Characterization of Substituted Phenol–Formaldehyde Resins Using Solid-State Carbon-13 NMR

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Synopsis

Crosslinked substituted phenol–formaldehyde resins were synthesized from cashew nut shell liquid, 3-*n*-pentadecylphenol and phenol with formaldehyde. The resulting resins were crosslinked and investigated using carbon-13 NMR in the solid state using cross-polarization, magic angle spinning, and dipolar decoupling. Comparisons were made between the spectra of pure phenol–formaldehyde and modified phenol–formaldehyde resins and it was shown possible to distinguish between the resins. It was also shown that the proton-dephased spectrum gave better spectral resolution for the substituted compounds. In addition, the solids carbon-13 technique verified that the degradation of the substituted phenolic resins occurs first with the degradation of the side chain in agreement with suggestions from earlier work.

INTRODUCTION

Polymers made from phenol and formaldehyde were discovered about 75 years ago[1,2] and are still used in a wide variety of applications[3,4] and even fibers.[5] Our interest in these compounds is because of their use in composites. The properties of materials made from these may be altered by modifying the chemical constituents and/or the processing conditions. Among the most convenient ways of altering the properties of phenol–formaldehyde resins are copolymerizations using substituted phenolic or aldehyde monomers. Substitution on the phenolic ring with an alkyl group can "soften" these resins. We have previously studied how various alkyl groups in substituted phenolics affect the thermal stability of the resin.[6] Of specific interest to us is the characterization of alkyl-substituted phenolics containing 15 carbon atoms. These may be derived from cashew nut shell liquid (CNSL) and are the basis for binder resins and friction particles in composite friction materials.

CNSL is isolated from cashew nut shells mainly grown in Brazil or India. An excellent review of its chemistry exists.[7] About 30–35% CNSL is present in the shell, which amounts approximately to 67% of the nut.[8] The components of CNSL have been characterized by a number of techniques including proton NMR, ultraviolet (UV), infrared (IR), and chromatography.[7-11] The major component of raw CNSL is anacardic acid, a hydroxy carboxylic acid with an alkyl substituent meta to the hydroxyl functionality. Decarboxylation of

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anacardic acid occurs during heating and processing of raw CNSL. This process yields distilled CNSL which is comprised of: cardanol, a meta-substituted phenol (> 86%); cardol, a meta-substituted resorcinol (2–5%); and other minor components (< 6%) including 4-methyl dihydricphenol. In addition to ring heterogeneity, the alkyl chains contain 15 carbons but consist of mixtures of saturated (< 1%), monoene (39%), diene (16%), and triene(45%). The percentages are based on the work of Tyman and Jacobs[8] but some uncertainty as to the actual percentages of each exists.[7]

In order to further understand the relationship between structure and properties of substituted phenol–formaldehyde resins, more detailed characterization of them must be made. Due to the insolubility of the cured resins, however, most chemical techniques are ineffective at chemical characterization. An exception to this is solids carbon-13 NMR analysis which has previously been used in the study of pure phenolic resins.[12–15] This technique also has the advantage of characterizing the materials in their native state.

In the present article, we report the characterization of meta-substituted phenol–formaldehyde polymers using carbon-13 NMR. Novolak-type prepolymers of substituted phenol–formaldehyde resins were prepared from distilled cashew nut shell liquid (consisting of cardanol and small amounts of cardol) and 3-n-pentadecylphenol (obtained by hydrogenation of cardanol). These prepolymers were subsequently cured with hexamethylenetetramine (HMTA) at high temperature to give crosslinked polymers. The crosslinked polymers were characterized by solids carbon-13 NMR, and the results compared to a standard phenol–formaldehyde resin.

