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RHEOLOGICAL CHARACTERISTICS OF MESOPHASE PITCH

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Abstract— Rheological characteristics of two pretreated petroleum pitches, during their transformation to mesophase, have been studied by using rotational viscometer. Simultaneously, the formation, growth, coalescence of mesophase spheres, and the alignment of coalesced mesophase were observed by Hot-Stage-Cinema-Microscope, discussed with the results of viscosity change and the Q.I. content. It is found that both pretreated pitches were Newtonian fluids at low temperature, but behaved pseudoplastics as increase of mesophase content above 390C. Shear thinning behaviour was also apparent in the shear rate range of 1.9-20 sec^{-1} at temperature above 390C. The apparent viscosity-temperature curves of this pyrolysed pitches were much affected by the pretreatment conditions.

INTRODUCTION

The rheological behaviour of pitches during heat treatment is of considerable technological significance, both in the low-temperature region where pitch/coke mixture are formed and in higher-temperatures where the carbonaceous mesophase grows and coalesces [1].

Bhatia et al. [2] have studied the rheological characteristics of coal tar and petroleum pitches in the range of 85-180°C. Didchenko et al. [3] have investigated the viscosity changes of pyrolysed petroleum pitches and found that there are maximum and minimum values on the viscosity-temperature curves above 400°C. Collet and Rand [4] have explained the variety of viscosity at high temperature was caused by formation, growth, and coalescence of mesophase spheres in pyrolysed pitch.

Fitzer [5] studied the viscosity and rheological properties of some pretreated pitches, and Balduhn [6] investigated rheological characteristics of pitches with sulfur addition.

Recently, many countries have tried to alternate the PAN precursor with mesophase pitch precursor for production of carbon fiber, and use the mesophase pitch as a matrix of carbon/carbon composites. For these purposes, the rheological properties of mesophase pitch were very important factors for extruding it to pitch precursor. But in view of the significance of the rheological behaviour of anisotropic pitches, it is rather surprising that only a few attempts have been made to investigate their rheological behaviours, especially in high temperatures. This might be partly because that raw pitches are composed of so much components and the properties are quite different from producing districts, processing sources, and so on.

Also, the mesophase formation, growth, and coalescence are different from pretreatments of raw pitches, heating conditions of pretreated pitches at high temperature.

Therefore, we have tried to investigate the rheological characteristics of Korean petroleum pitches with increasing the heat treatment temperature and set up the extruding conditions of anisotropic pitch to produce the mesophase pitch precursor for carbon fibre. Different shear rates have been used to elucidate the non-Newtonian behaviour of the mesophase pitch.

EXPERIMENT

Materials

Raw petroleum pitch(Yukong Limited, Korea) was pretreated in a high temperature-high pressure reactor to a temperature of about 400°C with different heating rates and conditions.

During this time, the pitch was continuously stirred and nitrogen gas was continuously bubbled through the pitch. PP-1 and PP-2 are the two pretreated samples and their characteristic properties are listed in Table 1. Q,I (Quinoline insoluble) content of raw petroleum pitches was negligible, but Q,I of pretreated pitches was considered as a mesophase produced during the pretreatment.

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Table 1. Properties of pretreated pitches.

	S.P* (℃)	Q.I. (wt %)	C/H/N (wt%)	Mw	C/H (mol ratio)	density	V.C.** (wt%)
PP-1	159	9.6	93.73 5.16 0.4	780	1.51	1.16	25.16
PP-2	97	2.8	92.36 5.58 0.7	502	1.32	1.17	39.06

* Softening point measured by Ring and Ball method.

** Volatile content measured by ASTM (D271-40)

Equipment

Rotational viscometer (Brookfield Co., L.V.F type) which is similar to that of Collet and Rand [4] was fitted with a coaxial cylinder measuring system, as shown in Figure 1. The system was heated by an electrical sources, controlled by an Eurotherm linear-temperature-time variable rate programmer and the temperature was recorded during heat treatment.

Nitrogen gas was continuously supplied to the system and emitted with other volatile products through a gap surrounding the spindle shaft. The radius of spindle is 0.95 cm, and the length is 6.5 cm. A guard aparted 1.2 cm from the center of spindle shaft was attached to the measuring head of the viscometer like a figure 1. With the rotational viscometer, the shear rate and shear stress of fluid can be expressed in the following equations [2,7,8].

