
Phenolic resins (IV). Thermal Degradation of Crosslinked Resins in Controlled Atmospheres

J. Bouajila, G. Raffin, S. Alamertery, H. Waton, C. Sanglar and
M. F. Grenier-Loustalot*

Service Central d'Analyse, USR 059, CNRS, Echangeur de Solaize BP 22, 69390 Vernaison, France

Received: 7 August 2002 Accepted: 26 November 2002

SUMMARY

The study involved the thermal degradation of phenolic resins in controlled atmospheres (inert and oxidizing). Its aim was to characterize volatile organic compounds (VOC) and inorganic compounds released during heat treatment. The methods used were thermogravimetry coupled with thermodesorption/gas chromatography/mass spectrometry (TG/TCT/GC/MS) and thermogravimetric analysis coupled with infrared (TGA/IR). At the end of the heat cycle, residues were characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (solid state ^{13}C NMR (CP/MAS)). The data show that the synthesis conditions of the crosslinked resins, the controlled environment and the temperature of the degradation heat cycle, all affect the composition of volatile compounds and residues at the end of the cycle. The data have enabled us to propose decomposition reaction mechanisms for these resins in oxidizing and inert environments.

1. INTRODUCTION

The characteristics of phenolic resins and their fields of application^{1,2} can be correlated with their thermal properties. Resin properties are usually controlled before and after the gel point, but for several years work has been done on their thermal degradation in order to determine the composition of gases released and their relationship to the conditions used to prepare resins³⁻¹⁵.

The present chemical characterization of resins after their thermal degradation involved the volatile compounds released and the solid residues. The thermal behavior of resins depends on the degradation atmosphere (inert or oxidizing) and the temperature¹⁴. Several phenolic resins were prepared (reactants, formaldehyde/phenol ratio (R), type of catalyst, cross-linking heat cycles, pH, temperature, etc.) and were degraded in different conditions (atmosphere, temperature, etc.)³⁻¹⁵.

This work is the continuation of studies on the properties of resins prepared using different conditions of synthesis and heat treatment¹⁶⁻¹⁸. The purpose of the thermal degradation of these resins was to characterize the molecules released in different atmospheres and at different temperatures. Analyses of degradation residues were carried out to determine their changes at different temperatures. The determination of the composition of volatile compounds released and their quantification provides information on the toxicity of these side products. The structures of compounds released and those of the residues have enabled us to propose degradation reaction mechanisms for cross-linked networks.

2. EXPERIMENTAL PART

2.1 Products

The products and preparation of resins and thermohardened resins have been described elsewhere¹⁸.

* Corresponding author. Tel: +33-4-78-02-22-62 Fax: +33-4-78-02-41-74. E-mail address: mf.grenier-loustalot@sca.cnrs.fr

2.2 Experimental Techniques

2.2.1 Thermogravimetry Coupled with Thermodesorption/Gas Chromatography/Mass Spectrometry (TG/TCT/GC/MS)

The analytical TG/TCT/GC/MS set-up consisted of three parts: the heat cycle oven, the thermodesorber (TCT) and the GC/MS.

The oven used for degradation was composed of a quartz tube surrounded by a heating resistance (T_{\max} : 850°C). The sample was placed in a platinum pan, in turn placed in a pan support at the extremity of a tube with a quartz extension. The support with the sample equipped with a thermocouple (control of sample temperature) was placed in the middle of the oven. The flow-rate of carrier gas (helium or air) inside the quartz tube was adjustable and controlled, about 10 mL.min⁻¹ at the outlet of the adsorbent tube. This adsorbent tube was placed at the oven outlet throughout the degradation cycle to adsorb volatile compounds released during degradation. The degradation cycle for each analysis was one minute at 30°C followed by a 5°C.min⁻¹ gradient up to the desired final temperature and terminated by a one minute isotherm at this temperature. The temperature ranges used for all resins in the inert atmosphere were 30-120°C, 120-200°C, 200-300°C, 300-400°C, 400-500°C, 500-600°C, 600-700°C and 700-850°C. In the oxidizing atmosphere (air) the 600-700°C and 700-850°C ranges were not used because the resins degraded completely before 600°C.

