

The effect of formaldehyde to phenol ratio on the curing and carbonisation behaviour of resole resins

K. Lenghaus, G.G. Qiao, D.H. Solomon*

Polymer Science Group, Department of Chemical Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia

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Abstract

Two resole-type phenol formaldehyde resins were synthesised with a formaldehyde to phenol (FP) molar ratio of 1.2 and 1.8 and their structure on curing examined by ^{13}C CP-MAS solid state NMR. The FP = 1.8 material was considerably more complex than the FP = 1.2 material. This has been interpreted as due to the formation and subsequent cleaving of ethers in the FP = 1.8 system. The structural changes in each resole after heating were observed by ^{13}C CP-MAS NMR up to 500°C, and their surface areas after carbonisation at 1000°C were measured using N_2 and CO_2 gas adsorption. The FP = 1.2 material was found to possess narrower micropores than the FP = 1.8 material. These results are significant for those industries where the high-temperature behaviour of phenol formaldehyde materials is important. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Phenol-formaldehyde; Carbonisation; Resole

1. Introduction

Phenol formaldehyde resins are used across a range of industries, their many different applications reflecting the way in which this superficially simple system can be adapted to meet different requirements. The increasing use of phenol formaldehyde resins as binders in refractory systems [1,2] is, in part, a response to health and safety concerns with pitch-based binders, and the recognition that the flow and adhesive properties of phenol formaldehyde resins, and their behaviour during curing and carbonisation, make them well suited to this application.

Phenol formaldehyde resins are formed by either the acid- or base-catalysed addition of formaldehyde to phenol [3]. A resin generated under base-catalysed conditions, and with a molar ratio of formaldehyde to phenol greater than one, is termed a resole. This material will harden on heating, without the addition of a crosslinking agent, to generate a hard, insoluble polymer, though under some circumstances additional crosslinking agents may be added.

Many different structures have been identified within cured resole resins [3]. The most common crosslink is the methylene bridge, though ethers can also be present

in significant amounts [3,4]. Phenoxy bridges [5], and carbonyl and methyl groups [5–8], have also been identified within the cured structure.

Model studies have shown that the ether can react with unsubstituted phenol to generate a phenoxy bridge [9]. Reaction of the ether bridges has also been suggested as the source of the observed carbonyl and methyl functionalities observed in a cured resole [5,7,8]. An alternative proposal [6] involves the oxidation of hydroxymethyl groups, and scission of methylene bridges, respectively. Carbonyl and methyl groups can be regarded as broken crosslinks, and may well affect the final properties of the carbonised resin by reducing the degree of crosslinking and by decomposing more readily at high temperatures. If the structure of the cured resin is to be controlled, it is important to understand the processes which result in these types of group and their subsequent behaviour at higher temperatures. However, there have previously been no reports attempting to fully relate the initial resin formulation to its behaviour during curing and carbonisation.

This paper compares the curing and carbonisation behaviour of two resole-type resins with a molar formaldehyde to phenol (FP) ratio of 1.2 and 1.8. It will focus on the formation of carbonyl and methyl groups during curing, and the differences between the two materials up to carbonisation at 1000°C.

* Corresponding author. Tel.: +61-3-9344-8200; fax: +61-3-9344-4153.
E-mail address: d.solomon@chemeng.unimelb.edu.au (D.H. Solomon).

