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Reduction in Thermoplasticity of Illinois No. 6 Coal by Heat Treatment in Refluxing Chlorobenzene

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When soaked in solvent, the organic portion of coal undergoes swelling and extraction induced by the disruption of intra- and intermolecular interactions, and shrinks re-forming interactions in subsequent removal of solvent while the extracted material is resorbed into/onto the shrinking gellike solid. Irreversible disruption and re-forming of molecular interactions may alter the conformational arrangement of molecules. Soaking of bituminous coals in refluxing chlorobenzene has been found to bring about conformational rearrangement to let molecules therein be more strongly associated than before the soaking,^{1–5} which has been evidenced by the decrease of pyridine extractability,¹ solvent-swelling ratio,² specific heat,³ and the increase in Einstein temperature.⁴ Another characteristic of the soaking in chlorobenzene is that the solvent extracts only small portions of coals, several mass percents at most.³ For examining the influence of the conformational arrangement on properties of coal, the extraction during the soaking should be minimized, since it more or less results in the separation of extractable material from nonextractable one that is a macroscopic rearrangement beyond the molecular scale. Thus, in regard to the extent of extraction, the employment of chlorobenzene has an advantage to that of more powerful solvents such as pyridine.

The above-described characteristics of the chlorobenzene soaking can be applied to the examination of the influence of the initial conformational arrangement on properties of coals upon heating to temperatures relevant to their conversion. The molecular mobility is a fundamental property for thermoplasticity of bituminous coals, many of which soften when they are heated over 600 K. If the molecular association formed through the chlorobenzene soaking could survive at the above temperature, the association more or less hinders the motion of molecules thus leading to the suppression of thermoplasticity. Larsen et al.⁵ heat-treated Illinois No. 6 coal in tetralin at 623 K and found its conversion into pyridine-soluble material is lowered by the preceding soaking in chlorobenzene. This result shows that the soaking reduces the solvent accessibility of the coal even at 623 K and strongly suggests a possibility of the reduction of molecular mobility when heated beyond a glass transition temperature of the coal around 400 K.⁶ In the present study, an examination was made of the

effect of the chlorobenzene soaking on the molecular mobility of Illinois No. 6 coal upon heating to 800 K by means of a proton magnetic resonance thermal analysis.⁷

An Argonne Premium Coal Sample, Illinois No. 6, was used for the experiment. The sample was dried at 383 K under vacuum and used for the treatments. The dried coal is hereafter referred to as IL. In the solvent soaking treatment, 2 g of the sample was heat-treated in 150 mL of chlorobenzene at 388 K under slightly pressurized argon atmosphere for 336 h. After the soaking, chlorobenzene was removed by rotary evaporation at 318–328 K and the treated coal was further dried at 1 Pa and 388 K until a constant mass was reached. The elemental analysis of the treated coal (denoted as IL-S) showed that a small amount of the solvent (2.3 g/100 g-IL) was retained in the coal. IL was also subjected to the Soxhlet extraction with chlorobenzene at 388 K for 48 h under argon atmosphere. The mass fraction of extracted material was 6 g/100 g-IL. The vacuum-dried extraction residue, referred to as IL-R, contained 2.3 g/100 g-IL of chlorobenzene.

Proton magnetic resonance⁷ was adopted to evaluate the molecular mobility of the coal samples on the basis of molecular mobility. A known amount, about 0.5 g, of IL was heated in atmospheric nitrogen flow at a rate of 100 mL-STP/min in a quartz tube (i.d. 8 mm) that was placed vertically in an NMR probe. The heating rate and peak temperature were 4 K/min and 800 K, respectively. During the heating, the ¹H NMR measurement was in-situ performed on a spectrometer (Bruker, CXP-40) using a resonance frequency of 38.27 MHz. The spin–spin relaxation signals were recorded after a single 90° pulse. Values for the pulse width, repetition time, and number of scans were 5 μs, 1 s, and 64, respectively. From the analysis of the observed signals, the change in the atomic fraction of mobile hydrogen in the specimen with time was determined. The signals could be deconvoluted into two components showing a slow exponential decay and a rapid Gaussian decay. In general, relaxation of mobile hydrogen existing in liquid is expressed by an exponential decay function with a longer spin–spin relaxation time, *T*₂, while that of immobile or rigid hydrogen in solid by a Gaussian decay function with a shorter *T*₂. Here, the atomic fraction of mobile hydrogen, *f*_{Hm}, is calculated by

