Rheological Characterization of Pitch and Binder Matrix with Different Concentrations of Fine Particles

Roozbeh Mollaabbasi[1], Lene Jensberg Hansen[2], Thierno Saidou Barry[3], Tor Grande[4], Seyed Mohammad Taghavi[5], Donald Ziegler[6], Houshang Alamdari[7]
1. Postdoc Researcher
3. Master Student
5. Assistant Professor
7. Associate Professor
Aluminum Research Centre REGAL, Laval University, Québec, Canada
2. Master Student
4. Professor
Department of Materials Science and Engineering, NTNU Norwegian University of Science and Technology, Trondheim, Norway
6. Program Manager-Modeling
Alcoa Corporation: Aluminium Center of Excellence, Alcoa Technical Center, Pittsburgh, USA
Corresponding author: roozbeh.mollaabbasi.1@ulaval.ca

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 and reduces the overall porosity of the coarse particles. The rheological properties of the binder matrix are among the most important parameters that affects the final quality of the anode with respect to the anode paste recipe, the interaction of the binder matrix with the coarse particles and operational conditions. Different parameters such as particle size distribution of fine particles, concentration of fine particles and forming temperature are governing 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 are considered to simulate real conditions and improve the understanding of the viscoelastic behaviour of the binder matrix.

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

1. Introduction

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

The rheological properties of pitch and binder matrix are one 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 as well as their tendency to agglomerate [10].

In this article, 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.

2. Materials and Method

2.1. Sample preparation

Calcined petroleum cokes with the density of 2.057g/cm³ and coal tar pitch with the density of 1.31g/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 cm^2/gr, are produced using a laboratory steel ball mill for 30 minutes to mill the coarse coke particles with a size range of -2.38+1.41 mm.

The granulometric distribution of particles and BN are measured by 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 in 178 °C for 10 minutes. Twelve samples with fine particle concentrations of 5, 10, …, 60 wt. % were 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 preformed at eight concentrations of fine particles (medium concentration) due to limitations of this method. While 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 (control 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.

$$\tau = \kappa \dot{\gamma}^{n}, \quad (1)$$

where τ, κ, $\dot{\gamma}$ and n are shear stress, consistency index, shear rate and power law index respectively. Table 2 shows the rheological parameters of pitch and binder matrix, considering the power law model. Results show, the pitch is a Newtonian fluid at all the studied temperatures, shown by the power index being unity. Adding the fine particles decreases the power index and the rheological properties of binder matrix deviate from Newtonian fluid. We will explain the results, including the effects of temperature and fine particle concentration more deeply below. It is worth mentioning that the rotation tests are performed up to 35 wt.% of the fine particles due to limitation of this method at high concentration suspensions.

Table 2. Rheological parameters of pitch and binder matrix, considering 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	0.98
	35	66.660	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 versus shear rate. In each panel, the temperature is T = 166 °C (a), 178 °C (b) and 190 °C (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 binder matrix, the shear stress increases with shear rate, and increasing the temperature decreases the shear stress. Comparing 0 and 35 wt.% shows that the shear stress increases with increasing fine particle concentration at fixed temperature. The shear stress of the binder matrix decreases with increasing the temperature. It means that the viscosity of the binder matrix drops with increasing the temperature.