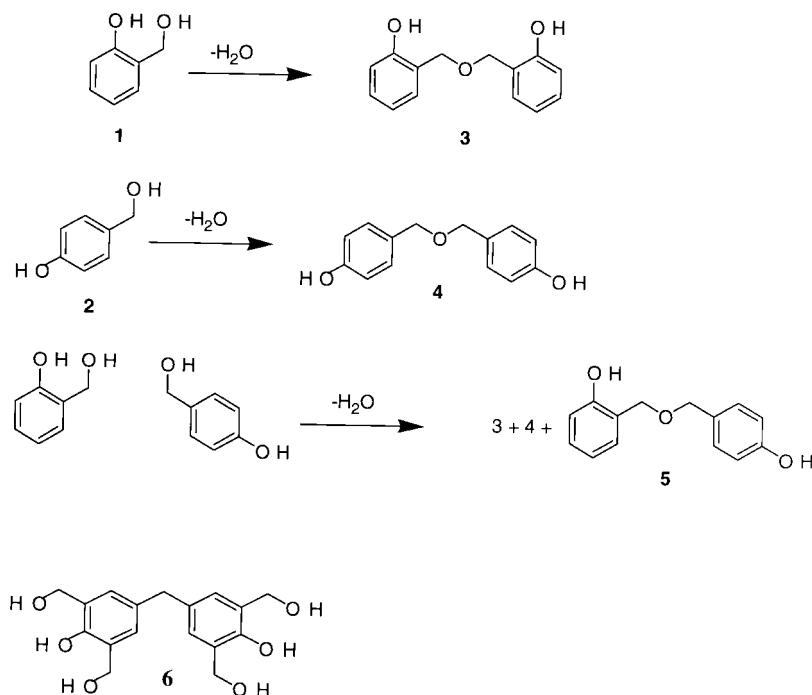


Fig. 1. Reaction scheme (unbalanced) for the generation of high ether material. The crosslinking agent bis(3,5-dihydroxymethyl-4-hydroxyphenyl)methane (**6**, or referred to in text as THBF) is also shown.

2. Experimental

Phenol, 2-hydroxy-benzylalcohol (**1**), 4-hydroxy-benzylalcohol (**2**) and bis(4-hydroxyphenyl)methane (bisphenol-F) were obtained from Aldrich and sublimed before use.

2.1. Synthesis and curing

2.1.1. Bis(3,5-dihydroxymethyl-4-hydroxyphenyl)methane (**6**)

Bis(4-hydroxyphenyl)methane (bisphenol-F, 21.84 g), aqueous formaldehyde (37%, 70.83 g), NaOH (4.34 g) and water (75 ml) were stirred at room temperature for 24 h. The mixture was then extracted with ethyl acetate and the solvent removed under vacuum. Column chromatography (silica, ethyl acetate) followed by recrystallisation of the rear component (isopropyl alcohol/hexane) gave 7.11 g (20%) of bis(3,5-dihydroxymethyl-4-hydroxyphenyl)methane (Fig. 1, **6**) (tetrahydroxymethyl bisphenol F, THBF) mp = 153–155°C ([10], 144°C) ¹H NMR (CD₃OD) δ = 3.78 (2H), 4.65 (8H), 6.97 (4H) ¹³C NMR (CD₃OD) δ = 41.63, 62.24, 128.29, 128.70, 134.35, 153.03 IR ν (cm⁻¹) = 3294, 2889, 1616, 1489, 1215, 1070, 987 MS *m/z* 320 (M⁺, 4%), 302 (20%), 284 (11%), 254 (20%), 237 (35%), 209 (28%), 181 (22%), 165 (48%), 84 (100%) elemental requires C:63.74, H: 6.29, found C: 63.69, H: 6.52

2.1.2. Phenol resins, FP = 1.2 and 1.8

Phenol was stirred with NaOH (0.02 molar equivalents),

formaldehyde (37% w/w aqueous solution) and water for 6 h at 110°C. The resin was then extracted with ethyl acetate, dried and cured. The purpose of the extraction step was to remove NaOH, and avoid any effect on curing [3] and carbonisation [11] it might have. Curing up to 205°C was by a previously described temperature cycle [12].

2.1.3. Model resins; ether bridges oriented *ortho-ortho*, *ortho-para* and *para-para*

2-hydroxy-benzylalcohol (**1**), 4-hydroxy-benzylalcohol (**2**) and a 1:1 mixture of each were heated at 120°C for 4 h. This was designed to give mixtures (Fig. 1) with a high content of ether bridges oriented *ortho-ortho* (**3**), *para-para* (**4**) and a mixture of all three possible orientations (**3**, **4**, **5**), and this was confirmed by solution ¹³C NMR.

Each of the mixtures was then divided into two and hardened in one of two different ways. Mole equivalents were calculated based on the molecular weight of the simple ether dimer; 230 g/mol.

2.1.4. Hardening method 1

Conc. HCl (36%, 0.1 g) was added to aqueous formaldehyde (37%, 10.01 g). Addition of the acidified aqueous formaldehyde (37%, 0.8 mol equiv.) to the mixtures followed by stirring and heating (90°C for 30 min), gave a hardened material whose ¹³C CP-MAS showed to contain hemiformal groups in addition to ethers, allowing investigation into what role, if any, hemiformals might have on the post-curing structure.

