Coal Plasticity at High Heating Rates and Temperatures

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Abstract

Effects of pressure, temperature, and coal type on coal plasticity were investigated. Seven coals, from the Argonne premium sample bank ranging from lignite to low volatile bituminous, were studied. Elevated pressures, up to 10 atm of helium, did not affect coal plasticity, but reducing pressure from atmosphere to vacuum resulted in diminished plasticity, i.e. a shorter plastic period and a higher minimum apparent viscosity. It is hypothesized that high pressure inhibits mass transport of metaplast to tar vapors, but also favors metaplast repolymerization into coke and char. Higher holding temperature decreased the coal plastic period. It is hypothesized that higher temperature increases mass transport of liquid metaplast to tar vapors and metaplast repolymerization to coke and char. Heating rate had essentially no effect on the individual softening temperatures of five different plastic coals. Possible explanations are that, depending on coal type, metaplast generation, by chemical bond breaking or physical melting, or both, is not strongly affected by heating rate. In particular, for medium and low volatile bituminous coals, there is evidence that generation of the metaplast responsible for initial softening involves largely chemical bond breaking as opposed to physical melting.

Introduction

A high temperature plastometer with a new cone-shaped shearing disk is being used to measure the apparent viscosity of molten coals as affected by pressure, temperature, time, and coal type. Seven coals, from the Argonne National Laboratory premium coal sample bank, are being studied: Beulah-Zap lignite (ND), Wyodak subbituminous (WY), Illinois No. 6 hvb (IL), Pittsburgh No. 8 hvb (PT), Lewiston-Stockton hvb (WV), Upper Freeport mvb (UF), and Pocahontas No. 3 lvb (PO). In this study, all hvb, mvb, and lvb coals show very good plastic behavior, but ND and WY coals did not exhibit any plasticity. For the plastic coals, the findings will help explain how pressure, temperature, and coal type affect the formation and depletion kinetics of the liquid metaplast which is primarily responsible for coal plasticity.

Pressure Effects

Using a constant heating rate of 400 K/s and a holding temperature of 1098 K, the plastic behavior of Argonne coals was studied at vacuum, 1 atm helium, 10 atm helium, and 50 atm helium.

Compared to the runs at 1 atm helium, the runs with different coals at vacuum displayed lower plasticity (higher minimum viscosity and shorter plastic period) as seen in Figures 1 and 2. The lower plasticity in vacuum is hypothesized to be due to enhanced mass transport of metaplast to tar vapors.

ND: Beulah-Zap Lignite
WY: Wyodak Subbituminous
IL: Illinois No. 6 hvb
PT: Pittsburgh No. 8 hvb
WV: Lewiston-Stockton hvb
UF: Upper Freeport mvb
PO: Pocahontas No. 3 lvb

Figure 1: Plastic period (period when the viscosity of molten coal is below 50000 Pa•s) of different coals at vacuum, 1 atm helium, 10 atm helium, and 50 atm helium. Heating rate of 400 K/s and holding temperature of 1098 K. ND and WY coals do not exhibit any plasticity.

Plastic Period vs. % C dmmf

ND: Beulah-Zap Lignite
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Figure 2: Maximum plasticity (minimum viscosity) of different coals at vacuum, 1 atm helium, 10 atm helium, and 50 atm helium. Heating rate of 400 K/s and holding temperature of 1098 K. ND and WY coals do not exhibit any plasticity.

Maximum Plasticity vs. % C dmmf

Compared to the runs at 1 atm helium, the runs with different coals at elevated pressures (10 atm and 50 atm helium) did not display any change as seen in Figures 1 and 2. Fong (1986) also observed similar results in his work on Pittsburgh No. 8 coal. It is hypothesized that high pressure inhibits mass transport of metaplast to tar vapors, but also favors metaplast repolymerization into coke and char (Griffin, 1989). Here, these two effects apparently compensate to give no net effect on plasticity.

From these findings, it seems that increasing pressure of inert gas above atmospheric does not play a major role in coal plasticity at high temperatures where the rate of depletion of liquid metaplast by mass transport is believed to be small compared to that by chemical processes. However, at extremely low pressure (such as vacuum), mass transport is greatly enhanced, and the metaplast depletion via this route becomes significant enough to diminish plasticity as seen above. At lower temperatures, where metaplast depletion kinetics are slower, increasing inert gas pressure above 1 atm may reduce plasticity by slowing metaplast transport from the coal and thus providing more time for metaplast depletion by secondary reactions.

