

Sulfur- and nitrogen-containing phenol-formaldehyde co-resites for probing the thermal behaviour of heteroatomic forms in solid fuels

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In order to probe the formation of sulfur- and nitrogen-containing gases during the pyrolysis and combustion of coals and other solid fuels, non-softening model substrates are required. In this respect, phenol-formaldehyde (PF) resins are ideal since they readily facilitate the incorporation of individual heteroatomic functions into a highly crosslinked matrix. A series of sulfur- and nitrogen-containing co-resites have been prepared using phenol with, as the second component, thiophene, dibenzothiophene, diphenylsulfide, benzyl phenyl sulfide, thioanisole, 8-hydroxyquinoline and 2-hydroxycarbazole. A mole ratio of 3 : 1 (phenol : heteroatom-containing component) was adopted in order to ensure that a reasonably high degree of crosslinking was achieved. Resoles containing diphenyldisulfide were also prepared but, due to the comparable bond strengths of the S–S and C–O linkages, a curing temperature of only 130°C was used to avoid cleavage of the disulfide bond. The virtually complete elimination of ether and methylol functions from the resoles by curing at 200°C was monitored by solid-state ¹³C nuclear magnetic resonance (n.m.r.) spectroscopy. The resultant resites were also characterized by sulfur K-edge X-ray absorption near-edge structure (XANES) spectroscopy, X-ray photoelectron spectroscopy (X.p.s.) and differential scanning calorimetry (d.s.c.). Simple air oxidation was found to selectively convert the aliphatic-bound sulfur to a mixture of sulfones and sulfoxides. Applications of the resites in fuel science are described. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

In order to obtain insights into the complex reactions which occur during the thermal breakdown of coals^{1,2} and other solid carbonaceous materials, such as oil shale^{2,3} and biomass^{4,5}, detailed structural information about the starting material and an understanding of how the different functionalities present behave under processing conditions are required. To achieve the latter aim, model-compound studies performed in both the vapour and liquid phases have been used extensively⁶. However, a major drawback with such studies is that the radicals generated via bond homolysis are mobile and free to diffuse independently prior to further reaction. In contrast, for solids such as coals and oil shales many of the reactive intermediates remain covalently attached to the crosslinked macromolecular framework. Thus, their reactivities are subject to diffusional restraints and are likely to be somewhat different from those encountered in fluid-phase

model-compound studies. Furthermore, for pyrolysis and combustion studies in open systems, the use of non-softening substrates that remain in the reactor is essential.

In order to explore the effects of restricted mobility in free-radical reaction pathways during coal liquefaction, Buchanan and coworkers pioneered work on model compounds immobilized on silica^{7,8}. It was recognized that these substrates also have considerable potential for modelling solid fuel pyrolysis phenomena, including the behaviour of sulfur and nitrogen forms with respect to the formation of H₂S, NH₃ and HCN during carbonization and SO_x and NO_x during combustion. In preliminary work it was established that the SiO–C bond linking the substrate to the surface is reasonably stable and does not cleave below 500°C⁹. Immobilized samples of thiophene, dibenzothiophene, diphenylsulfide, benzyl phenyl sulfide and thioanisole were subsequently prepared and used as calibrants¹⁰ in temperature programmed reduction (TPR), a thermal technique used to specify organic sulfur forms from their characteristic reduction temperatures^{11,12}.

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Cured phenol-formaldehyde (PF) resins were identified as another flexible class of materials that could also be used for investigating pyrolysis and combustion phenomena in the solid state, since a wide spectrum of hydrocarbon and heteroatomic moieties can readily be introduced into their macromolecular framework. In this present study, a series of sulfur- and nitrogen-containing co-resoles and resites have been synthesized using phenol with, as the second component, thiophene, dibenzothiophene, diphenylsulfide, benzyl phenyl sulfide, thioanisole, quinoline and carbazole. The elimination of ether and methylol functions from the resoles by curing at 200°C has been monitored by solid-state ¹³C nuclear magnetic resonance (n.m.r.) spectroscopy. The cured resites have also been characterized by sulfur K-edge, X-ray absorption near-edge structure (XANES) spectroscopy, X-ray photoelectron spectroscopy (X.p.s.) and differential scanning calorimetry (d.s.c.). It is demonstrated that aliphatic-bound sulfur can be converted to a mixture of sulfones and sulfoxides with a reasonable degree of selectivity by simple air oxidation.

EXPERIMENTAL

Synthesis of precursors

The hydroxy-sulfur compounds used to prepare the resins were 2-(4-hydroxybenzyl) thiophene, 2-hydroxydibenzothiophene, 4-hydroxythioanisole, 4-hydroxydiphenyl sulfide, benzyl 4-hydroxyphenyl sulfide, 4,4'-dihydroxydiphenyl sulfide and 4,4'-dihydroxydiphenyl disulfide. Of these, 4-hydroxythioanisole was the only commercially available precursor. For the nitrogen-containing resins, commercially available 8-hydroxyquinoline and 2-hydroxycarbazole were used.

In order to prepare 2-(4-hydroxybenzyl)thiophene, a Wolff-Kishner reduction was conducted on 2-methoxybenzoyl thiophene (10 g), using 95% hydrazine hydrate, potassium hydroxide and diethylene glycol to yield 5 g of colourless 2-(4-methoxybenzyl)thiophene (b.p. 188–190°C/14 mmHg). This compound was then demethylated by refluxing for 20 min in 20 g of redistilled pyridine hydrochloride. After cooling, the reaction product was extracted in diethyl ether and purified by vacuum distillation. This yielded 4 g of 2-(4-hydroxybenzyl)thiophene, which was recrystallized from petroleum ether to yield shiny colourless prismatic crystallites (m.p. 58°C, b.p. 195–200°C).

