Crosslinking chemistry of curing carbon composites containing novolac/furfuryl alcohol resins and carbon black or mesophase pitch as additives

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ABSTRACT

The crosslinking chemistry was studied for producing carbon composites using carbon black or mesophase pitch as additives and a binder containing novolac and furfuryl alcohol (FA) resins and hexamethylene tetramine (HMTA) as a crosslinker. Curing the composites to 205 °C generated FA, water and ammonia as the major volatile species released from the systems due to evaporation, condensation of FA and crosslinking reactions between the resins and HMTA, respectively. Carbon black or mesophase displayed a minimal effect on the chemical nature of the volatiles released from the curing. However, the carbon black particles, which were homogeneously distributed in the cured composite, produced a broad distribution of chemical environments and structures of the binder networks, and the chain motions of the binder were also modified. Mesophase pitch on the other hand was likely to participate in curing reactions of the resin phase and heterogeneous phase structures were detected only on a scale as small as ~2 nm in the composite.

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1. Introduction

As the initial synthetic resins developed over a century ago, phenolic and furfuryl alcohol (FA) resins have been commercially used in varies applications from commodity and construction materials to high technology industries due to its characteristic properties such as excellent mechanical strength, dimensional stability, solvent resistance and flame retardance. The chemistry and applications of these resins has been studied over several decades [1–7]. Comprehensive research has been conducted to investigate the curing and baking chemistry for phenolic and FA resins by using model compounds and commercial resins. ^{13}C and/or ^{15}N enriched crosslinkers such as formaldehyde or hexamethylene tetramine (HMTA) were also used to enhance the signals derived from the crosslinkers which made it possible to detect various intermediate structures formed during the crosslinking reactions and thus identify the reaction pathway of the resins [8–21].

When novolac and FA resins are combined in application as a binding agent, liquid FA can act as a solvent for solid novolac where the viscosity of the binder system can be controlled by varying the amount of FA, therefore, processing and mechanical performance can be greatly improved especially when the system is used to fabricate carbon composites, reduction composites and refractories in the metal industries. The binder resins would also form amorphous carbon eventually upon heating to high temperatures with high carbon yield. However, when the resins are used in fabricate carbon composites, the carbon additives should also play a role in the crosslinking and carbonization reactions due to interactions between the resins and the carbon additives. Some carbon additives may also participate in the reactions during the curing or baking at high temperatures, thus, the reaction pathways, the reactivity and morphology of the final carbon composites will be significantly varied. Understanding the chemistry and the morphology behaviour along with the curing and baking process for these systems are fundamentally important to design/modify the performance of the carbon composites, but this has not been investigated thoroughly.

The inter-reaction pathways of the novolac/HMTA/FA mixing systems and the formation of highly crosslinked polymer networks containing both phenol and furan rings were reported in conjunction with the carbonization chemistry of the resin systems [22,23]. Leveraging the methodologies and knowledge gained from these previous studies on resin-only systems, we have conducted research on curing and baking carbon composites using novolac/HMTA/FA resins as the binder with carbon black and mesophase pitch 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 the capability to develop extended graphitic crystallinity [24–29]. Crosslinking chemistry of these carbon composites during curing process up to 205 °C was studied and reported in this paper, to explore the chemical nature of the volatiles released during the

curing, reaction pathways and structures formed in the solid phase of the cured composites. [13]C- and ^{15}N-enriched HMTA was used as a crosslinker in the binder phase and the results were compared to those of binder-only system for understanding the factors derived from carbon black or mesophase additives. The study of carbonization process of these carbon composites and thereafter the significantly different performance of these carbon materials will be published on later dates.

2. Experimental

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 pitch (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. The obtained synthetic mesophase pitch sample was derived from naphthalene with particle size D [3,4] of 24.9 μm and softening point of 275–295 °C. All raw materials were used as received without purification or any further treatment.

The formulations of the novolac/HMTA/FA binder and composite samples are listed in Table 1. Solid novolac and HMTA were dissolved in FA liquid under mechanical stirring at a speed of 1050 rpm in a water bath (maintained at room temperature to avoid temperature increase during mixing which could cause curing) over 3 h to achieve a homogenous liquid binder (NHF-R). Carbon black or mesophase was then mixed with the NHF-R binder in a high speed mixer at a speed of 3000 rpm for 2–3 min to produce carbon black (NHF-C) or mesophase pitch (NHF-M) green composite samples. These samples were then cured on a small scale (3–5 g) in glass vials placed in a Memmert oven with a Eurotherm programming controller following a slow curing cycle (Table 2) up to 205 °C/4 h. The weight losses of the cured samples collected along the curing process at different curing temperatures were measured after cooling down to room temperature.

2.2. Characterization techniques

The fracture surface of the cured 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.