Temperature Effects

Temperature-time history effects on coal plasticity were studied in two ways: by varying the holding temperature or the heating rate. To study the effects of holding temperature, the heating rate and pressure used were 400 K/s and 1 atm helium, respectively. With different holding

temperatures, the maximum plasticity, i.e. minimum viscosity, of different coals was unchanged. However, higher holding temperature decreased the plastic period (the period when the viscosity of molten coal is below 50000 Pa•s) for all coals (Figure 3). For example, increasing the holding temperature from 898 K to 1098 K decreased the plastic period from 6.9 s to 1.9 s. It is hypothesized that higher temperatures diminish plasticity by increasing mass transport of liquid metaplast out of the coal and augmenting repolymerization of metaplast to coke (Fong, 1986).

To study the effects of heating rates, the holding temperature and pressure used were 1098 K and 1 atm helium, respectively. At this stage, the heating rate effect on the softening temperature (temperature when the viscosity of molten coal first reaches 50000 Pa•s) was studied. For each coal, the heating rate has essentially no effect on the softening temperature (Figure 4). This seems to indicate that for a given coal the initial generation of metaplast is independent of heating rate and further suggests, especially for hvb coals where the softening temperature is below 650 K, that the initial phase of softening probably occurs by physical melting of the pyridine extractables initially present in the parent coal (Fong, 1986). For example, other workers have found that for hvb coals pyridine extractables account for 25-30% of the total mass in the parent coal (Fong, 1986 and Niksa, 1991; see also Niksa and Kerstein, 1991, for background). Little or no dependence of softening temperatures on heating rate was observed experimentally by Fong (1986) and theoretically by Oh et. al (1989) for Pittsburgh No. 8 hvb coal.

ND: Beulah-Zap Lignite
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Figure 3: Plastic period (period when the viscosity of molten coal is below 50000 Pa•s) of different coals at different holding temperatures. Heating rate of 400 K/s and 1 atm helium. ND and WY coals do not exhibit any plasticity.

Plastic Period vs. Holding Temperature

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Figure 4: Softening temperature (temperature when the viscosity of molten coal first reaches 50000 Pa•s) of different coals at various heating rates. Holding temperature of 1098 K and 1 atm helium. ND and WY coals do not exhibit any plasticity.

Softening Temperature of Different Coals

The existence of different softening temperatures for different coal types could reflect different metaplast melting points for the different coals, different kinetics of metaplast generation, or both. Further work including quantitative modeling of plasticity kinetics and experimental determinations of melting points of metaplast or reasonable surrogates (e.g. pyridine extracts of raw coal) would shed further light on these possibilities.

The similarity in softening temperatures of hvb coals (approximately 630 K) suggests that the overall rates of generation of the metaplast responsible for initial softening are also similar. For hvb coals which have a high yield of pyridine extracts from the raw coal, most or all of this metaplast may be generated by physical melting. However, the UF mvb coal also has a similar softening temperature (approximately 650 K), but has a much lower initial weight fraction of pyridine extractables (i.e. 7%, Snape and Bartle, 1989). It is hypothesized that the UF mvb coal generates a major fraction of the metaplast needed for initial softening by chemical bond breaking and further, that the kinetics of this process is very rapid.

The PO lvb coal has a much higher softening temperature (740 K). This is probably due to the lack of metaplast generation by physical melting since the PO coal only has an initial fraction of pyridine extractables of 1%. The coal begins to soften only when the temperature is high enough for the metaplast generation by chemical bond breaking to become important.

Solomon et. al (1992) reported for four of the same Argonne sample bank coals studied here, softening temperatures measured with a Gieseler plastometer at an apparent heating rate of 3 K/s. Their softening temperatures and those of the present study agree qualitatively, and the results are consistent with the picture that heating rate has little effect on the softening temperatures of individual coals.

Future Work

Data on effect of heating rate on the plastic period and molten coal solidification will be discussed, with a view toward a better understanding of metaplast generation and depletion kinetics. A multiple independent parallel reaction (MIPR) kinetics model will be used to predict the magnitude and duration of plasticity of different coals. The kinetics parameters of the MIPR model will be fitted from the available data using a nonlinear regression program. The relationships between simple indices of coal type (e.g. elemental content and fraction of labile bridges) and observed plasticity will also be investigated.

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