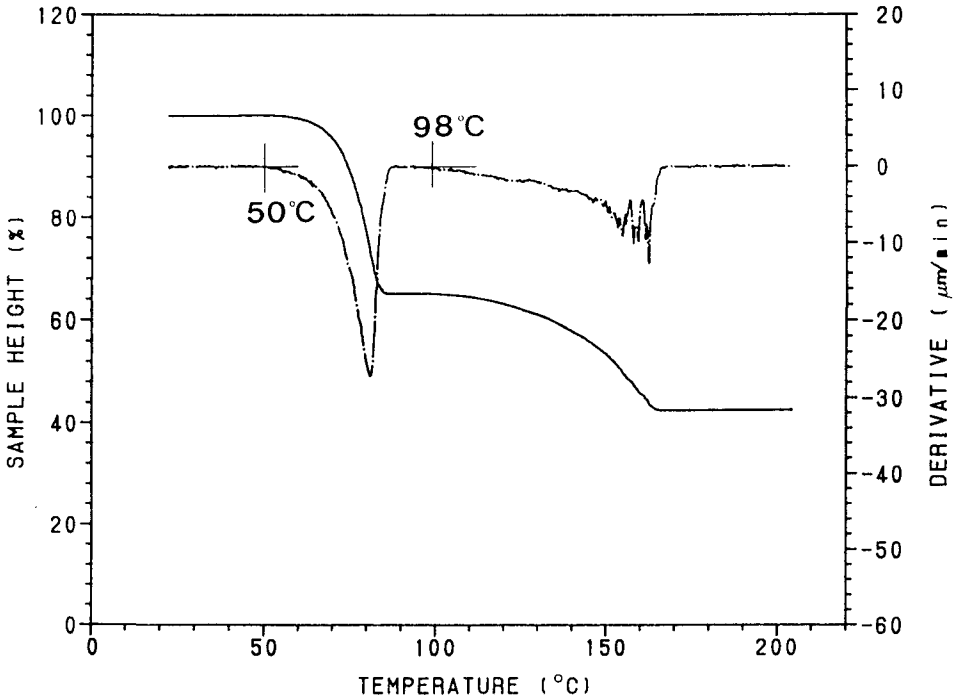

Fig. 5 TMA curve for the coal-tar pitch

enable the TMA ram to push all the pitch sample out of the tube, even at 200°C. The reproducibility of TMA curves was good for both petroleum pitch and coal-tar pitch samples.

Some materials exhibiting plastic behavior do not flow until the applied shearing stress exceeds a minimum value. This minimum shearing stress τ_y, designated as the yield stress required for Bingham flow [4], is though to be the cause preventing the ram moving to the bottom of the TMA tube. From the force balance point of view, when the maximum shear stress resulting from the loading of the ram becomes less than the yield stress of a Bingham fluid, flow in the TMA cell gap will be stopped.

To estimate the yield stress, one has to know the shear stress distribution along the annular gap of the TMA cell. This shear stress distribution, $\tau(r)$, was not derived in Bikerman's analysis. However, it may be obtained as follows.

The force balance in the direction of the Z axis in Fig. 1 for the infinitesimal annulus leads to:

$$hr\frac{d\tau(r)}{dr} + h\tau(r) - pr = 0 \tag{5}$$

where, as before, p is the pressure acting on the annulus and results from the loading, F. For simplicity, the surface tension acting on the top end of the infinitesimal annulus is ignored.

Equation (5) is a differential equation describing the shear stress distribution along the annulus. Its solution is:

$$\tau(r) = \frac{pr}{2h} + \frac{c_1}{r} \tag{6}$$

Equation (6) shows the shear stress distribution along the annular gap of the TMA cell. In particular, it is noted that when the integral constant C_1 is set to zero, $\tau(r)=pr/2h$ is the shear stress distribution for a pipe flow of length h under pressure p [4].

The constant C_1 can, however, be determined by assuming the case of a Newtonian fluid, in which $\tau(r)$ equals $\eta dv(r)/dr$, since Eq. (6) is a universal formula independent of the nature of the fluid in the annulus.

$$v(r) = \frac{pr^2}{4h\eta} + \frac{c_1}{\eta} \ln r + c_2 \tag{7}$$

where $v(r)$ is the velocity of the fluid in the annulus.

From the boundary conditions that at $r=a$, $v(r)=V$ and at $r=b$, $v(r)=0$, one obtains,

$$c_1 = \left(V - \frac{p(a^2 - b^2)}{4h\eta} \right) \frac{\eta}{\ln(a/b)} \tag{8}$$

where V is the downward velocity of the ram in the TMA cell. When the ram stops, V is zero.