EXPERIMENTAL

Distilled CNSL (amber-colored liquid) and 3-n-pentadecylphenol (pink to white solid) were used as received from the Cardolite Corp. (Newark, NJ). 3-n-Pentadecylphenol was produced by the hydrogenation and subsequent distillation of distilled CNSL. The crosslinked polymers were prepared as follows[6]: Into a three-neck reaction kettle, phenol (or substituted phenol) and sulfuric acid (46%) were charged. The contents were stirred and heated to 77°C at which time paraformaldehyde and mineral spirits (ca. 45 mL/mol of paraformaldehyde used) were added. The reaction mixture was heated to 95°C for 30 min and isopropanol added. The isopropanol/water azeotrope was then distilled off. The prepolymers were dried in a vacuum oven and later cured with hexamethylenetetramine (6.5% of the weight of the dry prepolymer) for 1 h at 105°C. These materials were then post-cured at 180°C for 3 h. The ratio of phenol/paraformaldehyde/sulfuric acid used was typically 1/0.7/0.008, respectively.

The ^{13}C-solid-state spectra were obtained on a VXR-200 spectrometer operating at 50.3 MHz for [13]C. The solids spectra were taken using the Varian PLE probe with cross-polarization (CP), dipolar decoupling (DD), and magic angle spinning (MAS). The CP/MAS/DD spectra were obtained with a 1 ms contact time, 1 s repetition time, and spinning of about 3.5 kHz using bullet-type spinners. The high power decoupler field strength was measured to be about 11 G (46 kHz). The magic angle was adjusted to within 0.1° by monitoring the change in line width of the aromatic region of a hexamethyl-

benzene spectrum with a change in angle. Since solid-state spectra gave rise to intense spinning sidebands, TOSS method of sideband suppression[16] was utilized to eliminate (or reduce) sideband interference and aid in the interpretation of the spectra. Accurate knowledge of spinning rate was determined by observing the sidebands produced without TOSS. The proton dephased spectra were taken using a modified TOSS sequence.[17] For our spectrometer[18] this amounts to the final delay in the TOSS sequence (100 μs in this case) during which the high power decoupler is gated off. This results in protonated carbon suppression originally reported by Opella and Frey.[19] The spectra are referenced with respect to tetramethylsilane via external solid hexamethylbenzene. The total experimental time for obtaining a sideband suppressed ^{13}C spectrum was typically 3–4 h per sample.

The liquid-like spectra were taken with the CP/MAS probe operating in a single pulse mode. Low power (1 W) decoupling (gated on during acquisition only) was used with 90° (10 μs) pulses. A 20,000 Hz spectral width was used for all spectra along with double precision accumulation. The MAS spectra are shown on an expanded scale.

RESULTS AND DISCUSSION

Different types of ^{13}C-spectra for solid materials of three crosslinked resins, phenol: formaldehyde (P–F), cashew: formaldehyde (C–F), and 3–n-pentadecylphenol: formaldehyde (PDP–F) resins have been obtained. Figure 1 shows the NMR spectra of the solid samples with low power scalar decoupling (i.e., liquid-like). The different ratios of the aliphatic/aromatic resonances in C–F or PDP–F and P–F is clearly observed. Although no CP/MAS/DD has been employed, the methylenes of the alkyl chains of C–F and PDP–F have moderately narrow peaks. In fact some chemical shift resolution is observed beyond the aliphatic/aromatic separation. This indicates that even in its crosslinked state the long alkyl chains remain fairly flexible. These crosslinked polymers tend to be "softer" as compared to those cured phenolics with no alkyl substitutions. The molecular motions of the alkyl chains could be partially responsible for this effect. However, the aromatic resonances of all three materials appear to have similar linewidths under these conditions. In the C–F spectrum there are two resolved resonances in the "aromatic" region only one of which is found in each of the PDP–F and P–F spectra. We believe that the higher ppm resonance is due to the olefinic carbons which undergo faster motion than the aromatic carbons and appear sharper. However, it is difficult to analyze the line shape because it contains contributions from a number of overlapping chemical shift powder patterns and residual dipolar couplings.

