Effect of erucic acid on the rheological and surface properties of coal tar pitch

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Abstract

Coal tar pitch (CTP) was modified using erucic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{COOH}$, and the rheological and surface properties of the modified CTP were evaluated. The effect of erucic acid was investigated using a rotational viscometer as well as by drop and weight tests. The modified CTPs were characterized by Fourier transform infrared spectroscopy and scanning electron microscopy following a carbonization process. The results showed significant differences in several properties between the CTP and modified CTPs, such as decreases in viscosity, wetting temperature, and softening point when erucic acid content was 1 – 3 wt. % of CTP. An improvement in bonding between the coke and the modified CTP can be achieved when the coke value remained 62%. Moreover, a modification mechanism was proposed to explain the physical plastification of CTP modified with erucic acid.

Keywords: coal tar pitch, erucic acid, rheological property, adhesion

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1. INTRODUCTION

The development and production of high-performance carbon materials need a high quality binder such as coal tar pitch (CTP), which is one of the most common aromatic binders for the production of anodes and electrodes, and also acts as the precursor of carbon–carbon composites [1,2]. The diverse application of CTP is attributed to its high carbon content, softening point, significant graphitization capability, and adhesion property. However, the application of CTP is greatly affected by its poor rheological characteristics and a narrow range of suitable operating temperatures, which increase both the mixing and baking temperatures, thus worsening the plasticity of the thickener and deteriorating the graphitization ability. Thus, several methods have been described to modify CTP in order to improve its rheological and surface properties, such as thermal treatments in inert or oxidative atmospheres [3,4], blending of additives such as petroleum coke [5], carbon black [6], iodine [7], and phenolic resin [8], as well as the addition of polymers such as polystyrenes [9].

In the last decade, studies have focused on the use of additives that are green, inexpensive, or waste materials to modify CTP. Several studies [10–12] on the properties of the blends prepared by mixing petroleum pitch with CTP in several proportions have been reported. Further, CTP has been modified using commercially available materials such as polyacrylonitrile (PAN) [13], divinylbenzene [14,15], carbon nano-fiber [16], terephthalaldehyde [17], and poly (vinyl chloride) [18,19]. However, the abovementioned studies were based on the chemical synthesis of additives, with few studies based on additives derived from natural products such as corn, rice husks, and pine tree. Li and coworkers [20,21] reported that the addition of furan resin decreased the softening point of CTP, while the carbon yield remained

unchanged, resulting in better flow ability. Further, they proposed a modification mechanism for CTP blended with furan resin. Kiser [22] modified CTP using biodiesel fuel and found that the viscosity of the resulting CTP changed remarkably; as the viscosity decreased, the softening point decreased and the carbon yield increased. Lin and coworkers [23,24] modified CTP using rosin and bismaleimide (BMI) with obvious improvements in rheological characteristics and anisotropy on carbonization.

Erucic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{COOH}$, is produced naturally (together with other fatty acids) by diverse green plants. Compared with other mineral oils, erucic acid is more readily biodegradable and can be converted into surfactants or lubricants. Besides, erucic acid, a monounsaturated mega-9 fatty acid, is less easily polymerized than other oils and hence easy to store and use. Furthermore, erucic acid is cheaply available. In this study, we modified CTP using erucic acid. The effects of the content of erucic acid on CTP and the properties of the modified CTP were investigated.

2. MATERIALS AND METHODS

2.1 Materials and modification

The CTP (diameter < 0.074 mm) was obtained from Shanxi Hongte Chemical Co., Inc. It has a softening point of 114.3°C and a coke yield of ca. 61.9 wt. %. The quinoline insolubles (QIs) and toluene insolubles (TIs) were 8.5 and 28 wt. %, respectively. The value of ash was 0.19 % and carbon/hydrogen (C/H) atomic ratio was 0.562. Erucic acid was obtained from Beijing Huaye Huanyu Chemical Co. Ltd. and added to CTP in proportions of 0, 1.0, 2.0, 3.0, and 4.0 wt. %. The modified CTPs were molded into columns (diameter and thickness =10.0 mm) after being mixed in a

reactor under stirring. The samples were labeled as PE₀, PE₁, PE₂, PE₃, and PE₄. Sample PE₀ represents the CTP without erucic acid. The needle coke used as the coke bed in both wettability and adhesive determination experiments was obtained from Shanxi Hongte Chemical Co., Inc., with a powder size of 0.15 – 0.5 mm.

2.2 Characterization

2.2.1 Rheological measurements

The viscosities of CTPs were measured using a rotational viscometer (SNB-A1, Shanghai Nirun Intelligent Technology Co., Ltd). The experiments were conducted by selecting the 27 rotor at 10 revolutions per minute (rpm), which then rose to 100-rpm when the temperature reached 180°C.

