

Rheological Study of Eucalyptus Tar Pitches

MARCOS J. PRAUCHNER,¹ VÂNIA M. D. PASA,¹ CHOYU OTANI,² SATIKA OTANI²

¹ Departamento de Química, Universidade Federal de Minas Gerais, Avenue Antônio Carlos, 6627 Belo Horizonte, Brazil

² Departamento de Física, Instituto de Tecnologia Aeroespacial, São José dos Campos, Brazil

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ABSTRACT: The development of advanced carbonaceous materials (ACMs) from biopitches is important to increase the revenue of the charcoal making industry and to stimulate the use of biomass, thereby attending to the appeals for environmental preservation. A pioneer study on the rheological behavior of eucalyptus tar pitches was carried out in this work. This behavior plays an important part in obtaining ACMs from pitch, particularly in the spinning step of carbon fiber production. Our results showed that biopitches have a strong dependence on the viscosity and temperature/softening point ratio. An Arrhenius-type law gave the activation energies for viscous flow. Different from conventional polymers, this energy was higher for more polymerized pitches because of their higher molecular stiffness. The results obtained by the Williams–Landel–Ferry equation showed that the viscosity can be associated with the free volume. Lower viscosities correspond to larger free volume. The plot of the apparent viscosity versus the shear time at constant temperature and shear rate showed that the pitches have a purely viscous flow. Experiments that changed the shear rate showed that biopitches behave as Newtonian fluids. Purely viscous and Newtonian behaviors are desirable for more stable spinning. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 900–908, 2002; DOI 10.1002/app.10096

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INTRODUCTION

The pitch based advanced carbonaceous materials (ACMs) will have an important role in the 21st century economy because an abundant and cheap raw material (an industrial residue) can be used to obtain materials with very interesting properties and a large number of applications. Examples are carbon fibers,^{1–4} carbon–carbon composites,^{2–6} anodes for lithium-ion batteries,⁷ and activated carbons.^{8,9}

Fossil pitches have been extensively studied as precursors of ACMs. However, so far the same studies have not been carried out for wood tar pitches, probably because their existence is practically restricted to Brazil, where the tropical climate favors forest growth. This country has an important steel industry, which produces about 6.3 million tons/year of pig iron. About one-fourth of this production uses charcoal as a thermoreducer, consuming around 6.6 million tons of charcoal in Brazil every year. About 67% of this charcoal is obtained from planted eucalyptus forests.¹⁰

During the slow pyrolysis of eucalyptus wood for charcoal production, the vapors that are generated are washed and condensed and form a tar, which when distilled produces a residue (about 50%) called eucalyptus tar pitch. This pitch is an

Correspondence to: V. Pasa (vanya@dedalus.lcc.ufmg.br).

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oligomer constituted basically of phenolic rings interlinked and highly substituted with elevated functionality and oxygen content. Further, they have a wide molar mass distribution.¹¹

The potential production of Brazilian eucalyptus tar pitches is about 250,000 tons/year, considering only planted forests. The development of the technology to produce ACMs from biopitches is important to increase the revenue of the charcoal making industry and to stimulate the use of biomass. This is ecologically advantageous because biomass is a renewable source of both energy and polymeric materials, and its use as an energy source gives rise to a closed carbon cycle.¹²

In this work a pioneer study on the rheological behavior of eucalyptus tar pitches was carried out. This behavior plays a very important role in the manufacturing process of carbon products from pitches, particularly in the spinning step of carbon fiber production, where the rheology influences the properties and homogeneity of the fibers that are produced. The experiments were conducted in static and transient modes. The apparent viscosity was measured in the static mode as a function of the temperature at a constant shear rate and as a function of the shear rate at constant temperature. In the transient mode the apparent viscosity was measured as a function of the shear time at constant temperature and shear rate. The viscosity is a measurement of the internal friction of a fluid caused by molecular attraction. This friction gives rise to fluid flow resistance¹³ and depends on the fluid molecular structure, average molar mass, and molar mass distribution.¹⁴

The pitches that were used had different degrees of polymerization after heat treating a precursor pitch.

