Rheological Characterization of Pitch and Binder Matrix at Different Fine Particle Concentration

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Abstract

Green anodes consist of coarse coke particles surrounded by a binder matrix, which is a viscoelastic material and is made of fine coke particles and coal-tar pitch. During the compaction process, the coarse particles rearrange while the binder matrix plastically deforms, reducing the overall porosity of the coarse particles. The rheological properties of the binder matrix are among the most important parameters that affect the final quality of the anode with respect to the anode paste recipe, the interaction of the binder matrix with the coarse particles, and the operational conditions. Different parameters such as the particle size distribution of fine particles, the concentration of fine particles, and forming temperature govern the rheological properties of the binder matrix. This paper is an extension of a previous work investigating the rheological properties of the binder matrix with fine coke particle concentrations up to 15 %. Here, the effects of higher fine particle concentrations (up to 60%) are considered to evaluate real conditions and improve the understanding of the viscoelastic behaviours of the binder matrix.

Keywords: Rheological characterization, pitch, binder matrix, high concentration.

1. Introduction

Carbon anode paste has a key role in the forming process, where pitch is used as a binder to fill the pores in coke aggregates and make strong coke-pitch bonds in the baked anode [1, 2, 3]. The chemical and physical properties of pitch, coke particles, and binder matrix affect the mixing and forming processes, consequently, the quality of the baked anode. Better understanding of the above parameters as well as the interaction between these materials may improve the quality of the anode [4, 5].

The rheological properties of pitch and binder matrix are among of the main parameters that affect the quality of the baked anode [6, 7]. Pitch is a Newtonian material at high temperature (166 °C and 190 °C) [7] and the mixture of pitch, fine, and coarse particles (anode paste) is considered as a granulo-viscoelastic material [8, 9]. The rheological properties of the anode paste depend on pitch content, concentration of the fine particles, coke particle size distribution, shape, and roughness of particles as well as their tendency to agglomerate [10].

The rheological properties of the pitch and the binder matrix at three different temperatures and a wide concentration range of fine particles are measured experimentally and the results are presented in this article.

2. Materials and Method

2.1. Sample preparation

Calcined petroleum cokes with the real density of 2.057 g/cm³ and coal tar pitch with the density of 1.31 g/cm³, provided by the anode manufacturing plant, are mixed to make the binder matrix samples. The fine particles, with the Blaine number (BN) of 4000 cm²/g, are produced using a laboratory steel ball mill for 30 minutes to mill the coarse coke particles to a size range of -2.38 +1.41 mm.

The granulometric distribution of particles and BN are measured using a RO-TAP sieve analyser and Malvern Mastersizer 2000, respectively. Table 1 shows the size distribution and Blaine number of fine particles. A Hobart N50 mixer installed in a furnace is used to mix fine particles and the pitch at 178 °C for 10 minutes. Twelve samples with fine particle concentrations from 5 wt% to 60 wt% with the concentration interval of 5% (5, 10, 15,…, 60 wt%) are prepared.

Table 1. Size distribution and Blaine number of fines particles.

Size range (µm)	+150	-150+106	-106+75	-75+53	-53+38	-38
wt%	3.1	11.5	15.6	18.7	14.6	36.5

2.2. Rheological characterization

A Discovery Hybrid Rheometer (DHR-3), equipped with two 20 mm Peltier parallel plates, is used to characterize the rheological properties of the pitch and binder matrixes. The gap thickness is 1000 µm. The rotation and oscillation tests are performed to deliver the viscous and elastic properties of the samples. Three temperatures are chosen for the rotation and oscillation tests. The rotation tests are performed at eight concentrations of fine particles (medium concentration) due to limitations of this method. However, the oscillation tests are performed at twelve concentrations of fine particles (high concentrations).

3. Results and discussion

3.1. Rotation tests

In order to characterize the rheological properties of the pitch and the binder matrix with the rotation method (controlled shear rate), eight concentrations of fine particles at three temperatures are tested. The power law model (Equation (1)) is used to correlate the rheological behaviour of the pitch and the binder matrix:

$$\tau = \kappa \dot{\gamma}^{n}, \tag{1}$$

where τ, κ, $\dot{\gamma}$, and n are the shear stress, consistency index, shear rate, and power law index, respectively. Table 2 shows the rheological parameters of pitch and binder matrix fitted to the power law model. The results show that the pitch is a Newtonian fluid at all the studied temperatures, shown by the power law index of unity. Increasing the fine particle concentration decreases the power law index and the rheological properties of binder matrix deviate from a Newtonian fluid at high concentrations. Below, the results are explained in more detail. The rotation tests are performed up to 35 wt% of fine particles due to limitation of this method at high concentration suspensions.

