Rheological Characterization of Pitch and Binder Matrix

Roozbeh Mollaabbasi[1], Thierno Saidou Barry[2], Seyed Mohammad Taghavi[3], Donald Ziegler[4] and Houshang Alamdari[5]
1. Postdoc Researcher
2. Master Student
3. Assistant Professor
5. Associate Professor
Aluminum Research Centre REGAL, Laval University, Québec, Canada
4. Program Manager-Modeling
Alcoa Corporation: Aluminum Center of Excellence, Alcoa Technical Center, Pittsburgh, USA
Corresponding author: roozbeh.mollaabbasi.1@ulaval.ca

Abstract

The quality of carbon anode used in the production of aluminum is highly linked to its recipe and processing parameters. The anode compaction process is one of the critical processing steps, affecting the final density and homogeneity of the anode. A large number of parameters such as raw materials (pitch, binder and coke) properties and operational conditions affect the densification process. The combination of fine cokes and pitch results in a highly viscous material (binder matrix) which surrounds large coke particles. The binder matrix is deformed during the compaction, moving between larger coke particles, and penetrating inside their pores. Therefore, the rheological properties of the binder matrix are of primary importance in the compaction process. These rheological properties may, in turn, be affected by the binder recipe; i.e. particle size distribution of fine coke, pitch/coke ratio and processing temperature. In this work, we experimentally study the effects of mixing temperature and pitch/coke ratio on the rheological properties of the binder matrix. The data generated in this work may give a global picture of the binder matrix rheology as well as an understanding of its viscoelastic behavior.

Keywords: Rheological characterization, pitch, binder matrix.

1. Introduction

Anode is one of the most important parts in Hall Héroult process that reacts as reducing agent [1]. In order to manufacture a green anode, coke particles and pitch are blended, mixed and compacted by vibro-compactors or presses. Then, the green anodes are baked to produce the final anodes. During this 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 physical and chemical properties of coke particles, pitch and binder matrix have crucial roles in the paste quality and consequently the quality of the baked anode. Better understanding of those properties and interactions between materials during the mixing process could improve anode properties [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]. Anode paste (mixture of the pitch, fine and coarse particles) is considered as a granulo-viscoelastic material. Pitch at room temperature is a solid material that behaves as a Bingham plastic at low temperature and as a Newtonian fluid in temperature between about 140 °C and 230 °C [7, 8]. The concentration of particles modifies the rheological behaviour of the paste. Hulse [9] mentioned that green anode paste has a granulo-viscoelastic behavior that depends on temperature, pitch content, coke particle size distribution, shape and roughness as well as their tendency to agglomerate.
In this article, the rheological properties of the pitch and the binder matrix at three different temperatures and four concentrations of fine particles are measured experimentally.

2. Materials and Method

2.1. Sample preparation

Calcined petroleum cokes and coal tar pitch are mixed to make the binder matrix samples that are received from the anode manufacturing plant. The density of coke and pitch are 2.057g/cm³ and 1.31g/cm³ respectively. Coarse cokes with a size range of -2.38+1.41 mm are milled in a laboratory steel ball mill for 30 minutes to produce fine particles and desired Blaine number (BN). 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. Three samples with fine particle concentrations of 5, 10 and 15 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	BN (cm^2/gr)
wt. %	3.1	11.5	15.6	18.7	14.6	36.5	4000

2.2. Rheological characterization

The rheological characterization of pitch and binder matrix are measured using a Discovery Hybrid Rheometer (DHR-3), equipped with two 20 mm Peltier parallel plates. The gap thickness is 1000 µm. This rheometer is able to perform the rotational and oscillational tests to measure different rheological properties of fluid such as viscosity, first normal stress difference, elastic modulus, viscous modulus etc.

3. Results and discussion

The rheological properties of the pitch and binder matrix are measured in four concentrations of fine particles and three temperatures. We use the power-law model (Equation (1)) in order to correlate the rheological behaviour of the pitch and the binder matrix (low concentrations of fine particles).

$$\tau = \kappa \dot{\gamma}, \qquad (1)$$

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. 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.

Table 2. Rheological parameters of pitch and binder matrix, considering the power law model.