The adsorption system was composed of a quartz tube packed with three adsorbent phases: Carbosieve SIII, Carbotrap and Carbotrap C (Varian/Chrompack TCT 16097). At the end of trapping, the adsorbent tube was placed on a thermodesorber (TCT (Varian/ChrompackPTI/TCTCP4010)). Desorption conditions on the TCT were T (rod): 250°C, T (trap): -150°C, T (desorption): 300°C, t (desorption): 20 minutes, P (He): 107 kPa, T (trap injector): 280°C and T (column head): 280°C. The flow-rate was 10 mL.min⁻¹.

Compounds were injected at 280°C in less than one minute, separated on a gas chromatography column and analyzed by ion trap mass spectrometry.

Separations were on a Varian Star 3400 Cx chromatograph. Chromatographic conditions were a 30°C isotherm for 10 minutes, a 30 to 320°C temperature rise with a gradient of 4°C.min⁻¹ and an 8 minutes isotherm at 320°C. Total analysis time was

90 minutes. The chromatographic column was Delta-3 (Macherey Nagel), 30 m long, internal diameter 250 µm, film thickness 0.25 µm. The mass spectrometer (Varian Saturn GC/MS/MS 4D) was adjusted for an emission current of 12 µA and electron multiplier voltage between 1900 and 2100 V. Trap temperature was 170°C and that of the transfer line was 280°C. Mass scanning was from 20 to 650 amu.

2.2.2 Thermogravimetric Analysis (TGA)

Polymerized resins were studied with a TA Instrument Hi-Res 2950 apparatus. Analyses involved samples weighing about 15 mg in a platinum pan. Analyses were carried out under nitrogen or air at a flow-rate of 90 mL.min⁻¹ in the oven and 10 mL.min⁻¹ on the balance. The gradient of the heat cycles was 5°C.min⁻¹ from 30 to 900°C under air and 30 to 950°C under nitrogen.

2.2.3 Thermogravimetric Analysis Coupled with Infrared Absorption Spectroscopy (TGA/IR)

Thermal diagrams of the resins were recorded with a TA Instrument 2050. Analyses involved samples weighing about 15 mg in a platinum pan. Analyses were carried out under nitrogen or air at a flow-rate of 80 mL.min⁻¹ in the oven and 10 mL.min⁻¹ on the balance. The gradient of the heat cycles was 5°C.min⁻¹ from 30 to 900°C under nitrogen or air. The temperatures of the cell (KBr window) and the transfer line were 250°C.

Infrared spectra were obtained with a Nicolet Nexus equipped with a Globar source (SiC) and Michelson Ge/KBr separator. The detector was an MCT-A (mercury, cadmium, tellurium). Acquisition was with HAPP-GENZEL apodization, accumulation was 16 scans and resolution was 4 cm⁻¹.

2.2.4 Fourier Transform Infrared Absorption Spectroscopy (FTIR)

Infrared absorption spectrometry in transmission mode was carried out with a Nicolet 5SXC equipped with a Globar source (SiC) and Michelson Ge/KBr separator. The detector was a DTGS (deuterated triglycine sulfate). Fourier transform was with HAPP-GENZEL apodization. For analyses, about 1 mg of sample was added to 200 mg of KBr, ground and pressed into a pellet under a pressure of 10 tons. Samples were analyzed at room temperature with an accumulation of 32 scans and a resolution of 4 cm⁻¹.

2.2.5 Solid State Nuclear Magnetic Resonance (Solid State ^{13}C NMR (CP/MAS))

Solid resins were analyzed on a Bruker ARX300 instrument equipped with a cross-polarization/magic angle spinning (CP/MAS) accessory. Samples were ground to a very fine powder and placed in 7 mm diameter ZrO_2 cups. A CP/MAS pulse sequence was used with suppression of side bands. Contact time was 1 ms, the interval between pulses was 4 s and rotation was 4 kHz. About 200 accumulations were necessary to obtain an interpretable spectrum in terms of the S/N ratio. Chemical shifts were recorded with reference to that of glycine carbonyl at 175 ppm (external standard).

