GLASS TRANSITION TEMPERATURE OF MODIFIED COALS

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INTRODUCTION

Coals are macromolecular solids (1). Although they are not polymers in the sense they possess a repeat unit, they do possess several properties typical of synthetic crosslinked macromolecular networks (2). The crosslinks are thought to be covalent in nature. Hydrogen bonds (3,4) and intermolecular polarization forces (5,6) can be important associative forces as well.

Coals behave as glassy materials at room temperature (2). In the glassy state, macromolecular motion is impeded and only short segmental motion of the polymer chain is possible. The glassy state of a material is characterized by its glass transition temperature, T_g, the temperature at which the polymer changes from a glass to a rubber. A rubber is characterized by significant macromolecular mobility compared to the glassy state. The practical utility of polymers and their different properties depend heavily on their glass transition temperatures. Thus, an important area of research is to understand how different molecular features affect the glass transition temperature.

This research is based on the premise that the glass transition temperature is a fundamental property of coals as well, and that it may have an important relation to several other coal properties. For example, the diffusivity of organic solvents in polymers increases by several orders of magnitude at the glass transition temperature (7). If the same concept can be applied to coal, the advantages of lowering the glass transition temperature of coal to enhance coal reactivity are obvious, particularly if the reaction is thought to be diffusion-controlled. Peppas _et_ _al_. have demonstrated that coals swollen with pyridine exhibited lower glass transition temperatures than unswollen coals (8). In this research, we are primarily concerned with the impact of the network of hydrogen bonds in coals on their glass transition temperatures. Both differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) were utilized to establish the importance of hydrogen bonding to T_g for two Argonne premium coals.

EXPERIMENTAL

Sample Preparation. Argonne premium Illinois and Wyodak coals were obtained in sealed ampoules from Argonne National Laboratory. Both coals were dried overnight under vacuum at 105°C. Analysis found: Illinois #6; C, 65.6%; H, 4.7%; N, 1.2%: Wyodak; C, 67.5%; H, 4.99%; N, 0.84%. The coals were alkylated according to the method of Liotta (3) using tetra-_n_-butylammonium hydroxide and the appropriate alkyl iodide in THF. One sample was exposed to THF with no alkylating agent and is identified as the THF blank. Both elemental and IR analysis confirmed that alkylation had occurred.

Differential Scanning Calorimetry (DSC). The DuPont 910 DSC was used to measure the glass transition temperatures of the samples. Samples were heated from ambient to 600°C at a heating rate of 10°C/min. The system was purged with nitrogen at a rate of 100 mL/min to provide an inert atmosphere. Sample sizes of 5 mg or less were used. The DuPont 2000 Thermal Analysis System was used to analyze the data. Heat flow was plotted as a function of temperature. The glass transition temperature is indicated by a change in the baseline curve in a negative direction. The analysis package identified the inflection point of the change in the curve and this inflection was reported as T_g.

Thermal gravimetric analysis (TGA). The Shimadzu HT 50 TGA was used to monitor weight loss as a function of temperature. The samples were run under nitrogen at a flow rate of 100 mL/min and heated from ambient to 550°C at a heating rate of 10°C/min.

Thermomechanical Analysis (TMA). The DuPont 943 TMA was employed to assess the softening characteristics of the coals. The TMA uses a weighted probe that will penetrate the sample due to the softening which indicates the onset of the glass transition. Probe displacement is plotted as a function of temperature and the softening point is indicated by a negative probe displacement. The macroexpansion probe was used on the TMA. The coal samples were obtained in powdered form. Flat-bottom aluminum DSC pans were used to hold the samples. The coal powder was packed into the pans to a thickness of about 2-3 mm. Typical sample weights were about 20 mg. The pans were then placed in the TMA under a 100 g weight load. This was done to ensure that settling of the sample would be complete. Probe displacement was monitored as a function of time at ambient temperature to insure that the sample was well-packed into a pellet. A 10 g weight was then applied and the cell was purged with nitrogen at a rate of 300 mL/min to obtain an inert environment. The sample was heated at a rate of 10°C/min to a temperature just below the temperature of significant weight loss as indicated by the TG curves.

