MOLECULAR ASSOCIATION AND NETWORK STRUCTURE OF COAL

Yuzo Sanada
Ex-Center for Advanced Research of Energy Technology, Hokkaido University,
Sapporo, 060-8628, Japan

Keywords: coal, network structure, molecular association

Introduction

More than three decades ago, Sanada and Honda have treated coal as a three-dimensional network comprised of macromolecular arrays. Since that time, the concept has been followed by many investigators with various approaches as a gauge of coal macromolecular structure. In this paper, a brief overview of our works on macromolecular network structure of coal has been made.

The recent investigations about molecular and network structure by interactions of coal and electron acceptors have been described.

Hardness, Young's Modulus and Mechanical Properties of Coal [1-3]

The Vickers and Knoop indentation hardness and microstrength of coals of every rank have been determined. The hardness number increases with rank, and reaches a maximum at about 80 per cent carbon content. Hardness then decreases with rank for bituminous coal, shows a minimum at about 90 per cent carbon content, and thereafter suddenly increases again for anthracite as shown in Figure 1. Approximate values of Young's modulus (static) of coals are deduced from the hardness numbers and are order of $10^{9\text{-}10}$ dyne/cm^2.

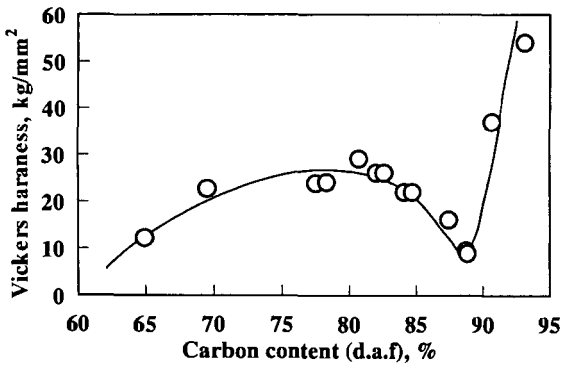

Fig. 1 Relation betweenVickers hardness number and rank of coal

The Shore dynamic hardness of coals has also been determined. The relation between Shore hardness and rank of coal shows a maximum at about 80 per cent carbon and a minimum at about 90 per cent carbon content like that static indentation hardness number and rank of coal. The fraction of elasticity and plasticity of coals is deduced from the impact and rebound energies of the free drop indenter. Approximate values of Young's modulus (dynamic) of coals are deduced as well. The calculated dynamic modulus is larger than the static one. The facts imply that coal is one of viscoelastic materials like synthetic high polymer. It is suggested that the mechanical deformation occurred during hardness measurements is mostly governed by non-covalent bonding in the coal structure.

The change of microstrength index versus rank of coal is similar to those of Vickers hardness number and the deduced Young's modulus. The almost similar relationship between the spin-lattice relaxation time derived nuclear magnetic resonance spectroscopy and rank of coal was found as shown in Figure 2.

Temperature Dependence of Knoop Hardness and Glass Transition [4-7]

When amorphous polymers are heated, in general, they show a minimum of indentation hardness,

a maximum of logarithmic decrease of the pendulum, and a change of slope of volume-temperature curve at the glass transition point or zone. We have attempted that the glass transition like phenomena for coal by various measurements, that is, temperature dependence of indentation hardness, decrease of pendulum and volume change method together with wide line NMR at lower temperature range, where there are not occurring any remarkable chemical reactions.

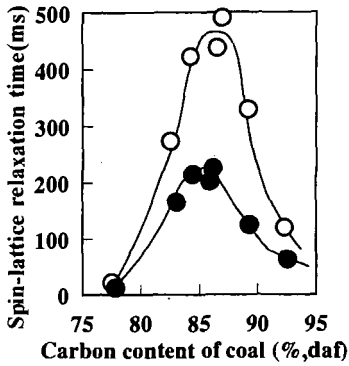

Fig. 2 Relation between ^{1}H-spin-lattice relaxation time and rank of coal. ● in air; ○ in vacuo

The relation between the Knoop hardness number, Hk, of air-dried coals and temperature is shown in Figure 3. For both brown and bituminous coals, Hk decreases with temperature increase to a minimum at about 50℃ and 100℃, respectively and increases with temperature up to 160℃. A small hump is observed at about 80℃ for brown coal. The specimens heated to 160℃ were allowed to cool in an ordinary atmosphere, then hardness was again measured at room temperature (closed circle in Figure 3). Bituminous coals and anthracite showed almost similar values to the original specimens. This implies the process is reversible step up to 160℃. On the other hand, the Hk value of brown coal became clearly high. The irreversible step is due to moisture release resulting the structure changes. We conclude that the characteristic points thus obtained with the various methods are brought by glass transition of coal.