Concentration of fine particles (wt.%)	T (°C)	κ (Pa.s^n)	*n* (-)
0	166	07.26	1
	178	02.54	1
	190	01.34	1
5	166	12.64	0.93
	178	04.95	0.94
	190	01.13	0.96
10	166	14.68	0.93
	178	06.09	0.94
	190	01.17	0.95
15	166	19.76	0.91
	178	06.99	0.92
	190	03.51	0.93

Figure (1) shows the shear stress versus shear rate. In each panel, the temperatures are T = 166 °C (blue square), 178 °C (black circle) and 190 °C (red triangle). The concentration of fine particles is constant in each panel, 0, 5, 10 and 15 wt.% from a to d, respectively. At each concentration, the shear stress increases with shear rate, and increasing the temperature decreases the shear stress. Comparing 0 and 15 wt.% shows that the shear stress increases with increasing fine particle concentration at fixed temperature. The solid lines correspond to the power law model parameters fitted to the data.

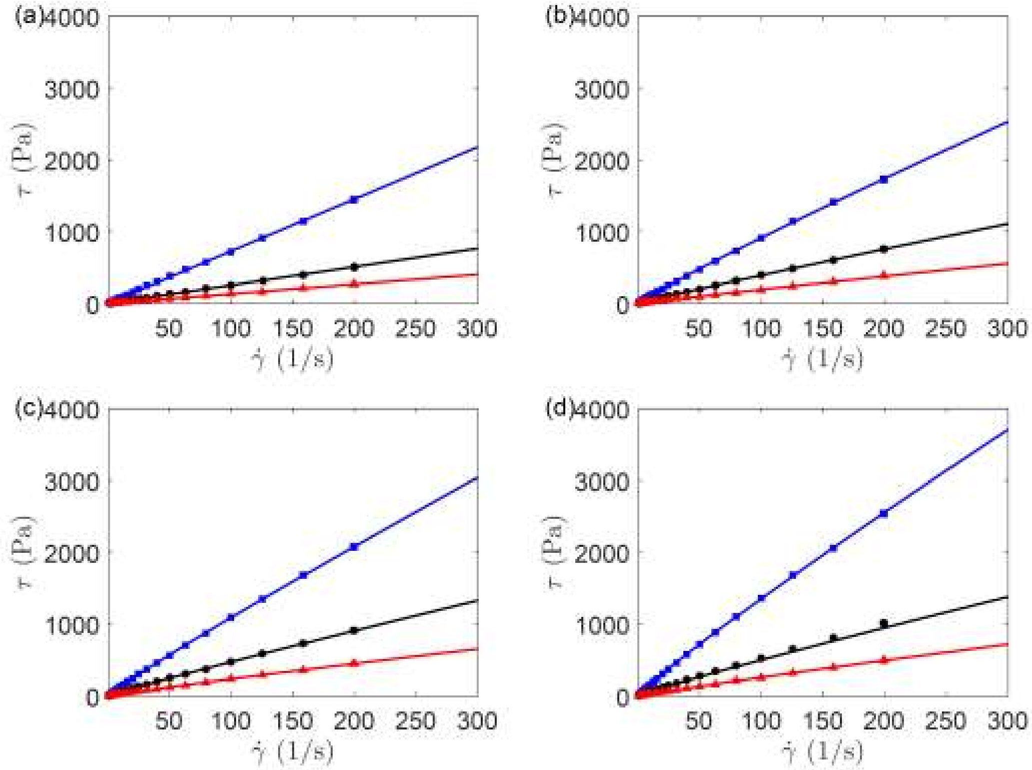

Figure 1. Shear stress versus shear rate. In each panel, the temperature is T = 166 °C (blue square), 178 °C (black circle) and 190 °C (red triangle). The concentration of fine particles is constant in each panel and it is 0 wt.%, 5 wt.%, 10 wt.% and 15 wt.% from a to d.

Figure (2) shows the viscosity, the shear stress divided by the shear rate ($\mu = \frac{\kappa\dot{\gamma}}{\dot{\gamma}}$), of the pitch and the binder matrix at different concentration of fine particles and temperature versus shear rate. In each panel, the temperature and concentration are as above. Results show the viscosity of the pitch is not depend on the shear rate; it is a Newtonian fluid. The viscosity of pitch decreases by increasing the temperature from 7.26 Pa.s at 166 °C to 1.34 Pa.s at 190 °C. The paste becomes increasingly shear thinning as the fine particle concentration increases. Here, the shear thinning diminishes as the temperature is increased. This is shown more clearly in Figure 3, where the shear thinning is nearly non-existent in the 190 °C case.