Table 2. Rheological parameters of pitch and binder matrix fitted to the power law model.

T (°C)	Concentration of fine particles (wt%)	κ (Pa.s^n)	n (-)
166	0	7.266	1.00
	5	12.640	0.93
	10	14.680	0.93
	15	19.760	0.91
	20	19.880	0.90
	25	25.970	0.90
	30	31.440	0.88
	35	56.660	0.87
178	0	2.545	1.00
	5	4.957	0.94
	10	6.094	0.94
	15	6.992	0.92
	20	7.589	0.92
	25	10.240	0.91
	30	12.620	0.90
	35	18.800	0.89
190	0	1.341	1.00
	5	2.437	0.96
	10	3.270	0.94
	15	3.514	0.93
	20	3.571	0.93
	25	5.174	0.92
	30	6.289	0.91
	35	9.667	0.90

Figure (1) shows the shear stress as a function of the shear rate for the different mixtures at different temperatures ((a) 166 °C, (b) 178 °C, and (c) 190 °C). The concentration of fine particles in the binder matrix increases in the arrow direction from 0 to 35 wt%. The solid lines correspond to the power law model parameters fitted to the data. At each concentration of the binder matrix, the shear stress increases with increasing shear rate and decreases with increasing temperature. Comparing the results of 0 and 35 wt% demonstrates that the shear stress of binder matrix increases with increasing fine particle concentration at a fixed temperature and decreases with increasing temperature at a given concentration. This means that the viscosity of the binder matrix reduces with increasing temperature.

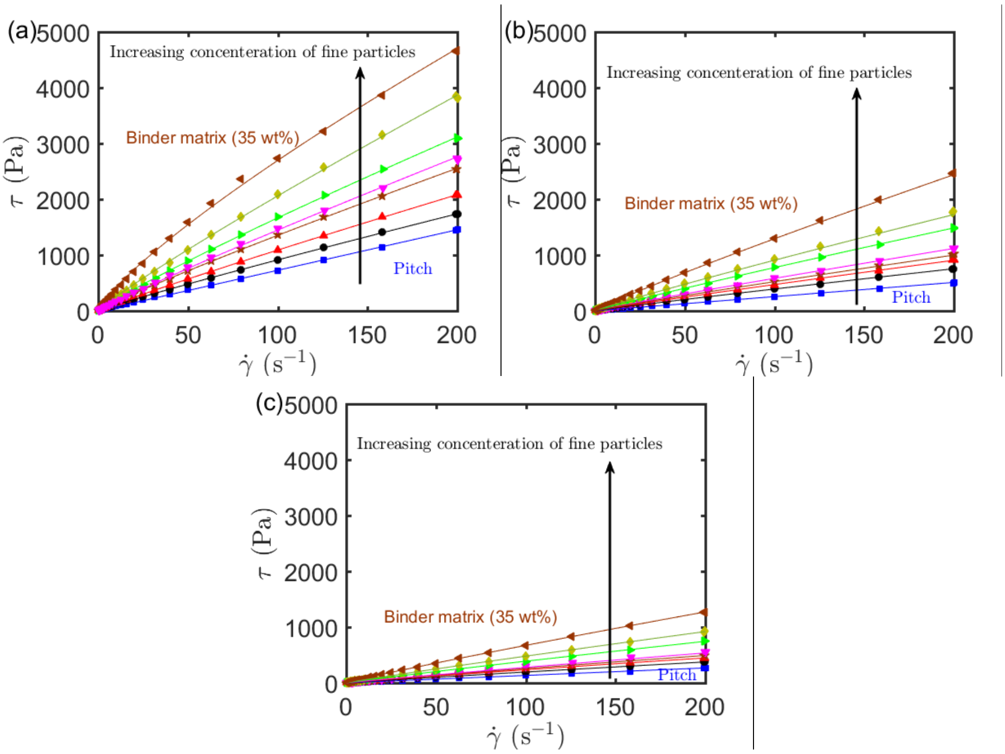

Figure 1. Shear stress vs shear rate at the temperature of (a) 166 °C, (b) 178 °C, and (c) 190 °C (The concentration of fine particles in the binder matrix increases in the arrow direction from 0 to 35 wt%).