RESULTS

Elemental Analysis. The O-alkylated coals were analyzed for carbon, hydrogen, and nitrogen. The hydrogen/carbon ratios for the various coals were consistent with the addition of approximately 6 alkyl groups per 100 carbons for the Illinois #6 coal. For the Wyodak coal, elemental analysis indicated addition of approximately 8 methyl groups per 100 carbon. FT-IR analysis of the O-alkylated coals indicated reaction had occurred as evidenced by the increased C-H absorption at 2900 cm^{-1}, reduction of the O-H absorption at 3300-3600 cm^{-1}, and the appearance of an absorption at 1700 cm^{-1} which is attributable to the C=O of esters formed from carboxylic acids.

DSC Results. A typical DSC thermogram obtained using the dry, whole Illinois #6 coal is presented in Figure 1. Note that there is an increasing negative heat flow into the sample relative to the aluminum oxide reference. The glass transition is identified by the slope shift that occurs near 300°C. Its onset temperature of 295°C was reported as T_g. These results are consistent with those of Peppas et al. for a coal of similar rank (8).

The results for both coals and their alkylated derivatives are summarized in Table I. For the Illinois #6 coals, all reported values are the average of at least five measurements, except for the THF blank (no alkylating agent), which is the average of only two measurements. For the Wyodak coals, only three measurements were made. The effect of O-methylation is to decrease T_g by 100°C for the Illinois #6 coal and 75°C for the Wyodak coal. The effect of the alkyl chain length is not significant for the Illinois #6 coal, although there is clear tread of decreasing T_g with increasing chain length. Exposure of the Illinois #6 coal to THF solvent results in a lower T_g by 50°C.

TG Results. The percent weight loss versus temperature curves for the Illinois #6 coals are presented in Figure 2. Weight loss for the dry, whole coal and the THF blank (no alkylating agent) is not significant until nearly 400°C, which is significantly above the reported T_g's for these coals. This result indicates that no major thermal degradation of the coal occurred before T_g, consistent with the results of Peppas et al (8).

Initial weight loss for the O-alkylated coals occurs at much lower temperatures than the whole coal. Approximately 5-10% of the weight loss occurs in the range of 200-350°C for these coals. An additional 15-25% weight loss occurs in the region of 350-550°C. These coals are clearly much more volatile than the whole coal, which is consistent with other studies (3). It appears that these coals are in a rubbery state, however, before any significant weight loss occurs, since their T_g's are all near 200°C as measured by DSC.

TMA Results. The whole and O-methylated coals were analyzed by TMA in order to assess their softening characteristics. The DSC results indicated that the O-methylated coal should soften at a much lower temperature than the whole coal. This expectation was confirmed. The results on the Illinois #6 coals are shown in Figure 3, where the probe displacement (dimensional change) is plotted against temperature. Note that the O-methylated coal softens at a much lower temperature than the whole coal. Similar results were obtained on the corresponding Wyodak coals.

DISCUSSION

The lowering of T_g by O-methylation of the coal is most probably attributed to the disruption of the hydrogen bond network known to exist in these coals. The hydrogen bonds serve as crosslinks between macromolecular chains and represent an important attractive force that should restrict chain mobility. That their disruption by O-alkylation lowers T_g of the coal is therefore not surprising. The effect of THF solvation on T_g is also substantial, although not as large as O-alkylation. This effect might attributed to a partial disruption of the hydrogen bond network by THF, which is a known hydrogen bond acceptor. THF is also expected to swell the coal substantially. When the THF is removed, not all of the disrupted hydrogen bonds are expected to reform.