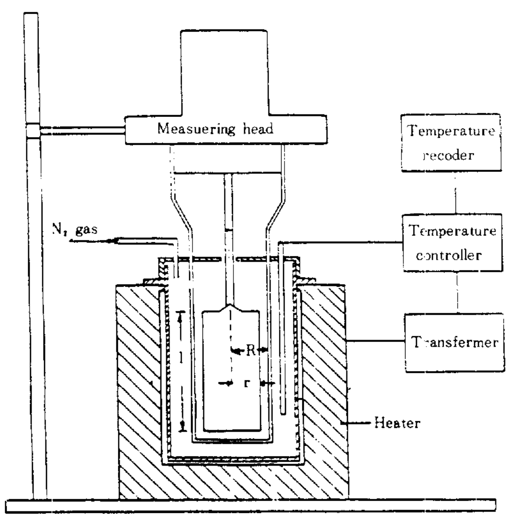

Fig. 1. Diagrammatic representation of the measuring system.

Shear rate: $$\dot{r} = \frac{2\omega R^2}{(R^2 - r^2)} \quad (1)$$

Shear stress: $$\tau = \frac{M}{2\pi r^2 l} \quad (2)$$

Where M represents the torque acting on the spindle of radius r and length l when rotating with a constant angular velocity ω. R is a radius of outer cylinder.

For Newtonian fluid, the apparent viscosity can be written as,

$$\eta = \frac{\tau}{\dot{r}} = \frac{M}{4\pi l W}\left(\frac{1}{r^2} - \frac{1}{R^2}\right) \quad (3)$$

There are many rheological equations for non-Newtonian fluids, and among them, the shear stress can be written as following the Ostwald de Waele equation [9].

$$\tau = K' \cdot \dot{r}^{n'} \quad (4)$$

Where K' is a flow consistancy index, and n' is a flow behaviour index. When a plot of shear rate vs shear stress is constructed in a log-log paper, flow behaviour index can be gained with slopes and flow consistancy index can be gained with the intercepts on the stress axis, if the plotting show straight lines.

Procedure

The pretreated pitches were preheated up to about softening point before fitting the viscosity measuring system, then heated according to programmed heating rates of which determined on the basis of TGA and pretreatment results.

The heating rates were 3°C/min from room temperature to 300°C, 1°C/min up to 390°C, and 0.4°C/min up to 550°C.

At viscosity measuring temperature the rotation speeds of spindle were varied from 6 to 60 rpm and the resultant torques were measured to calculate the shear stress.

Mesophase formation, growth, and coalescence in pyrolysed pitches were investigated with HSCM(Hot-Stage-Cinema-Microscope) which was controlled as same heating conditions as those of viscosity measuring conditions. The percentages of quinoline insoluble(Q,I) was determined by the method of Singer [10].

RESULTS AND DISCUSSION

Temperature dependence of viscosity

The apparent viscosity changes of two pretreated petroleum pitches up to 500°C were plotted in Figure 2.

Both materials have similar characteristics of viscosity macroscopically, but each has a different softening point and shows a different rheological behaviour above 390°C depending on the pretreatment conditions. The apparent viscosity change of PP-1 with respect to heat treatment temperature, the block of dotted line in Figure

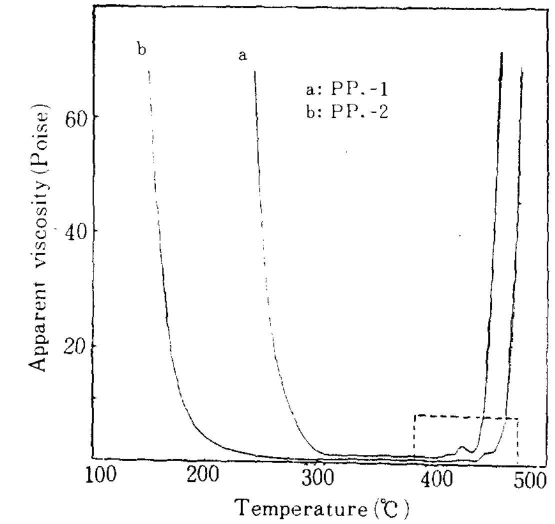

Fig. 2. Apparent viscosity of pretreated pitches with respect to heat treatment temperature.
Spindle speed:6 rpm

2, was shown in Figure 3.