In order to prepare 2-hydroxydibenzothiophene, dibenzothiophene was first brominated to yield 2-bromodibenzothiophene, which was then subjected to base hydrolysis¹³. For this step, 2-bromodibenzothiophene (3.6 g), sodium hydroxide (4.8 g), copper-bronze (3.2 g) and water (36 cm³) were mixed together and heated in a closed stainless steel tubing bomb (length = 20 cm, diameter = 2 cm) with vigorous shaking at 260°C for ca. 8 h. Following recovery, dilution of the reaction mixture, filtration and washing with water, the precipitate was then recrystallized from dilute aqueous methanol to give white crystals of 2-hydroxydibenzothiophene (m.p. 158–160°C). Gas chromatography (g.c.)–mass spectrometry (m.s.) analysis indicated a molar purity of 96.5%, with the major impurities being dibenzothiophene (ca. 1.0 mol%) and two isomers of dihydroxydibenzothiophene (ca. 2.0 mol%).

Benzene sulfinic acid was reacted with phenol using

a modification of Hinsberg's method¹⁴ for preparing 4-hydroxydiphenyl sulfide. The sodium salt of benzene sulfinic acid was dissolved in distilled water and concentrated hydrochloric acid was added to precipitate the acid. The latter (46.0 g) was then mixed with phenol (15.2 g) and heated in an oil bath (<100°C) for ca. 3 h with continuous stirring. A 10% solution of Na₂CO₃ (100 cm³) was then added to the dark red reaction mixture which was then steam-distilled to remove excess phenol. The flask contents were transferred into a beaker and then acidified with 2 M hydrochloric acid. A brown coloured resin and an oil layer were separated and the oil layer was extracted with ether (200 cm³ (×2)). The ether extract was washed with 10% Na₂CO₃ solution (100 cm³ (×3)) until the alkali layer became clear, and finally washed with water (100 cm³ (×2)) and dried over anhydrous magnesium sulfate overnight. The ether was evaporated off leaving a dark brown oil, i.e. the crude 4-hydroxydiphenyl sulfide. This crude product (43.8 g) was vacuum distilled at 6 mmHg in an oil bath at <220°C in order to prevent decomposition. The distillate fractions were slightly yellow in colour, which was probably due to impurities, and consequently were redistilled. Colourless oils were then obtained and, upon cooling, these formed white solids which were recrystallized from petroleum ether to give white crystals of 4-hydroxydiphenyl sulfide (m.p. 51–52°C).

Benzyl 4-hydroxyphenyl sulfide was prepared by reacting 4-hydroxythiophenol with benzylbromide¹⁵. Sodium hydroxide (10 g) was partially dissolved in methanol (25 g), and 4-hydroxythiophenol (34.7 g), also in methanol (25 g), was added to this stirred mixture. Benzyl bromide (2.7 g) was then added dropwise over a period of 45 min. The reaction proceeded vigorously and after the reaction mixture had been refluxed for 1 h, it was allowed to cool and then filtered. Methanol was evaporated to leave a yellow solid. This crude sample of benzyl 4-hydroxyphenyl sulfide was recrystallized from petroleum ether (100–120°C), leaving a white crystalline solid (m.p. 105–107°C), the yield being ca. 60 mol%.

4,4'-Dihydroxydiphenyl disulfide was synthesized by reacting 4-hydroxythiophenol (5.0 g) with dimethyldithiobis(thioformate) (5.0 g; this was prepared from a methanolic solution of potassium hydroxide and carbon disulfide) in the presence of pyridine (2.0 g) as catalyst¹⁶. The resulting solution was stirred for 1 min, allowed to stand for 15 min and evaporated to leave a crystalline yellow solid (yield = 2.70 g, 80 mol%). The crude solid was recrystallized from ethanol giving white crystals of 4,4'-dihydroxydiphenyl disulfide (m.p. 145–147°C).

Synthesis of the resins

The co-resoles were prepared by using a total phenol to formaldehyde mole ratio of 1:2.5, following established procedures^{17,18}. The mole ratio of phenol to the monohydroxy-substituted sulfur- and nitrogen-containing component was 3:1, so as to ensure that a reasonably high degree of crosslinking was achieved in the initial resoles. Sodium hydroxide was used as the catalyst in the condensation reaction at a mole ratio of 0.1 with respect to the phenol. Phenol, the monohydroxy-substituted sulfur- or nitrogen-containing phenol and formaldehyde (13.0 g of 37% formaldehyde) were mixed in a 250 cm³ 3-necked round-bottomed flask and stirred until all of the phenol was in solution. The mixture was then cooled

in an ice bath for ca. 10 min before sodium hydroxide (0.006 mol, 20 M) was added dropwise to the reaction mixture, which was then refluxed at 70°C for 30 min, and acidified with 85% lactic acid to pH 4–5 (indicated by universal indicator paper) before excess water was removed by vacuum distillation. The thick resinous material was poured into a capped container for curing in an oven purged with nitrogen gas that was initially set at 70°C for 4 days. The oven temperature was then raised to 130 and 200°C for additional 24 h periods. The resole containing dihydroxydiphenyl disulfide was prepared in a similar manner but without the addition of phenol, and was only partially cured at 130°C to avoid cleaving the relatively weak disulfide bonds.