EXPERIMENTAL

Production of Pitch

Wood chips (30–40 cm long) of planted eucalyptus forests (Minas Gerais, Brazil) were submitted to slow pyrolysis in industrial masonry ovens with a maximum pyrolysis temperature of about 400–500°C (12–14°C/h). The smoke was washed and condensed, producing a eucalyptus tar. The precursor pitch was obtained by vacuum distillation of this tar via a 3000-L boiler coupled to a fractionation column of four drilled plates. Homogenization of the mixture was accomplished through a centrifuge pump, which recirculates

the material available in the bottom of the boiler. The cut temperature was 180°C at 30–38 mmHg (corresponding to 260°C at 760 mmHg). The distillation time was about 8 h and the pitch yield was about 50% (w/w).

Heat Treatments

The pitches with different degrees of polymerization were obtained by heat treating the crude pitch (about 400 g) in a 1000-mL kettle vessel connected to a vigreux column and using an electric mantle. The pitch was homogenized using a mechanical stirrer, and the bulk temperature was measured. The treatments were conducted at 250°C for 2 and 4 h.

Differential Scanning Calorimetry (DSC)

DSC was used to determine the pitch glass-transition temperatures (T_g). The analyses were carried out in a Shimadzu DSC-50 calorimeter following ASTM D3418-82. The powdered samples (about 10 mg) were weighed into an aluminum pan, placed in the DSC cell, and heated at a rate of 20°C/min under a helium dynamic atmosphere (50 mL/min). As discussed in a previous work,¹¹ the first DSC scan of biopitches with a T_g near room temperature displays an endothermic peak overlapping with the glass transition. Accordingly, the samples were first heated from room temperature to 100°C and held at this temperature for 10 min to erase their thermal history. After cooling the samples and repeating the scan, only the glass transition appeared. In accordance with the ASTM norm, the determinations were made in duplicate and they did not differ by more than 2.5°C.

Softening Point (SP)

The SPs were determined using the ring and ball method following the ASTM D2398-73 standard test. In accordance with the standard, the tests were carried out in duplicate. If the measurements presented a difference larger than 1°C, the analyses were repeated.

Gel Permeation Chromatography (GPC)

GPC analyses were used to determine the molar mass distribution and the weight-average molar masses (M_w) of the soluble fraction of pitches in tetrahydrofuran (THF). The analyses were carried out in a Shimadzu LC-10AD liquid chro-

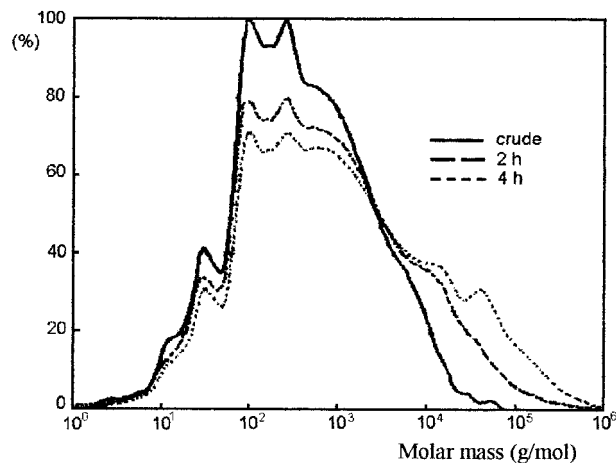


Figure 1 Molar mass distribution curves for crude eucalyptus tar pitch treated at 250°C for 2 and 4 h.

matographer coupled with a Shimadzu UV-VIS SPD-10AV detector at 254 nm and a Shimadzu C-R7A Chromatopac integrator with software for GPC calculations. The experiments were based on techniques developed for lignin analyses.¹¹ The elution was carried out in THF at 30°C and a flow rate of 1 mL/min using two coupled columns of polystyrene–divinylbenzene gel (Shim-pack GPC-8025 and Shim-pack 803). Injections of 20 μ L were made with the samples dissolved in the eluant (2 mg/mL). The calibration curve was built using polystyrene standards.

Rheological Studies

The apparent viscosity was measured using a Brookfield HADV-III digital rheometer and a Brookfield Thermosel accessory. The temperature was controlled by means of a Brookfield model 75 temperature controller. Rheocalc software was used for data acquisition. A SC4-21 spindle was used inside a cylindrical sample holder for all testing. The sample volume was 8 mL. Because of the strong effect of the temperature on the apparent viscosity, the pitch and spindle were both preheated for 30 min before the spindle was lowered into the sample. In addition, 30 more min were allowed for temperature equilibrium before the spindle was rotated.