3 RESULTS

3.1 Degradation of Resins in an Inert Atmosphere

The degradation of the resins in an inert atmosphere was studied by identifying volatile compounds (by TG/TCT/GC/MS and by TGA/IR) and also by identifying degradation residues (by infrared absorption spectrometry and by solid state ^{13}C NMR (CP/MAS)).

3.1.1 Characterization of Volatile Compounds

3.1.1.1 Degradation of Phenolic Resins Determined by TG/TCT/GC/MS

The TGA study of crosslinked resins was carried out at room temperature and at 950°C (Figure 1). VOC were trapped in the temperature ranges of 30-120°C, 120-200°C, 200-300°C, 300-400°C, 400-500°C, 500-600°C, 600-700°C and 700-850°C.

There were more VOC identified at each temperature range for resins subjected to cycle 1 than cycle 2. The advancement of cross-linking reduces the release of VOC before degradation of the phenolic network. According to the chromatograms obtained after trapping between 25-120°C, 120-200°C and 200-300°C, only traces of compounds were released (Figure 2 and Table 1). The TGA thermograms of resins prepared with cycle 2 exhibited a plateau between 200-300°C, indicating that in this temperature range the phenolic network is very stable. Trapping VOC in the 300-400°C range showed the presence of a large number of compounds (Figure 2), resulting from degradation of the phenolic network. The VOC eluted between 20 and 35 reach a maximum intensity between 400 and 500°C (Figure 2).

Figure 1 TGA diagram of resin S1-cycle 1 obtained in an inert atmosphere (N_2)

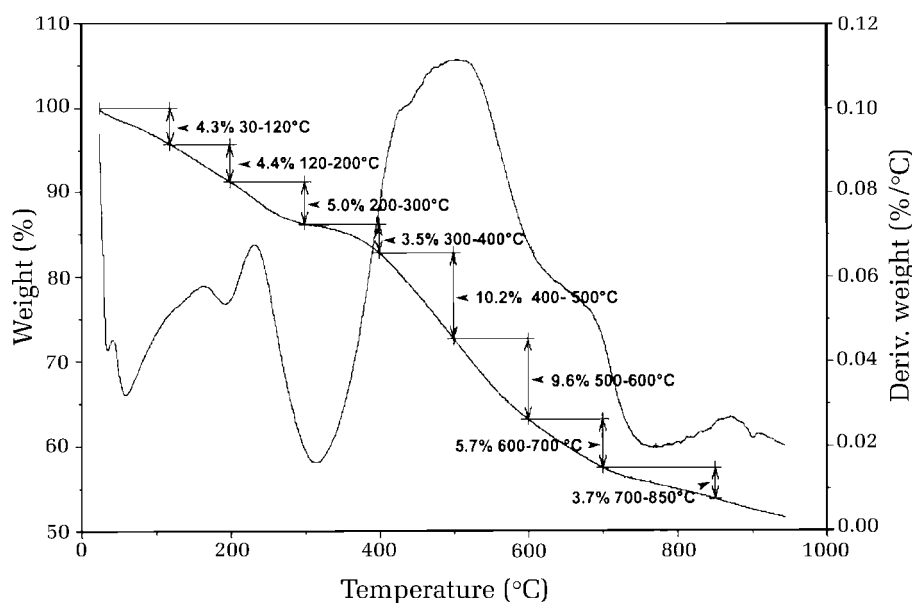


Figure 2 GC/MS chromatograms for different temperature ranges, obtained during the degradation of resin S1-cycle 1 in an inert atmosphere