Characterization

The C, H and N contents of the PF resins were determined by using a Perkin Elmer 2400 Analyser, while sulfur determinations were carried out using a Sulphanazo III instrument. The chloroform and methanol solubilities of a number of the resoless and resites were determined by heating small samples under reflux.

Solid-state ^{13}C n.m.r. spectra of the resoless and cured resites were obtained by using a Bruker MSL100 instrument, operating at a frequency of 25 MHz for carbon. The cross polarization–magic angle spinning (CP/MAS) technique was used, with the contact time being 1 ms with a recycle delay of 1.5 s between successive contacts. Samples (250 mg, <250 μm) were packed inside a 7 mm diameter zirconia rotor for the analysis. Typically, 1000 scans were accumulated and spectra were processed using a line broadening factor of 30 Hz.

D.s.c. measurements were carried out on a Mettler DSC-30 system. The sensor on the instrument consisted of a five-fold Au–Ni thermopile mounted on a glass disc. Temperature calibration was achieved by using the melting points of indium, lead and zinc standards. The sample (~10 mg) was weighed inside a standard aluminium pan with a cold welded lid, two pin holes were pierced through the lid to allow for evaporation of water and other volatiles. The carrier gas was nitrogen, at a flow rate of 50 $\text{cm}^3 \text{min}^{-1}$. The sample surface was heated from 30 to 300°C at a rate of 10°C min^{-1} in three consecutive scans. The furnace was cooled in between each scan with the aid of liquid nitrogen; the cooling rate was also 10°C min^{-1} .

Mild air oxidation of the sulfur-containing resites was carried out by the method used by Gorbaty *et al.*¹⁹. The sample (<75 μm) was spread in a thin layer in a large Petri dish and exposed to air in an oven kept at $125 \pm 0.5^\circ\text{C}$ for 5 days. XANES measurements on the sulfur-containing resoless and resites before and after air oxidation were performed at Daresbury Synchrotron Laboratory on the soft-X-ray beamline 3.4. The spectra were recorded in transmittance mode using a Si(III) double crystal monochromator and a Stern–Heald type detector. The energy scale was calibrated with respect to elemental sulfur, with the $s \rightarrow p$ peak maximum in the sulfur XANES spectrum being assigned a value of 2472.0 eV. Sample (<20 mg, <75 μm) and pure graphite (~40 mg, for conductivity) were blended in an agate mortar and pestle. A few millimetres of acetone were added to the mixture and the latter was then pipetted on to an aluminium sample plate, thus forming a thin layer. The sample plates were slotted into the edge of the rack

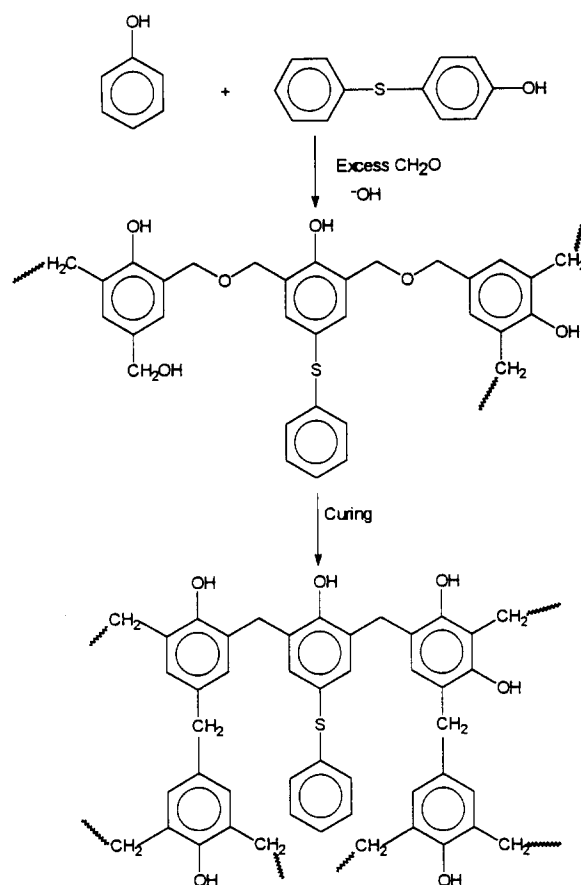


Figure 1 Incorporation of diphenyl sulfide into the structure of the co-resole, and the resultant resite

inside the sample chamber (which held up to nine plates). The sample chamber was evacuated to $<10^{-8}$ mmHg pressure before the beamline was opened.

X.p.s. of the benzyl phenyl sulfide-containing resite before and after air oxidation was carried out on a home-built system with a 100 mm hemispherical analyser, and using a non-monochromatic aluminium anode as the $\text{AlK}\alpha$ radiation source. Samples (100–200 mg) were dusted on to a metallic sample block by double-sided non-conducting tape and were analysed at pressures of ca. 10^{-8} mmHg.