The power law index of the samples at different fine particle concentrations are plotted with respect to temperature in Figure (2). The results show that increasing the concentration of the fine particles decreases the power law index, resulting in a non-Newtonian behaviour. Consequently, the binder matrix behaves as a shear thinning material. Deviation from Newtonian behaviour decreases with increasing the temperature. The rheological properties of the suspensions depend on several parameters such as the rheological properties of the base fluid, the density difference between the base fluid and particles, the size and shape of the particles as well as the solid concentration [11]. Stickel and Powell [11] have mentioned that most suspensions are shear thinning at low and intermediate shear rates due to an ordered particle structure, and they have a disordered particle structure at higher shear rates.

It is worth mentioning that the viscosity of the binder matrix can be calculated using:

$$\mu = \frac{\kappa \dot{\gamma}^n}{\dot{\gamma}}. \quad (1)$$

As the binder matrix is a shear thinning fluid, its viscosity decreases with increasing shear rate (the results are not shown due to lack of space).

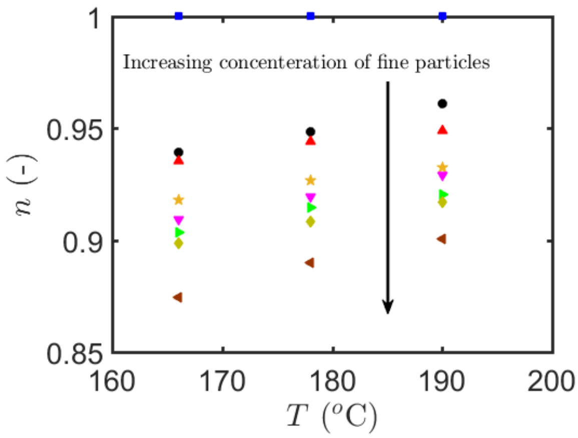

Figure 2. Power law index vs temperature (The concentration of fine particles in the binder matrix increases in the arrow direction from 0 to 35 wt%).

3.2. Oscillation tests

The oscillation method (frequency sweep) is used to measure the viscous and elastic properties of the pitch and the binder matrix at different fine particle concentrations (0 to 60 wt%) and different temperatures. The storage modulus, G', represents the elastic properties of the material [11,12].