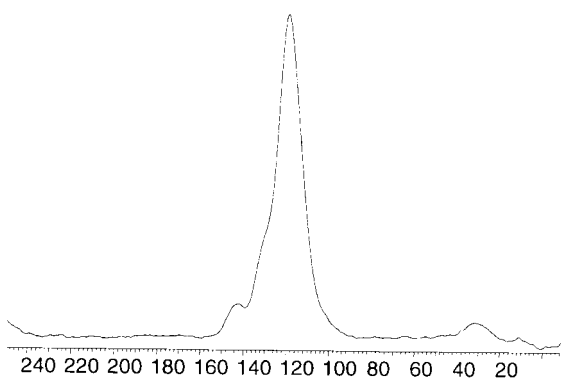
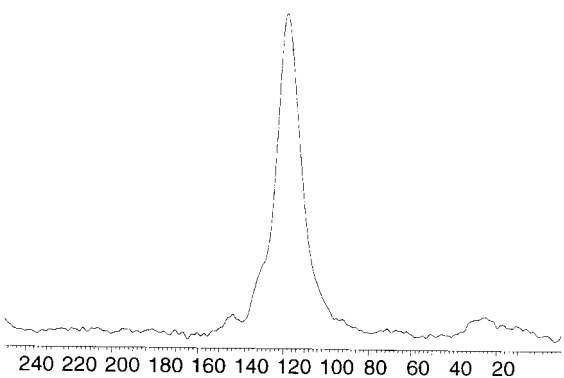
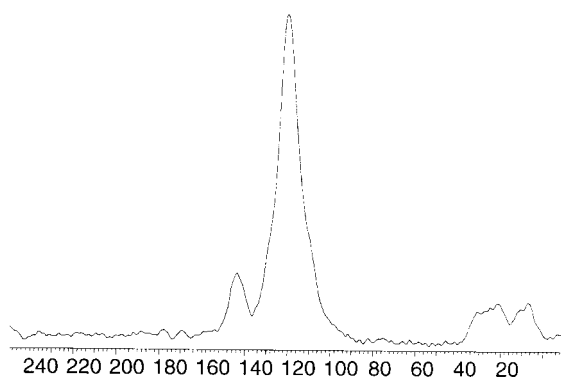
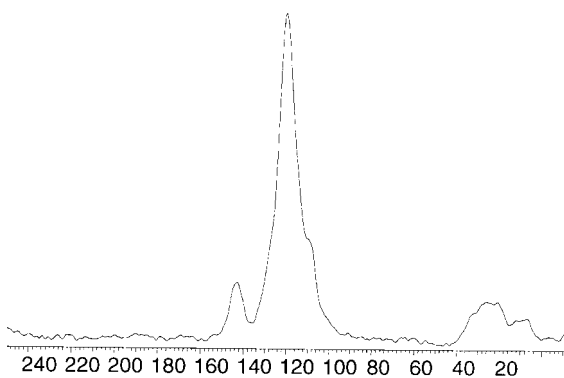
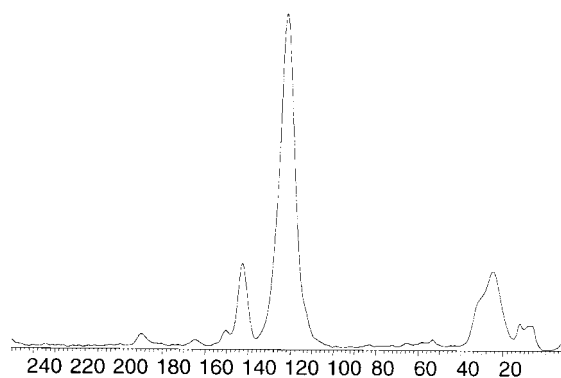
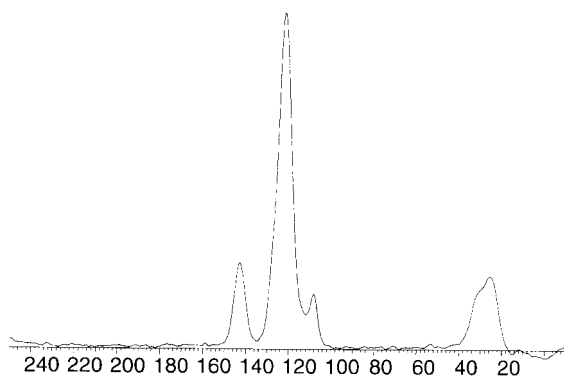


Fig. 2. FP = 1.2, from top to bottom: (1) after thermal curing; (2) after 400°C; and (3) after 500°C.

