Carbon composites with novolac/furfuryl alcohol resins as binders: 2. carbonization chemistry and morphologies of the composites after baking

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ABSTRACT: Different carbon composites with novolac and furfuryl alcohol resins in conjunction with a crosslinker hexamine (HMTA) as a binder were baked up to 1000 °C. The volatiles released during the process (mainly at 300 – 700 °C) were furfuryl compounds, phenol-benzene species, methane and ethane and other small molecule species such as moisture, CO₂, CO and ammonia. Carbon black additives reduced the amount of furfuryl and phenolic species released during the baking, and thus enhanced the carbon yield for the composites and decreased the level of dimensional shrinkage of the final amorphous carbon. In addition, carbon black shifted carbonization reactions of the binder to lower temperatures and resulted in a broad distribution of chemical environment and structures of the polymer segments of the binder due to strong interactions between the resin segments and the carbon black particles. On the other hand, mesophase took part in the carbonization with the resin binder. The porosity and therefore the level of dimensional expansion of the obtained amorphous carbon were reduced as compared to mesophase-only system.

Key words: carbon composites, carbonization chemistry, novolac resins, furfuryl alcohol resins, carbon black, mesophase
1. **INTRODUCTION**

Phenolic and furfuryl alcohol (FA) resins have been commercially used in various industrial applications [1-7]. Since the resin binder would form amorphous carbon upon heating to high temperatures with high carbon yield thus providing strong bonding strength to the composites at high temperatures, the resins have been applied as binder in producing various carbon composites [8-14]. Combination of novolac and FA resins, where the binder viscosity can be controlled by mixing different amount of liquid FA with solid novolac resins, the bonding capability, mechanical properties and processing performance of the carbon composites can be significantly improved. However, due to the complexity of the composite system, many details of the chemistry and factors influencing the curing and carbonization processes are still not fully known or understood, especially the additive effect on the curing and carbonization pathways and the interaction and/or inter-reaction behaviour between the binder and additives during the process. Understanding the chemistry and the morphology behaviour with the curing and baking process are fundamentally important to design/modify the performance of the carbon composites, but this has not been investigated thoroughly.

Comprehensive studies have been conducted to investigate the curing and baking chemistry for phenolic and FA resins to detect various intermediate structures formed during the crosslinking/carbonization reactions and thus identify the reaction pathway of the resins [12-27]. The inter-reactions of novolac/HMTA/FA mixing systems and the formation of highly crosslinked polymer networks containing both phenol and furan rings were studied in conjunction with the carbonization chemistry of the mixing resin system [28,29]. The studies of the carbonization behaviour of carbon/phenolic resins composites were also reported in literature [30-32]. Leveraging the methodologies and knowledge gained from these studies,
we have conducted research on curing and baking carbon composites using novolac/HMTA/FA resins as the binder while carbon black and mesophase as carbon additives. Carbon black is commonly used as additives to modify the mechanical and binding/processing performance of carbon composites, while mesophase pitch is an important precursor to produce advanced carbon composites with capability to develop extended graphitic crystallinity [32-34]. Following a previous paper on crosslinking chemistry of these carbon composites during curing process up to 205 °C [35], this paper will focus on the carbonization chemistry of the baking process up to 1000 °C to explore the chemical nature of volatiles released during the baking, reaction pathways, structures formed for the baked composites, and the morphology obtained for the finally obtained carbon composites. The effects on the carbonization derived from carbon black or mesophase additives were also examined and discussed.