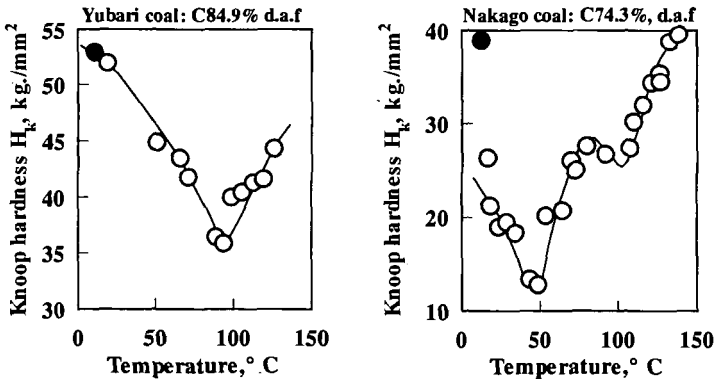

Fig. 3 Tempaerature dependence of knoop hardness of coals

Swelling Equilibrium and Three-Dimensional Network comprosed of Macromolecular Arrays [8-10]

Through the investigations above mentioned, a concept is motivated that coal as a three-dimensional network comprised of macromolecular arrays. Since that time, the concept has fostered into the thermodynamics governing solvent swelling as a gauge of coal macromolecules.

The swelling equilibrium of coal by pyridine at 25.0℃ was investigated. The molecular weight per crosslinked unit, Mc, of coal was estimated by applying the equation of Flory-Rehner. [Miss calculations were appeared in the original paper. These are corrected by the experiments separately [11, 12]. The results are summarized and shown in Figure 4. The value of Mc of coal over the range 65 to 80 per cent carbon content (d.a.f.) is almost constant. For bituminous coal, Mc increases suddenly with rank to a maximum at about 85 per cent for Japanese coal, then decreases with increase of rank. This relation coincides well with that between maximum fluidity,

measured by Gieseler plastometer, and rank of coal, as shown in Figure 5. It is suggested that the degree of crosslinking is an important factor in determining the thermal properties of coal.

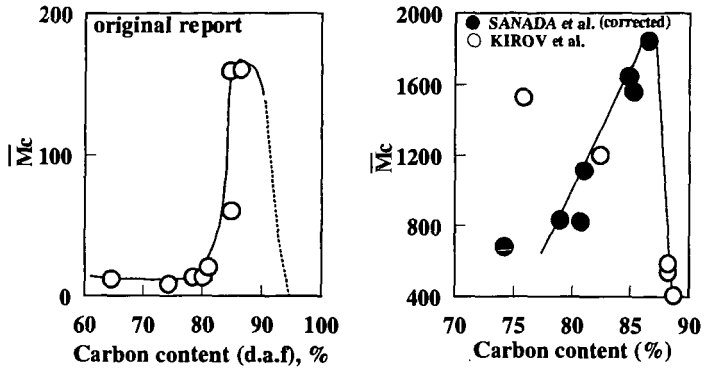

Fig. 4 Relation between moclecular weight per crosslinked unit and rank of coal

The equilibrium swelling of coal by various solvents has also been investigated. For brown coal and bituminous coals, the equilibrium swelling degree, Q, increases with increase of the solubility parameter, δ, of the solvent, reaches a maximum at about δ =10.8, and then decreases with increase of δ as shown in Figure 6. Applying the theory of regular solution, it is estimated that the cohesive energy density of coals over the range from 65 to 87 per cent carbon content is the values between 100 and 140 cal/cm^3 (δ =10 to 12).

