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3,5-Dimethylphenol resole resins: their structure and mechanism of thermal decomposition leading to graphitisation

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Abstract

Novel model compounds based on 3,5-dimethylphenol were used to determine the structure of graphitisable 3,5-dimethylphenol resins. The base catalysed reaction of 3,5-dimethylphenol with formaldehyde was found to give a solid, which CP-MAS ^{13}C NMR showed to have a predominately linear structure, highly condensed but with few crosslinks. Model studies showed that the 3,5-dimethylphenol material was readily able to form xanthene type structures, unlike phenol derived material. The presence of xanthene structures can account for the unusual properties of 3,5-dimethylphenol derived resins, including oxygen sensitivity and graphitisability. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Graphitisable; 3,5-Dimethylphenol; Xanthene

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1. Introduction

Polymers are finding increasing use as binders for refractory materials [1]. Phenol-formaldehyde resins are particularly useful in this application since they can be formulated to cure (crosslink) on heating to yield materials which are chemically resistant when cured and give a high carbon yield on carbonisation. However, the mechanism of carbonisation is not well understood. In particular, there are few systematic studies investigating the interaction between resin formulation, curing and carbonisation conditions and the structure of the carbon obtained subsequently.

Carbon precursors can be broadly divided into two different classes; graphitisable and non-graphitisable. Graphitisable materials develop a graphitic structure on heating to temperatures approaching 3000°C. Phenol-formaldehyde resins are precursors for non-graphitic carbon [2]; carbon that remains highly disordered even on heat treatment to 3000°C.

Graphitisable materials pass through a liquid crystalline (LC) phase while carbonising [3], and it is probable that this ordered fluid phase is necessary for graphitisation to occur [4]. At its onset, parallel aromatic sheets start to form and grow. As the temperature is increased, this short range order extends to larger and larger scales, the distance between aromatic sheets starts to approach that of graphite and ripples in the aromatic sheets are smoothed out [5]. Phenol derived resins are not observed to pass through this LC phase [2]. The extended, rigid network formed on the curing of a phenol-formaldehyde resin presumably works against the formation of a fluid phase during carbonisation. So it is something of a puzzle that, although phenol based resins are not graphitisable, 3,5-dimethylphenol resins are reported to be graphitisable [6–8].

The processes occurring during the carbonisation of 3,5-dimethylphenol resins have been studied using novel model compounds. These 3,5-dimethylphenol resin models, combined with solid state NMR techniques [9–11], have provided new insight into the processes occurring during the carbonisation of 3,5-dimethylphenol resins.

2. Experimental

Phenol, 3,5-dimethylphenol (**1**), bis(2-hydroxyphenyl)-methane (**2**) and (2,4′-dihydroxyphenyl)methane (**3**) were obtained from Aldrich and sublimed before use.

2.1. Synthesis of model compounds from 1

3,5-Dimethylphenol (**1**, 10.1846 g) was added to distilled water (4.19 g), aqueous formaldehyde solution (37%w/w, 2.07 g) and conc. HCl (0.14 g). The mixture was stirred under mild reflux for 210 min in a 100 ml round bottom flask fitted with an air condenser. The crude product was

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extracted into ethyl acetate (3 equiv.). After removal of ethyl acetate, the unreacted **1** was removed by sublimation at 45°C and <1 Pa pressure.

The remaining material (4.01 g) was then separated into three fractions by column chromatography, eluant 1:1 hexane–ethyl acetate with 5% methanol. The first fraction (2.526 g, 24%) was the *ortho–ortho* methylene dimer (**4**), the middle fraction (1.172 g, 11%) was the *ortho–para* methylene dimer (**5**) and the final fraction (0.3 g, 3%) was the *para–para* methylene dimer (**6**).

