Rheological Characteristics of Mesophase Forming Pitch Materials Up to 500°C

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INTRODUCTION

Carbonaceous mesophase formed by thermal treatment of pitches is known as an essential intermediate in production of high modulus carbon fibres or needle coke, because it can be deformed by mechanical means in the temperature range between 300-500 °C [1,2,3]. The appearing shear stresses during the deformation of the liquid crystals cause high degree of preferred orientation in the resulting bulk mesophase. This preferred orientation is transferred quantitatively into the final carbon product. The flow behaviour of the carbonaceous mesophase itself is only qualitatively known from optical observations of mesophase pitch, i.e liquid crystals within surrounding isotropic pitch. For optimization of the process conditions to achieve the intended preferred orientation in the bulk mesophase the rheological behaviour of the isotropic pitch up to temperatures when the mesophase is formed and coalesces as well as the influence of increasing mesophase content on the rheology should be known.
COLLETT and RAND [2] as well as BALDUHN and FITZER [3] have shown Newtonian behaviour for pitches up to 250°C and non-Newtonian above 250 °C. Thixotropic flow characteristics have been observed by BARR et al. [4] and also by COLLETT and RAND [2] for some mesophase pitches whereas pseudo-Newtonian and non-Newtonian flow behaviour have been reported by NAZEM [5,6] for a variety of mesophase pitches. But Nazem described the rheological behaviour only from log/log plots of apparent viscosity vs. shear rate instead of shear rate vs. shear stress diagramms necessary for complete understanding of the flow behaviour. As far as isotropic pitches up to temperatures of 180 °C are concerned, BHATIA et al. [7] have found that all pitches, pure or mixed with different carbon additives, do not behave rheologically as Newtonian fluids but as Bingham plastics with a certain small yield stress. We have recently reported on rheological measurements with an improved co-axial cylindrical viscosimeter up to 500 °C [8,9]. Unlike reported earlier [2,3] by us and other authors we did not observe now an intermediate maximum/minimum in apparent viscosity with increasing temperature neither with different pitches nor with separated pitch fractions, though such an intermediate maximum/minimum could be expected for the temperature intervall when the isotropic/anisotropic phase transformation occurs in mesophase pitches. Therefore new measurements of the rheological behaviour of various pitches have been performed with this improved equipment and are described here. The results were evaluated for determination of the real viscosity of homogeneous pitches and of mesophase pitches with increasing content of liquid crystals.

EXPERIMENTAL

Equipment The viscosimeter is a Contraves Rheomat 30 with a shear rate range of 0.06 - 452 s^{-1}, in principle the same as used by BALDUHN and FITZER previously [3] only modified according to the new DIN 53019 (rotor with 70 mm height and 45 mm diameter and a gap between rotor and cup of 1.8 mm). The difference in shear rate across the gap is less than 7 % according to calculations. The mentioned improvement consisted of a better alignement of the co-axial cylindrical system and mainly of a much preciser temperature control [9]. This improvement was achieved by controlling the temperature with thermocouples placed in the copper coating around the outer wall of the cup.

Procedure It is most important that a controlled volume of test material fills the gap during the whole measuring procedure. The temperature of the sample is controlled with an accuracy within ±1 °C. The rotation of the cylinder was started after heating up to the desired temperature. For each shear rate constant torque values were achieved after a few minutes. The flow behaviour of the sample at a particular temperature was measured by stepwise increase as well as decrease of the rotor's shear rate. This procedure was repeated for all pitches at various temperatures until solidification. A constant flow of nitrogen was maintained over the pitch surface during the whole run.

Sample materials As shown in Table 1 three various commercial pitches were used, namely a binder pitch for electrode manufacture, a special prepared coal tar infiltration pitch (after filtration purification) and a commercial petroleum pitch (Ashland A-240). The last samle material was varied by heat treatment at various temperatures.