The shear stress distribution in the case of $V=0$ is then written as,

$$\tau(r) = \frac{pr}{2h} + \frac{p(b^2 - a^2)}{r4h \ln(a/b)} \tag{9}$$

On the other hand, the force balance for the ram in the Z axis direction leads to:

$$p = \frac{F}{\pi \left(2a^2 - \frac{b^2 - a^2}{2\ln(b/a)} \right)} \tag{10}$$

Equations (9) and (10) are the formulae showing the stress distribution along the annulus gap of a TMA cell. In the case of a narrow gap in the TMA cell, one can obtain:

$$p \simeq \frac{F}{\pi a^2} \tag{11}$$

$$\tau(b) = -\tau(a) = \frac{p}{2}\left(\frac{\delta}{h}\right) \tag{12}$$

where, $\delta = b - a$ and represents the clearance of a TMA cell (see Appendix).

Equation (12) suggests that, when the clearance of a TMA cell is very small compared with the diameters of the tube and ram, the maximum shear stress, which is the driving force pushing the fluid out, is linearly proportional to the loading pressure applied to the ram and to the clearance. The height of sample fluid in the gap, on the other hand, is inversely proportional to the shear stress.

The yields stress may therefore, be estimated from Eq. (12) (putting $h = H = 12$ mm, $\delta = 0.025$ mm and $p = 100$ kPa as typical values):

$$\tau_y = \frac{p}{2} * 0.0025/12.0 = 104.0 \text{ Pa}$$

This value is reasonable compared with an observed yields stress of 600 Pa using a newly developed stress controlled rheometer for A240 mesophase pitch at 240°C [5]. Such a small yield stress would hardly be detected in a conventional rheometer.

Conclusion

The tube-compressive mode of TMA has proved to be a useful tool to characterize a pitch. In particular, the glass transition and softening temperatures, as well as the rheological behaviour above the softening point, can be measured in a single experiment. The glass transition temperatures show good agreement between DSC and TMA determinations. In addition, this technique has the feature of being simple in concept and of producing relatively rapid results with high sensitivity and high reproducibility.

Experiments on softened coal-tar pitch successfully detected Bingham behaviour, which is not detectable in a conventional rheometer, since the yield stresses measured were small (of the order of 100 Pa).

However, since softening temperature is not a thermodynamic transition and a TMA fluidity curve (the curve after softening) is affected by the clearance of the cell as indicated by Eqs (1) and (12), this requires TMA cells to be accurately fabricated and standardized if results from different laboratories are to be compared. As in other TMA modes, a successful TMA experiment is only possible when the loading is correctly selected. In the case of pitches, p = 100 kPa

was found to be suitable. In addition, the thickness of the TMA cell restricts heating and cooling rates in order to eliminate inhomogeneous phenomena.

Furthermore, a TMA curve should be interpreted with care for a volatile or reactive material, since the movement of the ram will be affected by the pressure of any gases produced during the experiment. However, it is already clear that this novel technique has wide application to the characterization of pitch (and many related materials).

Appendix

$$\ln(a/b) = \ln(1 - \delta/b) = -\frac{\delta}{b} - \frac{1}{2}\left(\frac{\delta}{b}\right)^2 - \frac{1}{3}\left(\frac{\delta}{b}\right)^3 - \ldots. \quad \text{(A1)}$$

or

$$\ln(a/b) = -\ln(1 + \delta/a) = -\left[\frac{\delta}{a} - \frac{1}{2}\left(\frac{\delta}{a}\right)^2 + \frac{1}{3}\left(\frac{\delta}{a}\right)^3 - \ldots.\right] \quad \text{(A2)}$$

$$\frac{(b^2 - a^2)}{b^2} = 2\frac{\delta}{b}\left(1 - \frac{\delta}{2b}\right) \quad \text{(A3)}$$

$$\frac{(b^2 - a^2)}{a^2} = 2\frac{\delta}{a}\left(1 + \frac{\delta}{2a}\right) \quad \text{(A4)}$$

Substituting Eq. (A1) and Eq. (A3) or Eq. (A2) and Eq. (A4) into Eq. (9), one obtains $\tau(b)$ and $\tau(a)$. Substituting Eq. (A2) and Eq. (A4) into Eq. (10), Eq. (12) is obtained.

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Zusammenfassung — Mittels spezieller thermomechanischer Analyse (TMA) kann Pech auf reproduzierbare Weise und mit hoher Empfindlichkeit charakterisiert werden. In einem einzigen Experiment ermöglicht diese Technik die gleichzeitige Bestimmung der Glasumwandlungstemperatur, der Erweichungstemperatur und des rheologischen Verhaltens von Pechproben. Die Ergebnisse von einem typisch australischen Kohlenteerpeches zeigen Übereinstimmungen mit dem Verhalten einer Bingham-Flüssigkeit oberhalb der Erweichungstemperatur mit einer Streckspannung der Größenordnung von 100 Pa. In einem ähnlichen Test weist eine Petroleumpechprobe keine Streckspannung auf.