The CP/MAS/DD spectra of all three compounds are shown in Figure 2. The phenol–formaldehyde spectrum is virtually the same as previously reported.[12–15] Two distinct methylene bridge peaks are observed corresponding to the ortho–ortho, occurring at around 27 ppm, and the other ortho–para bridge, occurring at around 35 ppm. These peaks were assigned based on the article by Bryson et al.[15] The spectrum of C–F and PDP–F show much more intense aliphatic resonances with their major peak at 31 ppm, corresponding to the methylenes of the side chain and the methylene bridges. The methyl
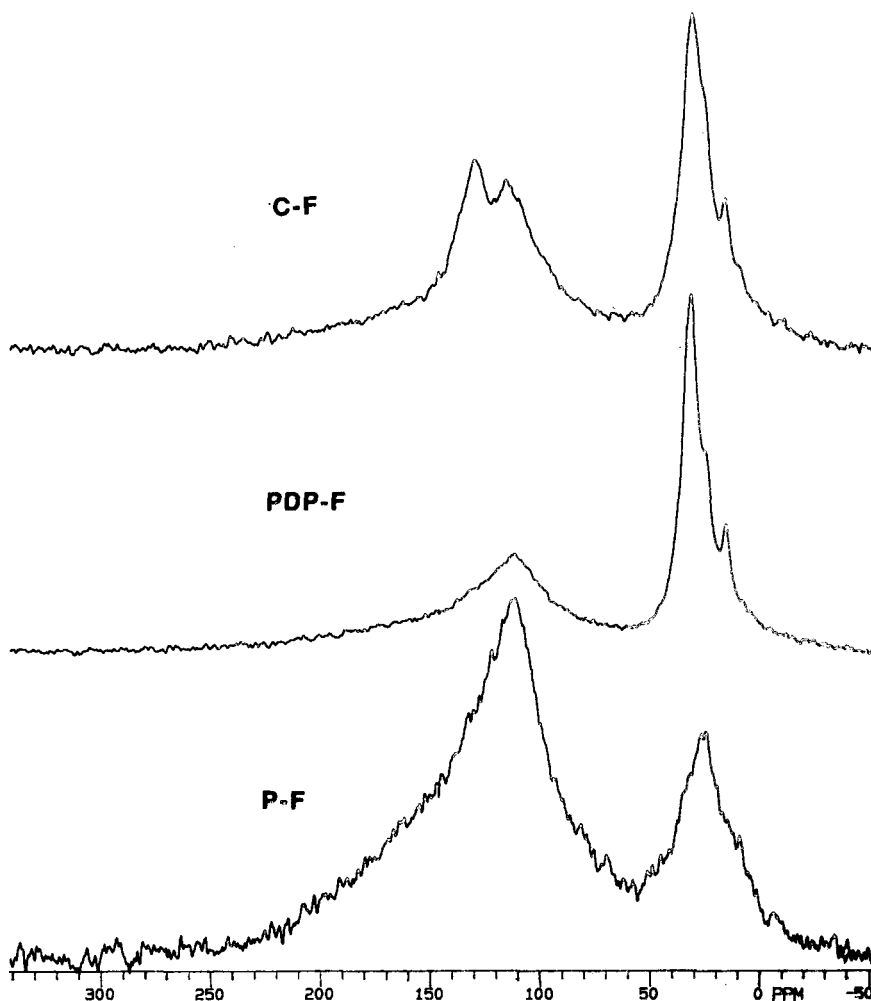
Fig. 1.   Liquid-like ^{13}C spectra of phenol–formaldehyde (P–F), 3-n-pentadecylphenol–formaldehyde (PDF–F), and cashew–formaldehyde (C–F).

groups are also observed and are rather narrow. In C–F, resonances due to the substituted aromatic and side chain double bonded carbon are observed but are not very resolved. For PDP–F only the former is present. The assignments of all carbon resonances given on the spectra refer to the structures shown in Figure 3 and summarized in Table I.