Fig. 3. FP = 1.8 from top to bottom: (1) after curing; (2) after 400°C; and (3) after 500°C.

2.1.5. Hardening method 2

THBF (0.2 mol equiv.) was mixed with each of the three ether mixtures (approx. 400 mg of each). Aqueous HCl solution (0.018%, 1.0 g) was then added, followed by stirring and heating at 90°C until hard. This gave a cross-linked material without hemiformal groups.

The goal in both cases was a crosslinked resin with an equivalent FP of 1.8.

The model resin systems were then ground and small samples of each (≈ 100 mg) were placed in a preheated oven. The temperatures used are given in the results. After

4 h the samples were removed and a CP-MAS ^{13}C solid state NMR spectrum was obtained.

2.2. Carbonisation conditions

Ground samples of the FP = 1.2 and 1.8 resins were heated at 50°C/h to 300, 400 and 500°C under an inert (Ar) atmosphere, and held for 4 h at the target temperature. A CP-MAS ^{13}C solid state NMR spectrum was then taken. Samples for surface area analysis were prepared by heating

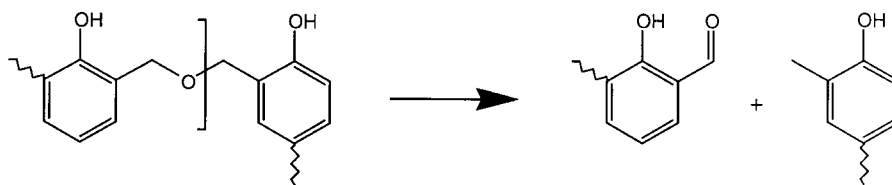


Fig. 4. The scission of an ether bridge to simultaneously generate an aldehyde and a methyl group [5,7,8].

unground cured resin to 1000°C at 50°C/h, with no hold time at 1000°C.

2.3. Analysis

Solution state ^{13}C NMR was run on a Varian Unity 400 MHz machine. Solid state NMRs were obtained using an INOVA 300 with 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 . All NMR spectra are reported on ppm scale. Nitrogen and carbon dioxide adsorption isotherms were run on a Micromeritics ASAP 2010.

3. Results and discussion

3.1. Curing

There are significant differences between the ^{13}C CP-MAS spectra of the cured resins with a formaldehyde/

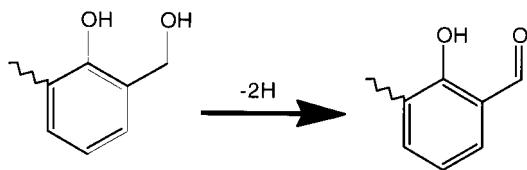


Fig. 5. The oxidation of a hydroxymethyl group to an aldehyde [6].

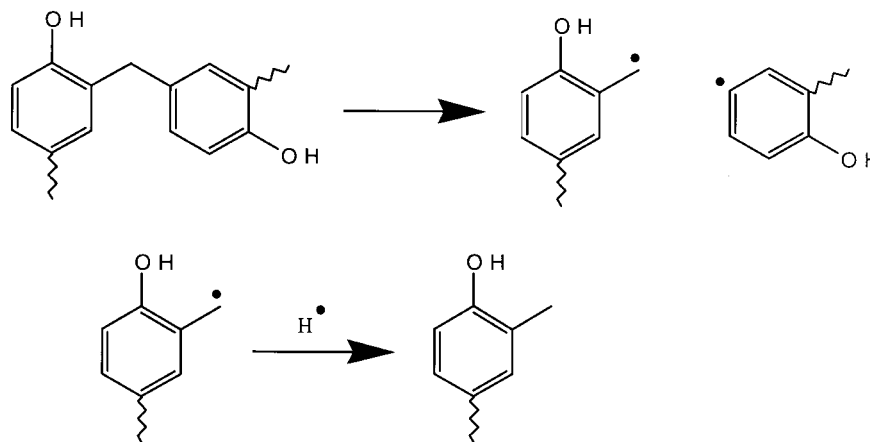


Fig. 6. The breakup of a methylene bridge leads to the generation of a methyl group [6].