RESULTS AND DISCUSSION

Sample Physical–Chemical Characterization

The heat treatments give rise to pitch polymerization. This effect can be established by the re-

duction in the amount of shorter molar mass molecules and the increase in the amount of high molar mass molecules, which can be verified by the GPC curves (Fig. 1). This polymerization brought about enhancements in the estimated M_w values (Table I). However, these values should be taken into account only in a comparative way because, as previously discussed,¹¹ some experimental difficulties make pitch GPC analyses not absolute.

Polymerization was followed by increases in the T_g and SP (Table I). The T_g is the temperature at which the molecules get enough energy for medium- and long-range motions. The SP is an arbitrary measurement, which provides an indication of the temperature at which the material gets adequate viscosity to flow in a plausible range time. Although these two properties are related to each other,¹⁵ SP has been demonstrated to be more useful for dealing with pitches, because the measurements are easier to make and more accurate. Moreover, sometimes it supplies more valuable information for material processing. For example, it indicates the maximum temperature at which a pitch artifact can be treated without deforming and provides an estimate of the temperature range for pitch spinning.

Viscosity Dependence on Temperature

Many experimental difficulties appeared during the rheological studies. The main one concerns the instability verified in the viscosity measurements that is due to bubble formation. These bubbles result from continuous volatile release during pitch heating. Because small and volatile molecules are present even in the sample with a higher degree of polymerization (Fig. 1), the higher the temperature, the higher the viscosity instability, regardless of the sample. This can be established in the apparent viscosity versus the shear time plots (Fig. 2), in which the higher the

Table I Weight-Average Molecular Weight (M_w), Softening Point (SP), and AI Values for Crude Eucalyptus Tar Pitch Treated at 250°C

Treatment Time (h)	$M_w \times 10^3$ (g/mol)	T_g (°C)	SP (°C)
Crude pitch	2.1	26	76
2	4.2	29	97
4	5.4	33	119

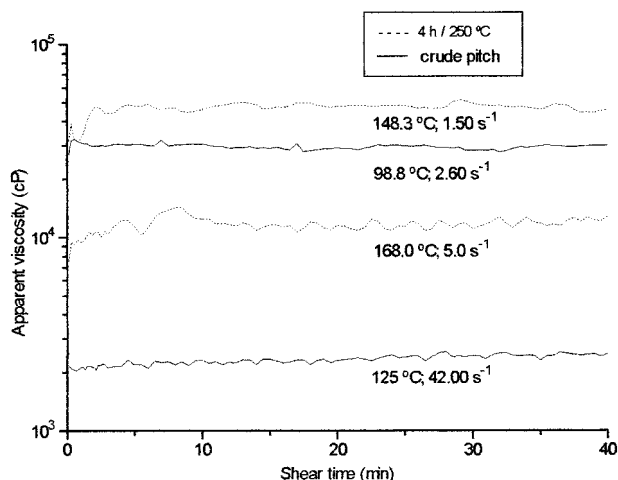


Figure 2 The apparent viscosity as a function of the shear time at constant temperature and the shear time for crude eucalyptus tar pitch treated at 250 °C for 4 h.

measurement temperature, the more oscillation in the respective curve. This sort of problem also occurs with fossil pitches¹⁶ but only at higher temperatures, because their molecules are larger and, consequently, less volatile. To minimize the experimental errors resulting from viscosity instability, the measurements in the static modes were always carried out in triplicate.

With increasing temperature the thermal movement of pitch molecules becomes more rapid and random and intermolecular interaction forces decrease, leading to decreasing viscosity.¹⁴ The plots of the apparent viscosity versus the temperature (Fig. 3) show that there is a large depen-

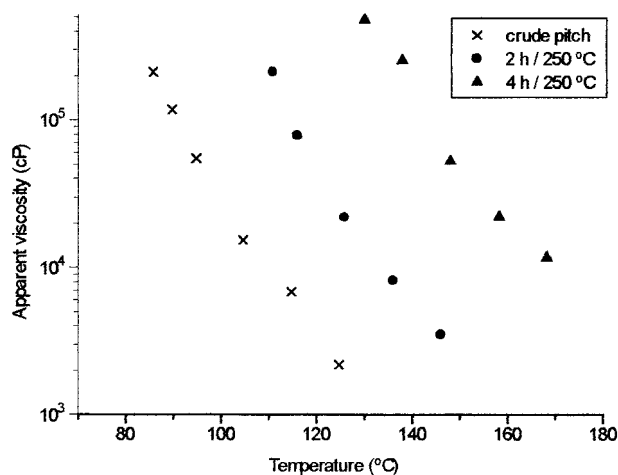


Figure 3 The apparent viscosity as a function of the temperature for eucalyptus tar pitches.