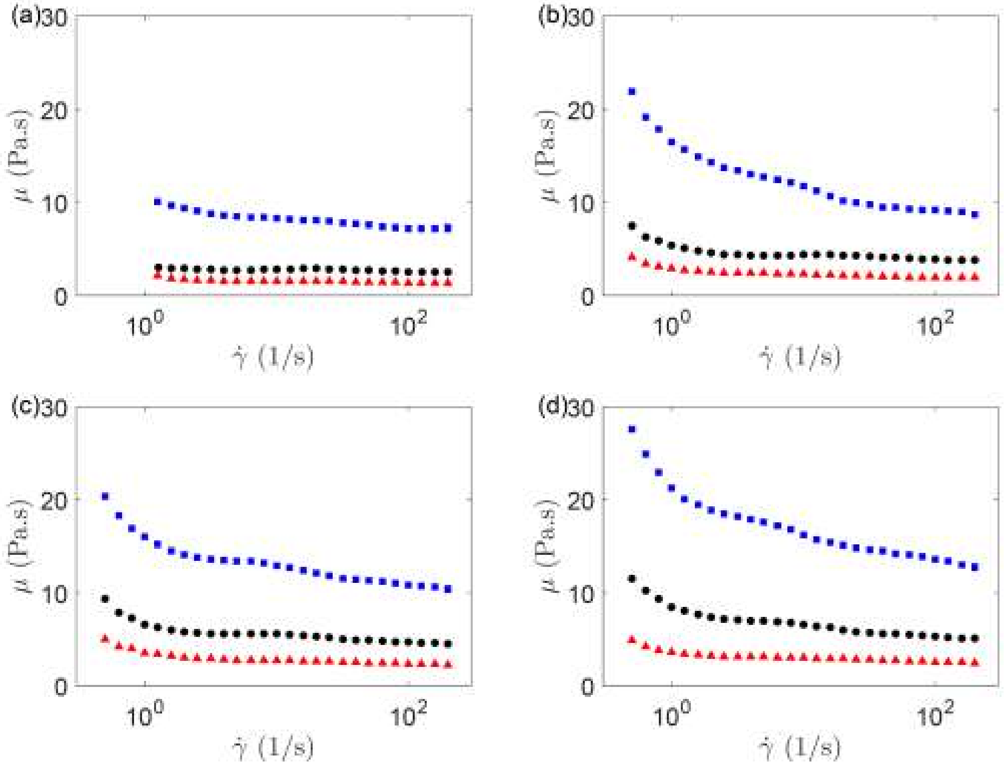

Figure 2. Viscosity versus shear rate. In each panel, the temperature is T = 166 °C (blue square), 178 °C (black circle) and 190 °C (red triangle). The concentration of fine particles is constant in each panel and it is 0 wt.%, 5 wt.%, 10 wt.% and 15 wt.% from a to d.