2. Methods

2.1. Raw materials and sample preparation

Novolac resin (Resinox GC 1848), hexamethylene tetramine (HMTA) and furfuryl alcohol (FA: UCAR C34) were obtained from Huntsman Chemical Australia, Merck Pty Ltd and Orica Australia respectively. Carbon black and mesophase (AR Resin MP-P) were supplied by CanCarb Ltd Canada and Mitsubishi Gas Chemical Company Inc. Carbon black aggregates were crush into small particles by a blender just before use, and the particle size D[4,3] (volume weighted mean) was 9.44 μm. The particle size D[4,3] of the mesophase sample was 24.9 μm. All raw materials were used as received without purification or any further treatment.
The formulations of novolac/HMTA/FA (NHF) binder and composite samples are listed in Table 1. The procedure of green composite preparation and composite curing has been described in a previous paper [35]. Solid novolac and HMTA were dissolved in FA liquid under mechanical stirring at a speed of 1050 rpm over 3 hrs to achieve a homogenous resin solution (NHF-R). Carbon black or mesophase was then mixed with the solution using a high speed mixer at a speed of 3000 rpm for 3-4 min to NHF-C or NHF-M composite samples. These samples were then cured on a small scale (5 – 8 g) in glass vial following a slow curing cycle [35] up to 205 °C in a Memmert oven with a Eurotherm programming controller. The cured samples were cooled down to room temperature naturally and taken from the glass vials. Baking was then conducted using a home-made furnace at a rate of 50 °C/h from room temperature to a target temperature such as 300, 350, 400, 450, 500, 600, 700, 800, 900 and finally held at 1000°C for 2h. The weight losses of the samples collected at different temperatures were measured after cooling down to room temperature and combined with the weight loss data in curing. The diameter values of these samples were also measured before and after baking.

2.2. Characterization techniques

The fracture surface of the baked composite samples was examined by Philips FEI XL-30 SFEG scanning electron microscopy (SEM). The samples were mounted onto SEM stages with double-sided conductive tape and then sputter coated with gold of 20 nm thickness under argon atmosphere. The electron beam with an accelerating voltage of 5 kV was used to produce high definition images. Elemental analysis of the baked samples was conducted by Chemical & Micro Analytical Service Pty. Ltd. (CMAS, Belmont VIC 3216 Australia).
The X-ray Diffraction (XRD) experiment was conducted using a Siemens D5000 XRD with copper radiation at 40 kV and 30 mA over a 20 range of 10 to 40 degree with a 0.03 degree step and a 4 second step time. A graphite monochromator was used in the diffracted beam.

TGA-FTIR results were acquired using a TA SDT Q Series Explorer (Q600) TGA connected to a Nicolet Nexus 670 IR Spectrometer in an inert atmosphere (nitrogen gas). A small amount of each pre-cured sample was ground into find powder and placed in the TGA sample pan (~30 mg) and heated following an accelerated baking rate (500 °C/h) to 1000 °C then held isothermally for 5 min. Volatiles generated from heating samples in the TGA furnace were transferred through the interface into the FTIR spectrometer maintained at 180°C. Infra-red spectra were acquired continuously with KBr Beam splitter, resolution of 4 cm\(^{-1}\) and 365 scans for each spectrum.

\(^{13}\)C/\(^{15}\)N 97 – 98 % enriched HMTA (synthesized by Sigma-Aldrich as requested) was used instead of conventional HMTA to prepare the samples for high-resolution solid-state NMR experiments in order to enhance the signals derived from HMTA. All NMR measurement was conducted at room temperatures using a Varian Unity plus-300 spectrometer at resonance frequencies of 75 MHz for carbon-13 and 30 MHz for nitrogen-15 under conditions of cross polarization (CP), magic angle sample spinning (MAS) and high-power dipolar decoupling (DD). The 90° pulse-width was of 5.8 µs while the contact time was 3 ms. The rate of MAS was at a value around 7 – 8 kHz and no spinning side band was observed for \(^{15}\)N spectra when using such a MAS rate. The chemical shift of \(^{13}\)C spectra was determined by taking the carbonyl carbon of solid glycine (176.3 ppm) as an external reference standard. For \(^{15}\)N spectra, the enriched HMTA resonance at 44 ppm was taken as an external reference.

3. Results and discussion
3.1. Morphology of the baked carbon composites

Baking NHF-R and NHF-C to 1000 °C resulted in formation of carbon materials with SEM images of sample fracture surface shown in Fig. 1. A homogeneous, amorphous morphology was obtained for NHF-R with a minimal number of pores and pore size less than 1 μm (Fig. 1 A). The SEM image of NHF-C sample after baking to 1000 °C shows that carbon black particles were homogeneously distributed in the amorphous binder phase with pore size less than 1 μm (Fig. 1 B and C). Porous morphology was obtained for NHF-M sample during the baking (Fig. 2 A – E) and the pore size was around 5 – 50 μm. Large pore size was most prominent when the sample was baked to 400 – 600 °C. However, the mesophase in the NHF-M system did not form fibrous carbon (diameter of 100 μm with layer-by-layer structures) as it did when baked alone (Fig. 2 F). This suggests mesophase did not follow its own thermal carbonization pathway and could take part in the carbonization reactions with the NHF-R binder during the baking process.