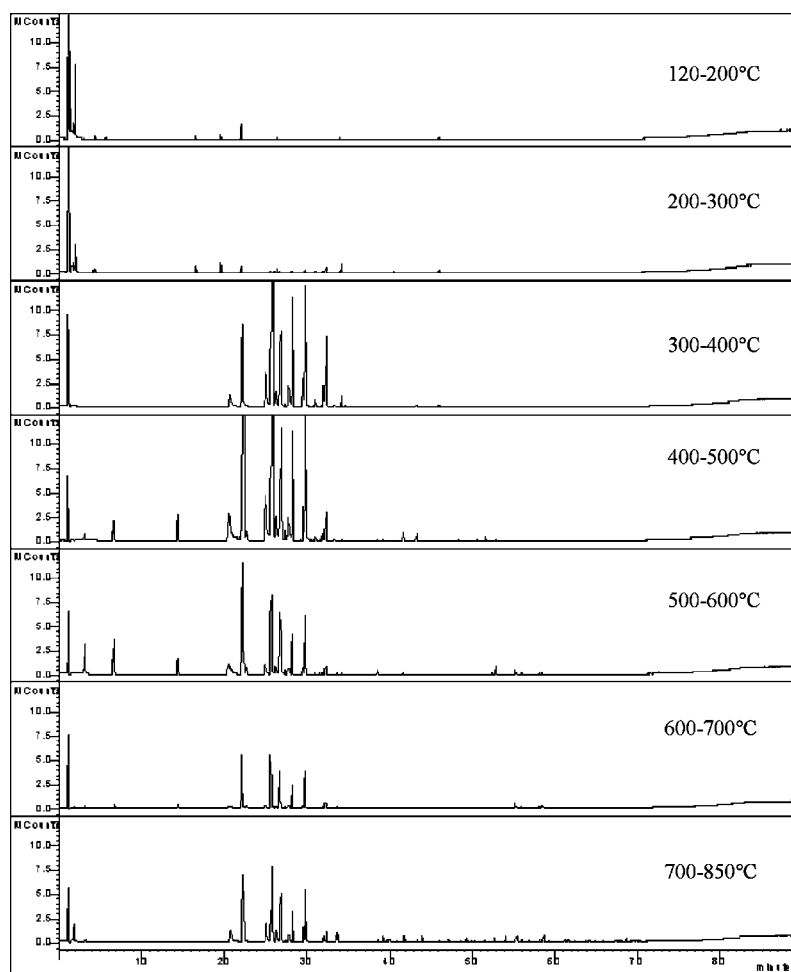


Table 1

TG/TCT/GC/MS attribution of VOC trapped during the degradation of all resins in an inert atmosphere in several temperature ranges (30-120°C, 120-200°C, 200-300°C, 300-400°C, 400-500°C, 500-600°C, 600-700°C and 700-850°C).