2.2.2 Wettability measurements

The wetting behavior of the samples was determined by the wet drop test using an apparatus which was proposed by Couderc et al. [25], and then successfully used in wetting behavior of pitch and coke [26], as shown in Figure 1. The samples were positioned evenly on a flat bed of coke. The bed containing the CTP columns were then placed in a furnace, and heated according to the following temperature/time profile: (i) heating at 1°C min⁻¹ up to 80°C for 20 min, and (ii) from 80 to 200°C at 0.5°C min⁻¹. A video camera was programmed to capture images every 10min.

(Insert Figure 1 here)

2.2.3 Adhesive measurements

Figure 2 shows the measurement of the adhesion ability of CTPs, similar to the test procedure proposed by Kravtsova [27]. The samples, pitch columns (weight, m₁≈1.0g), were placed on the center of a small coke bed made of weighing bottle and

coke particles. The system was heated in an oven for 1h, cooled, and the sample was weighed, which was denoted as m_2 .

(Insert Figure 2 here)

2.2.4 Softening point and Carbon yield

Softening points were measured using a Mettler Toledo apparatus according to the GB/T 2294-1997 standard procedure. The carbon yield was determined by the GB/T 8727-2008 standard procedure; the temperature could reach up to 550°C.

2.2.5 Microstructure characterization

Fourier transform infrared (FTIR) spectra were recorded using a Nicolet 6700 FTIR spectrometer with a resolution of 4 cm^{-1} and a scan rate of 32 s^{-1} . Samples PE_0 and PE_3 were prepared in KBr with a modified CTP to KBr ratio of 1:100. The samples were carbonized to measure the carbon yields. The representative samples ($\text{PE}_{0,1,3}$) were characterized by scanning electron microscopy (SEM) using a Quanta 250 microscope.

3. RESULTS AND DISCUSSION

The modified CTPs demonstrated distinct characteristics such as viscosity, wettability, softening point, and carbonization yield. These characteristics affect their commercial use; therefore, CTP needs to be modified.

3.1 Effect of erucic acid on the rheological property of CTP

Figure 3 shows the viscosity vs. temperature profile of CTPs modified with erucic acid. Compared with PE_0 , the viscosity of modified CTPs (such as PE_{1-4}) decreased to different extents. A significant decrease in the viscosity was observed

before 170°C. Above 170°C, the viscosity of PE₄ decreased by 300 and 150 mPa·s compared with those of PE₀ at 190 and 200°C, respectively, i.e., PE₀ would require a higher temperature (up to 10°C) to achieve the same viscosity as PE₄. Thus, the addition of a small amount of erucic acid significantly decreased the viscosity of the modified CTP.

(Insert Figure 3 here)

Viscosity reflects the friction between the adjacent layers of the fluids moving at different velocities because of the internal molecular friction. The effect of temperature on viscosity is very complicated. The relationship between temperature and viscosity at a constant shearing rate can be expressed by the Arrhenius equation as follows:

$$\eta_s = A \exp[\Delta E_\eta / (RT)] \quad (1)$$

Where E_η is the flow activation energy, kJ/mol; R is the gas constant per mole, in this case 8.314 J/ (K·mol); T is the thermodynamic temperature, K; and A is a constant related to the raw material, known as the pre-exponential factor. Thus, equation (1) can be expressed as follows:

$$\lg \eta_s = \lg A + \Delta E_\eta / (2303R) \times (1/T) \quad (2)$$

When temperature is low, the value of viscosity is large, so the 10-rpm rotating speed was enough to obtain the accurate viscosity value; When temperature is increased above 180°C, the decrease of viscosity is obvious, and thus the 100-rpm rotating speed was required to guarantee the reasonable measurement of viscosity value. The flow activation energy decreased with an increase of A, especially when 1 wt. %

erucic acid was added into CTP. Only a slight amount of surfactant will improve the level of sensitivity because the flow activation energy is a reflection of sensitivity between viscosity and temperature. In contrast, the flow activation energy of sample PE₄ increased to 88.92 kJ·mol⁻¹ with the addition of 3 wt. % erucic acid at 100-rpm rotating speed. This is because erucic acid, CH₃(CH₂)₇CH=CH(CH₂)₁₁COOH, is a polar molecule with a linear asymmetric structure. The molecular structure of CTP containing nonpolar aromatic molecules was destroyed when polar erucic acid molecules were added. This, in turn, decreased the interactions among the CTP molecules, thus decreasing the transition energy of CTP. Therefore, the flow activation energy of the modified CTPs decreased. The linear erucic acid molecules possibly strengthened the interactions among the CTP molecules when their quantity was increased to 4 wt. %, thus increasing the flow activation energy. Therefore, the optimum quantity of erucic acid was 3 wt. %, considering the temperature and rotating speed comprehensively.