2.1.1. Bis(2-hydroxy-4,6-dimethylphenyl)methane (4)

mp = 175°C, ^{1}H NMR ($CDCl_3$): $\delta = 2.21$ (6H), 2.31 (6H), 3.91 (2H), 6.48 (2H), 6.59 (2H), ^{13}C NMR ($CDCl_3$): $\delta = 20.28$, 20.84, 23.59, 114.62, 120.83, 124.31, 137.12, 138.1, 153.88; IR (KBr disc) ν (cm^{-1}) 1621, 1576, 1460, 1310, 837; MS: *m/z* 256 (M^+, 30%), 135 (100%), 122 (22%), 107 (13%), 91 (18%); accurate mass = 256.14625 $^{12}C = 17$, $^{1}H = 20$, $^{16}O = 2$, dev (ppm) = −0.29; Elemental analysis (%) found C 79.63, H 7.66; $C_{17}H_{20}O_2$ requires C: 79.65, H: 7.86.

2.1.2. (2-Hydroxy-4,6-dimethylphenyl-4′-hydroxy-2′,6′-dimethylphenyl)methane (5)

mp = 168–169°C, ^{1}H NMR (acetone): $\delta = 1.93$ (s, 3H), 2.14 (s, 6H), 2.16 (s, 3H), 3.94 (s, 2H), 6.40 (s, 1H), 6.48 (s, 2H), 6.54 (s, 1H); ^{13}C NMR (acetone): $\delta = 19.95$ (CH_3), 20.85 (CH_3), 20.88 (CH_3), 26.74 (CH_2), 114.24 (CH), 115.75, 115.84(CH), 123.6 (CH), 129.56, 136.24, 138.63, 138.73, 155.64, 155.97; IR (KBr disc) ν (cm^{-1}) 3440–3402 (w), 3020, 2955, 2924, 2857, 1610, 1596, 1585, 1464, 1300, 1028, 833; MS: *m/z* 256 (M^+, 45%), 135 (100), 122 (20), 107 (7); Elemental analysis (%) found C 79.70, H 7.80; $C_{17}H_{20}O_2$ requires C: 79.65, H: 7.86.

2.1.3. Bis(4-hydroxy-2,6-dimethylphenyl)methane (6)

mp = 287–289°C (m,d); ^{1}H NMR ($CDCl_3$): $\delta = 2.04$ (s, 12H), 3.85 (2H), 6.45 (4H) ^{13}C NMR (CD_3OD/d6 acetone): $\delta = 21.418$ (CH_3), 30.905 (CH_2), 116.364 (CH), 130.215, 138.950, 156.042; IR (KBr disc) ν (cm^{-1}) 3400–3000, 2962, 2941, 2925, 1612, 1485, 1302, 1140, 1028, 845; MS: *m/z* 256 (M^+, 30%), 241 (18), 207 (12), 134 (100); Elemental analysis (%); found C 79.58, H 8.01; $C_{17}H_{20}O_2$ requires C: 79.65, H: 7.86.

2.1.4. 1,3,6,8-Tetramethylxanthene (7)

Compound **1** (306.4 mg) and **4** (35.4 mg) were placed in a glass ampoule, which was then flushed with argon. The ampoule was then sealed and heated in an oven to 250°C at 100°C/h, and held at 250°C for 4 h. The recovered product mixture was then sublimed (45°C, <1 Pa), which removed **1** (282.8 mg). The remaining material was separated by rotary chromatography using chloroform as the eluant, and gave two fractions; 8.7 mg in the first fraction and 28.7 mg in the second. The rear fraction was identified as **4**. The first fraction was identified as the xanthene **7** (26%). mp = 130°C reported [12] 120–121°C ^{1}H NMR ($CDCl_3$): $\delta = 2.01$ (6H), 2.32 (6H), 5.88 (2H), 6.57 (2H), 6.73 (2H); ^{13}C NMR ($CDCl_3$): $\delta = 19.01$ (CH_3), 20.95 (CH_3), 23.36 (CH_2), 114.22 (CH), 115.49, 124.70 (CH), 136.91, 136.95, 151.20; IR (KBr disc) ν (cm^{-1}) 3019, 2964, 2922, 2859, 1623, 1585, 1447, 1381, 1138, 1062; MS: *m/z*238 (M^+, 68%) 237 (86), 223 (100), 118 (17), 104 (37).