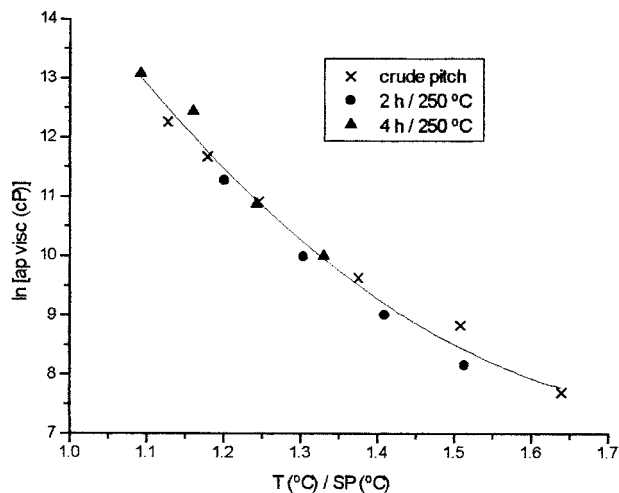


Figure 4 The apparent viscosity as a function of the temperature/softening point (T/SP , °C) ratio for eucalyptus tar pitches.

dence between the biopitch viscosity and the temperature. An increase of 5 °C in the temperature gives rise to a viscosity reduction of 50–60%. As a result, rigid temperature control is needed during pitch spinning.

An interesting result was obtained while plotting the apparent viscosity (η_{ap} , cP) as a function of the ratio of the measurement temperature over the sample SP (T/SP , °C). The curves are brought approximately together for all pitches (Fig. 4), and it is possible to establish the following general relation:

$$\ln \eta_{ap} = 43 - 39(T/SP) + 11(T/SP)^2 \quad (1)$$

Therefore, the SP and the consequent polymerization degree of eucalyptus tar pitches can be estimated from viscosity measurements. Moreover, if the SP of a given sample is known, the temperature for a given viscosity, such as that necessary for spinning, can be estimated.

The relation above leads to the conclusion that, apart from considerations about other factors such as the facility for stabilization and carbonization yield, it would be more suitable to use pitches with a low softening point in carbon fiber production, because lower temperatures are necessary to reach the spinning viscosity, thus reducing bubble formation and making the process more stable.

The effect of temperature on the viscosity of melt polymers is very complex. Several mathematical formulations of this effect have been pre-

sented in the literature, but none has held for every arbitrary polymer over the whole range of temperatures, mainly at temperatures below the melting point. For temperatures far over the melting point of a given polymer, usually the temperature dependence of the viscosity follows an Arrhenius-type law:

$$\ln \eta = \ln A + E_{\eta}/RT \quad (2)$$

where A is a constant, E_{η} is the activation energy for viscous flow, and R is the gas universal constant.

This expression is interpreted by means of the hole theory of liquids.¹⁷ The E_{η} is an energy barrier, which the molecules need to overcome to jump from an unoccupied site to another. This is called the shearing activation energy, and for low molar mass liquids it is related to the heat of vaporization because the removal of a molecule from the environment of its neighbors forms part of both processes. In this way, the larger the molecules, the stronger the interactions and the higher E_{η} . However, for high molar mass molecules the E_{η} levels off at a value independent of the molar mass, because for long chains the flow is carried out by successive jumps of segments until the whole chain has shifted.