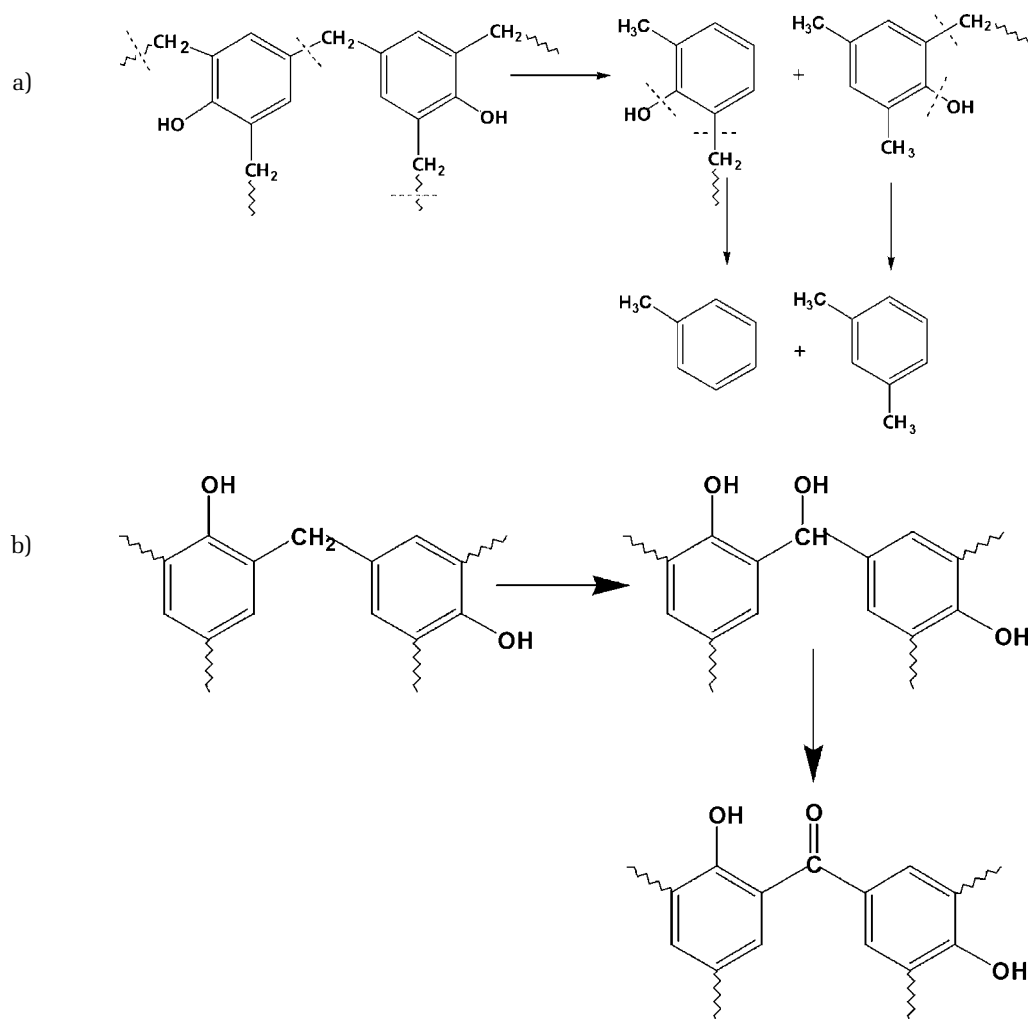
Mass losses recorded by TGA in these temperature ranges confirm these data (Figure 1). In the range of 600-700°C, the intensity of VOC was lower (Figure 2) than between 700 and 850°C. Considerable quantities of polycyclic aromatic hydrocarbons (PAH) (eluted between 38 and 70 minutes) started to appear in the 400-500°C range. Their compositions changed as a function of degradation temperature (Table 1). These PAH reached a maximum (concentration and number of compounds) in the 700-850°C range. Large quantities of toluene and m-xylene formed between 400 and 500°C (Figure 2). Their intensities reached a

maximum between 500 and 600°C and then decreased progressively. These compounds arise from a rupture of methylene bridges, then from phenolic hydroxyl functions (Figure 3a).

Phenol, and mono-, di- and trimethylated phenols were the major compounds released in all the temperature ranges (Table 1).

The study of VOC by TG/TCT/GC/MS was qualitative, and so we can not fully explain the influence of the

Figure 3 (a) Reaction mechanism of rupture at the level of methylene bridges and phenolic hydroxyls. (b) steps in the oxidation of the methylene bridge to carbonyl in an inert atmosphere



preparation conditions of the crosslinked resins (ratio R, type of catalyst and cross-linking heat cycle) on the formation of each of the VOC.