2.2. Resin synthesis

Phenol and 3,5-dimethylphenol were used to make resins of formaldehyde to phenol (FP) mol ratio = 0.8, 1.0 and 1.2. Phenol or 3,5-dimethylphenol (10 g) was dissolved in water (5 ml) and NaOH (0.02 mol/mol phenolic). The appropriate amount of aqueous formaldehyde (37% w/w) was then added and the mixture stirred under nitrogen at mild reflux. The reaction mixture containing 3,5-dimethylphenol formed a solid after 60 min, while the reaction mixture containing phenol started to separate into two liquid layers after 150 min. The reaction was stopped at each of these times, respectively.

2.3. Carbonisation

Carbonisation was carried out under flowing argon in ceramic crucibles. Unless otherwise indicated in the text, heating was at 4°C/min to 1500°C, held at 1500°C for 2 min followed by natural cooling to room temperature.

2.4. Characterisation and analysis

Melting points are uncorrected. ^{1}H- and ^{13}C NMR for characterisation were made on a 400 MHz Varian Unity spectrometer using Pulse Field Gradient and Broad Band probes, respectively. Mass spectra were obtained from a V.G. Micromass 7070F spectrometer at 70 eV, and elemental analyses were carried out on a Carlo Erba 1108 CHNO–S analyser. Solid state NMRs were obtained using an INOVA 300 with Magic Angle Spinning (MAS) at 10 kHz in SiN spinners with Kel-F caps, pulse width = 4.1 μs, contact time = 3 ms, recycle delay = 3 s. For the CH_2 and CH edited spectra, the dipolar decoupling was interrupted for 60 μs, and for the CH_2 edited spectra the depolarisation time was 27 μs. X-ray diffraction data was obtained from a Philips PW1800 Powder diffraction system using a low background plate, silicon as an internal standard, with a Cu emission tube.

Volatile emission data was obtained at the University of Alicante, Spain. The sample was placed in a temperature controlled vertical furnace and heated to 800°C at 5°C/min. A carrier gas (He, 50 ml/min) was used to carry the volatiles evolved to a Balzers Varicube MSC 200 quadrupolar mass spectrometer for analysis.

3. Results and discussion

To our knowledge, there have been no previous reports comparing the structure of resins obtained from 3,5-dimethylphenol with those obtained from phenol under comparable reaction conditions. The results reported here were obtained from a combination of ^{13}C solution and solid state NMR. Phenol and 3,5-dimethylphenol derived model compounds were used to investigate the differences between these two materials leading up to liquid crystal (LC) formation in 3,5-dimethylphenol, which is reported in Ref. [8], to occur at 420°C.

3.1. Identifying methylene bridge orientation in 3,5-dimethylphenol resins

It is well established in the literature that the *ortho–ortho*-CH_2 methylene bridges give a ^{13}C NMR signal around 30 ppm, the *ortho–para* CH_2 gives a ^{13}C NMR signal around 35 ppm and the *para–para* CH_2 has a ^{13}C NMR signal around 40 ppm [13–17]. The structure of phenol formaldehyde resins has been studied using these assignments [18–24]. The methylene bridges between 3,5-dimethylphenol units do not fit this model. The CH_2 resonances in the model compounds were established by the DEPT experiments to be 23.59 (**4**, *ortho–ortho*), 26.74 (**5**, *ortho–para*) and 30.91 (**6**, *para–para*). These novel compounds allowed the structure of the 3,5-dimethylphenol resin to be more easily obtained than might have otherwise been possible.

3.2. 3,5-Dimethylphenol resin structure

The reaction conditions that generated a viscous liquid resole from phenol produced a hard, brittle solid from 3,5-dimethylphenol. This material was only partially soluble in 1:1 methanol–acetone, with the insoluble material forming a transparent gel. The formation of a gel rather than full solubility, plus the brittleness of the material, suggested that the solid was relatively highly condensed at this early stage of resole formation, but not heavily crosslinked; it would appear that 3,5-dimethylphenol rapidly condenses to form a predominately linear material. Much greater rate of reaction between 3,5-dimethylphenol and formaldehyde than phenol and formaldehyde has been reported previously [25], consistent with the observations made here.

Solution state ^{13}C NMR (Fig. 1) of the soluble portion showed traces of *ortho–ortho* and *ortho–para* oriented methylene bridges. Signals that could be attributed to hydroxymethyl groups were not identified in large quantities, although the solvent peaks due to methanol interfered considerably in the spectrum. The limited amount of material in the solution further supports a highly condensed structure.