Figure 5 shows the plotting of $\ln \eta_{\text{ap}}$ versus the reciprocal temperature for the pitches studied. The linear aspect of the curves shows that the

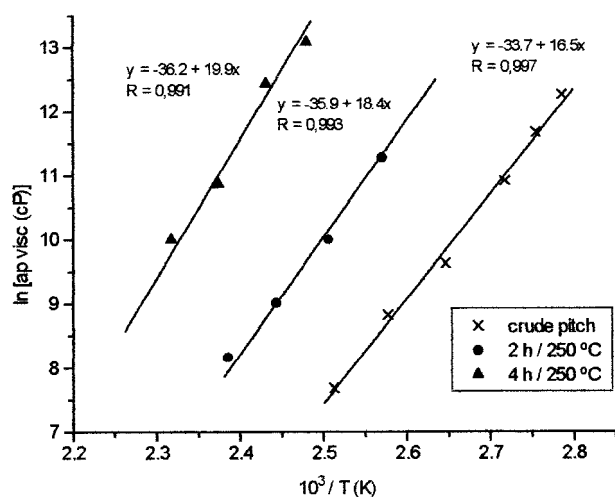


Figure 5 The natural logarithm (\ln) of the apparent viscosity as a function of the reciprocal temperature for crude eucalyptus tar pitch treated at 250°C for 2 and 4 h.

Table II Parameters of Arrhenius-Type Law for Crude Eucalyptus Tar Pitch Treated at 250°C

Treatment Time (h)	A (cP)	E_{η} (kJ/mol)
Crude pitch	1.7×10^{-15}	133
2	2.3×10^{-16}	150
4	2.3×10^{-16}	166

dependence of the apparent viscosity on the temperature in the range studied follows an Arrhenius-type law. Therefore, the A and E_{η} for each pitch sample were calculated (Table II) from the respective curves. The values are listed in Table II. If the A and E_{η} are known, the apparent viscosity of a pitch sample can be estimated at any temperature by eq. (2).

The results showed that the E_{η} increases with the increasing degree of polymerization of the pitch instead of leveling off. This probably occurs because the movements of isolated segments in the larger molecules of more polymerized pitches become more difficult. Further, the polymerization process not only gives rise to polymerization, but it also affects the material molecular structure, increasing the aromaticity due to the release of aliphatic side chains.¹¹ As sp^3 links in aliphatic side chains display reduced rotation energy, which by its turn facilitates molecular movements, the higher aromaticity of more polymerized pitches contributes to make their molecular motions more difficult and increase E_{η} .

Biopitches have larger E_{η} than is usual for conventional polymers. For example, from the curves of the viscosity versus $10^3/T$ provided by Fleurot and Edie,¹⁶ an E_{η} of 82 kJ/mol can be estimated for nylon 6. Considerations about polarity and molecular interactions aside, this can be attributed to the higher stiffness of pitches due to their 3-dimensional structures and elevated aromaticity. A higher E_{η} represents the higher sensibility of the apparent viscosity to temperature changes.

Nazem¹⁸ calculated the E_{η} for an isotropic petroleum pitch as 161 kJ/mol. This value is similar to those calculated for eucalyptus tar pitches, in spite of the more polar structure of the latter. Some factors such as their lower average molar mass or their higher content of sp^3 links should compensate the higher polarity.

Table III Parameters of WLF Equation for Crude Eucalyptus Tar Pitch (SP = 76°C)

	T_r (°C)							
	76	80	85	90	95	100	105	110
C_1	20.5	20.3	20.0	19.7	19.4	19.2	18.9	18.7
C_2 (°C)	349	353	358	363	368	373	378	383
$f_r \times 10^2/B$	2.12	2.14	2.18	2.20	2.23	2.27	2.30	2.33

Williams–Landel–Ferry (WLF) Equation

The WLF equation¹⁹ describes the reduced variables shift factor (A_T) of polymers for two given temperatures (a reference temperature T_r and another temperature T) in terms of empirical parameters. The A_T relates not only to the time for a transition (t_r and t), but also to many other time-dependent quantities. The most important one is the viscosity. Therefore,

$$\begin{aligned} \log(A_T) &= \log(\eta/\eta_r) \\ &= \frac{-B/2.303f_r(T - T_r)}{f_r/\alpha_f + T - T_r} \\ &= \frac{C_1(T - T_r)}{(C_2 + T - T_r)} \end{aligned} \quad (3)$$

where B is a constant, f_r is the fractional free volume at T_r , and α_f is the expansion coefficient of the free volume.