Shown in Figure 4 is the proton dephased spectra of the three crosslinked phenolic resins. In this experiment the decoupler was turned off for 100 μs after the cross-polarization and TOSS sequence but prior to data acquisition and high power decoupling. This had the effect of dephasing the protonated carbons. This technique is primarily effective for nonmobile carbons. Mobile carbons like methyl, and some methylene groups, are often not suppressed because of semirapid molecular motion. This is obvious in Figure 4 as the carbons of the methyl and methylenes of the alkyl chains are not effectively suppressed using this technique. In addition, this sequence is not totally
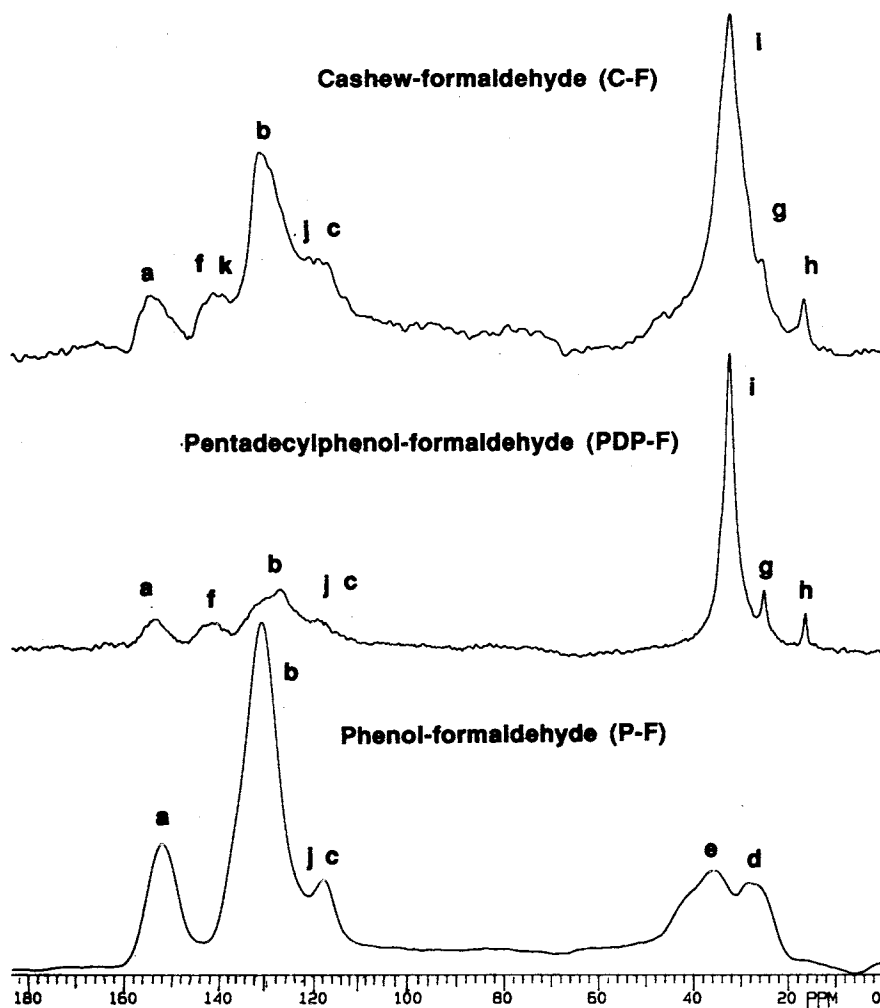
Fig. 2. Solid-state ^{13}C-NMR spectra of phenol–formaldehyde (P–F), 3-n-pentadecylphenol-formaldehyde (PDF–F), and cashew–formaldehyde (C–F) using CP/MAS/DD and TOSS.

effective at removing spinning sidebands. In P–F only the nonprotonated carbons show increased intensity. These are fairly rigid structures. For PDP–F and C–F the major resonances enhanced are the nonprotonated aromatics; however, there are still very significant contributions from the flexible side chains due to their flexibility. In fact, the proton dephased spectra of C–F and PDP–F show better spectral resolution with two well-defined methyl and methylene peaks. Only the C–F spectrum shows a shoulder on the methylene resonance at around 27 ppm due to the carbons next to the double bonds. In addition, the carbons corresponding to the double bonds in C–F are also better resolved than the CP/MAS/DD case.