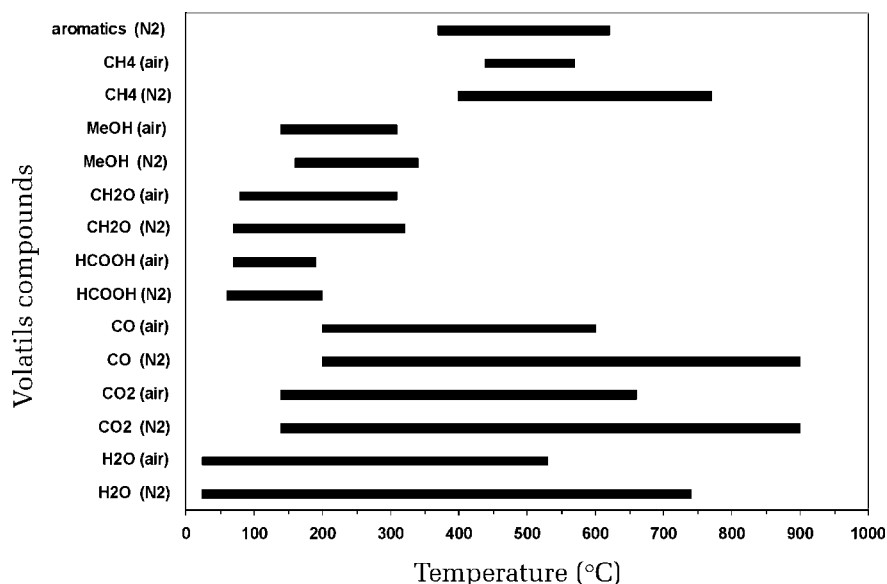
3.1.1.2 Degradation of Phenolic Resins Determined by TGA/IR

The TGA/IR analysis of crosslinked resins enabled the identification of the most volatile low molecular weight compounds (H₂O, CO, CO₂, CH₂O, HCOOH and MeOH).

Water was detected between 25 and 740°C (Figure 4) from all resins. Small quantities were released between 25 and 120°C: this water was chemically adsorbed in the porous network. Between 120 and 380°C, the

quantity of water released depends on the polymerization heat cycle. It arises from condensation between residual hydroxymethyl functions (auto-condensation) and from that between hydroxymethyl and free ortho or para positions, according to mechanisms presented elsewhere¹⁶. The quantity of water released from resins subjected to cycle 2 was very low compared to that of cycle 1. The cross-linking of cycle 1 resins was less advanced. The third phase of water release occurred between 380 and 740°C for all crosslinked resins. Based on TGA analyses, degradation of the phenolic network (rupture of methylene bridges and release of aromatic compounds) occurs around 380°C. As a result, starting at this temperature decomposition of the resins involves the formation of water, a finding confirmed by published data³⁻¹⁵.

Figure 4 Temperature ranges of release in an inert (N_2) and oxidizing atmosphere (air) of volatile compounds from crosslinked resins, analyzed by TGA/IR



The release of formaldehyde depends on the cross-linking heat cycle. The first loss between 70 and 210°C occurred only for resins subjected to cycle 1. It arises from the small quantities of formaldehyde trapped at temperatures $T < 120^\circ\text{C}$ and from transformations of dimethylene ether bridges into methylene bridges. The second loss of formaldehyde was observed for all the resins between 180 and 320°C. Formaldehyde arises from polyoxymethylene chains, oligomer hemiacetals, hemiformals and dimethylene ether bridges that are transformed into methylene bridges.

In most resins, formic acid is released in very small quantities, even none at all from S2-cycle 2 and S4-cycle 2. This compound was released in the 60-200°C range (Figure 4). The loss may result from the oxidation of free formaldehyde.

Methanol was released from all resins between 160 and 340°C (Figure 4). It arises primarily from methanol hemiacetals and methoxyhemiacetals of phenol and oligomers. The network formed from methylene bridges and dimethylene ether bridges does not release methanol in this temperature range. Methanol release is slightly different depending on the cross-linking heat cycle.

Carbon monoxide was released at temperatures higher than 200°C from all phenolic resins (Figure 4). It forms in four temperature ranges. The first loss was minor between 200 and 340°C and may arise from polyoxymethylenes and oligomer hemiacetals. The second, third and fourth losses are in the respective ranges of 340-470°C, 470-700°C and 700-900°C. The quantity of carbon monoxide released was proportional to temperature. Beyond 380°C, the principal source of CO was the degradation of the phenolic network.

Carbon dioxide was released between 140 and 900°C in several steps (Figure 4). CO₂ may have the same origin as CO. The largest quantity of CO₂ is released primarily between 380 and 530°C, i.e. during the degradation of the phenolic network.