^{13}C CP-MAS solid state NMR (Fig. 2) shows a small shoulder in the spectrum at 30 ppm, presumable due to *para–para* methylene bridges. The larger signal from 26 to 20 ppm is assigned to signals from the *ortho–para* and *ortho–ortho* bridges. The spectrum confirms that the material has a predominantly linear structure; highly condensed but only lightly crosslinked. Hydroxymethyl groups were only present at low levels, and heating the resin to 200°C was sufficient to completely remove these (Fig. 3). Note that the methylene peak is slightly better resolved in this spectrum than in Fig. 2.

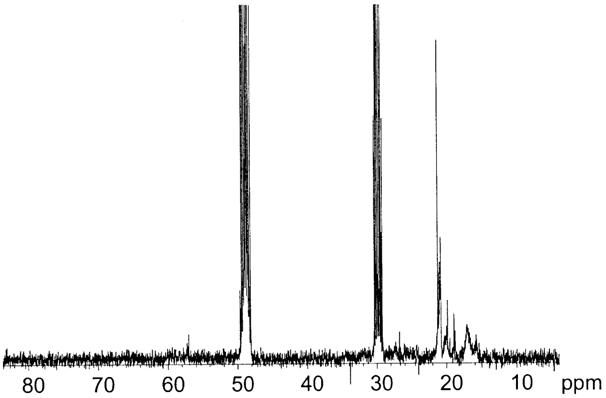

Fig. 1. ^{13}C solution state NMR of the FP = 1.2 resin obtained from 3,5-dimethylphenol (**1**). Solvent is mixed deuterated methanol (49 ppm) and acetone (30 ppm).

The structure of the resin from 3,5-dimethylphenol is quite unlike the resole resin obtained from phenol (Fig. 4) under the same conditions. Phenol based resoles do not contain the amount of methylene bridges observed with the resins obtained from **1** unless cured. Owing to the highly crosslinked material curing produces [16], the cured resole resins are tough, and insoluble in all solvents.

3.3. Model compound reactions

Since the structure of the resin from 3,5-dimethylphenol was found to be dominated by *ortho–ortho* and *ortho–para* methylene bridges, the model compounds studied for their behaviour were the *ortho–ortho* dimer **4** and the *ortho–para* dimer **5**. The phenol analogues **2** and **3** were used for comparison. 3,5-Dimethylphenol (**1**) and phenol were also

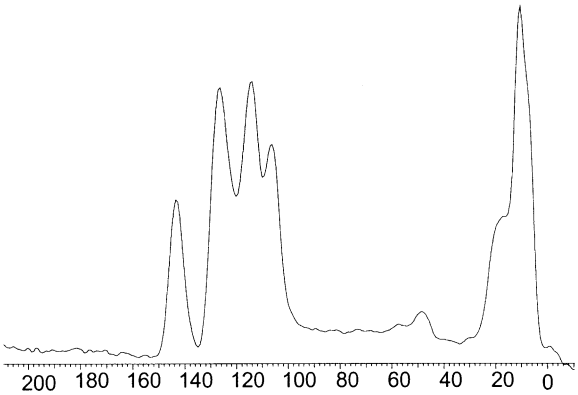

Fig. 2. CP-MAS ^{13}C spectrum of the condensed resole resin, FP = 1.2, obtained from 3,5-dimethylphenol (**1**). The small signal around 50 ppm is assigned to hydroxymethyl groups.

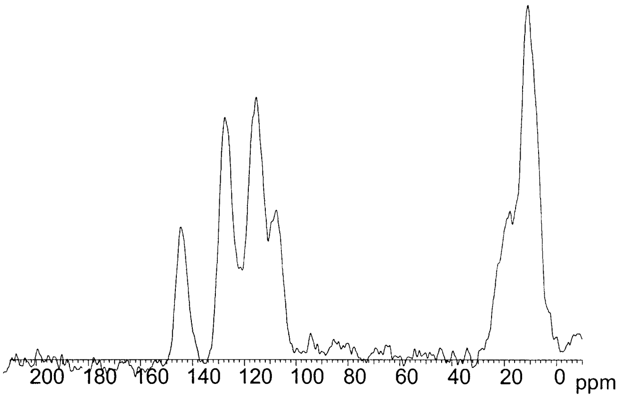

Fig. 3. The resin from Fig. 2 after heating to 200°C. The signals previously visible around 50–60 ppm (Fig. 2) are now gone.

heated to establish any differences in behaviour between the monomers and the dimers.