RESULTS

The shear rate ($\dot{\gamma}$) vs. shear stress (τ) plots at various temperatures for the filtered coal tar pitch (CTP) are shown in Fig. 1a,1b,1c as typical example for all

Table 1 Characterization of used pitch materials

Sample	S.P. °C	C/H	T I %	Q I %	β-resin %
Binder Pitch	89	2.08	36	15	21
CTP	80	1.82	26	0	26
Petroleum Pitch	115	1.44	10	0	10
HTT 410 °C	145/165	1.74	52	22	30
HTT 420 °C	176/204	1.91	70	31	39
HTT 425 °C	206/271	1.93	80	50	30

non heat treated pitch samples. For better understanding, the flow diagrams are represented for three temperature ranges, i.e. 100-150 °C, 170-470 °C and finally 490-510 °C. As seen in Fig. 1a, the flow curves for the temperatures 100, 110 and 150 °C deviate only slightly from Newtonian behaviour, but nevertheless, they must be considert as typical for Bingham plastics with a yield value τ_o and a plastic viscosity η_{pl}. The experimental data were fitted by the least square method to the rheological equation of Bingham plastics

$$\tau - \tau_o = \eta_{pl} \cdot \dot{\gamma}$$

The yield stress τ_o decreases with increasing temperature slightly, from 1.8 Pa at 100 °C to 1.2 Pa at

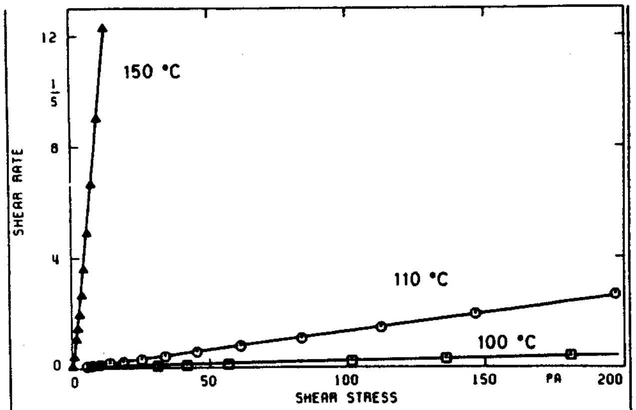

Fig. 1a FLOW CURVES OF THE FILTERED COAL TAR PITCH (CTP) 100 - 150 DEG C

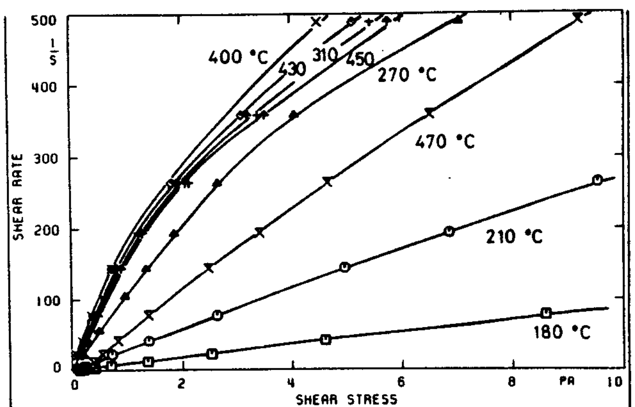

Fig. 1b FLOW CURVES OF THE FILTERED COAL TAR PITCH (CTP) 180 - 470 DEG C

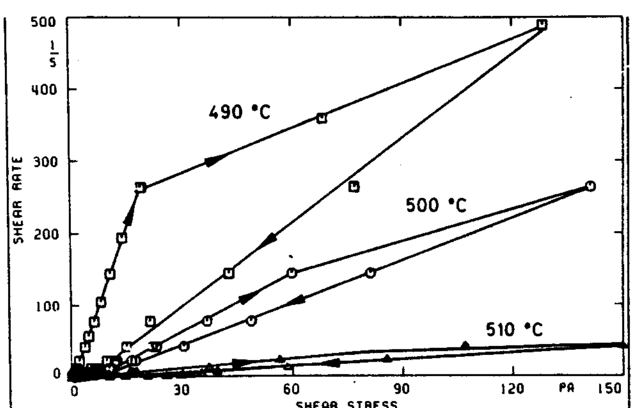

Fig. 1c FLOW CURVES OF THE FILTERED COAL TAR PITCH (CTP) 490 - 510 DEG C

150 °C. The plastic viscosity η_{pl} shows a strong decrease with increasing temperature, i.e. from 440 Pa•s at 100 °C to 0.9 Pa•s at 150 °C. With increasing test temperatures the coal tar pitch behaves still as Bingham plastic as shown in Fig. 1b. Additionally, a bendingof the flow curves between 170 and 470 °C towards the stress axis for shear rates higher than 77.5 s^{-1} were observed. This deviation is explained as being caused by TAYLOR whirls [10] but not by a dilatant flow behaviour of the pitch.

