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INTRODUCTION

The thermoplasticity of coals and the formation of mesophase from pitches are key phenomena in their respective utilisation in high temperature carbonisation to produce blast furnace coke and as precursors for producing high performance carbons. Although standard empirical tests are widely used to ascertain plasticity and softening behaviour, they do not easily relate to the actual structural changes that occur. In this sense, NMR is definitive in that molecular parameters are monitored, i.e. the amount and mobility of hydrogen. Indeed, high temperature ^1H NMR has successfully been used to investigate the motion of coals in-situ during carbonisation, where parameters reflecting the spin-spin relaxation times T_2 s, have been correlated with plasticity (1,2). Further, ^1H NMR can also monitor the loss of hydrogen resulting from devolatilisation and aromatisation and consequently the technique has been referred to as "proton magnetic resonance thermal analysis" (PMRTA) (1,2). However, the other ^1H relaxation parameters, i.e. spin-lattice in the laboratory and rotating frames, T_1 and $T_{1\rho}$, can also be a source of information about molecular motion for coals (3). This paper addresses the changes in all the ^1H relaxation parameters as a function of temperature which have been followed both in-situ and at ambient temperature for a coking coal and coal-derived and petroleum pitches. Bulk carbon skeletal parameters derived from solid state ^{13}C NMR for the coals and pitches investigated are also reported in the Proceedings (4).

EXPERIMENTAL

The in-situ ^1H NMR measurements were performed on a Australian coking coal, a thermally treated coal tar pitch and Ashland A-240 petroleum pitch using a Bruker MSL-100 spectrometer at a field strength of 2.4 Tesla. A Doty probe was used for the high temperature measurements where the 90° pulse width varied with temperature between $2.8\mu\text{s}$ at ambient to $6\mu\text{s}$ at 500°C . About 30-50 mg of sample was packed in a zirconia rotor which was placed horizontal in the stator. A flow of $15\text{ dm}^3\text{ min}^{-1}$ of dry nitrogen was used to transfer the heat to the samples and to remove the volatiles escaping through a small ventilation hole in the rotor.

The ambient ^1H NMR experiments on the pretreated samples were carried out using a Bruker broadband probehead and a 90° pulsewidth of $1.2\mu\text{s}$. A suite of partially carbonised coal (PCC) samples prepared using a Juraneck furnace over the temperature range $325\text{-}625^\circ\text{C}$, and coal tar pitches (CTP) preheated between $250\text{-}380^\circ\text{C}$ and under vacuum (80-125 mm. Hg) have been analysed. A 5 mm o.d. borosilicate glass tube filled with ca 50-80 mg of sample was placed horizontal in the probe. At ambient temperatures, the relaxation parameters were obtained using single point acquisition, but for the high temperature experiments, the generally low sensitivity meant that the conventional accumulation of a series of whole FIDs had to be employed.

RESULTS

Partially carbonised coals Figure 1 compares the peak widths at half height, $\Delta H_{1/2}$ and the T_1 s measured in-situ at temperatures up to 500°C . The initial softening of the coal between 200 and 250°C , probably resulting from the solvent-extractable material present, and the temperature range of maximum fluidity at $350\text{-}390^\circ\text{C}$ are reflected by the changes in $\Delta H_{1/2}$ (proportional to $1/T_2$). During the fluidity range, the peak width of the plastic phase is only about one-tenth that for the initial coal (Figure 1). However, inert material giving a broad peak is also evident during the fluidity range and this accounted for ca 20% of the total hydrogen. After the onset of resolidification, the peak width of the plastic phase increases to reach a value similar to that of the initial coal by ca 450°C (Figure 1).

The changes in T_1 are quite different from those in $\Delta H_{1/2}$. The initial increase up to 250°C probably arises from the desorption of paramagnetic O_2 trapped within the coal. Above 250°C , the T_1 falls steadily until at 450°C , it is much less than that of the initial coal (Figure 1). The development of plasticity in the coal should reduce its correlation time so that T_1 decreases significantly. However, the increase in the concentration of free radicals will also give rise to a decrease in T_1 (3). The fact that resolidification does not reverse the fall in T_1 indicates that the relaxation mechanism is dominated by the free radicals present.