Spindle speeds are 6, 12, 30, and 60 rpm. In the figure the viscosities were increased slowly from 390°C to 410°C, decreased up to 418°C after 410°C, and increased rapidly to 425°C, decreased again to 435°C, and then increased continuously up to the infinite. The results of maximum and minimum values on the vis-

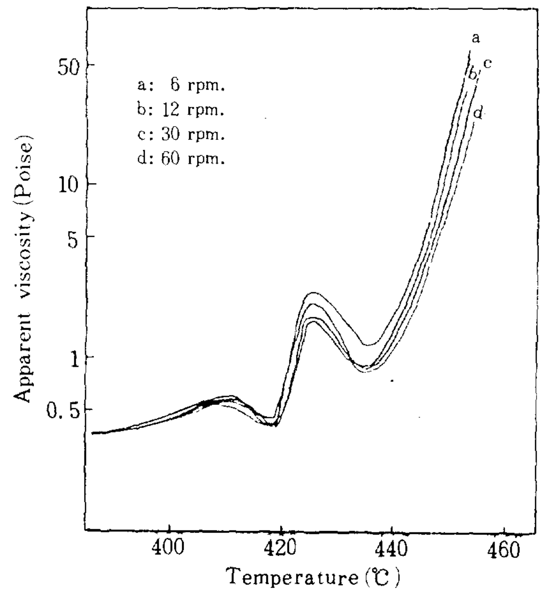

Fig. 3. Apparent viscosity of PP-1 with respect to heat treatment temperature.

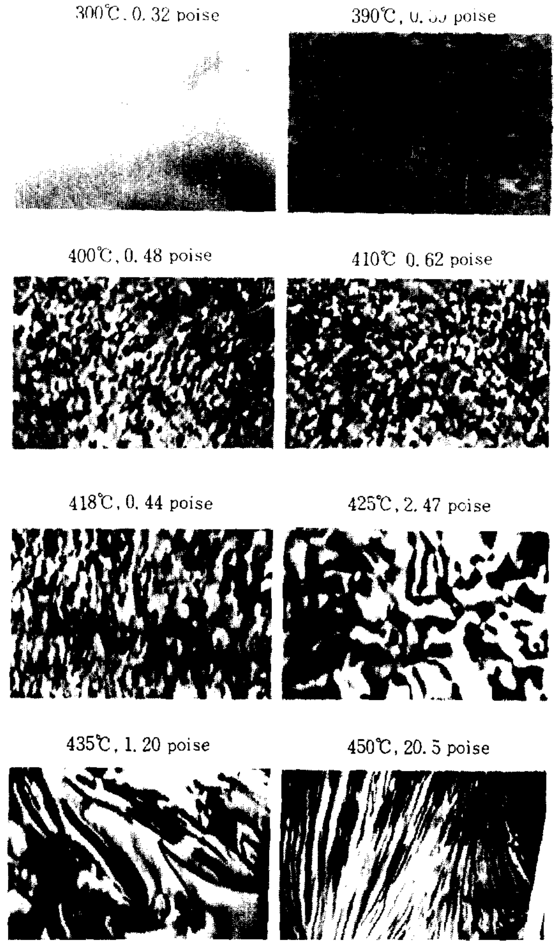

Fig. 4. Observation of mesophase pitch for PP-1.

cosity-temperature curves were similar to those of Didckenko [3], Collet [4], but this PP-1 shows the peak twice apparently. These phenomena can be explained in detail on the observation of Hot-Stage-Cinema-Microscope in Figure 4.

The small mesophase spheres being formed in the pyrolysed pitch near 390°C have slowly transformed the isotropic phase to anisotropic phase made the mobility dull as the reports of Lewis [11]. Lewis has compared pitch-mesophase systems to unstable emulsions. If this analogy is retained, it is clear that, at temperature below 410°C, the pitches can be considered as emulsions of mesophase droplets dispersed in a continuous isotropic liquid phase.

From about 410°C, the dehydrogenation and the polymerization of PP-1 becomes rigorous and the volatilization rate becomes maximum up to 418°C. As the mesophase content increases, coalescence occurs more readily and the particles become more irregular in shape until at about 418°C.

As increasing the mesophase shpere sizes, the apparent viscosity decreases and the mobility becomes more fluid.

Krevelen and Schuyer [12] have reported that the apparent viscosity have a minimum value at a temperature corresponding to the maximum rate of volatilization.

At temperature about 418°C, the volatilization becomes weak and the coalesced mesophase rapidly makes an interlocked network with isotropic liquid, simultaneously the viscosities increase rapidly up to 425°C. Above about 425°C, there appears to be a phase inversion and the mesophase becomes the continuous phase within which droplets of the isotropic phase are dispersed. Then the interlocked network of two-phase moves again and makes a alignment along the stream of mesophase.

Therefore, the viscosities decrease again. Han [13] have reported that two-phase polymer melts also exhibit a maximum in apparent viscosity when an interlocked structure is apparent prior to phase inversion and Sherman [14] have also observed a maximum in the apparent viscosity of water-oil emulsions at a concentration near to the phase inversion value.