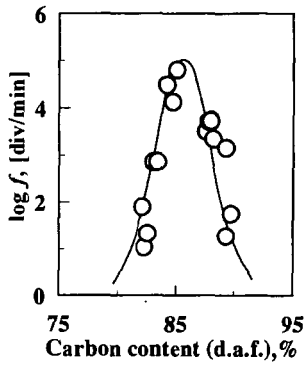

Fig.5 Changes of Gieseler maximum fluidity as a function of coal rank

In polar solvents the equilibrium swelling degree of coal is almost constant over the range from 65 to 87 per cent carbon content and decreases suddenly with further increase of rank. In non- or slightly- polar solvents, on the other hand, Q increases gradually with increases of rank up to a maximum at about 87 per cent carbon and then decreases. The value of Q for polar solvents increases remarkably with the increase of temperature. Polar solvents form 'coal-solvent' contacts readily by breaking and

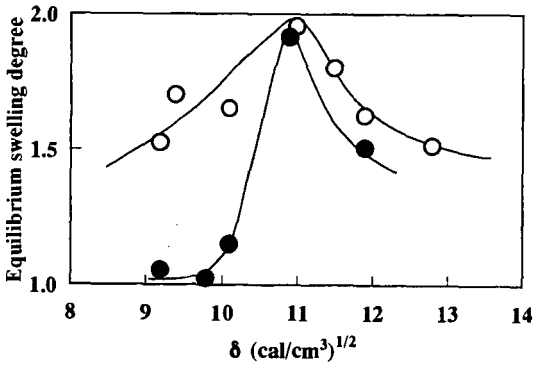

Fig. 6 Relation between equilibrium swelling degree of bituminous coal and solubility paramerters of solvents at 25.0°C ,○, (C81.1%); ●, lignite(C65.1%)

/or relaxing the hydrogen bonds in coal. It appears that cohesive forces in coals show a distinct minimum at about 85 to 87 per cent carbon content.

Interactions of coal with various solvents are investigated by means of solvent extraction at the boiling points as well as hardness of solvent-immersed coal. Conclusion obtained is similar to that of swelling measurements.

Molecular Association [12,13]

The thermodynamic behavior of coal is, of course, a macroscopic property. The macroscopic approach examines energy changes in systems with no regard to molecular structure. On the other hand, the microscopic approach examines the molecular structure of coal and related intermolecular interactions.

Interaction energies between molecules are the functions of (1) permanent dipole, (2) induced dipole and (3) dispersion forces. Ionization potential, I, polarizability, α, dipole moment, μ, and distance between the molecules, r, are the most fundamental properties. Figure 7 shows the changes of polarizability and dipole moment together with hydrogen bond energy versus coal rank. Contributions of dipole moment and hydrogen bonding are dominant at the low rank of coal, while polarizability developed by condensed aromatic rings in the structure for high rank coal is important for π-π interactions. The contributions of polarizability, hydrogen bonding and dipole moment for medium rank coal are less important. The relationships between grindability and thermal fluidity of coal and rank are able to explain from the trends with rank as shown in Figure 7.

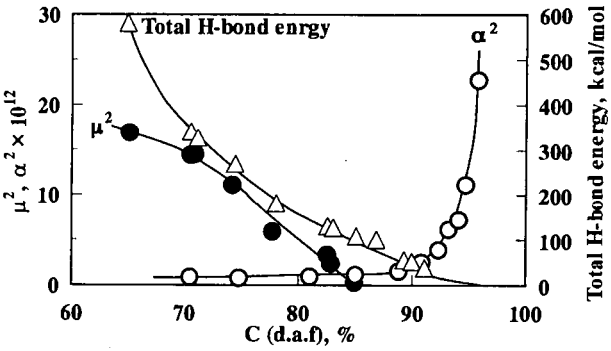

Fig. 7 Relation between molecular association factors and rank of coal

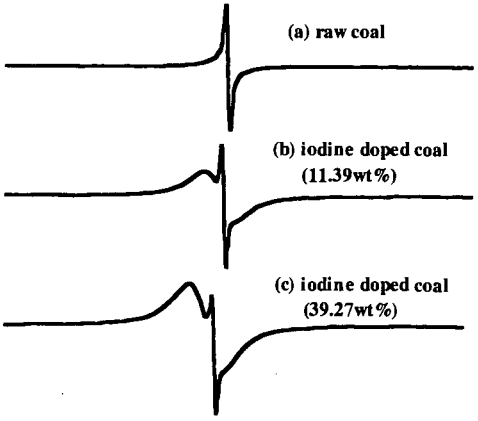

Fig. 8 ESR spectra of raw and iodine doped Upper Freeport(UF) coal

Charge Transfer Complex [15-19]

Coal is consisting with various molecules. It is likely that some of coal molecules behave electron deficient and others sufficient in nature at the solid state. The fact suggests that charge and/or electron transfer are generating between the both. This causes perhaps one of molecular association forces.