phenol (FP) ratio of 1.2 (Fig. 2) and 1.8 (Fig. 3). There is no peak at 110 ppm in the FP = 1.8 resin, indicating complete substitution at the *ortho* position [13,14], unlike in the FP = 1.2 resin. The cured FP = 1.8 resin contains methyl (10 ppm), phenoxy (150 ppm) and carbonyl groups (190 ppm) [5,6] while the cured FP = 1.2 resin does not. Interrupted decoupling [15,16] identifies the carbonyl in this material as an aldehyde.

There are two mechanisms to be found in the literature to explain the observed carbonyl and methyl groups. One uses fragmentation of an ether bridge [5,7,8] to create an oxidised product and a reduced product; that is, the simultaneous generation of carbonyl and methyl groups (Fig. 4). The second mechanism [6] has the carbonyl generated by oxidation of a hydroxymethyl (Fig. 5), and the methyl created by scission of a methylene bridge (Fig. 6).

The differences between FP = 1.2 and 1.8 materials do not support the latter interpretation at typical curing temperatures (up to 200°C). If the carbonyl and methyl groups were derived from hydroxymethyl and methylene bridges, respectively, then the carbonyl and methyl intensities should change in proportion with the FP ratio. But they are undetectable in the FP = 1.2 material, while they are readily apparent in the FP = 1.8 material. It is also unlikely that hydroxymethyl groups will survive to sufficiently high temperatures to be oxidised. These are quite labile groups, readily generating quinone methides which subsequently react to give ether or methylene bridges [9]. Clearly this mechanism cannot be the primary source of carbonyl and methyl groups.

To test the mechanism based on ether fragmentation, the materials with ether bridges in various orientations, *ortho-ortho* (3), *para-para* (4) and *ortho-para* (5), were heated to different temperatures. The CP-MAS spectra obtained from these materials showed that the carbonyl group is detectable after 4 h at 160°C and always appears first, and this observation is clearly not consistent with the previously proposed ether fragmentation mechanism, which requires simultaneous formation of the carbonyl and methyl functional groups. The CP-MAS spectra of the material containing all three possible ether orientations and crosslinked with THBF is an example. At the hardened stage and after heating at 160°C for 4 h (Fig. 7) the formation of carbonyl groups (190 ppm) without the corresponding generation of methyl groups can be seen.

The different behaviour of the FP = 1.2 and 1.8 material shows that the formation of carbonyl and methyl groups is in some way dependent on the formaldehyde content of the starting resin. Hemiformal groups have been found in resol resins, and it was considered possible that they might be contributing to the formation of either or both the methyl and carbonyl groups, since the hemiformal content would be expected to increase with a higher initial formaldehyde content. However, the materials with large quantities of hemiformal groups were not observed to produce either methyl or carbonyl groups at a lower temperature than the THBF-cured materials.

Other points of difference between the FP = 1.2 and 1.8 resins were considered. Phenoxy bridges, shown to be a product of ether exchange at a bridging ether [9], are evident in the FP = 1.8 resin, and not in the 1.2 resin, and it was concluded that the FP = 1.8 material contained significantly more ether bridges than the FP = 1.2 material at some stage of the curing process. Hydroxymethyl phenols react faster with formaldehyde than unsubstituted phenols [17–23], and hence hydroxymethyl groups are not distributed evenly on all phenol rings in the resin; instead, a mixture of heavily hydroxymethyl substituted and much less substituted phenols is created. The formation of dibenzyl ether bridges requires hydroxymethyl groups on separate phenols. The distribution of hydroxymethyl groups makes this situation less likely in the FP = 1.2 resin, compared with the FP = 1.8 resin, than a simple consideration of the formaldehyde to phenol ratio would indicate.