The broad XRD curves shown in Fig. 3 indicated that baking NHF-R, -C and –M all resulted in amorphous carbons. The graphitic crystallinity was minimal after baking to 1000 °C. The sharp peaks in the patterns were due to Al₂O₃ impurities, possibly picked up from the Al₂O₃ sample-holder during baking.

The weight loss and sample dimensional changes (shrinking or expanding) of NHF-R, -C and –M samples during the baking process are shown in Fig. 4. The major proportion of the weight loss (volatile release) occurred below 700 °C. NHF-R released the highest amount of volatiles during the baking, followed by NHF-M, and NHF-C releasing the lowest amounts of volatiles. Table 2 lists the weight loss data after baking the three systems up to 1000 °C. The total baking weight loss (volatile release) for NHF-R was 57 %, while that of NHF-C
was 30 % which is lower than that of NHF-R (assuming no weight loss contribution from carbon black). The high surface area of the carbon black would adsorb the resin segments thermally broken apart from the networks during the baking process and benefit the increase of carbon yield. Although carbonization of mesophase also generated weight loss [9,31,34], the value was lower than that from baking NHF-R resins, thus 47 % weight loss was detected for baking NHF-M sample. The increase in surface area in baking NHF-M sample (formation of porous structure) could also enhance volatile release for the sample.

Both NHF-R and –C samples experienced sample shrinkage during the baking process due to volatile release from polymer networks with minimal porous structures in NHF-R, while a dimensional expansion occurred to NHF-M sample in baking and a maximum expansion (~15%) was reached at 450 ºC (Fig. 4). Such dimensional expansion for NHF-M is consistent with the formation of porous carbon structures with large pore sizes as shown in Fig. 2 A – E. The molecular structures of small molecular weight aromatic mesophase compounds were similar [36] thus carbonization reactions all occurred within a small temperature range. The resulting volatiles released also occurred within this small temperature range, therefore produced significant porous structures and severe dimensional expansion [31,34]. After baking to above 500 ºC, dimensional shrinkage occurred as the pore size decreased with increased baking temperatures. The final sample expansion for NHF-M at 1000ºC/2h was 6 – 7 %. The carbon black particles generated additional micro-pore structures (Fig. 1 B and C) which compensated for the shrinkage of NHF-C to some extent (~10 % shrinkage at 1000 ºC as compared to 23 % for NHF-R).

3.2. Chemical natures of the volatiles released from baking
The large weight loss reflected a significant amount of volatiles released during the baking process. TGA-FTIR was used to study the evolution and chemical nature of these volatiles, where a faster baking rate (500 °C/h, 10 times faster than that in furnace baking) was used in order to enhance the signals detected in the measurement. The TGA weight loss data is also shown in Table 2 as a comparison. The faster baking process in TGA testing generated a lower amount of volatiles but the trend was similar to those observed in furnace baking.

FTIR spectra of NHF-R heated in TGA to various temperatures are shown in Fig. 5. The FTIR spectra were compared with standard library spectra available in the spectrometer software to determine chemical natures of the major products detected during the baking. The assignments are shown in Fig. 5. At 200 °C, water and furfuryl compounds (FUR) were the predominant volatiles released from the system. Although the sample was cured to 205 °C/4h before baking, sample grinding exposed the attached FA within the bulk sample and it was released with moisture when heated in the TGA. CO₂, CO and NH₃ were also generated with increasing temperatures in conjunction with CH₄, C₂H₆ and their low molecular weight homologues plus benzene products. Note that above 600 °C, most of these volatile species were still present, and the small molecular species (CO₂, CO, NH₃ and water) were detected until 1000 °C.