Table 1 Elemental compositions of the heteroatomic-containing resites and the disulfide resole

| Co-resite/resole | Composition ^a (%) | | | |
|---------------------------|------------------------------|-----|------|------|
| | C | H | S | N |
| Thiophene | 70.6 | 5.2 | 3.3 | n.d. |
| Dibenzothiophene | 72.3 | 4.2 | 5.4 | n.d. |
| Diphenyl sulfide | 72.4 | 4.9 | 5.2 | n.d. |
| Phenyl benzyl sulfide | 72.7 | 5.0 | 5.5 | n.d. |
| Thioanisole | 69.3 | 5.1 | 6.2 | n.d. |
| Diphenyl disulfide resole | 54.0 | 4.4 | 19.5 | n.d. |
| Carbazole | 74.2 | 5.5 | n.d. | 1.3 |
| Quinoline | 68.6 | 4.4 | n.d. | 2.4 |

^a n.d. = not determined

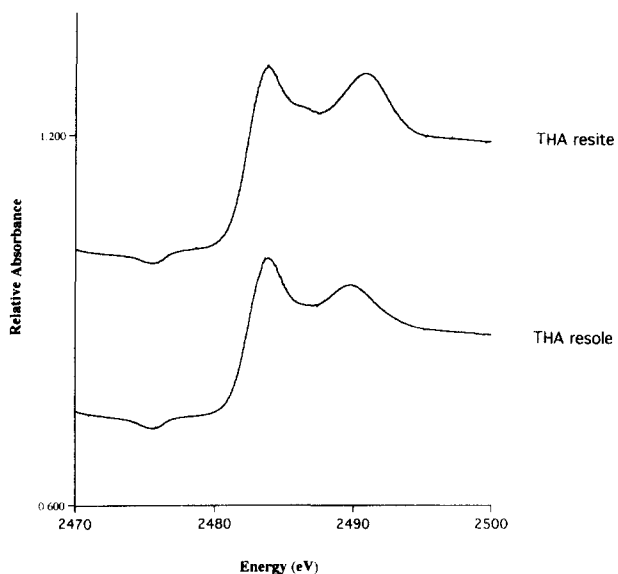


Figure 2 XANES spectra of the thioanisole resin before and after curing

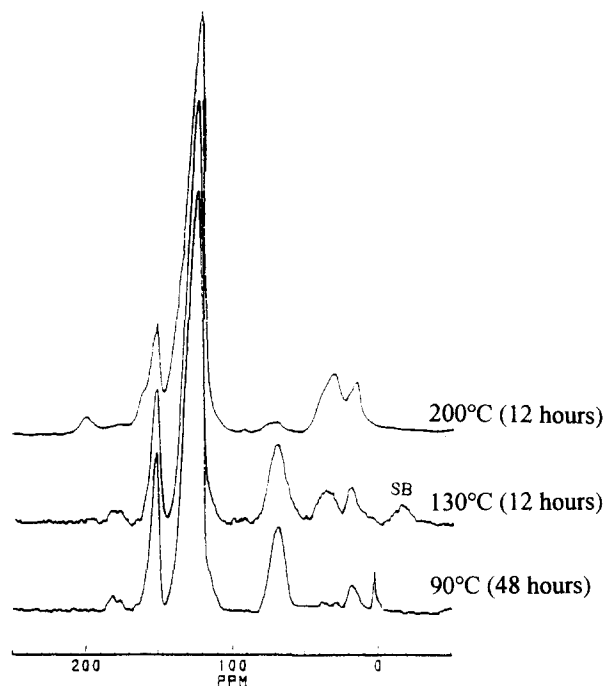


Figure 3 Solid-state ^{13}C n.m.r. spectra of a normal PF resin after various curing periods

RESULTS AND DISCUSSION

General considerations

The incorporation of diphenyl sulfide into a cured PF resole and the resultant resite is depicted in Figure 1. Clearly, the PF sulfur- and nitrogen-containing resites should have the same basic structure as normal co-resins. Novalak-based co-resins containing cresols have found applications as coatings and semiconductors where their antioxidant and adhesive properties are exploited^{20,21}. As mentioned earlier, a mole ratio of 3:1 for phenol to the heteroatom-containing component was adopted here to ensure that a reasonably high degree of crosslinking was

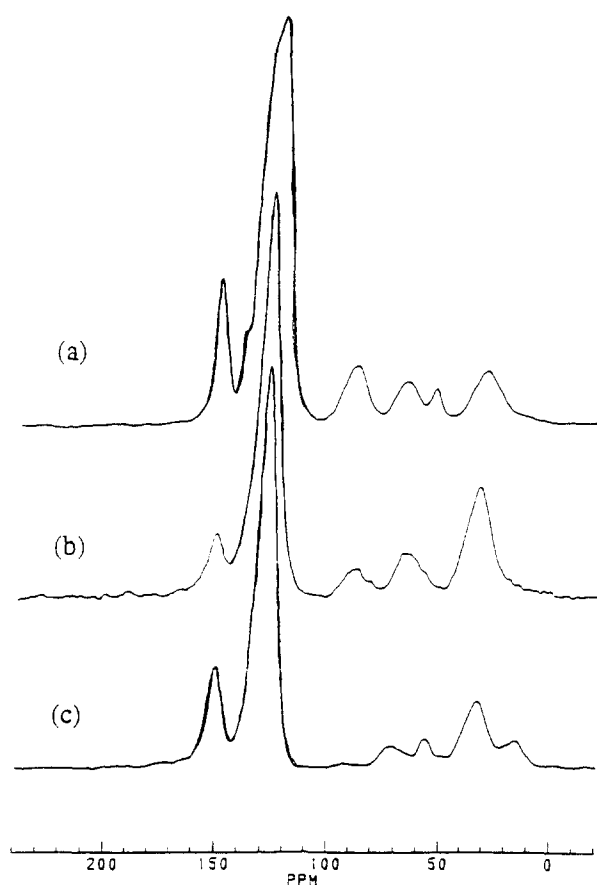


Figure 4 Solid state ^{13}C n.m.r. spectra of the partially cured (130°C) resites containing: (a) dibenzothiophene; (b) thioanisole, (c) phenyl benzyl sulfide

achieved and to ensure that the heteroatomic species were reasonably dilute in the macromolecular structure. As anticipated, the cured PF resins were all found to have low chloroform and methanol solubilities, i.e. below 1%.