When the model compounds were heated (under Ar) in separate sealed glass ampoules at 100°C/h to 200°C, and held at that temperature for 8 h, 3,5-dimethylphenol, phenol, **2**, **3** and **5** were found to be returned unchanged.

When **4** was heated to 200°C for 8 h, an insoluble brown material was formed. Solid state NMR of **4** (Fig. 5) was compared with the condensed material (Fig. 6). A new peak has appeared at 30 ppm in the condensed material. This was identified by a series of pulse sequences [9–11] as being due to a CH_2 resonance.

To investigate this reaction further, **4** was heated with an excess of 3,5-dimethylphenol (**1**). Since it had been previously shown that **1** would not react with itself, it was anticipated that any reaction products would be relatively simple, soluble and characterisable.

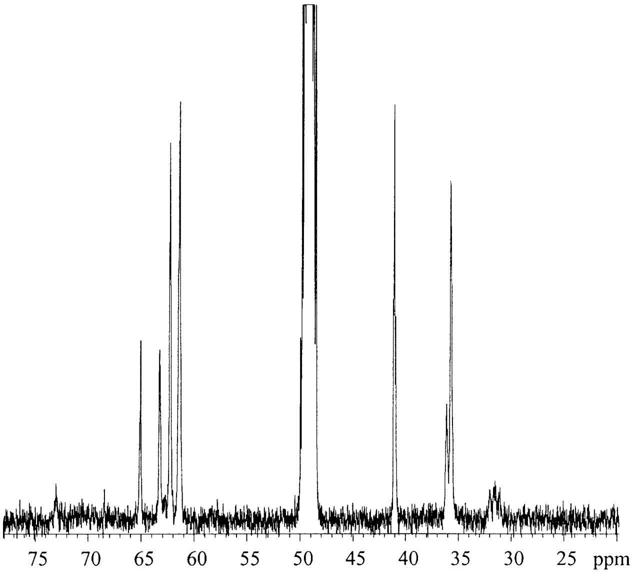

Fig. 4. ^{13}C solution state NMR of an uncured phenol resin. The peaks around 49 ppm are due to the solvent; deuterated methanol. Signals due to *ortho–ortho* (30–32 ppm), *ortho–para* (36 ppm) and *para–para* methylene bridges (41 ppm) are visible. The signals between 60 and 65 ppm are assigned to hydroxymethyl groups.

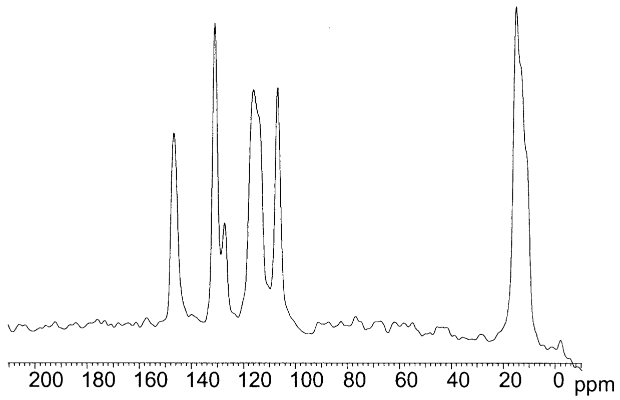

Fig. 5. ^{13}C CP-MAS spectrum of bis (2,4-dimethyl-6-hydroxyphenyl) methane (**4**).

3.4. Xanthene derivative of bis(2-hydroxy-4,6-dimethylphenyl)methane

Heating **4** in the presence of 10 equiv. of 3,5-dimethylphenol was found to give the xanthene derivative **7** (Fig. 7). The phenol dimer **2**, under the same conditions, did not form xanthene in detectable quantities. More forcing conditions are required, though yields are still very low [26].