(Insert Figure 4 here)

(Insert Table 1 here)

It was also found that whether CTP was modified or not, its flow activation energy decreased dramatically with an abrupt increase of rotating speed. This explains the shear thinning behavior of CTP.

3.2 Effect of erucic acid on the CTP wetting behavior

The wetting behavior of CTP and the modified CTP on the coke is a significant property because it provides information about the interactions between the CTP and coke during the mixing stage. When a typical CTP binder is positioned on a granular

bed of needle coke and then heated, it softens firstly and adopts a drop shape. Subsequently, it starts to spread and flows through the coke bed. Finally, the CTP is adsorbed in the coke bed completely. During heating, the contact angle between the CTP and coke bed decreases, changing from $>90^\circ$, 90° (wetting temperature), $<90^\circ$ to finally complete penetration. Based on the results of rheological property, 1–3 wt. % erucic acid was chosen to study the wetting behavior and adhesion property. The process of treatment to obtain the wetting angle between CTP and coke is shown in Figure 5. The relationship of wetting angle of the modified CTP and temperature is shown in Figure 6.

(Insert Figure 5 here)

(Insert Figure 6 here)

The process shown in Figure 5 demonstrated the conversion of the data from the image to number without manual measurement error. However, the comparison of contact angles and variation in CTP height with temperature was carried out, as shown in Supporting Information. This was due to the contact angle was instead of the variation in CTP height in some publications [26]. The contact angle decreased sharply when the temperature reached a certain point and above. However, the extent of variation in contact angle was negligible. Figure 6 shows that the wetting temperature decreased with an increasing amount of erucic acid. Although the relationship of wetting angle and temperature was not so clear, in fact, the wetting temperature (wetting angle equal to 90°) is the most important parameter for estimating wetting behavior. The wetting temperatures of PE₀ and PE₂ were 178 and

163°C, respectively; moreover, the wetting temperature of PE₃ reduced by 23°C in comparison with PE₀. The improvement of the wetting behavior of CTP with erucic acid is consistent with the rheological property resulting from the CTP with erucic acid. Low viscosity would accelerate the flow of CTP, and thus lead to the development of wetting behavior at lower temperatures. This is important for the production of a graphite electrode by improving the bonding of the CTP and coke at the mixing stage.

3.3 Effect of erucic acid on CTP adhesion characteristics

The effect of erucic acid on the adhesion characteristics of CTP was investigated by testing penetration behavior after the wetting process. The interaction between CTP and coke is difficult to describe accurately due to the permeability and roughness of the coke bed surface. Similar to wetting behavior, the adhesion characteristics are influential in establishing the ideal, optimum combination of CTP and coke. Herein, the penetration coefficient, W , introduced by Kravtsova et al [27] was used to describe the interactions between the CTP and coke as follows:

$$W = (\text{mass of coke and pitch agglomerate} - \text{mass of pitch}) / \text{mass of pitch} \quad (3)$$

In this study, $W = (m_2 - m_1) / m_1$; the results are shown in Figure 7. The soakage ratio of CTP remained essentially constant within the temperature range 140–180°C. However, the modified CTPs showed a large improvement. The change of soakage ratio in sample PE₁ was obvious, for instance, its soakage ratio at 170°C was 5 times than that at 160°C. Another significant observation was that the soakage ratio of PE₃ was at least 10 times that of PE₀ at 170°C. Although the addition of erucic acid significantly improved soakage ratio within the mid temperature region, this reached an optimum value after which an increase in the amount of erucic acid added had no

effect.

(Insert Figure 7 here)

According to the Langmuir theory, the active center of a solid surface in the adsorption process plays a significant role in attracting the adsorbate molecule. This function of the attractive force, similar to chemical bonding force, will be limited to the substrate scope of the adsorbate molecule, which would firstly form a monomolecular layer on the solid surface, and then become saturated. The monomolecular layer shields the attraction to eliminate the possibility of forming a multilayer. That is the reason why the penetration of the unmodified CTP was inappropriate. Erucic acid activated the surface between the CTP and coke; the coke surface formed a monolayer of erucic acid, thus stabilizing the plasticity of the thickener.

3.4 Effect of erucic acid on CTP softening point and coking value

Figure 8 showed that the softening point of the unmodified CTP was 114.3°C, whereas it changed to 109.1°C when CTP was modified with 1 wt. % erucic acid. The change in softening point when erucic acid was added demonstrated its plasticizing effect. Every 1 wt. % of erucic acid resulted in a decrease of 2°C in temperature. The coking value of the unmodified CTP was 61.9%, and the addition of erucic acid firstly increased this value and then decreased it. Thus, both the volatilization and reaction (copolymerization or polycondensation) improved the coking value to some extent. When the content of the additive was low, the effect of the reaction between the surfactant and CTP predominated, and subsequently the volatilization of CTP

overcame the effect. In particular, there is no fundamental change of the coking value of CTP in the presence or absence of erucic acid; however, the softening point decreased continuously, which is similar to the result reported by Xu et al [28].