The elemental analysis results for the co-resites are listed in Table 1. The partially cured resin containing dihydroxydiphenyl disulfide has a much higher sulfur content than the co-resites, since phenol was not used in the preparation (Table 1). Their sulfur and nitrogen contents are in the ranges 5–6% and 2–3% respectively, as predicted from the molar quantities used. Furthermore, the O/C, S/C and N/C atomic ratios remained constant throughout the curing period. The constant values of the S/C ratios suggest that the more labile (aliphatic) carbon–sulfur bonds have not been broken to any considerable extent by curing at the relatively high final curing temperature of 200°C that was used. These bonds should also not have been oxidized to a significant extent. Figure 2 shows the XANES spectra of the thioanisole resin before and after curing. Although a small shoulder from sulfones/sulfoxides is evident, it is estimated that these oxidized forms account for no more than 10% of the total sulfur.

All of the fully cured co-resites have carbon contents close to 70% (Table 1), with the contents of the volatile matter being between 45 and 60%. In relation to coals, these values and the C and O contents are close (superficially) to those of lignites¹. However, lignites clearly have a much more diverse array of oxygen

Table 2 ^{13}C n.m.r. peak assignments for the resoles and resites

| Chemical (ppm) shifts | Functional group assignment |
|-----------------------|---|
| 18 | Arylmethyl, <i>ortho</i> -position to phenolic OH |
| 30, 35, 40 | 2,2-, 2,4-, 4,4'-methylene carbon, respectively |
| 58-65 | Methylol carbon, <i>ortho</i> - or <i>para</i> -position to phenolic OH, ArCH_2OH |
| 68-73 | Dimethylene ether linkages; $\text{Ar}-\text{CH}_2-\text{O}-\text{CH}_2-$ |
| 95 | Hemiacetals, OCH_2O |
| 110-135 | Phenolic ring carbons other than C-OH |
| 152, 160 | Phenolic, (C-OH), aryl ether (C-O), respectively |

functionalities and substitution patterns, with phenols accounting for no more than half of the total oxygen, with carboxyls and carbonyls both being present in significant concentrations¹. Furthermore, probably as a result of the highly crosslinked state of the initial structure (both covalent methylene bridges and hydrogen-bonded crosslinks), the chars obtained from the PF resins have been found to have a much higher degree of closed porosity than both bituminous and lower-rank coals²².

X.a.n.e.s. spectroscopy has been used to ascertain the extent of the oxidation that may occur for the sulfidic moieties in the curing process. *Figure 2* indicates that, compared to the corresponding resole, the peak for the thioanisole-containing resite at ca. 2475 eV (9.5 eV wrt pyrite), which is attributable to sulfones (S(VI)), is somewhat more prominent in relation to the first-absorption sulfur peak, indicating that some oxidation has occurred during the curing process. It is estimated that the oxidized forms account for a maximum of ca. 10% of the total sulfur based on the relative molar response factors of ca. 1:3 for sulfide to sulfone peaks determined using model-compound blends. The same effect was observed for the phenyl-benzyl sulfide-containing resite. However, for the diphenyl sulfide and dibenzothiophene resins, the XANES spectra showed no evidence for any oxidation in the curing state (*Figure 2*).

^{13}C n.m.r. spectroscopy

In order to establish the most appropriate curing regime for the heteroatom-containing resins, a normal PF resin was used. *Figure 3* shows the solid-state ^{13}C n.m.r. spectra of this resin after various curing periods. There is no apparent difference in the spectra of the resin cured for 3 and 8 days at 90°C. However, raising the temperature from 90 to 130°C increased the intensity of the peaks at about 35 and 70 ppm, which were attributable to methylene and ether bridges, respectively (*Table 2*). After the resin has been cured at 200°C, the intensity of the peak at 70 ppm was vastly reduced, along with an increase in the peak at 35 ppm (*Figure 3*), indicating that ethers have largely been converted into methylene bridges. Interestingly, there appears to be a shoulder at 160 ppm which was assigned by Maciel *et al.*²³ to an aromatic carbon attached to an ether oxygen. Aryl ethers are likely to arise from condensation reactions involving two phenolic moieties. A peak at 18 ppm is evident, which has been attributed to an arylmethyl group which is *ortho* to the phenolic OH (*Table 2*).

Having established the optimum curing regime in terms of the elimination of ether bridges, the sulfur-containing

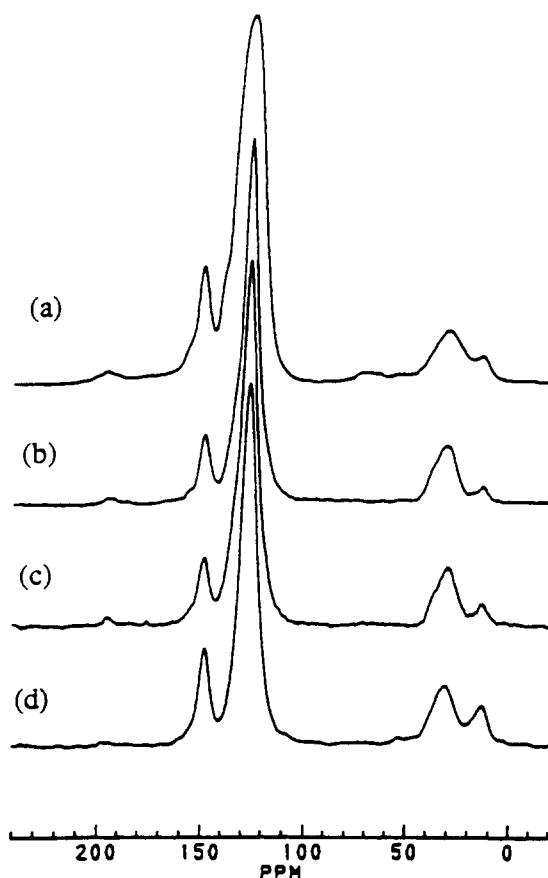


Figure 5 Solid state ^{13}C n.m.r. spectra of the fully cured (200°C) resites containing: (a) dibenzothiophene; (b) phenyl benzyl sulfide; (c) diphenyl sulfide; (d) thioanisole