It is probably significant that xanthene **7** had been synthesised previously using conditions that generally gave 2,2′-dihydroxydiarylmethane (i.e. methylene bridged) compounds except with, amongst others, 3,5-dimethylphenol [12]. Another important aspect of the xanthene compound is that such materials are readily oxidised to xanthen-9-ones [27]. If the formation of this compound or similar is an important intermediate in the carbonisation reactions of 3,5-dimethylphenol resins, then this would account for the reported oxygen sensitivity of such materials [5,7,28].

However, the 30 ppm peak cannot be due to **7**, since the CH_2 ^{13}C resonance of **7** is very close to that of **4**, and would not be separately resolved by solid state NMR techniques.

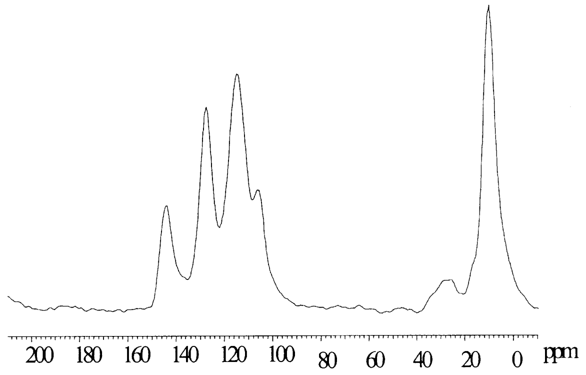

Fig. 6. ^{13}C CP-MAS spectrum of product obtained from **4** after heating at 200°C for 8 h.

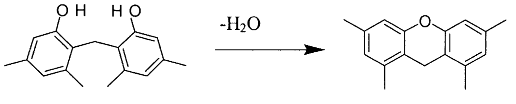

Fig. 7. The dehydration of **4** gives the xanthene **7**.

The new CH_2 resonance, plus the insoluble nature of the product, suggests that a crosslinking reaction has occurred, producing a condensed phenolic material. This is extremely unusual; since the dimer does not contain any functional groups conventionally associated with crosslinking at these temperatures. So far, it has not been possible to unambiguously identify the reaction or product responsible for the 30 ppm signal.

3.5. Carbonisation

An attempt was made to heat bis(2-hydroxy-4,6-dimethylphenyl)methane (**4**) in a furnace and collect the volatiles evolved for analysis by mass spectroscopy. However, **4** evaporated from the furnace at relatively low temperatures, and it was not possible to obtain reliable data. Instead, the FP = 1.2 resin from 3,5-dimethylphenol (**1**) was used. As noted earlier, the structure of this material and the dimer **4** is similar.

3.6. Carbonisation of resins from 3,5-dimethylphenol; volatiles evolved

Heating the 3,5-dimethylphenol resin from room temperature to 800°C showed that water was evolved with a peak at 200°C (Fig. 8) and again at 350°C. Solid state ^{13}C NMR had shown (Figs. 2 and 3) that the residual hydroxymethyl groups identified in the uncured material are readily removed by heating to 200°C. It is concluded that the water peak cannot be solely due to the condensation of these groups.

A comparison (Fig. 8) of the 3,5-dimethylphenol resin with the cured and uncured phenol formaldehyde resins shows a difference between 350 and 550°C. Water is being evolved in large quantities from the resin derived from phenol; this peak has been previously assigned to hydroxyl condensation [29]. In contrast, the generation of water by the resin obtained from 3,5-dimethylphenol (**1**) drops between 350 and 550°C. This difference in the carbonisation of the resins is further evidence for **1** having an efficient mechanism for losing hydroxyl groups. The appearance of a liquid crystal phase is reported [8] to occur at 420°C, this temperature corresponding to the region (Fig. 8) at which water being evolved from the 3,5-dimethylphenol resin is close to reaching its lowest point. The majority of the phenolic OH groups have been removed from the 3,5-dimethylphenol material. The subsequent rise in water being evolved is presumably due to the breakdown of other oxygen containing functionalities.