Rearrangement of this equation indicates that a plot of $(T - T_r)/\log(\eta/\eta_r)$ versus $(T - T_r)$ will yield a straight line with

$$C_1 = -B/2.303f_r = 1/\text{slope}; \quad (4)$$

$$C_2 = f_r/\alpha_f = \text{intercept/slope} \quad (5)$$

This sort of plot was made at several different reference temperatures (from SP to SP + about 35°C) for the three pitches studied. The respective

C_1 and C_2 values were determined (Tables III–V). The viscosity value at each temperature was taken from the equations for the curves in Figure 5 instead of directly using experimental values. In this way, distortions in the viscosity measurements were overcome. Knowing the C_1 and C_2 for a given reference temperature, the viscosity at any other temperature can be estimated if the viscosity at a particular temperature is known.

The f_r corresponding to each C_1 determined was estimated in terms of the constant B (Tables III–V). The results show that the free volume increases with increasing temperature. Therefore, the viscosity of pitches can be associated with the presence of free space in the material, in accordance with the free volume theory.²⁰ The lower viscosities of a pitch sample at more elevated temperatures can be explained by larger f_r . Moreover, considering B nearly constant for biopitch samples with different degrees of polymerization, the higher viscosity at the same temperature of more polymerized pitches can also be attributed to their smaller free volume, as shown in Table VI.

Viscosity Dependence on Shear Rate

The viscosity of materials constituted by large nonsymmetrical molecules usually depends on the shear rate (non-Newtonian behavior). In most cases the fluid displays decreasing apparent viscosity with increasing shear rate. This behavior is called pseudoplastic or shear thinning.¹³

Table IV Parameters of WLF Equation for Eucalyptus Tar Pitch Treated at 250°C (SP = 97°C)

	T_r (°C)							
	97	100	105	110	115	120	125	130
C_1	21.6	21.4	21.1	20.8	20.6	20.3	20.1	19.8
C_2 (°C)	370	373	378	383	388	393	398	403
$f_r \times 10^2/B$	2.01	2.03	2.06	2.08	2.11	2.14	2.16	2.19

Table V Parameters of WLF Equation for Eucalyptus Tar Pitch Treated at 250°C (SP = 119°C)

	T_r (°C)							
	119	125	130	135	140	145	150	155
C_1	22.0	21.7	21.4	21.2	20.9	20.7	20.4	20.2
C_2 (°C)	392	398	403	410	413	418	423	428
$f_r \times 10^2/B$	1.97	2.00	2.03	2.05	2.08	2.10	2.13	2.15

The apparent viscosity was measured while ranging the shear rate at constant temperature to assess if eucalyptus tar pitches behave as Newtonian or non-Newtonian fluids. The measurements were made to cover as large a range of shear rate as possible within the equipment torque range. The tests were carried out for the more and the less polymerized pitches at two different temperatures. In this way, both regions of higher and lower viscosity were covered for pitches of variable polymerization degrees.

However, the experiments were made difficult by the viscosity instability. To overcome this problem, the measurements were made quickly only at three given shear rates, so that there was insufficient time for considerable fluctuations to occur in the apparent viscosity during a scan. Further, to obtain more representative values, the scans were done in triplicate and the medium value for each shear rate was taken into account.

For all tests, regardless of the sample degree of polymerization and temperature, the curves showed a very small decrease in the apparent viscosity with increasing shear rate [Figs. 6(a), 7(a)]. In the shear stress versus the shear rate curves [Figs. 6(b), 7(b)], it was not possible to perceive the loss of linearity characteristic of non-Newtonian behavior. Therefore, it can be concluded that eucalyptus tar pitches display Newtonian behavior.

Isotropic materials usually display Newtonian behavior.^{18,21} On the other hand, fossil pitches

with a high degree of polymerization, mainly those having some mesophase content (nematic liquid crystals formed by the packing of large