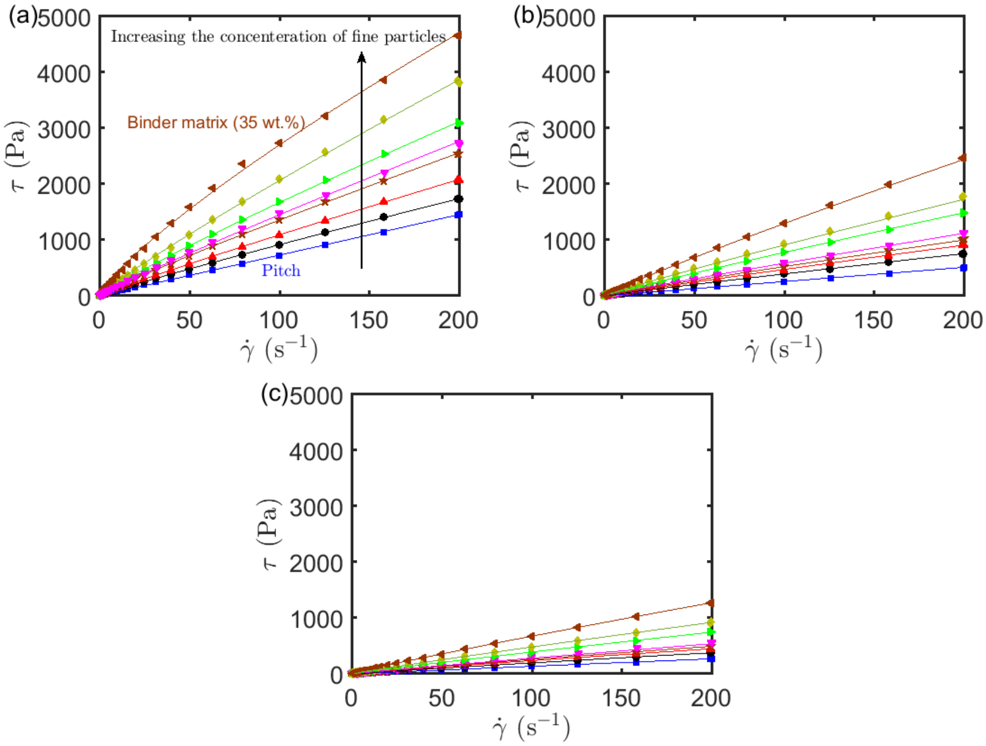

Figure 1. Shear stress versus shear rate. In each panel, the temperature is fixed as T = 166 °C (a), 178 °C (b) and 190 °C (c). The concentration of fine particles in the binder matrix increases in the arrow direction from 0 to 35 wt.%.

The power index of the samples at different concentration of the fine particles are plotted versus temperature in Figure (2). The results show increasing the concentration of the fine particles decreases the power index, rheological properties of the binder matrix deviate from Newtonian, and 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 mentioned that most the suspensions are shear thinning at low and intermediate shear rates due to an ordered structure of particles at low and intermediate shear rates and a disordered structure of the particles at higher shear rates [11].

It is worth mentioning that we can calculate the viscosity of the binder matrix using $\mu = \frac{\kappa\dot{\gamma}^n}{\dot{\gamma}}$. As the binder matrix is a shear thinning fluid, its viscosity decreases with increasing the shear rate (the results are not shown for brevity).

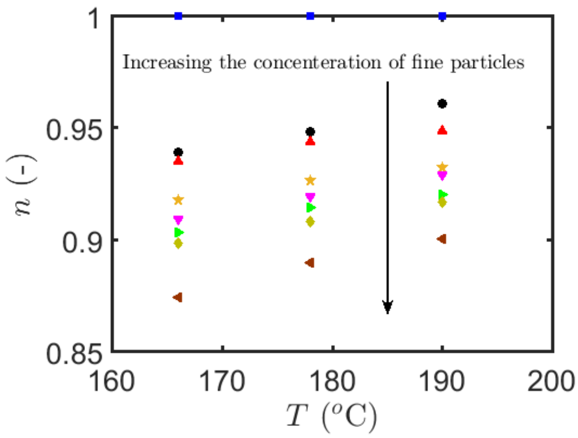

Figure 2. Power law index versus temperature. The concentration of fine particles in the binder matrix increases in the arrow direction from 0 to 35 wt.%.

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 concentrations (0 to 60 wt.%) of the fine particles and temperatures. The storage modulus, G', represents the elastic properties of the material [11,12].