The length of the added alkyl group appears to have only a small effect on T_g, contrary to our expectations. We believed that the addition of longer alkyl groups might disrupt noncovalent interactions other than hydrogen bonding that might exist between the macromolecular chains, thereby lowering T_g even more. Either these interactions are not important or O-alkylation fails to disrupt them. In the future, we plan to examine the effects of C-alkylation (5) on the glass transition temperatures of coals to explore this aspect more fully.

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TABLE I

Glass Transition Temperatures of Modified Coals

Coal	T_g, °C Illinois #6	Wyodak
Whole	300±5	276
THF Blank	247	---
O-Methylated	198±13	203
O-Butylated	185±7	---
O-Octylated	178±14	---

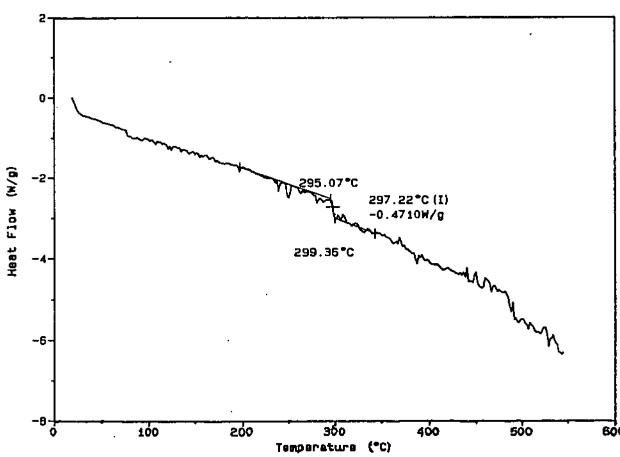

Figure 1. DSC Curve of Dry, Whole Illinois #6 Coal.

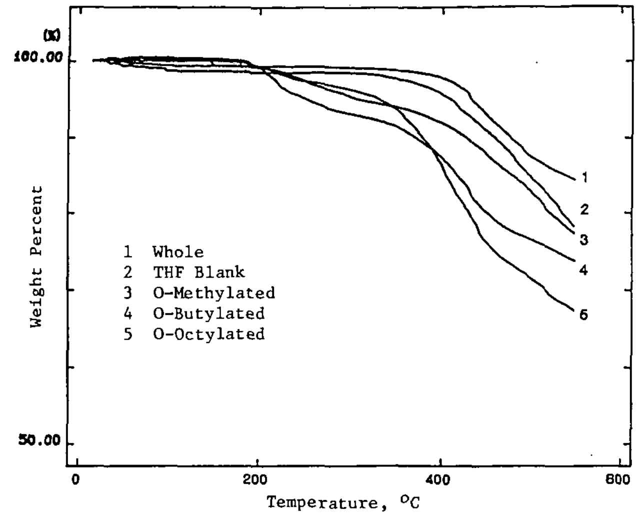

Figure 2. TGA Curves of Illinois #6 Coals.

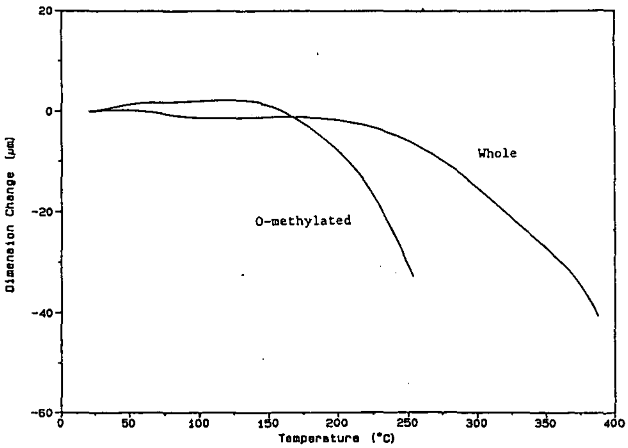

Figure 3. TMA Curves of Illinois #6 Coals