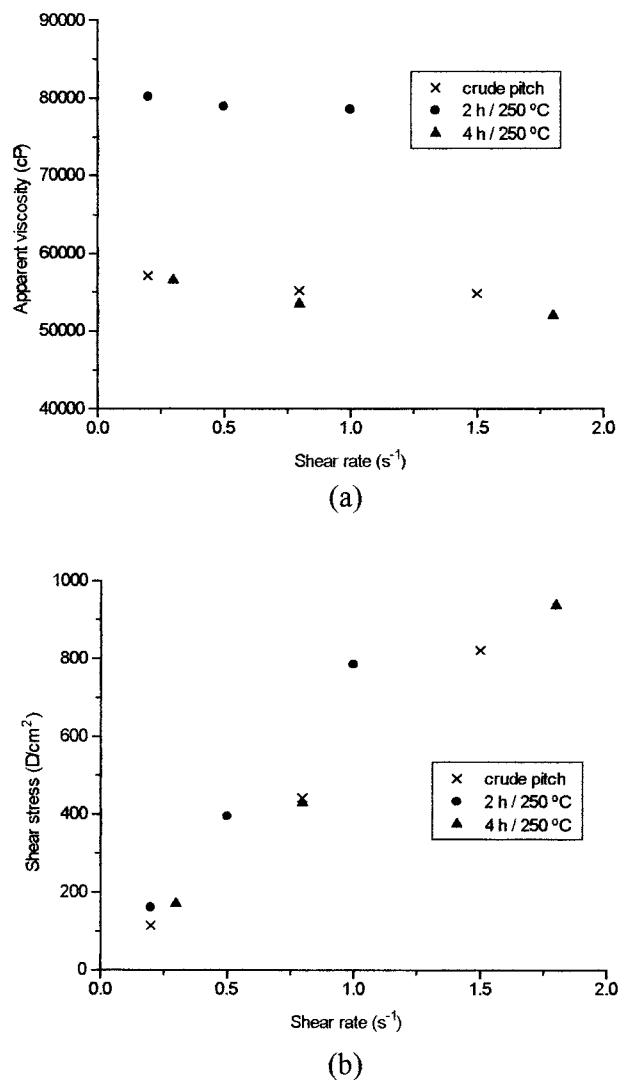


Figure 6 The (a) apparent viscosity and (b) shear stress as a function of the shear rate for crude eucalyptus tar pitch treated at 250°C for 2 and 4 h. The rheological experiments were carried out at 94.8, 115.9, and 148.0°C (temperatures corresponding to regions of high viscosities).

Table VI Viscosity and Free Volume at 120°C for Crude Eucalyptus Tar Pitch Treated at 250°C

	Treatment Time (h)		
	Crude	2	4
η (cP)	3.5×10^3	5.4×10^4	1.8×10^6
$f_r \times 10^2/B$	2.39	2.14	1.98

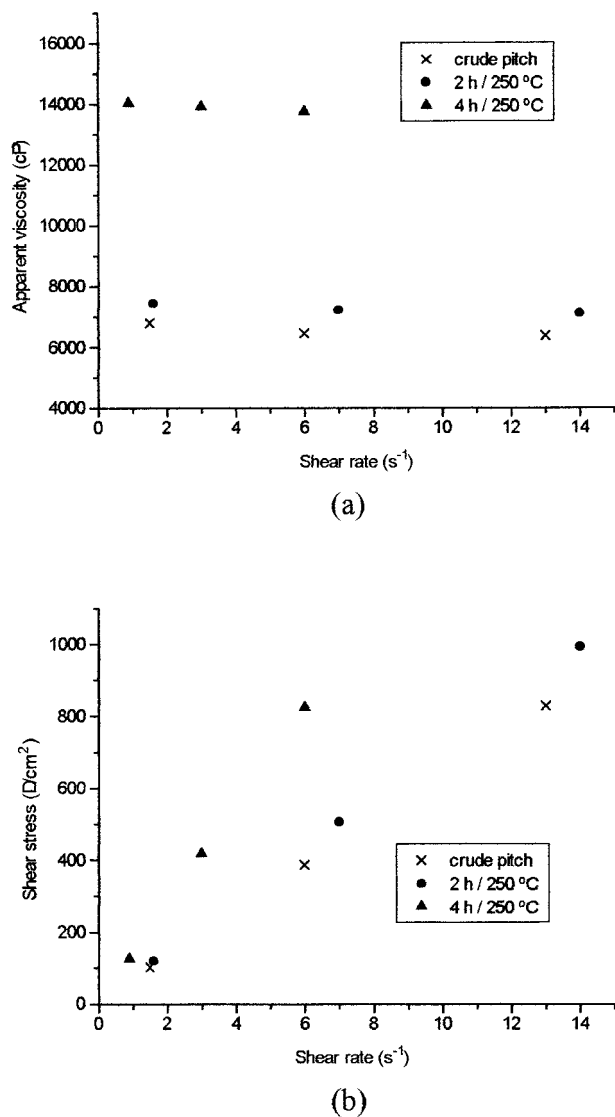


Figure 7 The (a) apparent viscosity and (b) shear stress as a function of the shear rate for crude eucalyptus tar pitch treated at 250 °C for 2 and 4 h. The rheological experiments were carried out at 114.8, 135.9, and 168.3 °C (temperatures corresponding to regions of low viscosities).