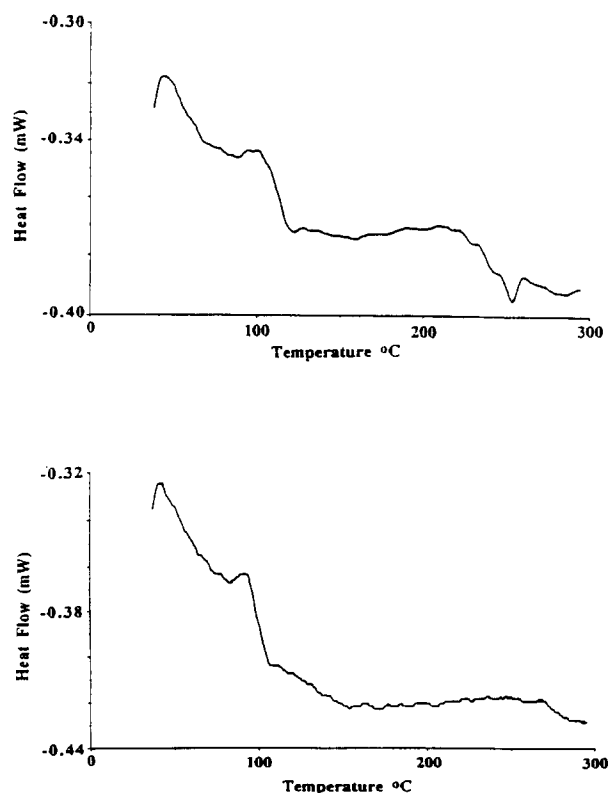


Figure 6 D.s.c. scans for the dibenzothiophene- (top) and diphenyl-sulfide (bottom)-containing resites

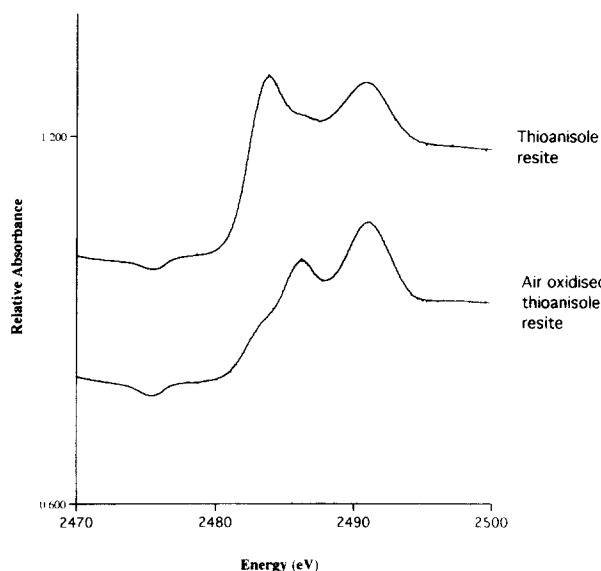


Figure 7 X.a.n.e.s. spectra of the thioanisole-containing resite before and after air oxidation

co-resoles were cured and Figures 4 and 5 show, respectively, the spectra of the resultant partially and fully cured resites (130–200°C). After curing at 130°C, the proportions of ether, ethylene bridges and methylol constituents vary considerably in the different sulfur-containing resins. However, the intensities of the peaks in the 55–80 ppm range arising from a methylol carbon directly attached to the *ortho*- or *para*-position of the phenol ring and dimethylene ether carbons are significant in relation to the principal methylene-bridge carbon peak at 38 ppm. In addition, two of the resins that were analysed displayed another prominent C–O peak close to 90 ppm, due to hemiacetal carbons (O–CH₂–O). The spectra of the fully cured resites only contain aliphatic carbon peaks centred at 18 and 38 ppm, with no discernible peaks remaining at 70 ppm from ether linkages. The 18 ppm peak is also evident in the partially-cured phenyl-benzyl-sulfide-containing resin (Figure 4). The shoulder at 160 ppm arising from aryl ethers seems to increase slightly with curing temperature, as found for the normal PF resin (Figure 3). Indeed, the spectra for the normal and sulfur-containing resites cured at 200°C are remarkably similar, with no discernible ether peaks remaining at 70 ppm.

Fourier transform infra-red (FTi.r.) spectroscopy has provided confirmatory evidence that the concentrations of ether groups in the resites were very low. All of the resins that had been partially cured at 130°C gave rise to peaks at 1050 cm⁻¹, due to the C–O bonds, but these peaks disappeared upon curing at 200°C. These results are generally consistent with the early work by Hanus and Fuchs²⁴ on the condensation reactions of *para*-substituted phenols which indicated that the methylene bridges dominate over the benzyl ether linkages at temperatures above 130–150°C. Although a number of side-reactions occur above 150°C, there was no evidence from ¹³C n.m.r. spectroscopy that quinones had been formed in significant concentrations^{25,26}. Indeed, the major side-reaction identified here for the normal and sulfur-containing resites involved the formation of an

arylmethyl moiety which gave the characteristic peak at 18 ppm in all of the spectra of the fully cured resites (Figures 3 and 5). For the dibenzothiophene- and diphenyl-sulfide-containing co-resites, its intensity is approximately one quarter of that of the methylene peak at 35 ppm. In the case of the thioanisole co-resite, the intensity of the 18 ppm peak is somewhat greater due to the contribution from S–CH₃.