Table 1 lists the relaxation parameters determined at ambient temperature for some of the partially carbonised coal samples. For samples carbonised above *ca* 350°C, the T_1 decreases continuously with increasing carbonisation temperature indicating again that, at high temperatures, the relaxation mechanism is dominated by the free radicals present. The changes in T_2 and $T_{1\rho}$ at ambient temperature are much less marked than those in T_1 .

Pitches At ambient temperature, thermal treatment of coal tar pitch gives rise to decreases in both T_1 and $T_{1\rho}$, but no significant variation in T_2 (Table 1). These changes are thought to arise again from the higher concentrations of free radical species, rather than the increases in softening point (reflecting the higher concentrations of toluene-insolubles) brought about by thermal treatment. As anticipated, the $\Delta H_{1/2}$ decreases (T_2 increases) markedly after softening in-situ as shown in Figure 2 for the petroleum pitch. Little weight loss occurs below 300°C when a moderately slow heating rate is employed. A significant loss of volatiles occurs above 300°C before the rapid onset of mesophase formation at 400°C. By 450°C, mesophase formation is nearly complete with only 10% mobile (isotropic) material remaining (Figure 2) which disappeared after a further isothermal period of 20 min. Isothermal experiments on coal tar pitch in-situ showed that mesophase formation does not begin to occur until temperatures well above 370°C.

CONCLUSION

The results have confirmed the ability of high temperature NMR to follow carbonisation in-situ, through changes in peak width (T_2) and the decreases in hydrogen concentration. Changes in thermal relaxation times (T_1) would appear to be dominated by free radical concentrations.

ACKNOWLEDGEMENTS

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Table 1: Relaxation parameters for partially carbonized coals (PCC) and coal tar pitches (CTP) at ambient temperature.

Sample	Temp./°C	T_1 /ms	$T_{1\rho}$ /ms	T_2 /us
Coal	-	178	7.2	36
PCC-1	351	162	6.6	43
PCC-2	468	76	4.2	45
PCC-3	611	20	6.1	55
Heat-treated CTP-1	250	735	19.7	21
Heat-treated CTP-2	380	380	7.2	18

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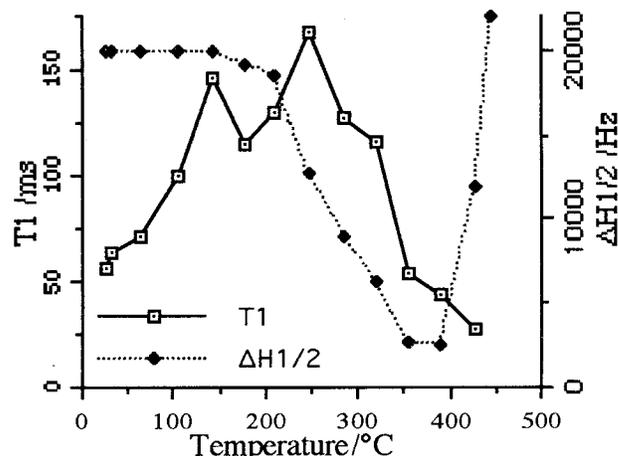


Figure 1. Variation of the T_1 and peak half-width with temperature for the coking coal in-situ.

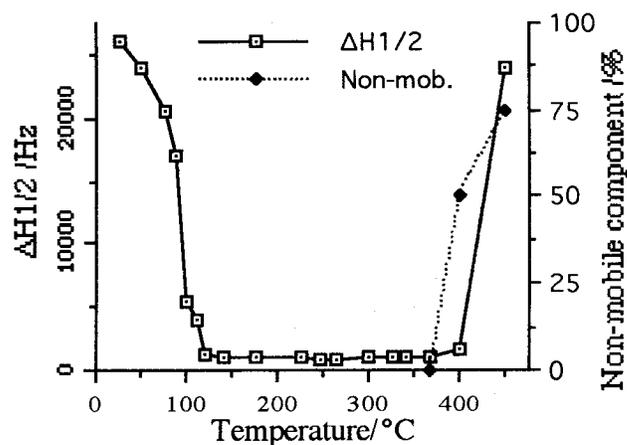


Figure 2. Variation of peak half-width and mesophase development with temperature for the petroleum pitch.