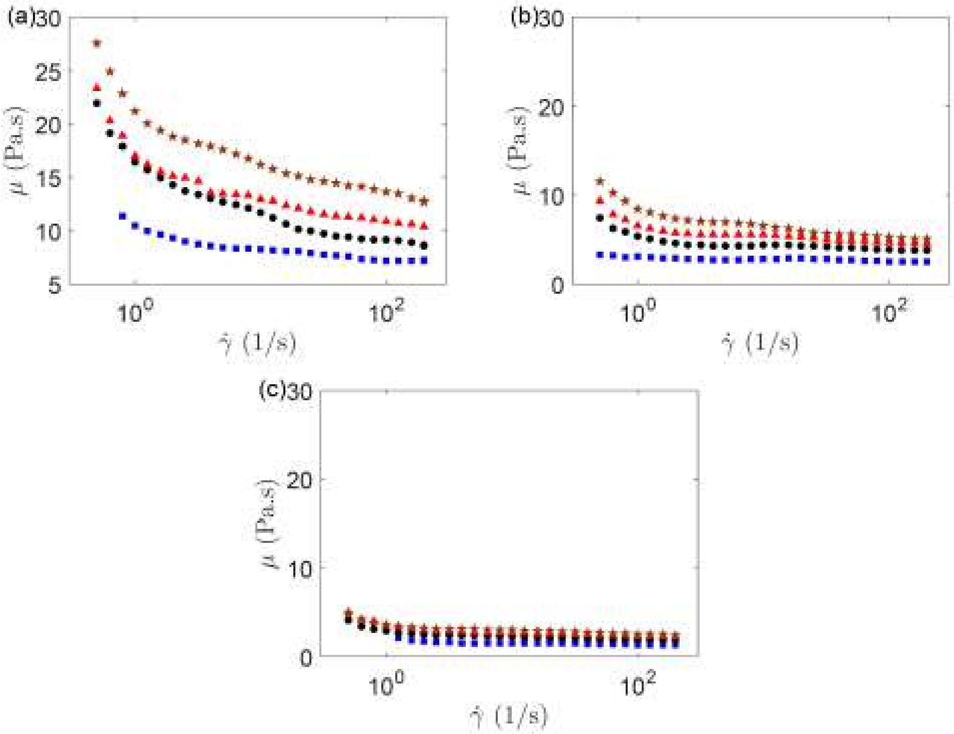

Figure 3. Viscosity versus shear rate. In each panel, the concentration of fine particles is 0 wt.% (blue square), 5 wt.% (black circle), 10 wt.% (red triangle) and 15 wt.% (brown star). The temperature is constant in each panel and T = 166 °C, 178 °C and 190 °C from a to c.

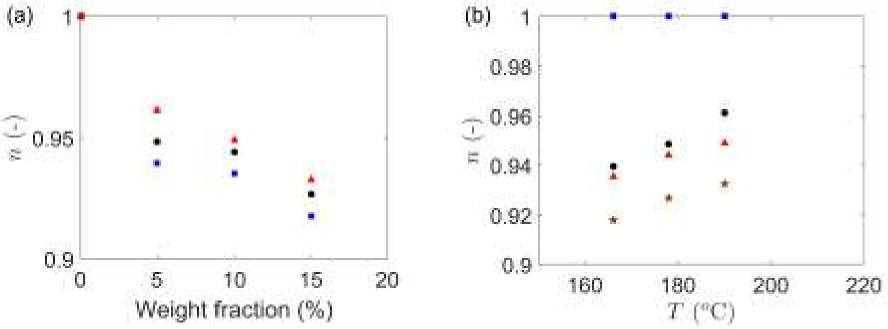

Figure 4. Power law index versus concentration of fine particles (a) and temperature (b). In panel a, T = 166 °C (blue square), 178 °C (black circle) and 190 °C (red triangle). In panel b, the concentration of fine particles is 0 wt.% (blue square), 5 wt.% (black circle), 10 wt.% (red triangle) and 15 wt.% (brown star).

Figure (4a) shows the effect of temperature and concentration of fine particles on the power law index. Figure (4a) shows, the rheological properties of fluid deviate from Newtonian by increasing the concentration of the fine particles. This effect is observable in all temperatures. In addition, Figure (4b) shows the effect of temperature on the power law index; the deviations due to the particles increase at lower temperature.

Figure (5) shows the Viscosity of the binder matrix at different concentration of fine particles at low shear rate (red square) and high shear rate (brown triangle). Here, the axis has been adjusted to volume fraction to allow comparison with theory. The temperature is constant in each panel at 166, 178 and 190 °C from a to c. The solid line shows the viscosity of suspensions of spheres in Newtonian media [10]. Guth modified the Einstein correlation in order to explain the reinforcing effect of elastomers as:

$$\mu = \mu_0(1 + 2.5\phi + 14.1\phi^2), \tag{2}$$

where, μ_0 and ϕ are the viscosity of base fluid (pitch) and volume concentration of fine particles respectively. There is a good agreement between the results of correlation and experimental one at high shear rate ($\dot{\gamma}$ = 100 (1/s)) at high temperature but the correlation is not able to predict the experimental results at low shear rate ($\dot{\gamma}$ = 1 (1/s)). The deviation of experimental results from the correlation in high shear rate decreases by increasing the temperature as the binder matrix behaving similar to Newtonian fluid at higher temperature.