The ether bridge can split to give a quinone methide and a hydroxymethyl phenol; for instance, heating bis-(2-hydroxy-3,5-dimethylbenzyl)ether [9] at 150°C under N₂ for 28 h will allow the equivalent quinone methide trimer [24] to be isolated in 14% yield. So, at a late stage in the curing process, at a relatively high temperature, hydroxymethyl groups can reappear from ether bridges. Assuming that oxidation of hydroxymethyl groups is faster at these high temperatures than generation of quinone methides, this would result in the carbonyl groups observed.

The quinone methide can react at a free aromatic site to give a methylene bridge, or potentially with another quinone

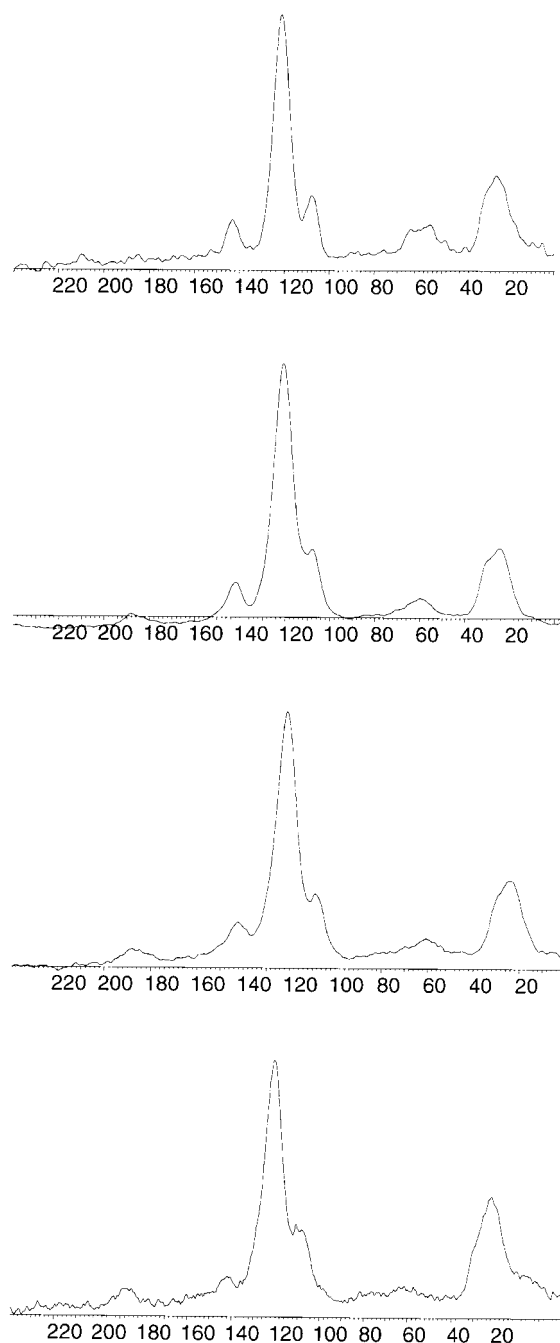


Fig. 7. The mixed ether material, crosslinked with THBF and acid hardened. From top to bottom: (1) after hardening; (2) after 4 h at 160°C; (3) after 4 h at 180°C; and (4) after 4 h at 200°C.

methide to give Diels–Alder products [9,24]. The Diels–Alder products also contain carbonyl groups. The quinone methide tetramer [24], which has two different carbonyl centres, was used to show that interrupted decoupling will correctly identify the quaternary carbon centres.

If it is possible for quinone methides to be reduced to methyl phenols, we would predict this to be more strongly favoured, from a kinetic perspective, when the quinone methide is generated in a highly crosslinked material with