Since many of these polymers are used in moderate to high temperature applications, their thermal behavior is of some importance. We have previously shown that the thermal stability of substituted phenolics decreased with the length of the alkyl-chain group.[6] However, the mechanism of degradation
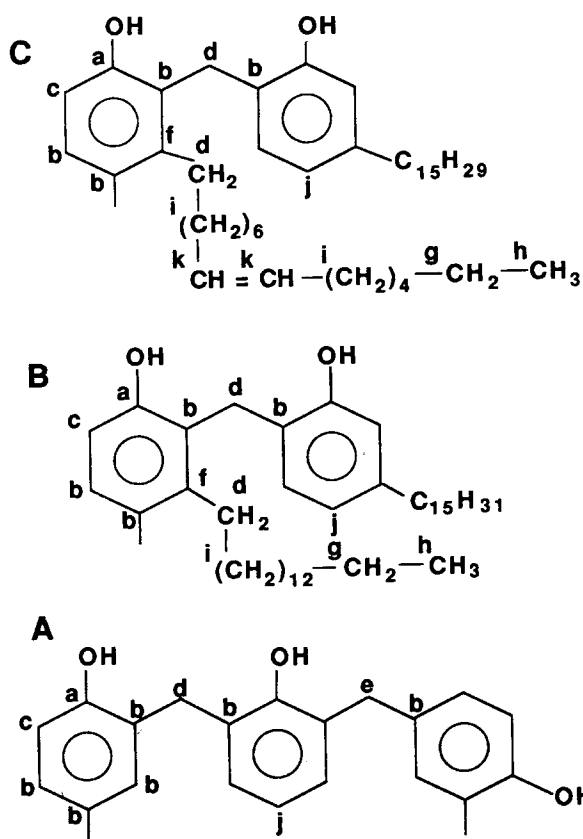
Fig. 3. Structural assignments of solid-state ^{13}C-NMR spectra. The letter designations used here are used to assign the spectra in Figure 2. The structures shown are the simplest representation of the crosslinked resin for (A) phenol–formaldehyde (P–F), (B) 3-n-pentadecylphenol-formaldehyde (PDP–F), and (C) cashew-formaldehyde (C–F).

is not established using thermogravimetric analysis. In Figure 5 we show a series of ^{13}C-solid-state NMR spectra with CP/MAS/DD of C–F, which has been subjected to thermal degradation at different temperatures and for different time periods in the presence of air. The bottom spectrum is that of a crosslinked polymer and the others are those of the sequentially degraded polymer. The intensities of the methylene peaks diminish as the amount of heating is increased. These resonances are virtually absent at a temperature of 400°C. The aromatic resonances, however, show a relative increase in intensity with some loss of resolution. Consequently, we feel that the side chain methyl and methylenes degrade first as the temperature is increased. The structures that remain after heating are probably rather complicated aromatic structures with higher thermal stability than the original resin. In these experiments we do not observe the carbonyl functionalities upon heating, found in previous experiments using carbon-13-labeled materials. This is because the concentration of these appears to be quite small. The hydroxyl functionality also does not appear to degrade upon heating the resin to 400°C. The broadness of the resonances after heating is likely due to further crosslinking of the material

| Chemical shift (ppm)[a] (resin found in)	Carbon	Description
15 (PDP–F, C–F)	h	$—CH_2—\underline{C}H_3$ (side chain)
24 (PDP–F, C–F)	g	$—\underline{C}H_2—CH_3$ (side chain)
31 (PDP–F, C–F)	i	$—\underline{C}H_2—\underline{C}H_2—CH_2—$
27 (P–F)	d	Ortho–ortho methylene bridge
35 (P–F)	e	Ortho–para methylene bridge
117 (all)	c	Unsubstituted ortho-C
120 (all)	j	Unsubstituted para-C
130 (all)	b	Unsubstituted meta or substituted ortho or para position
138 (C–F)	k	Unsaturated carbon on alkyl chain
141 (PDF–F, C–F)	f	Substituted meta-carbon
152 (all)	a	$\underline{C}—OH$ aromatic