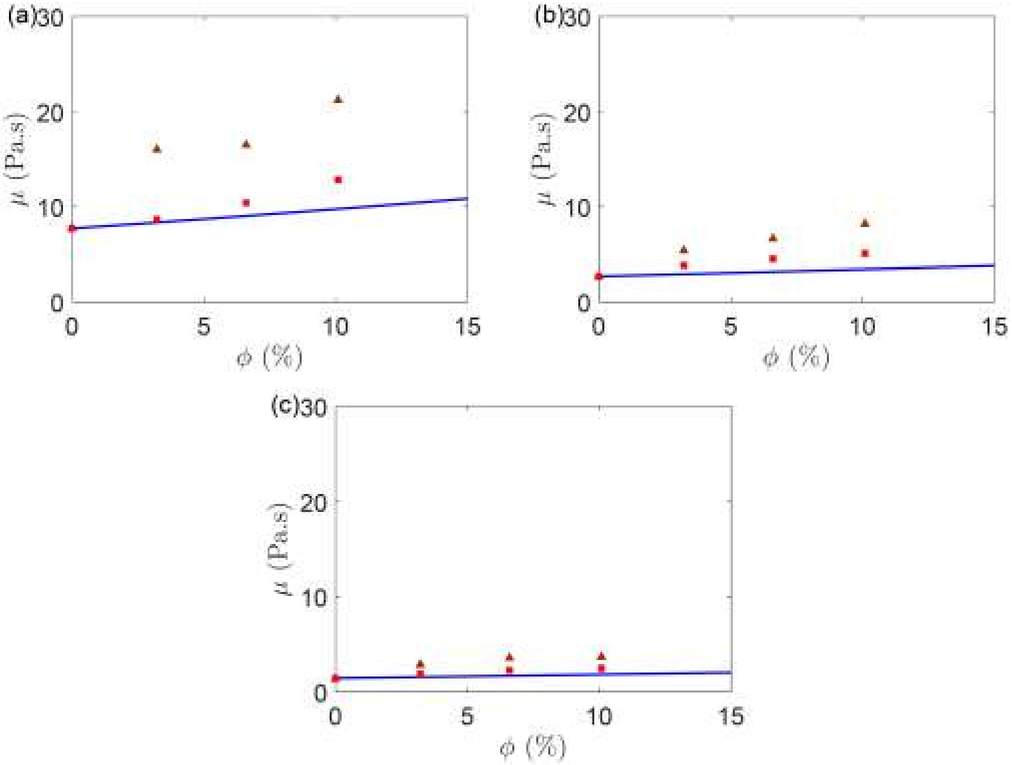

Figure 5. Viscosity of binder matrix versus concentration of fine particles at high shear rate (red square) and low shear rate (brown triangle). The temperature is constant in each panel and T = 166 °C, 178 °C and 190 °C from a to c. The solid line shows the viscosity of suspensions of spheres in Newtonian media.

We measure the first normal stress difference (N_1) directly by rheometer in order to study the elastic properties of the materials. The first normal stress difference is the difference between the normal stress in the flow direction (σ_{xx}) and the normal stress in the cross-film direction (σ_{yy}) [11]. The first normal stress difference is a measure of elastic effects [12]. Figure (6) shows the first normal stress difference versus shear rate at different temperature and concentration of fine particles. Increasing the concentration of fine particles increases N_1 and so the elastic effect. Adding even a small amount of fine particles increases the elastic effect of pitch dramatically (in each panel compare the blue squares and black circles). However, the effect appears to not be proportional to the particle concentration, as the differences between the curves with the loaded pitch are not so large. This effect is observable in all three temperatures.