Thermogravimetric analysis Fourier transform infrared spectroscopy (TGA–FTIR) results were acquired using a TA SDT Q Series Explorer (Q600) TGA connected to a Nicolet Nexus 670 IR Spectrometer in inert atmosphere (nitrogen gas). A small amount of each green composite sample (~30 mg) was placed in the TGA sample pan and heated following an accelerated curing cycle (listed in Table 2) to 205 °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 during the measurement with KBr Beam splitter, resolution of 4 cm^{-1} and 365 scans for each spectrum.

In order to enhance the nuclear magnetic resonance (NMR) signals derived from HMTA, ^{13}C and ^{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 following the same sample mixing and curing procedures. All NMR measurements were conducted at room temperatures using a Varian NMR300 System 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 1 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 adamantine peak at up-field (29.5 ppm relative to TMS) as an external reference standard. For ^{15}N spectra, the enriched HMTA resonance at 44 ppm [18] was taken as an external reference. [1]H spin–lattice (T_1) and spin–lattice relaxation times in the rotating frame ($T_{1\rho}$) were measured via ^{13}C resonances using pulse sequences reported previously [30]. Solution NMR spectra were also measured using the same spectrometer with 10 mm solution probe head.

3. Results and discussion

3.1. Chemical nature of the volatiles released from the curing

The weight loss data during the curing of the NHF-R, NHF-C and -M systems are shown in Fig. 1, reflecting the volatile released during the curing. The weight loss up to 90 °C were minimal for all
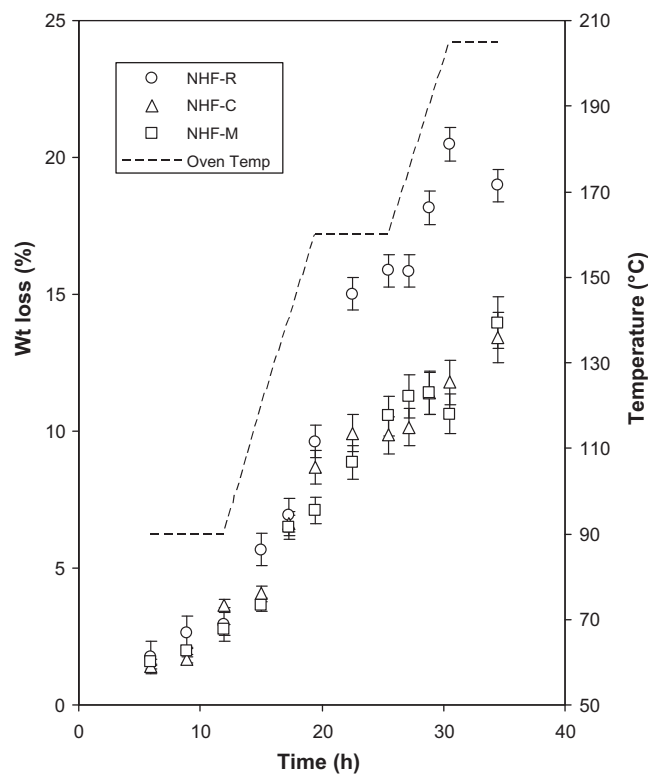

Fig. 1. Weight loss of NHF-R, -C and -M systems after curing to 205 °C/4 h.

samples, however, it increased rapidly when the curing temperature was increased. After curing to 205 °C for a total of 35 h, NHF-R (resin-only sample) produced 19% of weight loss, while NHF-C and -M (containing 63% of resins) generated 13–14% weight loss (corresponding to 21–22% resin loss when assuming no volatile release from carbon black or mesophase pitch).

TGA–FTIR measurement was conducted to examine the chemical nature of the volatiles released during the curing process. Due to the small scale testing for TGA analysis where only up to 30 mg samples could be packed into the TGA sample pan, a fast curing cycle listed in Table 2 was used to enhance the IR signal; all target temperatures remained the same as those used in oven curing, but
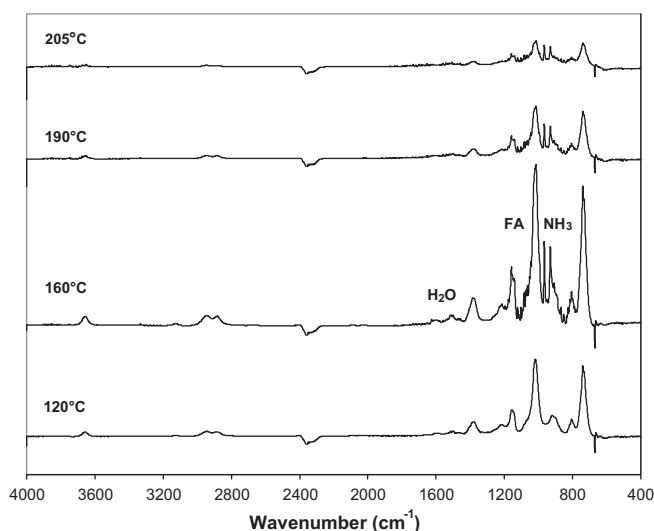

Fig. 2. FTIR spectra of volatiles collected at 120, 160, 190 and 205 °C/4 h during TGA testing for NHF-R sample.