$$f_{\text{Hm}} = \frac{I_{\text{L}}(0)}{\{I_{\text{L}}(0) + I_{\text{G}}(0)\}}$$

where *I*_L(0) and *I*_G(0) represent the initial signal intensi-

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(1) Nishioka, M.; Larsen, J. W. *Energy Fuels* 1990, 4, 100–106.

(2) Larsen, J. W.; Mohammadi, M. *Energy Fuels* 1990, 4, 107–110.

(3) Larsen, J. W.; Flowers, R. A.; Hall, P. J. *Energy Fuels* 1997, 11, 998–1002.

(4) Hall, P. J. *Energy Fuels* 1997, 11, 1003–1005.

(5) Larsen, J. W.; Azik, M.; Korda, A. *Energy Fuels* 1992, 6, 109–110.

(6) Mackinnon, A. J.; Hall, P. J. *Energy Fuels* 1995, 9, 25–32.

(7) Lynch, L. J.; Sakurovs, R.; Barton, W. A. *Fuel* 1986, 65, 1108–1111.

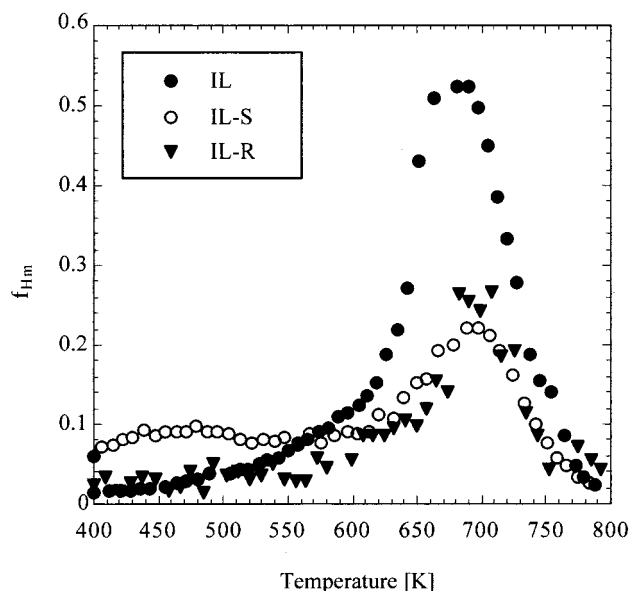


Figure 1. Fractions of mobile hydrogen to total hydrogen in IL, IL-S, and IL-R as a function of temperature.

ties arisen from the mobile and immobile hydrogens, respectively. The coal samples were also subjected to thermogravimetry. About 5 mg of the sample was heated in a thermobalance reactor (Mac Science Inc. model TG2000S) under the same conditions as in the ^1H NMR. In some experiments, IL-S and IL-R were heated to 473, 523, and 573 K and then cooled without holding the temperature, and the elemental compositions of the heat-treated samples were measured. The results showed that chlorobenzene retained in IL-S and IL-R was completely removed from them before the temperature reached 573 K. In addition to the ^1H NMR and thermogravimetry, the volumetric swelling ratios of IL and IL-S in pyridine were measured according to the method provided by Green et al.⁸ The swelling ratio for IL and IL-S were 2.8 and 2.2, respectively, and this reduction of the ratio confirms the conformational rearrangement induced by the chlorobenzene soaking as found in previous studies referred above.