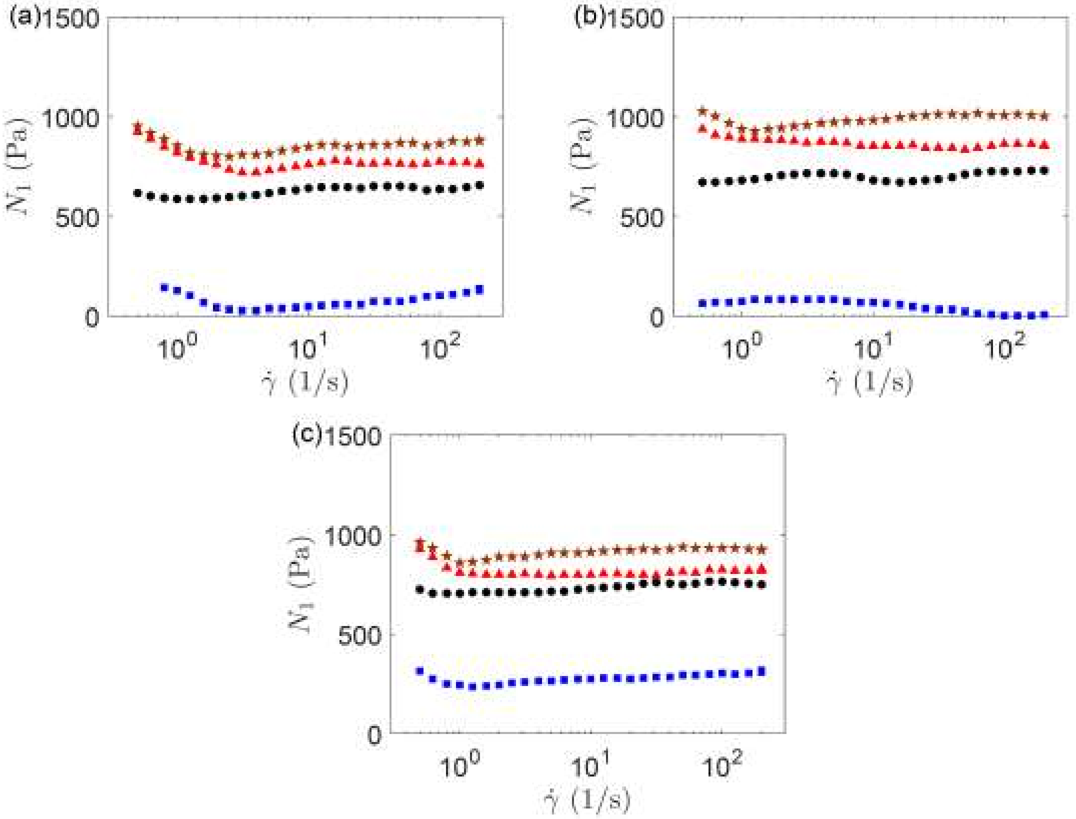

Figure 6. First normal stress difference versus shear rate. In each panel the concentration of fine particles is 0 wt.% (blue square), 5 wt.% (black circle), 10 wt.% (red triangle) and 15 wt.% (brown star). The temperature is constant in each panel and T = 166 °C, 178 °C and 190 °C from a to c.

4. Conclusion

The rheological properties of pitch and binder matrix is studied at three temperatures and four 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 non-Newtonian fluid and the rheological properties of the binder matrix deviate from Newtonian by increasing the concentration of the fine particles. The viscosity of the binder matrix decreases with increasing the shear rate and temperature. Finally, the elastic properties of the binder matrix are reinforced by increasing the concentration of the fine particles.

5. Acknowledgment

This research has been carried out at Université Laval, supported financially by an NSERC grant. The authors acknowledge Alcoa for the support of this work. We greatly thank. Dr. D. Picard, A. Eslami and G.Gauvin (Laval University) for very useful discussions.

6. References

1. F. Chevarin et al., Active pore sizes during the CO_2 gasification of carbon anode at 960 °C. *Fuel.* Vol. 178 (2016) 93-102.
2. K. Azari et al., Influence of coke particle characteristics on the compaction properties of carbon paste material. *Powder technology*. Vol. 257 (2014) 132-140.
3. U. Suriyapraphadilok, characterization of coal and petroleum-derived binder pitches and the interaction of pitch/coke mixtures in pre-baked carbon anodes. *Ph.D. Thesis* 2008, Pennsylvania state university.
4. A. N. Adams and H. H. Schobert, Characterization of the surface properties of anode raw materials. *Light Metals* (2004), 495-498.
5. B. Madjidi et al., Simulation of vibrated bulk density of anode-grade coke particles using discrete element method. *Powder Technology*. Vol. 261 (2014) 154-160.
6. B. Majidi et al., Discrete Element Method Modeling of the Rheological Properties of Coke/Pitch Mixtures,. *Materials.* Vol. 9 (2016) 334.
7. S. Hlatshwayo et al., Rheological behavior and thermal properties of pitch/poly(vinyl chloride) blends. *Carbon*. Vol. 51 (2013) 64-71.
8. St. Thibodeau et al., New insight on the restructuring and breakage of particles during unaxial confined compression tests on aggregates of petroleum coke. *Powder tehnology.* Vol. 253 (2014) 757-768.
9. K.L. Hulse, Rheological behavior, Anode manufacture: Raw materials, formulation and processing parameters, (2000) 283–334.
10. E. Guth, Theory of filler reinforcement. *Journal of Applied Physics*. Vol. 16 (1945) 20.
11. T. G. Mezger, The rheology handbook, 2^{nd} eddition (2006).
12. A. Eslami and S. M. Taghavi, Viscous fingering regimes in elasto-visco-plastic fluids. *Journal of Non-Newtonian Fluid Mechanics*. Vol. 243 (2017) 79–94.