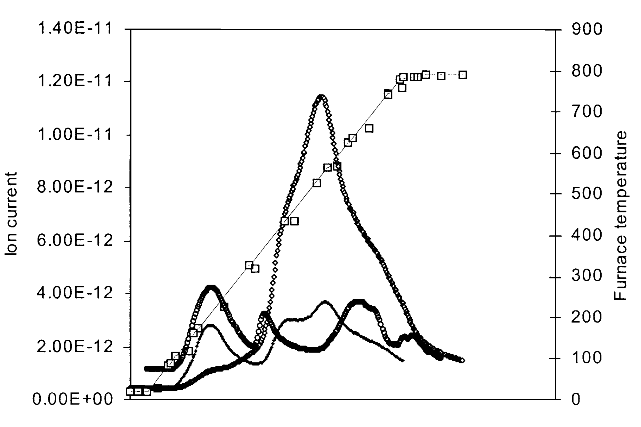

Fig. 8. The emission of water from uncured 3,5-dimethylphenol resin (open circles), uncured phenol resin (small squares) and cured phenol resin (open diamonds). The open squares show temperature readings (right side scale, °C) taken from a thermocouple inside the reaction vessel.

The sharp peak in water evolution at 350°C in the resin from 3,5-dimethylphenol (**1**) coincides with the appearance of the 30 ppm CH_2 peak in the solid state NMR spectrum of the resin from **1** (Fig. 9), allowing for the faster heating rate during the evolution of volatiles tending to offset the observed behaviour to higher temperatures.

The appearance of a peak at 30 ppm after heating (Fig. 9) is very similar behaviour to that observed for bis(2-hydroxy-4,6-dimethylphenyl)methane (Fig. 6) after heating to 200°C. The same experiment showed that the *ortho–para* dimer **5** was much less reactive than **4**. This suggests that the early carbonisation behaviour of 3,5-dimethylphenol resins is being dominated by its *ortho–ortho* oriented sections.

3.7. X-ray diffraction (XRD)

Resole resins obtained from phenol are not observed to be graphitisable, while resins from 3,5-dimethylphenol are observed to be graphitisable. Carbons obtained from these materials already have a clear difference in their internal structure following carbonisation to 1500°C, when examined by XRD (Fig. 10). It seemed possible that altering the amount of crosslinking in the resin precursor might have an effect on its graphitisation. However, when resins

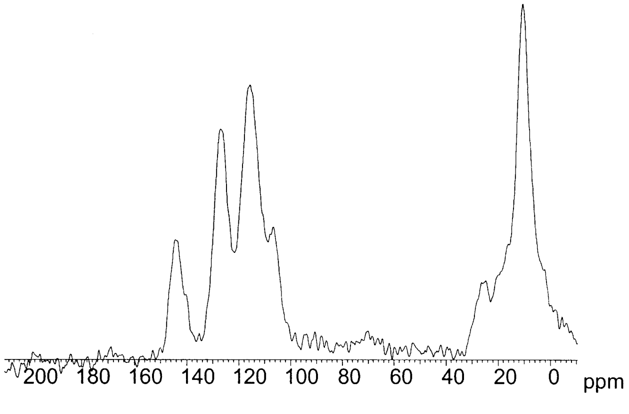

Fig. 9. After 4 h at 300°C, a CH_2 peak at 30 ppm is visible in the FP = 1.2 resole resin obtained from 3,5-dimethylphenol.

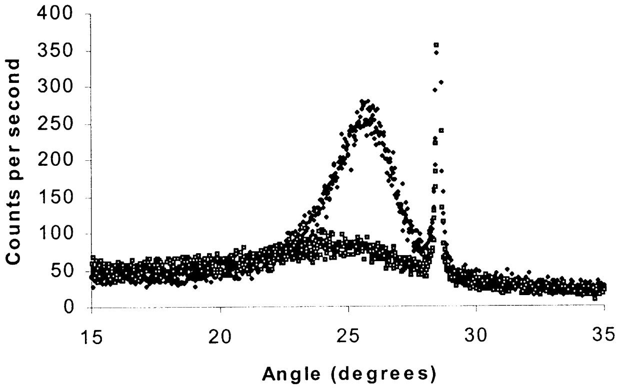

Fig. 10. XRD pattern of resins from 3,5-dimethylphenol (**1**) (upper trace) and phenol (lower trace) following carbonisation to 1500°C. The peak at 28° is due to silicon metal, used as an internal standard.

from phenol and 3,5-dimethylphenol with FP ratios of 0.8, 1.0 and 1.2 were carbonised to 1500°C, their respective XRD patterns did not alter.