Condensed aromatic ring compounds with iodine show a broad e.s.r. signal due to charge transfer. The e.s.r. intensities of them correlate to their ionization potential values. Our investigations for coal have been concentrating the area by means of e.s.r. spectroscopy. Broad e.s.r signal was separated from sharp one by curve deconvolution. Peak intensity of the broad component is increasing with the iodine content as shown in Figures 8 and 9. The intermolecular behaviors of coal have been discussed through the evidences above.

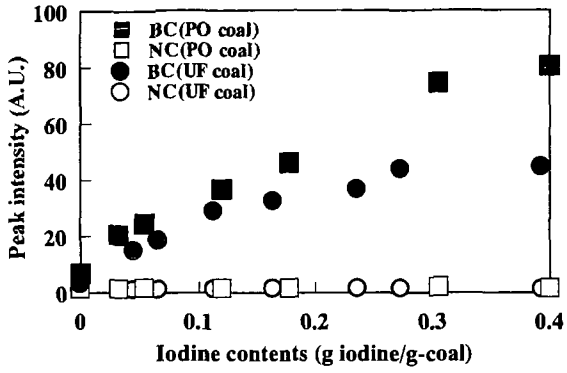

Fig. 9 Changes in peak intensity of iodine doped UF and PO coals ; BC: broad component, NC: narrow component

Acknowledgment

The author wishes to express his sincere thanks to Dr. H. Honda for his supervision at Resources Research Institute. The contributions of my coworkers and former students at RRI and Hokkaido University are most gratefully acknowledged.

References

1. Honda, H., Sanada, Y., Fuel, **1956**, 35, 451.
2. Honda, H., Sanada, Y., Fuel, **1958**, 37,141.
3. Yokono, T., Sanada, Y., Fuel, **1978** 57, 334.
4. Sanada, Y., Mochida, N., Honda, H., Bull. Chem. Soc. Jpn., **1960**, 33, 1479.
5. Sanada, Y., Honda, H., Nishioka, A., J. Appl. Polymer Sci., **1962**, 6, 94.
6. Sanada, Y., Honda, H., Fuel, **1962**, 41, 437.
7. Sanada, Y., Honda, H., Fuel, **1963**, 42, 479.
8. Sanada, Y., Honda, H., Bull. Chem. Soc. Jpn., **1962**, 35, 1238 & 1358.
9. Sanada, Y., Honda, H., Fuel, **1966**, 45, 295.
10. Sanada, Y., Honda, H., Fuel, **1966**, 45,451.
11. Kielov, N. Y., Oshea, J. M., Sergeant,C. D., Fuel, **1968**, 47, 415.
12. Green, T., Kovac, J., Brenner, D., Larsen, J. W., 'Coal Structure', **1982**, R. A., Meyers Ed.,Academic Press, p.199.
13. Sanada, Y., J. Fuel Soc. Jpn., **1963**, 42, 238.
14. Sanada, Y., Satou, M., J. Appl. Coal Petrology, Jpn., **1994**, 14, 29.
15. Sasaki, M., Sanada, Y., J. Jpn. Petrol. Inst., **1991**, 34, 218.
16. Sasaki, M., Kumagai, H., Sanada, Y., Energy & Fuels, **1992**, 6, 758.
17. Kaneko, T., Sasaki, M., Sanada, Y., 'Magnetic Resonance of Carbonaceous Solids', **1993**, Ed. R. Botto, Y. Sanada, Advances in Chemistry Series, 229, ACS, p.529.
18. Sanada, Y., Kumagai, H., Sasaki, M., Fuel, **1994**, 73, 840.
19. Sanada, Y., Kumagai, H., Mineo, T., Aizawa, S., Chiba, T., to be submitted.