Differential scanning calorimetry

Figure 7 show the results from scans of the thioanisole- and diphenyl-sulfide-containing resites. For all the PF resins, the first scan is significantly different from subsequent scans; this is primarily due to the loss of water in the temperature range from 50 to 150°C. A second-order process at ca. 110°C is then observed for all of the resins investigated and the characteristics of this process in terms of peak temperature, temperature range and the change in heat capacity, are listed in Table 3. These parameters are fairly similar for all of the samples investigated, with no structural correlation being evident between the partially and fully cured resites.

Second-order transitions have been observed at the same temperatures for both bituminous and low-rank coals, and these have been ascribed to glass-to-rubber transitions^{27,28}. Clearly, as for low-rank coals, the PF resins contain little solvent-extractable material and the phenomenon must therefore be attributed to features in the macromolecular structure. It is still uncertain as to the precise structural features which are responsible for the increase in molecular motion, although a disruption of the hydrogen-bonding network could well be a key factor in the change to a more rubbery structure in both the coals and the PF resins.

Air oxidation

XANES spectroscopy has already shown that the sulfidic moieties were not oxidized to a significant extent during the preparation of the resites (see earlier). However, aliphatic sulfides are clearly more susceptible to oxidation than aromatic (diaryl) sulfides and thiophenes and Gorbaty *et al.*¹⁹ have proposed that simple air oxidation is a straightforward procedure to resolve aliphatic and aromatic carbon-bonded sulfur in coals. To test this hypothesis, air oxidation was carried out on the sulfur-containing resites, and the extent of oxidation was then determined by XANES spectroscopy.

Table 3 Characteristics of the second-order process obtained from d.s.c.

| Sample | T_{tr}^a (°C) | ΔT_{tr}^b (°C) | ΔC_p^c (J g ⁻¹ K ⁻¹) |
|-------------|--------------------|---------------------------|--|
| Mequinenza | 109.0 | 15.1 | 0.30 |
| Co-resite E | 112.6 | 13.2 | 0.19 |
| Co-resite F | 96.4 | 10.0 | 0.19 |
| Co-resite H | 105.5 | 9.8 | 0.14 |
| Resite I | 108.8 | 13.9 | 0.33 |
| Resite J | 99.5 | 10.7 | 0.25 |
| Co-resole E | 107.3 | 13.0 | 0.43 |
| Co-resole F | 112.5 | 7.4 | 0.30 |
| Co-resole H | 106.7 | 10.9 | 0.68 |
| Resole J | 114.0 | 12.4 | 0.24 |

^a Mid-temperature point of the transition

^b Temperature range of the transition

^c Change in specific heat capacity

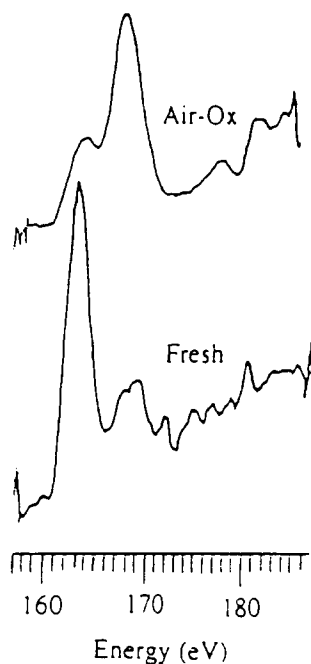


Figure 8 X.p.s. spectra of the phenyl-benzyl-sulfide-containing resite before and after air oxidation

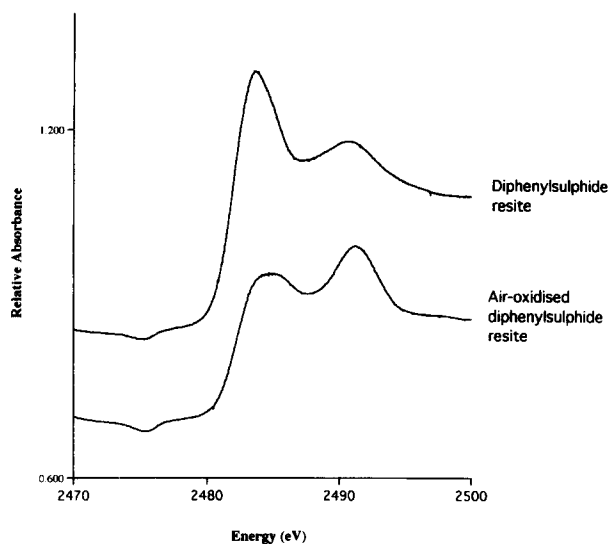


Figure 9 XANES spectra of the diphenyl-sulfide-containing resite before and after air oxidation

Figure 7 shows the XANES spectra of the fresh and 5-day air-oxidized thioanisole-containing resole, and the corresponding resite. The sulfur K-edge first-derivative absorption peaks for the initial resite and the resole are both observed at ca. 2466.30 eV (0.80 eV wrt pyrite). In the spectra of the air-oxidized samples, there are vast increases in the intensities of the absorption peaks at ca. 2470.50 and 2475 eV (5.0 and 9.50 eV wrt pyrite), due to the formation of sulfoxides and sulfones, respectively. As for the initial samples, sulfones are the dominant oxidized sulfur form which is present, and a rough estimate of the extent of oxidation in the resites has been obtained by taking the relative molar response factors of ca. 1:3 for the sulfide and sulfone peaks as described earlier for the initial resites.