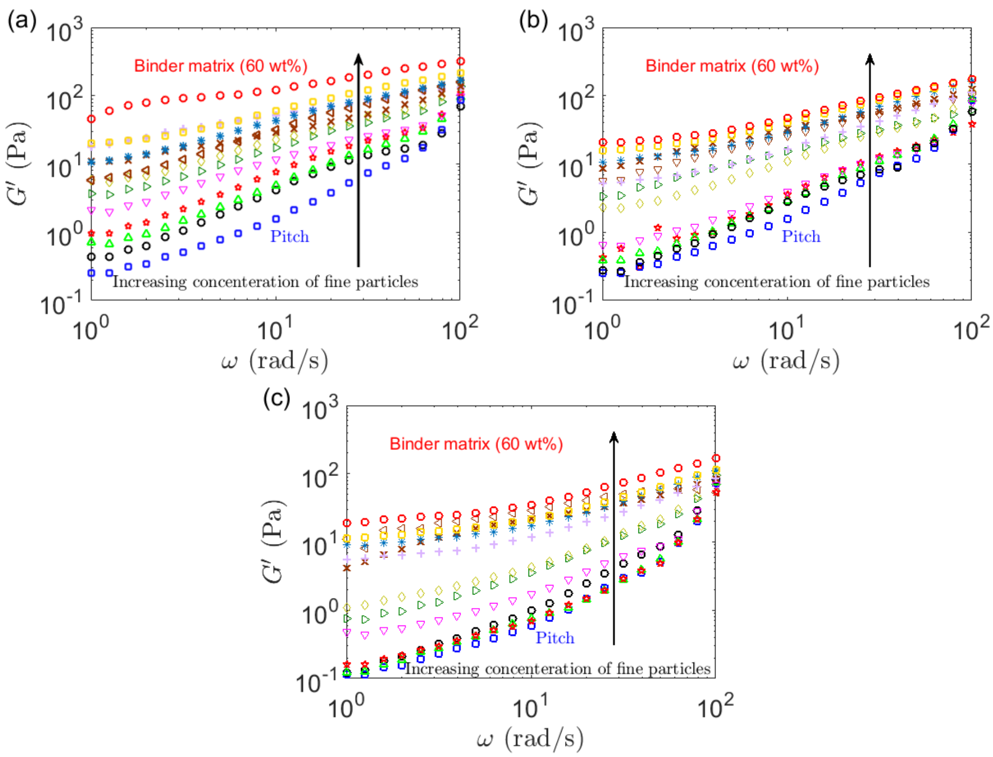

Figure 3. Storage modulus vs angular frequency at the temperature of (a) 166 °C, (b) 178 °C, and (c) 190 °C (The concentration of fine particles in the binder matrix increases in the arrow direction from 0 to 60 wt%).

The storage modulus of the binder matrix at different fine particle concentrations (from 0 to 60 wt%) as a function of the angular frequency is plotted in Figure (3) at different temperatures ((a) 166 °C, (b) 178 °C, and (c)190 °C). The results show that the elastic properties of the binder matrix increase with increasing fine particle concentration. Also, increasing the temperature decreases the elastic properties of the binder matrix at a fixed concentration of the fine particles (i.e., see the storage modulus of the binder matrix at the concentration of 60 wt% and at temperatures of 166 °C and 190 °C in this figure).

The loss modulus, G'', represents the viscous properties of a material [12,13]. Figure (4) shows the loss modulus of the pitch and the binder matrix as a function of the angular frequency at different fine particle concentrations and temperatures. Increasing the concentration of the fine particles increases the loss modulus. Also, the elastic modulus decreases with increasing temperature. This decrease is more significant at higher concentrations. Based on the results obtained for elastic modulus and loss modulus, it can be concluded that the binder matrix is a visco-elastic material and both viscous and elastic behaviours increase with increasing concentration of the fine particles.

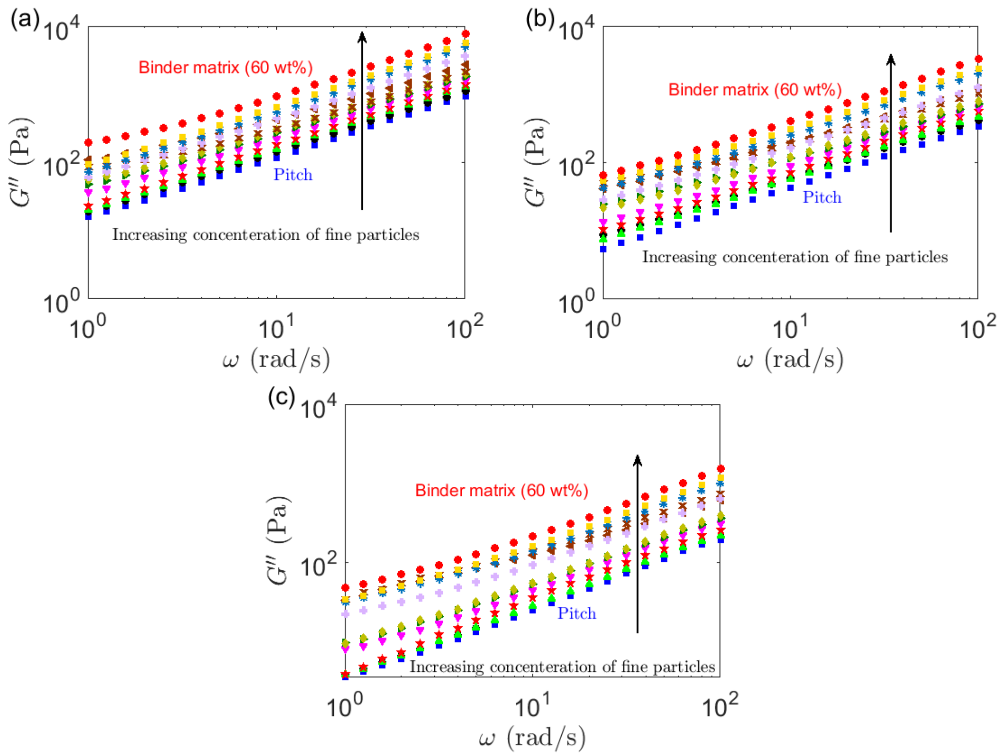

Figure 4. Loss modulus vs angular frequency at different temperatures (a) 166 °C, (b) 178 °C, and (c) 190 °C (The concentration of fine particles in the binder matrix increases in the arrow direction from 0 to 60 wt%).