In the interlocked microstructure the mesophase regions are randomly orientated and connected. But during flow these networks must be broken and this leads to greater energy dissipation than when the mesophase was in the form of discrete shperes [15].

However when the mesophase becomes the continuous phase, the anisotropic structure can be orientated much more easily in the direction of flow, leading to a decrease in the apparent viscosity.

Over the whole temperature range, polymerization is continuing in the pyrolysed pitch, producing even higher molecular weight species with a lower mobility. Hence, the apparent viscosity increased again very sharply indeed at higher temperature above 435°C, but the rotating speed of spindle was decreased by increase of mesophase content. Whittaker [16] have also reported that the rotating speed decreases rapidly when the mesophase content approaches 50%. The thermally produced QI matter in pyrolysed pitches is usually identified with the carbonaceous mesophase. Therefore the QI content can be correlated with mesophase content and apparent viscosity.

Figure 5 shows QI content of pyrolysed pitches with respect to heat treatment temperature.

QI content increased slowly from about 390°C, increased sharply between 410°C and 440°C, and then increased slowly after 440°C. In general, the content of mesophase spheres could be identified to the QI content and corresponded with the increase of the apparent viscosity till 410°C.

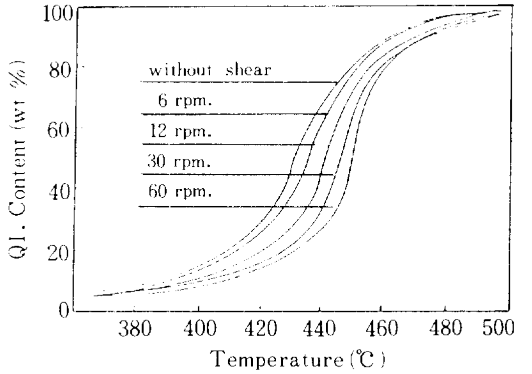

Fig. 5. Q. I. contents of PP-1 with respect to heat treatment temperature.

However, the viscosity change couldn't be correlated with QI content because of mesophase coalescence and mobility change, even though the content of mesophase could be equalized to QI content. Above 440°C, the viscosity increases sharply because of low mobility of anisotropic phase, but the QI content doesn't increase like a viscosity increase. Especially QI content could not be equalized to mesophase content at higher temperature, since some of isotropic pitch could be transformed to cokes directly.

In this study non-mesophase fraction of QI content which was formed at higher temperature couldn't be distinguished from QI content, because that fraction is out of interests. From the figure, the QI content of mesophase pitch without rotating the spindle is more than those with shearing. Besides, increase of the shear rate have delayed the transformation of isotropic phase to anisotropic phase.

Figure 6 is a plot of the apparent viscosity change of PP-2 with respect to the heat treatment. The mesophase spheres have appeared at about 400°C. Above 420°C, the mobility of pyrolyzed pitch becomes dull and the viscosity increases till 430°C.

At about 430°C, the pyrolysed pitch becomes much fluid and accompanied with rigorous polymerization and dehydrogenation reactions.

Then the pyrolysed pitch becomes viscous again above 440°C, and also the viscosity was rapidly increased as a result of forming an interlocked network of two-phase. However, the interlocked network of two-phase has broken slowly and orientated at near 448°C, but its mobility was not good as that of PP-1.

Rheological behaviours of pyrolysed pitch

To investigate the rheological behaviours of the mesophase pitches depending on the increase of heat treatment temperature, the viscosities of PP-1 were

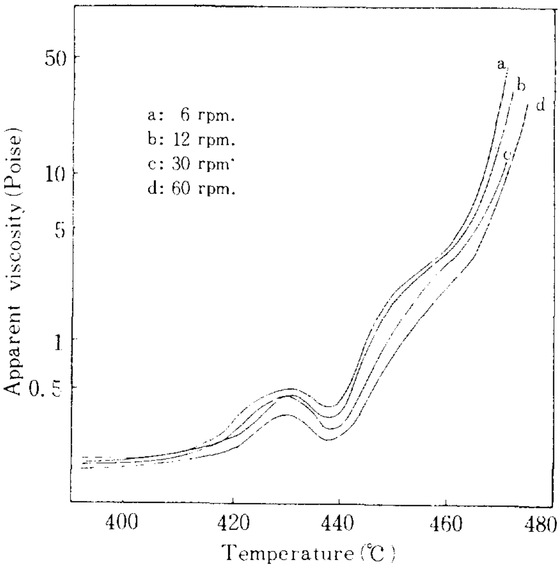

Fig. 6. Apparent viscosity of PP-2 with respect to heat treatment temperature.

measured at various spindle speeds and temperatures. Simultaneously the shear rates and the shear stresses were calculated by using the equation (1) and (2). Figure 7 is a plot of the apparent viscosity with respect to the spindle speeds at each temperature. Though the shear rates were changed, the viscosities were constant from 300°C to 390°C.