The results of NHF-C and –M were similar to those observed for NHF-R system but their relative intensities displayed some different patterns. Fig. 6 shows the relative IR intensities of the volatiles released at different baking temperatures for the three different systems. For NHF-R, release of furfuryl compounds (FUR) reached a maximum at 300 °C, but there was FUR in the volatiles up to 1000 °C. CO₂ and CO components in the volatiles reached their maximum intensities at 460 °C. Benzene/phenol species and CH₄, C₂H₆ were observed above 400 °C and reached their maximum intensities at 560 °C. Water vapor was
released from the system across a wide temperature range although the relative intensity was low, while NH$_3$ displayed two maximum peaks at 500 and 770 °C.

For NHF-C, the volatile releasing behaviors of small molecular species such as CO$_2$, CO, CH$_4$, NH$_3$ and water vapor were similar to those of NHF-R, but the intensities of FUR and phenolic components in the volatiles were significantly decreased. These molecular species could be trapped on the surface of carbon black and then took part in the carbonization reactions to become part of carbon materials rather than being released as volatiles. The result of phenolic/furfuryl volatiles reduction is consistent with the high carbon yield for NHF-C sample. A significant difference for the NHF-M sample is the relative intensities of most volatile components became higher while the intensity of CO$_2$ was relatively lower. On the other hand, CO$_2$ and CO reached their maximum intensities at higher temperatures, while furfuryl/phenolic (FUR/Ph) and CH$_4$/C$_2$H$_6$ species reached their maximum intensity at lower temperatures as compared to those in NHF-R and –C systems. These differences could be attributed to the participation of mesophase in the carbonization process.

The TGA-FTIR experiment was conducted using fine powder samples with large surface area exposed to heating under an inert gas flow. The implication of this was easy for volatile to release from the system with reduced likelihood of participation in additional reactions and retention of these products in the resin system. Composites baked under large industrial scale baking processes would have smaller surface area to volume ratio and a longer volatile escape pathway especially for larger molecules containing furfuryl and benzene/phenol structures which would react in the resin phase and be retained in the system. Therefore, the results from current TGA-FTIR are only indicative of the species which would most likely form and be released as volatiles during the baking process.
3.3. Carbonization chemistry of the carbon composites

The carbon/hydrogen (C/H) atomic ratio is another important parameter in characterizing the carbonization process (aromaticity of carbons) for the formation of carbon materials from phenolic-furfuryl alcohol resins. The C/H ratio of the carbon black sample used in this study was 20.3, providing a good indication of the aromaticity of an amorphous carbon material. The C/H ratio for the mesophase sample used in this study before baking was 1.57, indicating the molecular weight was relatively small and comparable to the value of around 1.1 for NHF-R sample after curing to 205 °C/4h. The C/H ratio data of NHF-R, -C and –M systems after baking are shown in Fig. 7 A in conjunction with those of mesophase after baking to 900 °C (C/H ratio of 7.81). Significant increase in C/H ratio occurred above 600 °C for all the systems, and NHF-C reached a C/H ratio of 12.5 due to the contribution of carbon black. It is interesting to note that the C/H ratio of NHF-M also reach a C/H ratio of 10, higher than that of NHF-R (8.9). However, it is difficult to measure the contribution of mesophase in the NHF-M composite sample. The mesophase could follow a different carbonization pathway when baking with NHF-R.

Fig. 7 B shows the nitrogen-content (N %) values of the three systems after baking. The increase in N % in NHF-R at 400 – 600 °C was due to a larger weight loss of non-nitrogen-containing products as seen in TGA-FTIR study. The release of nitrogen-containing structures (e.g. NH$_3$) occurred mainly above 600 °C. A similar behaviour was observed in NHF-C and –M, although not that significant. After baking to 1000 °C, the nitrogen retention for the NHF-R, -C and –M systems were 35.4%, 35.3% and 39.9%, respectively. As the absolute N % content was very low in NHF-C and –M systems, the difference among these values was within error.
The examination of the chemical structures formed in the solid phase during the baking process of these composite systems should provide further understanding of the carbonization chemistry. High-resolution solid-state NMR spectroscopy provides a powerful tool to explore the chemical structures of such highly crosslinked systems. $^{13}$C CP/MAS spectra of NHF-R, -C and -M after baking to different temperatures are shown in Fig. 8 with greatly enhanced signals due its derivation from the use of $^{13}$C/$^{15}$N enriched HMTA. A strongly enhanced peak at 103 ppm was detected for NHF-R at 300 °C, its intensity further increased when temperature reached 400 °C. The resonances were assigned to >CH=CH< species which were derived from thermal dehydrogenation of methylene linkages (originally from HMTA) during baking. An increase in the methyl group intensity at 15 – 20 ppm was also observed with increasing temperature. Above 500 °C, a broad peak at 126 ppm was dominant as attributed to the formation of benzene structures while the methylene intensity was even lower than that of methyl groups. The intensities of methylene and methyl resonances became minimal when NHF-R was baked to 600 – 800 °C. These results were consistent with those reported previously [29]. After baking to 1000 °C, a broad peak over a wide frequency range was detected due to the formation of amorphous carbon materials, similar to that of carbon black as reported [35].