[a]All shifts are relative to TMS.
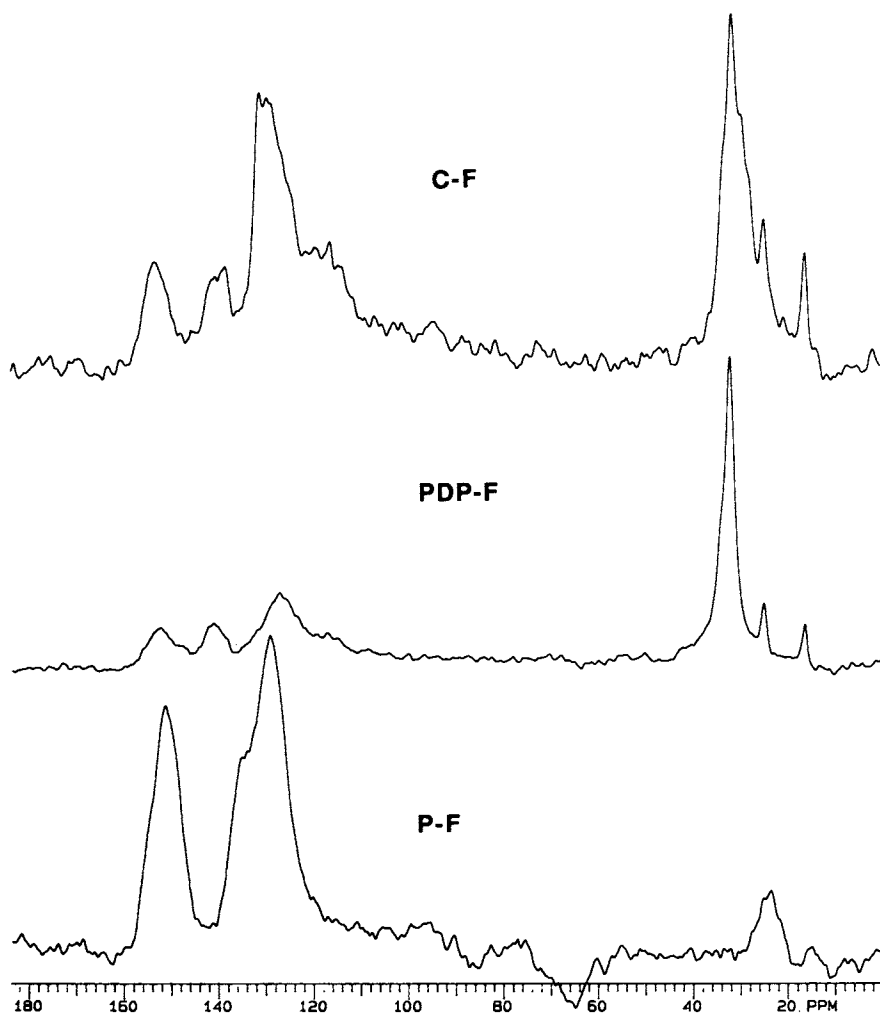
Fig. 4.   Proton-dephased TOSS ^{13}C-NMR spectra of phenol–formaldehyde (P–F), 3-n-pentade-cylphenol-formaldehyde (PDP–F), and cashew–formaldehyde (C–F). Incomplete spinning side-bands elimination is evident between 50 and 90 ppm.
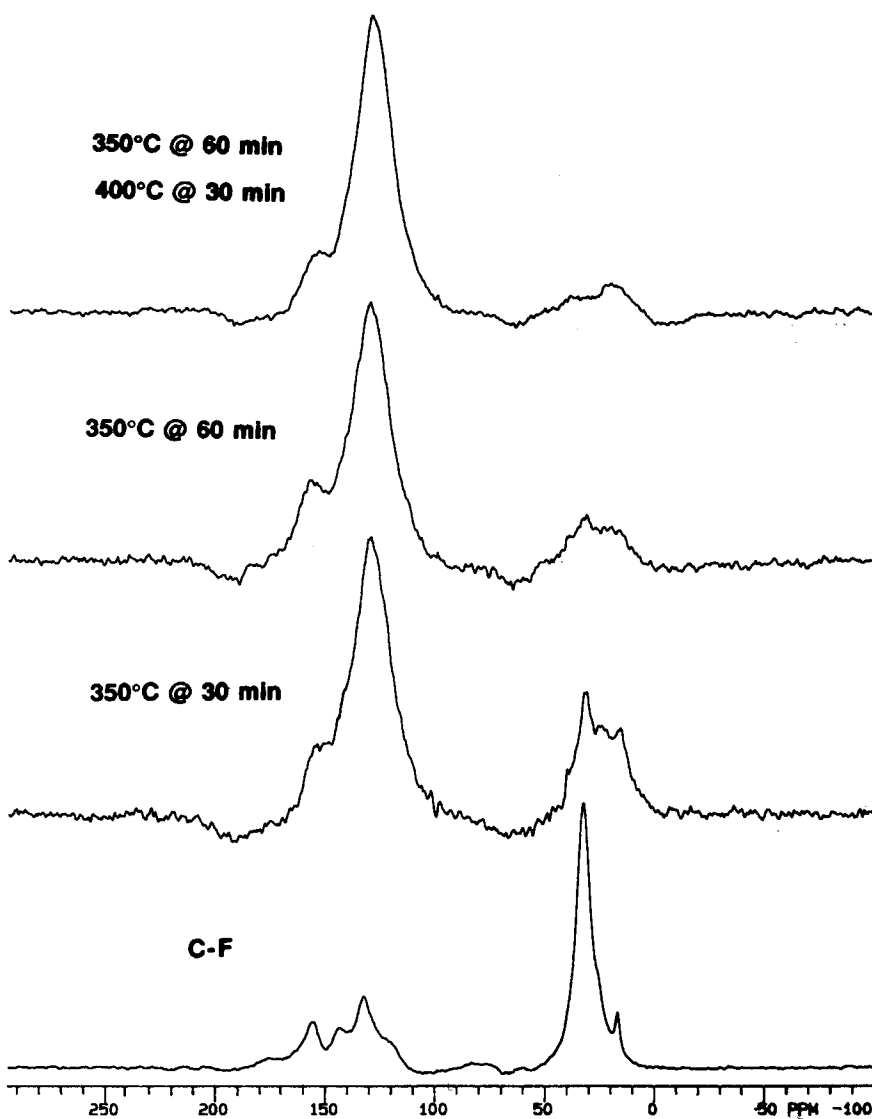
Fig. 5.   Solid-state ^{13}C-NMR spectra using CP/MAS/DD and TOSS of cashew formaldehyde (C–F) thermally degraded at different temperature and time periods noted in the figure. Note that that the chemical shift scale is different than the other spectra reflecting the broader resonances.

limiting mobility and the presence of a variety of different functionalities each with an individual chemical shift.

CONCLUSIONS

Solid-state carbon-13 NMR spectra with CP/MAS/DD is a useful tool for distinguishing between different phenol–formaldehyde resins. The proton dephased spectra of these resins provide much better spectral resolution compared to the ones with no proton dephasing. The ^{13}C-solid-state NMR

spectra with CP/MAS/DD can be used to follow the chemistry of degradation of cured phenolic resins. In agreement with our earlier conclusions based on thermogravimetric analysis, the side chains of these resins appear to degrade before the aromatic portions of the crosslinked polymer.

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