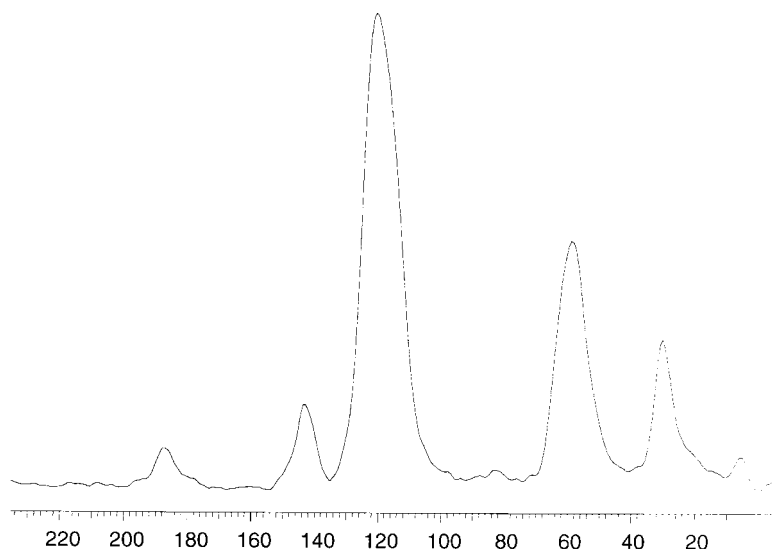


Fig. 8. THBF after 180°C, 4 h. The peak at 5 ppm is due to the formation of methyl groups in this material.

few or no free aromatic sites available for reaction; that is, when the quinone methide is unable to gain access to all but the nearest phenol rings and the reactive sites on those rings are already occupied. This extreme case can be tested by hardening THBF itself. As predicted, methyl groups (5 ppm, Fig. 8) are observable after 4 h at 180°C in this material, but still unobservable in the formaldehyde- and THBF-hardened resins at these conditions, and higher temperatures are required before methyl groups are observed (Fig. 7). The overall proposed mechanism is summarised in Fig. 9.

3.2. Early carbonisation: up to 500°C

Using CP-MAS ^{13}C NMR, the carbonyl groups in the FP = 1.8 material are seen to have disappeared following heating to 400°C (Fig. 3), and there is an increase in the intensity of the methyl carbons. Methyl carbons have appeared in the FP = 1.2 (Fig. 2) material, and it is concluded that between 300 and 400°C there is the onset of significant methylene bridge breakdown, resulting in the methyl groups [25]. The quantity of methyl groups in

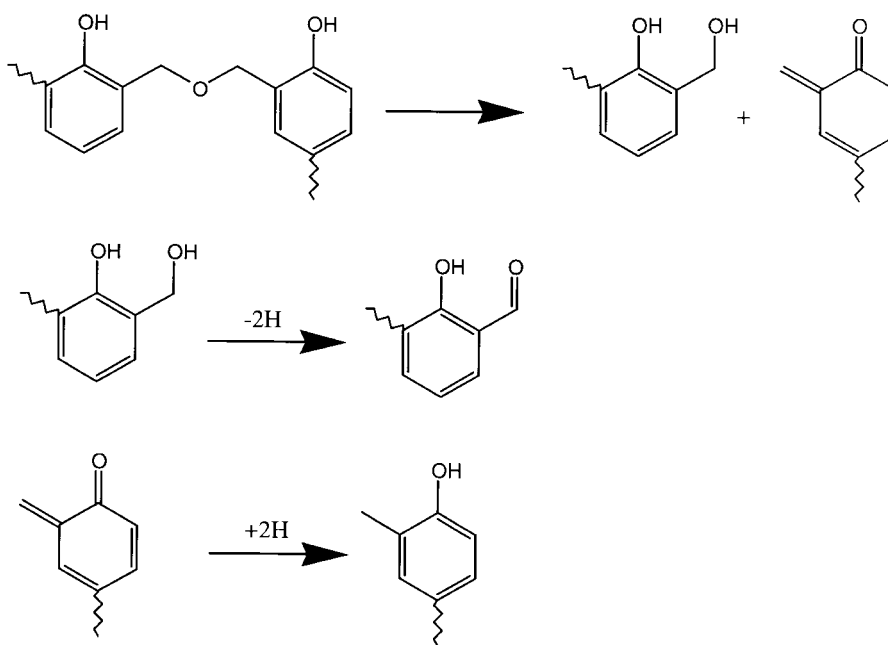


Fig. 9. Proposed mechanism of ether scission, generating a hydroxymethyl phenol and quinone methide, which subsequently react to give a carbonyl and methyl group, respectively.