The results obtained from solid-state NMR and TGA-FTIR studies indicated that the carbonization reactions of NHF-R occurred at 300 – 600 °C with the opening of furan rings and then converting to benzene rings. Dehydrogenation of the methylene linkages during the baking process resulted in formation of >CH=CH< species, then ultimately to benzene structures and finally producing carbon materials with increased C/H ratio. Methyl groups were also formed during the process, some of them thermally decomposing from the network and released as CH$_4$ or C$_2$H$_6$, as detected by the TGA-FTIR.
The behaviour of the NHF-M system was quite similar to that of NHF-R. For NHF-C, the $^{13}$C resonances all became broader, suggesting a broad distribution of chemical environment and structures due to the strong interactions between the resin segments and carbon black particles. The carbonization reactions also shifted to lower temperatures; the spectrum at 400 °C for NHF-C was similar to that at 500 °C for NHF-R or NHF-M, indicating dehydrogenation of methylenes occurred at lower temperatures when carbon black was used as additives in the systems.

The variation of nitrogen-containing structures of NHF-R and –M during baking was examined by $^{15}$N CP/MAS spectra, shown in Fig. 9. The major nitrogen-containing structures in NHF-R after heating to 300 °C were amides and imides (120 – 150 ppm). Small amounts of nitriles (~ 250 ppm) and imines (280 – 320 ppm) were also detected. Increasing temperature produced broad imides/amides peaks and the relative intensity of imines at 280 ppm was further increased after heating to 500 – 600 °C. NO$_2$ species were also detected at 450 ppm with the disappearance of the amides/imides resonances when NHF-R was baked to 800°C. Since the baking was conducted under an argon atmosphere, the oxygen necessary for oxidation could only come from the decomposition of the phenolic-furfuryl resin. The minor peaks at 30 – 60 ppm were due to amine species formed by thermal decomposition of the nitrogen-containing linkages in the network during the baking. After baking to 800 °C, three minor broad peaks were detected at 150, 300 and 450 ppm corresponding to residual imides, nitriles and -NO$_2$ species, respectively. The $^{15}$N signal of the samples baked to 1000 °C was too weak to be detected.

For NHF-C, the $^{15}$N signal was very weak and broad. Those spectra with poor signal/noise were not shown. The nitrogen-containing structures formed during carbonization process for NHF-M were similar to that of NHF-R (with $^{15}$N CP/MAS NMR spectra shown in Fig. 9). However, less imine and nitrile structures were formed for NHF-M.
as compared to that in NHF-R system, and the imide structure became the major nitrogen-containing constituent remaining until 600 °C. The signal was too weak to be observed when samples were baked above 800 °C. These nitrogen-containing structures with the majority being amides, imides, nitriles and \(-\text{NO}_2\), acting as impurities in the carbon materials, can only exist either as linkages between large pieces of carbon structures or at the edge of carbon structures.

Carbon black and mesophase played a different role in the carbonization process. A significant linewidth broadening occurred in $^{13}$C NMR spectra of baked NHF-C composite, indicating a wide distribution of chemical environments and structures and mobility reduction of polymer segments due to strong interactions between resin segments and carbon black particles. Such interactions also shifted certain carbonization reactions to occur at relatively lower temperatures as compared to those in NHF-R (the resin-only system). On the other hand, mesophase additives could take part in the carbonization process with NHF-R and generate homogeneous amorphous carbons, similar to those reported previously \[31,34\]. Such inter-reactions should broaden the carbonization temperature range of mesophase and reduce the porosity of the carbon materials thus the dimensional expansion was also reduced as compared to the carbon obtained from baking pure mesophase compounds.