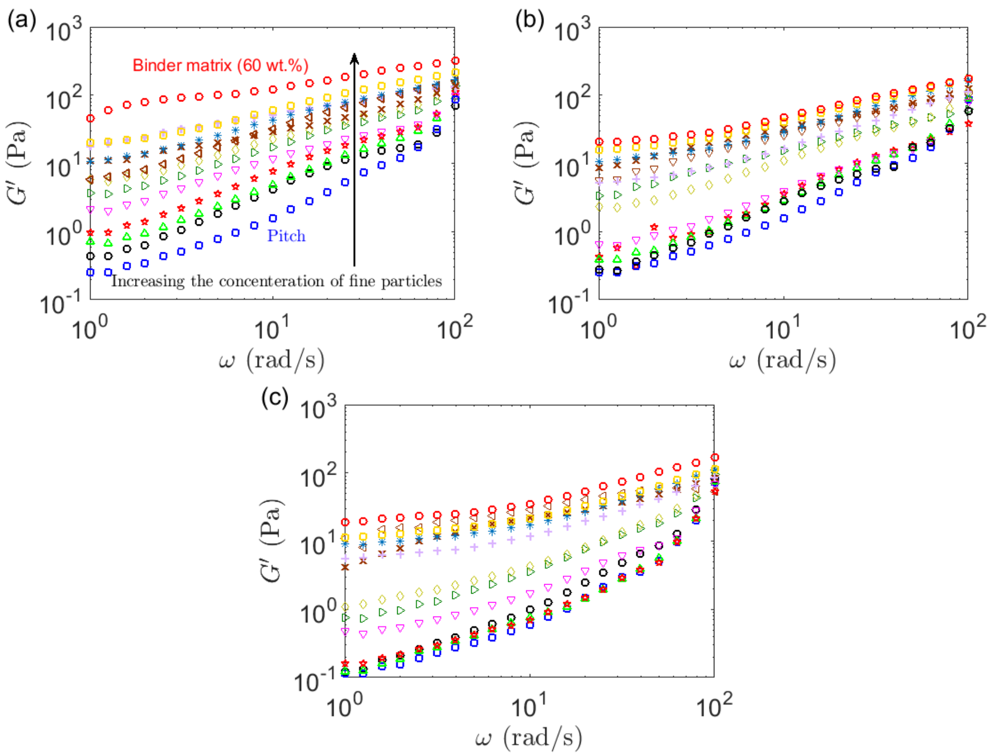

Figure 3. Storage modulus versus angular frequency.
The temperature is constant in each panel and T = 166 °C, 178 °C and 190 °C from (a) to (c). The concentration of fine particles in the binder matrix increases in the arrow direction from 0 to 60 wt.%.

The storage modulus of the binder matrix at different concentration of the fine particles (from 0 to 60 wt.%) versus the angular frequency is plotted in Figure (3). The temperature is fixed in each panel and T = 166 °C, 178 °C and 190 °C from (a) to (c). The results show the elastic properties of the binder matrix increases by increasing the concentration of the fine particles. In addition, increasing the temperature decreases the elastic properties of the binder matrix at a fixed concentration of the fine particles (i.e., compare the storage modulus of the binder matrix with 60 wt.% at 166 °C and 190 °C).

The loss modulus, G'', represents the viscous properties of the material [12,13]. Figure (4) shows the loss modulus of the pitch and the binder matrix versus angular frequency at different concentrations of the fine particles and temperature. Increasing the concentration of the fine particles increases the loss modulus. In addition, the elastic modulus decreases by increasing the temperature (it is more obvious at higher concentrations). With respect to the results of elastic modulus and loss modulus, the binder matrix is a visco-elastic material and both viscous and elastic behaviours increase by increasing the concentration of the fine particles.