planar molecules²²), usually display highly pseudoplastic behavior at low shear rates.^{23,24} Collet and Rand²⁵ suggested that coal tar pitches are initially Newtonian in character, but non-Newtonian behavior appears when the average molar mass increases as a result of the polymerization process and volatilization of low molar mass species. The more accepted reason for this is that shearing can orient the larger and more planar molecules. In this way, the higher the shearing, the higher the orientation, and the lower the flow

resistance.^{20,23} Consequently, it can be concluded that small and nonplanar molecules, which cannot be oriented by shearing, constitute eucalyptus tar pitches. This statement is in accordance with their relatively low M_w values (Table I) and their high degree of substitution and aliphatic carbon content verified earlier.¹¹

Transient Mode Studies

Fossil pitches having a high degree of polymerization and consequently a high quinoline insoluble content usually display thixotropic behavior. This behavior is characterized by a declining apparent viscosity at the time when the material is subjected to shearing at constant shear rate and temperature. Usually this effect is observed in the initial seconds or minutes after the spindle starts spinning and is attributed to the high degree of condensation and crosslinks among the molecules, which makes the material display an elastic component in the flow beyond the viscous one (viscoelastic behavior).^{14,25}

Viscous flow is a nonreversible process in which energy is dispersed as heat. By contrast, elasticity is a reversible phenomenon in which energy is stored as potential energy.¹³ The presence of this stored energy in the fluid can influence the properties and morphology of the final material.²⁴ Therefore, the viscosity of materials with thixotropic behavior depends on their history. Any motion that causes shearing, such as stirring or flow, can alter their apparent viscosity.

Experiments in transient mode were carried out to verify the presence or absence of elasticity in biopitches. Once more the experiments were carried out for the more and the less polymerized pitches at two different temperatures, so that both regions of higher and lower viscosity were assessed for pitches of variable degrees of polymerization. The shear rates were varied from test to test according to the equipment torque range. The results (Fig. 2) show that eucalyptus tar pitches, both less and more polymerized ones, do not display viscoelastic behavior in either the low or high viscosity regions. This is in accordance with the low average molar masses estimated for these pitches.

CONCLUSIONS

All eucalyptus tar pitch samples presented approximately the same relation between the appar-

ent viscosity and temperature/SP ratio. This suggests that it is more suitable to use pitches with a lower SP in carbon fiber production because lower temperatures will be necessary to reach the spinning viscosity, thus reducing bubble formation and preventing degradation, and consequently making the process more stable. On the other hand, it is necessary to point out that a low SP makes the thermostabilization of the as-spun fibers difficult, so that these two effects should be taken into account in choosing the precursor pitch, as discussed elsewhere.²⁷

Biopitches follow an Arrhenius-type law, which permits the estimation of their energy of activation for viscous flow. The results showed that, different from conventional polymers, biopitches with higher degrees of polymerization present higher E_{η} . Therefore, it can be concluded that the larger 3-dimensional molecules of more polymerized pitches and their higher aromaticity make the movement of isolated segments more difficult, hence increasing the E_{η} .

It was verified by means of the WLF equation that the free volume of pitches increases with increasing temperature. Being so, the viscosity of pitches can be associated with the existence of free space, in accordance with free volume theory.²⁰ Lower viscosities correspond to larger free volume.

Biopitches show a purely viscous flow, which is in agreement with their relatively small constituent molecules. Moreover, they display Newtonian behavior because the aromatic rings in their molecules are highly substituted, which makes them nonplanar. These results lend a good perspective on using wood tar pitches as precursors in carbon fiber production because purely viscous and Newtonian behaviors are desirable for more stable spinning and contribute to fiber homogeneity.

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