3.8. Xanthene and the liquid crystal phase

It is known that graphitisation is associated with the formation of a liquid crystalline phase during carbonisation. A liquid crystal, by combining the properties of order and fluidity, allows large scale rearrangement that favours the formation of graphite. Xanthene formation in the carbonising 3,5-dimethylphenol resin is probably important to the formation of this LC phase, and hence the graphitisation process, for a number of reasons.

Its formation removes hydroxyl groups from the carbonising resin at a relatively low temperature without increasing the amount of crosslinking in the resin, unlike the reactions that have been reported to occur in phenol. It is reasonable to conclude that highly crosslinked materials will find it difficult to form a LC phase, and this is supported by findings from other systems [30].

The formation of the xanthene group would reduce the amount of hydrogen bonding in the resin. Intermolecular hydrogen bonds contribute significantly to the viscosity of liquids in which they are present. Removing them, by removing phenolic hydroxyls, should help the formation of the liquid crystal phase.

The xanthene group will also produce flat ribbons of mixed aromatic and non-aromatic rings. Such structures will find it easier to arrange and begin to form the ordered layers of carbon that is an important intermediate step in the formation of graphite [31]. The xanthene group has been shown by ab initio calculation to prefer a flat conformation [32].

The formation of the xanthene group, in turn, would not be possible unless the resin obtained from 3,5-dimethylphenol was linked by a majority of *ortho–ortho* bonds. This suggests that phenol precursors with the *para* site blocked, which are forced to link *ortho–ortho*, might have interesting carbonisation properties. Our work in this area will appear in a subsequent publication.

Why the methyl groups have such a large influence on the chemistry of 3,5-dimethylphenol, including its much higher reactivity towards formaldehyde and its graphitisability, is difficult to understand. A comparison [6] of 3,5-dimethylphenol with 3-methylphenol and phenol found that 3-methylphenol is intermediate in its carbonisation behaviour between 3,5-dimethylphenol and phenol. It seems unlikely that the methyl groups would have a significant inductive effect on the aromatic ring, especially by comparison with the effect of the phenolic OH. Further investigation into why the methyl groups influence the carbonisation behaviour to such an extent is required.

4. Conclusions

Three novel model compounds were synthesised from 3,5-dimethylphenol (**1**). These were used to show that a resole type resin formed from 3,5-dimethylphenol had a highly condensed, predominately linear structure, linked by *ortho–ortho* and *ortho–para* methylene bridges. This is quite unlike the behaviour of phenol derived resole resins.

It was found that bis(2-hydroxy-4,6-dimethylphenyl)-methane (**4**) would form 1,3,6,8-tetramethylxanthene on heating in dilute solution, and would crosslink if heated by itself. ^{13}C CP-MAS solid state NMR showed that the crosslinked material had a new carbon resonance at 30 ppm, and this was shown to be due to a CH_2 group. Neither of these reactions occurred when bis(2-hydroxyphenyl)methane (**2**) was used. Solid state NMR was used to show that the resole resin from 3,5-dimethylphenol also had a CH_2 peak at 30 ppm when heated to 300°C.

It was concluded that the formation of a xanthene is a key step in the graphitisation of 3,5-dimethylphenol resins. Xanthene formation is an efficient way of removing heteroatoms. This step would not be possible if the 3,5-dimethylphenol resin were not significantly *ortho–ortho* linked. However, the *ortho–ortho* methylene orientation, though essential, is not sufficient. The methyl groups in the three and five positions also influence the xanthene formation process, as this reaction was not detectable in bis(2-hydroxyphenyl)methane (**2**) under comparable conditions.

The formation of the xanthene also offers an explanation for the reports [5,7,28] that contact with air must be avoided during the resin's synthesis and curing, if a graphitisable material is to be obtained. Oxidation sensitivity is entirely consistent with a xanthene compound being the key intermediate, since they can be readily oxidised to form a xanthen-9-one [27].

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