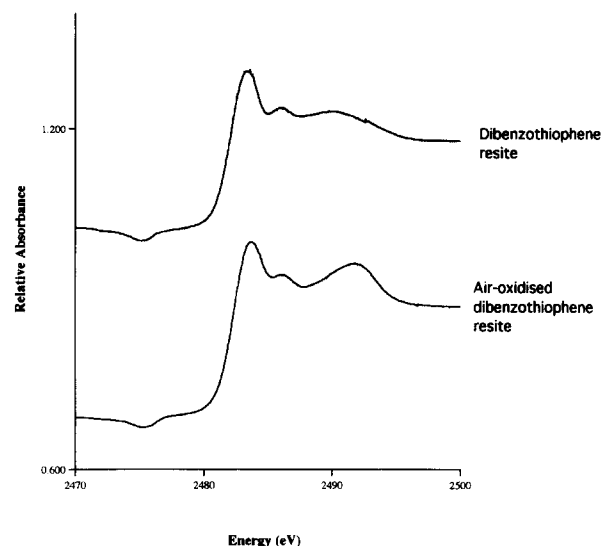


Figure 10 X.a.n.e.s. spectra of the dibenzothiophene-containing resite before and after air oxidation

The results were found to be consistent with those from the X.p.s. studies; Figure 8 shows that virtually complete oxidation has also been achieved for the phenyl-benzyl-sulfide-containing resite, with the sulfone peak (167–168 eV) dominating over that observed for the unreacted sulfide (163 eV).

On this basis, the oxidized sulfur forms are estimated to account for ca. 70% of the total sulfur for the thioanisole- and phenyl-benzyl-sulfide-containing resites. On the other hand, the XANES spectrum of air-oxidized diphenyl sulfide resite (Figure 9) displays only a relatively minor increase in absorption at ca. 2475 eV (9.50 eV wrt pyrite) from sulfone, which is estimated to account for ca. 15% of the total sulfur. At this low level of oxidation, the sulfoxide peak was not observable. As anticipated, the XANES spectra of fresh and air-oxidized dibenzothiophene resite (Figure 10) were nearly identical. Thus, virtually complete oxidation occurs only when the sulfur is bound to at least one aliphatic carbon. These results confirm that air oxidation is sufficiently selective to give a reasonable indication of the concentrations of aliphatic-bound sulfur in coals and other solid fuels.

Application of the PF resins in fuel science

Although van Krevelen was the first to use PF resins in coal science to account for the plasticity behaviour of different coals¹, the approach adopted here represents a new direction in fuel science for investigating, in a macromolecular environment, the behaviour of the individual functional groups present during the conversion processes. Clearly, since no one type of material can hope to adequately take account of all of the divergent structural features in coals, the aim has not been to synthesize a model for coal *per se*. The sulfur- and nitrogen-containing co-resites reported here are currently being used to address the following topics in fuel science:

1. In order to demonstrate unequivocally that the release of SO₂ during combustion is governed

primarily by the partition of the sulfur between volatile matter and char from the resins and not by the form of organic sulfur, temperature programmed oxidation (TPO) has been conducted on the sulfur-containing resins²⁹. The sulfur dioxide profile for the dibenzothiophene-containing resin overlaps those for the sulfidic resins investigated between 350 and 450°C, corresponding to the major release of volatile species²⁹.

2. In order to determine the characteristic reduction temperatures in temperature programmed reduction (TPR) studies for specifying the organic sulfur forms present in coals and to probe secondary reactions involving organic sulfur forms, pyrolysis tests have been conducted at both atmospheric and high pressure (15 MPa) on the sulfur-containing resins³⁰. Although the T_{MAX} values for hydrogen sulfide evolution from the primary C–S bond scissions in the resins are remarkably similar to those of their immobilized counterparts¹⁰, the extent of secondary reactions at high hydrogen pressures was found to be greater for the resins. For example, in the case of diphenyl sulfide, the continual release of H₂S at temperatures up to 600°C after the primary reduction event at 330°C indicates that much of the sulfidic sulfur is being converted into complex thiophenes. Compared to the immobilized substrates and, indeed, coals, this is considered to be attributable to the likelihood that intra-particle restrictions (much more closed porosity in chars)²² on the escape of volatiles would be considerably greater.
3. TPO has also been conducted on the quinoline and carbazole nitrogen-containing PF resites to compare the release of nitric oxide (NO) with coals. In the temperature range for char combustion, both the CO₂ and NO profiles for the resites lag considerably behind those reported previously for bituminous coals^{30,31}. It is probable that the additional non-covalent bond crosslinking and secondary reactions during pyrolysis induced by the nitrogen groups make the resultant chars even more intractable in terms of closed microporosity.

In addition, PF co-resites containing phenanthrene and naphthalene moieties have been prepared in order to ascertain the influence of the aromatic structure in coals on the release of polynuclear aromatic compounds during pyrolysis. Normal and diphenylmethane-containing resins have also been used to show the effect of OH substituents through keto–enol tautomerism on the ease of cleavage of diarylmethane linkages during coal liquefaction with hydrogen-donor solvents at temperature close to 400°C³².

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