Table 1
Surface areas (m²/g) and weight loss (%) following carbonisation to 1000°C

Resin	Weight loss (%)	Surface area N ₂	D–R surface area CO ₂	D–A surface area; exponent
FP = 1.2	50	52.5	371	355; 2.21
FP = 1.8	50	107	395	402; 2.02

the FP = 1.2 material is less than in the FP = 1.8 material after heating to 400°C. Following heating to 500°C the two materials are very similar in appearance by CP-MAS ¹³C NMR. There is almost complete loss of phenolic OH, shown by the disappearance of the peak at 150 ppm, and very little aliphatic carbon of any type remaining (Figs. 2 and 3).

The transition from 200 to 500°C showed that the structural differences detected by CP-MAS between the FP = 1.2 and 1.8 material persisted to 400°C, but rapidly disappeared at higher temperatures. In applications where 400°C represents the operating temperature limit this may be important, and should be considered when selecting a resin formulation.

3.3. Carbonisation to 1000°C

Resole resins are typically formulated with FP = 1.5–2.0 [3]. The thermal stability of phenol formaldehyde materials is related to their highly crosslinked structure, it would be reasonable to assume that higher crosslinking, and hence higher initial formaldehyde content in the resin formulation, would be advantageous during carbonisation. The results here suggest that this may not necessarily be the case (Table 1).

The hardened resins from FP = 1.2 and 1.8 were carbonised to 1000°C under Ar, and then analysed for surface area with N₂ and CO₂ adsorption. The N₂ adsorption data was fitted to the Langmuir isotherm, and the CO₂ data was fitted using the Dubinin–Radushkevich (D–R) and the Dubinin–Astakhov (D–A) equations [26].

The combination of N₂ and CO₂ isotherms has been successfully applied previously to obtain information regarding the micropore width of a range of carbons [27–29]. The accepted interpretation is that an N₂ surface area lower than that obtained with CO₂ indicates that the carbon's microporous structure is extremely narrow [29]. At 77 K, narrow micropores hinder the diffusion of N₂ into the carbon, and the isotherm obtained does not truly represent an equilibrium isotherm; such an isotherm may take many weeks to establish [26], and it is not viable for these to be routinely obtained under the conditions normally prevailing in working laboratories. The higher (273 K) temperature of CO₂ adsorption allows for more rapid diffusion into the micropore system, and hence a higher surface area than that obtained with N₂ under conditions of strongly hindered diffusion.

Based on this interpretation, the overall microporosity of the FP = 1.2 and 1.8 appears to be similar; the CO₂ surface areas are of similar magnitude. However, the micropore size

distribution is different. The micropores are narrower in the FP = 1.2 material than in the FP = 1.8 carbon. This conclusion is supported by the different surface areas obtained between N₂ and CO₂ as well as the larger exponent obtained from the D–A equation. The exponent in the D–A equation is inversely related to the standard deviation of the micropore size distribution [30–32]. The larger the exponent gets, the smaller the standard deviation and the narrower the micropore size distribution. The higher exponent in the FP = 1.2 carbon is indicative of a narrower microporosity in this material than in FP = 1.8.

These results were obtained without any attempt to optimise the carbonisation process. Although there are other reasons for having a higher FP ratio, principally to reduce the amount of free phenol present within the resin prior to curing, these results suggest that it would be worthwhile to investigate the effect of crosslinking on the carbonisation process further.

4. Conclusions

A cured phenol formaldehyde resin with an FP ratio of 1.2 was found to be much simpler in structure than a cured resin with FP = 1.8, with no carbonyl, phenoxy or methyl groups observed by ¹³C CP-MAS NMR. This has been interpreted as due to larger quantities of ether bridges present in the FP = 1.8 material than in FP = 1.2. It was shown that neither of the mechanisms previously described in the literature can adequately explain the formation of the methyl and carbonyl groups, and a different model of ether breakdown was proposed to explain the observations.

It was considered possible that the differences between the cured resins might have an effect on their carbonisation behaviour. Analysis by ¹³C CP-MAS NMR showed that differences between the two persisted after heating to 400°C, when methylene bridge degradation became significant. There were no substantial differences observable by ¹³C CP-MAS NMR after heating to 500°C for 4 h.

Differences in surface area and micropore structure were observed between the two materials after carbonisation to 1000°C, and it was concluded that the FP = 1.2 material had a narrower micropore structure and size distribution than the FP = 1.8 material.

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