(Insert Figure 8 here)

3.5 Modification mechanism of erucic acid modified CTP

FTIR spectra of the modified CTPs are shown in Figure 9. The bands at 740 and 814 cm^{-1} are attributed to the aromatic C–H bending vibration, whereas the bands at 1600 and 1438 cm^{-1} are attributed to the C=C stretching vibration. The bands at 2926 and 2853 cm^{-1} are attributed to the C–H stretching vibration of the CH_2 groups. Further, the band at 3040 cm^{-1} is attributed to the C–H stretching vibration in the benzene rings, whereas the broad band at 3424 cm^{-1} is attributed to the O–H stretching vibration. The FTIR spectra of PE_0 and PE_3 exhibited a similar pattern. Therefore, it can be demonstrated that the addition of erucic acid did not change the functional group of CTP.

(Insert Figure 9 here)

According to this study, a certain amount of erucic acid contributed to the plastification of CTP by decreasing the softening point and improving the rheological, wettability, and adhesion properties of CTP. CTP is a ‘pseudo solution’ of different types of hydrocarbons ranging from aliphatic paraffins to aromatic compounds, as proposed by Riggs, who used the theory of solubility for nonelectrolytes to explain

the stability of ‘pseudo solution’ [29]. However, the amphiphilic erucic acid molecules improved the isolation; the effect of the microstructure is shown in Figure 10.

(Insert Figure 10 here)

A series of processes may occur between CTP and erucic acid as follows: (i) Erucic acid firstly wets the porous surface of CTP, and then penetrates into the surface. (ii) Polar erucic acid molecules dissolve the other polar molecules on the surface of CTP. (iii) Thus, erucic acid gradually penetrates into the surface causing the strong internal stress, where definite activation energy was needed. (iv) Finally, the molecular structure of CTP was altered by erucic acid, because erucic acid coexisted with the CTP molecules as shown in Figure 10(PE₁₋₃). Several white substances were observed in the resulting structure after the physical change. Therefore, the molecular structure of CTP was altered by erucic acid, thus decreasing the friction among the molecules resulting in an increased flow ability of the CTP. This explains the entire process of the plastification of CTP.

4. CONCLUSIONS

The rheological and surface characteristics of CTP affect the mixing process between coke and CTP. CTP modified with erucic acid significantly reduced the mixing temperature by decreasing the viscosity, wetting temperature, and softening point, while improving the adhesion of the CTP and coke when the coke value remained unchanged at 62%. The optimum erucic acid amount was 3 wt. %, and a combination of several factors reduced the mixing temperature of the modified CTP

by 10 °C. The modification mechanism of erucic acid in CTP was proposed to be a physical plastification process.

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Captions of figures

Figure 1 Apparatus for wettability measurement of CTP.

Figure 2 Sketch of adhesive ability measurement of CTP.

Figure 3 Relationship of viscosity and temperature of CTP modified with erucic acid.

The viscosity of CTP from 170 to 210°C is zoomed on the right figure.

Figure 4 Relationship of $\lg \eta$ and $1/T$ of CTP modified with erucic acid. 1:10-rpm;

2:100-rpm.

Figure 5 Process of treatment to obtain the wetting angle between CTP and coke by Image-J Software.

Figure 6 Relationship of wetting angle of the modified CTP and temperature.

Figure 7 Relationship of soakage ratio of the modified pitch and temperature.

Figure 8 Effect of erucic acid on the softening point and coking value of CTP.

Figure 9 FTIR spectra of CTP in the presence and absence of erucic acid.

Figure 10 SEM images of CTP: (a) PE0, (b) PE1, (c) PE2, and (d) PE3.

Table 1 Linear regression parameter between temperature and viscosity of CTP modified with erucic acid.

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Sample	Rotating speed(rpm)	Constant (A)	Coefficient (R')	$\Delta E_{\eta}/\text{kJ}\cdot\text{mol}^{-1}$
PE ₀	10	−13.07	0.996	139.12
PE ₁	10	−10.86	0.992	120.42
PE ₂	10	−10.53	0.999	116.18
PE ₃	10	−9.90	0.999	110.13
PE ₄	10	−9.67	0.996	106.86
PE ₀	100	−7.35	0.999	89.72
PE ₁	100	−6.92	0.998	85.47
PE ₂	100	−6.44	0.991	80.24
PE ₃	100	−6.37	0.999	78.92
PE ₄	100	−7.55	0.991	88.92

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