Equation (2) is used to calculate the complex viscosity ($\boldsymbol{\eta}^*$) of the visco-elastic materials using the complex modulus ($\boldsymbol{G}^*$) and angular frequency as [13]:

$$|\eta^*| = \frac{|G^*|}{\omega}, \quad (2)$$

where $|\boldsymbol{G}^*| = \sqrt{\boldsymbol{G}'^2 + \boldsymbol{G}''^2}$.

Figure (5) presents the complex viscosity of the binder matrix with respect to the angular frequency at different fine particle concentrations and temperatures. The complex viscosity of the binder matrix increases with increasing concentration of fine particles and decreases with increasing angular velocity. It is worth mentioning that the complex viscosity of the binder matrix also decreases with increasing temperature and this decrease is more significant at higher concentrations of the particles.

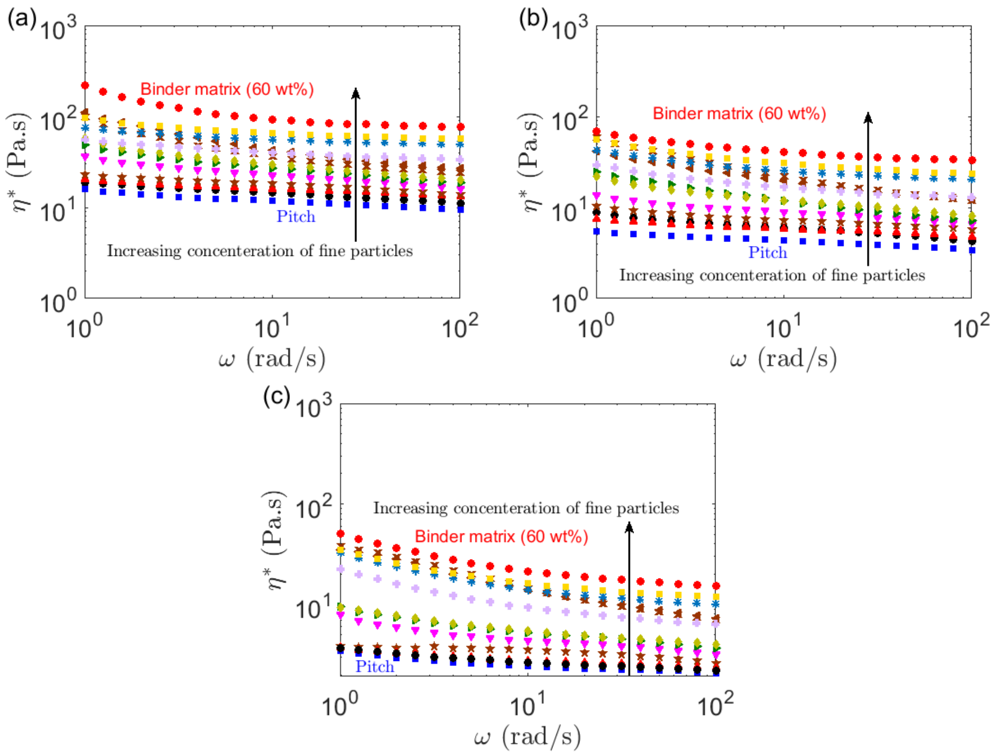

Figure 5. Complex viscosity vs angular frequency at different temperatures ((a) 166 °C, (b) 178 °C, and (c) 190 °C) (The concentration of fine particles in the binder matrix increases in the arrow direction from 0 to 60 wt%).

4. Conclusions

The rheological properties of pitch and binder matrix are studied at three temperatures and twelve fine particle concentrations. The results show that pitch is nearly a Newtonian fluid and its viscosity decreases with increasing temperature. The binder matrix is a visco-elastic fluid and both viscous and elastic properties of the binder matrix increase with increasing concentration of fine particles. Finally, the complex viscosity of the binder matrix increases with increasing concentration of the fine particles and decreases with increasing temperature. The results of this study will help improve the quality of anodes as the rheological properties of the binder matrix affect the baked anode properties.

5. Acknowledgements

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