It is apparent that carbon black and mesophase additives displayed contradictory effects on the carbonization behaviour of the binder phase. Application of both additives and manipulating their compositions with binders might be able to provide complementary benefits in a carbon composite to achieve its designed performance and desired properties in applications. Further research is required for understanding the behaviour of these mixing systems and to determine optimum carbonization conditions for such mixing systems in order to produce the designed structures of carbon composites and reduce the volatile release during the carbonization process.
4. Conclusion

Baking carbon composites with NHF-R as binder to 1000 °C generated amorphous carbons for both carbon black and mesophase composites with NHF-R as the binder. The volatiles released during the baking (mainly at 300 – 700 °C) were furfuryl compounds, phenol-benzene species, methane and ethane and other small molecules such as water vapor, CO₂, CO and ammonia. The participation of mesophase in the carbonization of the binder resins generated additional volatiles during the baking process and large pore sizes. However, the porosity and the level of dimensional expansion were reduced as compared to baking the mesophase-only system. On the other hand, the strong interactions between the binder resins and carbon black particles not only trapped a considerable amount of furfuryl and phenolic species in the system during the baking to enhance the carbon yield, but also shifted some carbonization reactions to lower temperatures and produced a broad distribution of chemical environment and structures of the binder segments in the final amorphous carbon. The dimensional shrinkage of the NHF-C composite was also lower than that of the binder-only system. Complementary performance/properties of a carbon composite could be designed and produced by using both carbon black and mesophase additives through manipulating their compositions with binders under optimum carbonization conditions.

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REFERENCES:


Table 1 - Formulations of the Binder or Composite systems in weight parts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Resinox</th>
<th>HMTA</th>
<th>C34</th>
<th>Carbons</th>
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<tbody>
<tr>
<td>NHF-R</td>
<td>24</td>
<td>5</td>
<td>34</td>
<td>0</td>
</tr>
<tr>
<td>NHF-C</td>
<td>24</td>
<td>5</td>
<td>34</td>
<td>37 carbon black</td>
</tr>
<tr>
<td>NHF-M</td>
<td>24</td>
<td>5</td>
<td>34</td>
<td>37 mesophase</td>
</tr>
</tbody>
</table>

Table 2 - Weight loss data after baking to 1000ºC

<table>
<thead>
<tr>
<th>Samples</th>
<th>NHF-R</th>
<th>NHF-C</th>
<th>NHF-M</th>
</tr>
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<tbody>
<tr>
<td>Baking wt loss (wt%)</td>
<td>57.2 %</td>
<td>36.9 %</td>
<td>47.1 %</td>
</tr>
<tr>
<td>TGA wt loss (wt%)</td>
<td>49.2 %</td>
<td>30.3 %</td>
<td>42.4 %</td>
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</table>
Fig. 1 - SEM images of NHF-R (A), NHF-C (B, C) after baking to 1000 °C.
Fig. 2 - SEM images of NHF-M after baking to 300 °C (A), 400 °C (B), 600 °C (C) and 1000 °C (D, E), and mesophase after baking to 900 °C (F).
Fig. 3 - XRD patterns of NHF-R, NHF-C and NHF-M after baking to 1000 °C.
Fig. 4 - Weight loss (A) and sample dimension extension (B) for NHF-R, NHF-C and NHF-M after baking to 1000 °C
Fig. 5 - FT-IR spectra of the volatiles released from NHF-R during TGA up to 1000 °C.
Fig. 6 - FT-IR relative intensities of volatiles released during TGA for NHF-R, NHF-C and NHF-M up to 1000 °C.
Fig. 7 - Atomic C/H ratio (A) and nitrogen content data (B) for NHF-R, NHF-C and NHF-M after baking to 1000 °C.
Fig. 8 - $^{13}$C CP/MAS NMR spectra for NHF-R, NHF-C and NHF-M after baking to 1000 °C
Fig. 9 - $^{15}$N CP/MAS NMR spectra for NHF-R and NHF-M after baking to 800 °C