It means that the shear stress of this pyrolysed pitch is linearly proportional to the shear rate on this range of temperature, and this pitch shows a Newtonian fluid characteristics.

McNeil [18] has reported that the flow properties of all types of coal tar pitches are Newtonian in character and that their rheological properties are adequately specified by one viscosity measurement at one temperature, which may be conveniently chosen to be the softening point of the pitch.

Collet [4] has also reported the pyrolysed pitches are Newtonian liquids at low temperatures, but non-Newtonian character appears at temperatures above 380°C. On the other hand, Bhatia et al. [2] suggested all pitches, pure or mixed with a carbon additive, are behave rheologically as Bingham plastics.

But their results were obtained between 85-180°C and they have also suggested that the yield stress and apparent viscosity both decrease with increase in temperature of the pitch.

In the Figure 7, the apparent viscosities were decreased as increasing the shear rates, and the pyrolysed pitch became shear-thinning because of mesophase formation, growth, coalescence, and alignment at

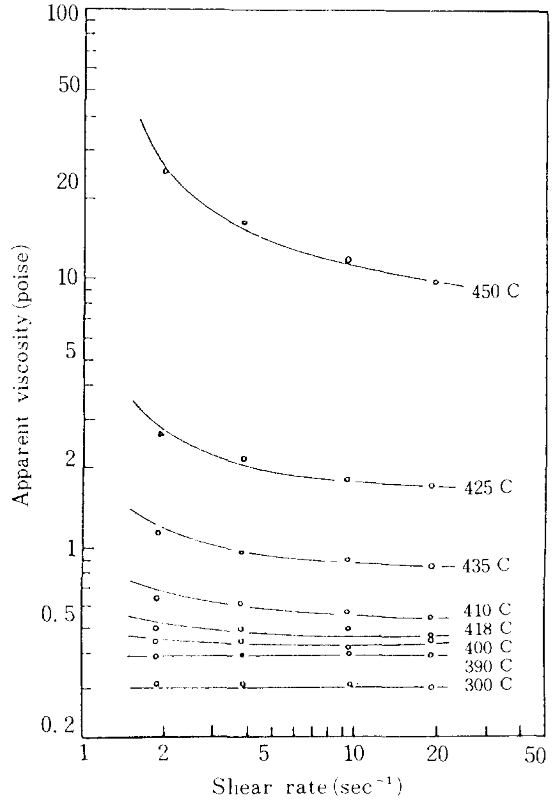

Fig. 7. Dependence of viscosity on shear rate for PP-1.

temperatures above 390°C.

White [17] has reported that the alignment of the mesophase molecules along the fiber axis during the drawing of fiber suggests that this phase should be shear-thinning. Didchenko et al. [3] have also observed shear-thinning behaviour at high temperature above 400°C. The relationship between shear stress and shear rate of this pyrolysed pitch could be plotted in a log-log paper, and the flow behaviour indexes(n′) could be obtained from the slopes. That results of PP-1 were listed in Table 2.

As the table shows the flow behaviour indexes are 1 at temperatures below 390°C and this isotropic phase acts as a Newtonian fluid. But the flow behaviour indexes became less than 1, and the anisotropic phase acts as a pseudoplostic fluid at temperatures above

Table 2. Flow behaviour indexes of PP-1.

Temp. (℃)	300	390	400	410	418	425	435	450
n′	1	1	0.96	0.94	0.97	0.84	0.88	0.70
K′	0.32	0.40	0.50	0.64	0.46	2.80	1.20	24.C

390°C. The changes of flow behaviour index and flow consistancy index are apparent when the interlocked network is composed of two-phase.

CONCLUSIONS

1. The apparent viscosity-temperature curves of pyrolysed petroleum pitches show the maximum and minimum values depending on the formation, growth, coalescence of mesophase spheres, alignment of coalesced mesophase, and solidfying of two-phase.
2. Pyrolysed pitches behave Newtonian fluid (the flow behaviour indexes are 1) at temperatures below 390°C in the shear rate range of 1.9-20 sec^{-1}, but pseudoplastics at temperature above 390°C.
3. Rheological behaviour of pyrolysed pitches is much affected by the pretreatment conditions, and phase transformation is delayed by increasing the shear rates.
4. The apparent viscosity and Q.I. content of petroleum pitches are both increased as increasing the pyrolysed temperature, but viscosity change couldn't be correlated with Q.I. content above 410°C.

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