Figure 1 shows f_{Hm} of IL, IL-S, and IL-R as a function of temperature. f_{Hm} in IL gradually increases from 0.02 to 0.1 in the temperature range from 400 to 600 K, which is followed by a sharp increase to a maximum of 0.52 at 690 K. For IL-S, f_{Hm} remains roughly constant around 0.1 at 400–600 K and increases to a maximum of only 0.22 at 700 K. The considerable difference in maximum f_{Hm} caused by the soaking treatment suggests that the difference in the initial molecular arrangement can result in the difference in the molecular mobility even at temperatures where the coal undergoes pyrolysis and carbonization. f_{Hm} for IL-R at 600–800 K is approximately equivalent to that in IL-S, while much smaller at lower temperatures. The difference in f_{Hm} at 400–600 K among the coals may be explained as follows. During the soaking treatment, chlorobenzene-extractable material is dissolved in the solvent, and in the following evaporation of the solvent, precipitates on the surface of swollen parent coal particles due to insufficient time to diffuse into the particles. Hence, the extractable material may not be associated with nonextractable macromolecules after the

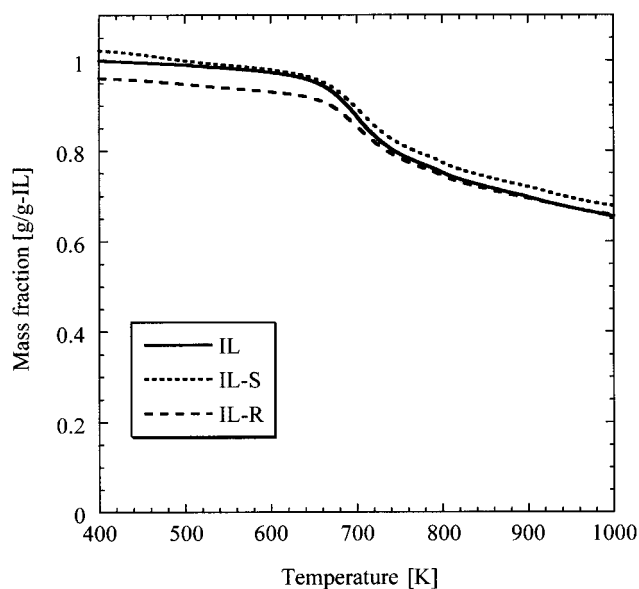


Figure 2. Changes in mass fractions of IL, IL-S, and IL-R with temperature.

evaporation as before the soaking but more or less isolated from the macromolecular phase. Such isolation makes the extractable material mobile and therefore increases f_{Hm} . The absence of the extractable material in IL-R is the reason for f_{Hm} for IL-R being distinctly smaller than that in IL-S. In addition, the isolation of the materials may accompany conformational rearrangement of macromolecules to form more thermally stable assemblies of them, in which extensive molecular motion is not allowed even at temperatures above 600 K.

Figure 2 illustrates the changes in the mass fractions of the coals with temperature. The mass fraction is indicated in the unit of g/g-IL. The initial fraction of IL-S is larger by 0.023 than that of IL due to retention of chlorobenzene in the former coal, and the decrease in the fraction seen at 400–550 K is ascribed to the evaporation of chlorobenzene. The initial fraction of IL-R, 0.96, results from the loss of the chlorobenzene-extractable material and the retention of the solvent. It should be noted that the fractions for IL and IL-S agree well with each other in the range from 600 to 700 K, where they exhibit much different molecular mobilities. This agreement indicates that the reduction of f_{Hm} induced by the soaking is not a result of enhanced evolution of tar, i.e., a major volatile product that would behave as liquid in the coal matrix.

The experimental results presented here demonstrate that the thermoplasticity of IL evaluated on the basis of molecular mobility is appreciably influenced through the physical rearrangement of macromolecules induced by the soaking in chlorobenzene that extracts only 6 mass % of material from the coal.

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(8) Green, T. K.; Kovac, J.; Larsen, J. W. *Fuel* **1984**, 63, 935–940.