Fig. 1c shows that the flow curve at 490 °C is different from those at lower temperatures. The flow curve at 490 °C is not reversible and consists of two parts, that is up curve and down curve. The up curve cracks off sharply at shear rates above 250 s^{-1} whereas for the down curve the shear stress is constantly decreased with decreasing shear rate. For test temperatures above 490 °C the flow behaviour is similar but the area which is surrounded by the up and down curve is reduced for flow curves at higher temperatures.

Fig. 2 shows the plastic viscosity derived from the slope of the flow curve against the reciprocal temperatures. Easily four temperature ranges can be observed. The first one is the melting region, the second range corresponds to the softening region, range three covers the minimum viscosity region and finally range four indicates solidification. For all parts of the curves in Fig. 2 the activation energy of flow can be calculated according to the equation

$$\ln \eta_{pl} = B + \frac{E_a}{R T}$$

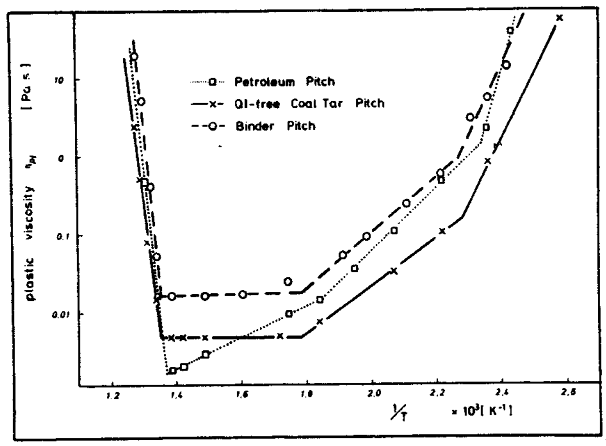

Figure 2 The plastic viscosity η_{pl} as function of $\frac{1}{T}$

These data are compiled in Table 2. It must be pointed out, that this formal activation energy of flow in the solidification range is negativ.

Finally, the effect of heat treatment on the petroleum pitch (Figure 3) is shown in the apparent viscosity curve against the measuring temperature. In the melting region a broad viscosity band is found for the heat treated samples whereas the original pitch shows the usual viscosity line as other thermoplastic materials. It should be pointed out, that these non constant curves with intermediate maxima/minima are only found for the melting temperatures but not for the solidification temperatures as described earlier [2,3]

Table 2 Activation energy of flow in kJ/mol

	melting	softening	min. viscosity	solidification
Binder Pitch	146	70	2.2	- 922
CTP	160	58	0.007	- 596
Petroleum Pitch	191	72	38	- 800

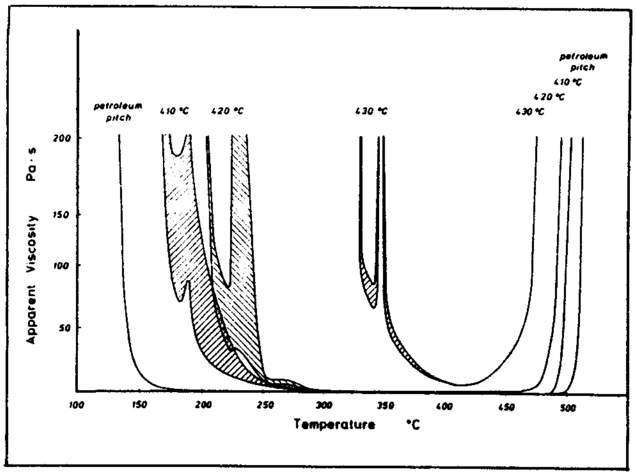

Figure 3 App. viscosity of the heat treated PP

DISCUSSION

The non-Newtonian flow behaviour, TAYLOR-whirls, shear thickening, temperature dependence of the plastic viscosity and the viscosity band for heat treated pitches will be discussed (see also [11]).

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