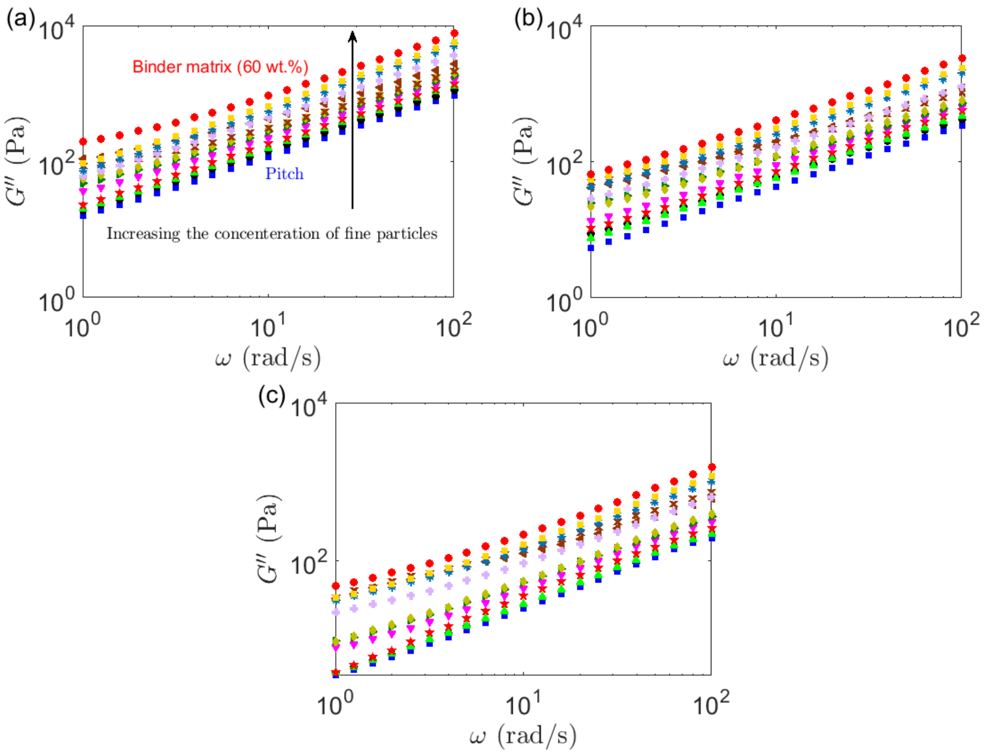

Figure 4. Loss modulus versus angular frequency.
The temperature is constant in each panel and T = 166 °C, 178 °C and 190 °C from (a) to (c). The concentration of fine particles in the binder matrix increases in the arrow direction from 0 to 60 wt.%.

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

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

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

Figure (5) plots the complex viscosity of the binder matrix versus angular frequency at different concentrations of the fine particles and temperatures. The complex viscosity of the binder matrix increases with increasing the concentration of the fine particles. In addition, the complex viscosity decreases with increasing the angular velocity. It is worth mentioning that the complex viscosity of the binder matrix decreases by increasing the temperature and it is more obvious at higher concentrations of the particles.

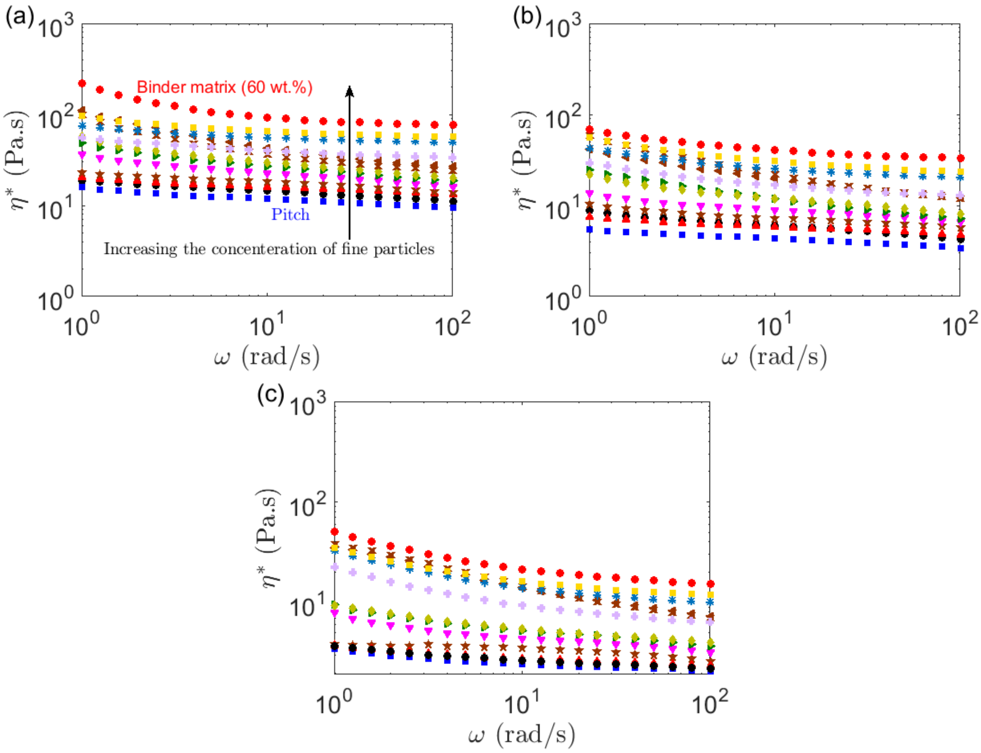

Figure 5. Complex viscosity versus angular frequency.
The temperature is constant in each panel and T = 166 °C, 178 °C and 190 °C from (a) to (c). The concentration of fine particles in the binder matrix increases in the arrow direction from 0 to 60 wt.%.

4. Conclusion

The rheological properties of pitch and binder matrix is studied at three temperatures and twelve concentrations of fine particles. The results show that pitch is a nearly Newtonian fluid and its viscosity decreases by increasing the temperature. Binder matrix is a visco-elastic fluid and both viscous and elastic properties of the binder matrix increases by increasing the concentration of the fine particles. Finally, the complex viscosity of the binder matrix increases by increasing the concentration of the fine particles and it is decreases by increasing the temperature.

5. Acknowledgment

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