Cyclic compounds (aromatic, PAH, etc.) were present between 380 and 620°C in all the resins. TGA/IR coupling did not enable the identification of each of these compounds, in contrast to TG/TCT/GC/MS coupling.

Methane was released between 400 and 770°C from all resins. It arises primarily from the decomposition of methylene bridges.

3.1.2 Characterization of Solid Residues by Fourier Transform Infrared Absorption Spectroscopy (FTIR)

The infrared spectra of degradation residues are highly dependent on the cross-linking heat cycle. All the resins from the same cross-linking cycle present the same spectra. The attribution²⁰ and changes (Table 2) of infrared bands for all the resins are listed in Table 2. Up to 400°C (Figure 5), there is little or no degradation of the network. When the temperature increases, the resins subjected to the two cross-linking heat cycles provide the same infrared spectra. Changes in the composition of residues as a result of heating enable several observations to be made:

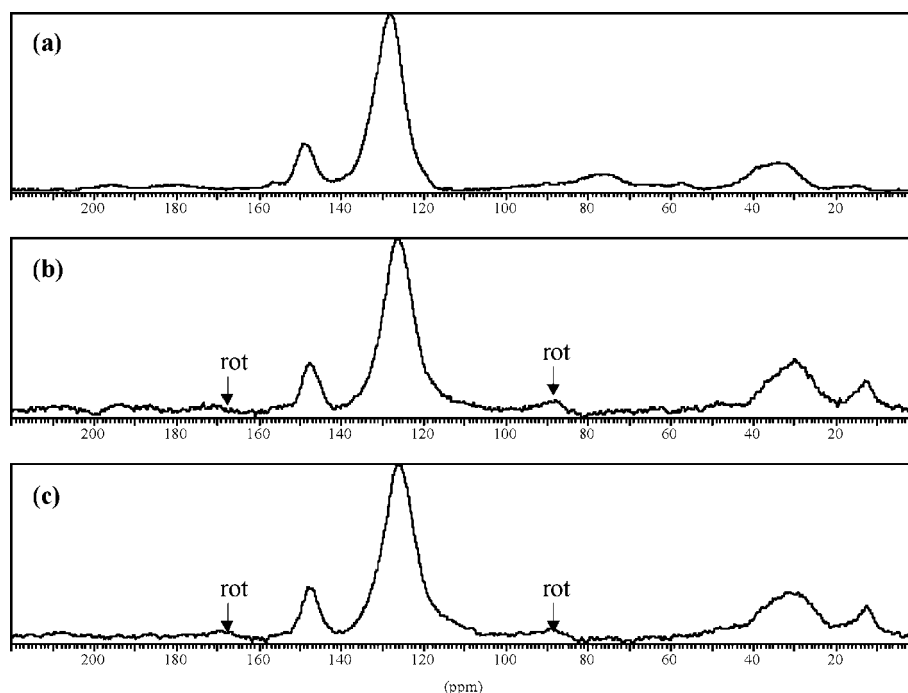
- for all crosslinked resins, the δ_{OH} band around 1355 cm^{-1} of primary alcohols disappears from

the residue at 300°C, resulting from condensations or a release of volatile compounds. This disappearance is concomitant with the decreased intensity of the elongation band of hydroxyls around 3500 cm^{-1} . The latter disappears between 500 and 600°C (Figure 5). Phenolic hydroxyls thus decompose between 300 and 600°C,

- the band between $1100\text{--}950\text{ cm}^{-1}$ ($\nu_{\text{C-O}}$ of primary alcohols and $\nu_{\text{C-O-C}}$ of ethers) disappears essentially at 200°C (S1 and S5) or 300°C (S2, S3, S4 and S6). These differences between resins confirm prior results¹⁸ on the advancement of resins S1 and S5 compared to the others. Changes in this band confirm the continuity of formation of methylene bridges, represented by ν_{CH_2} and δ_{CH_2} bands, that start to degrade between 500 and 600°C,

Table 2
Attribution of infrared frequencies observed in residues of thermal degradation in an inert atmosphere. Residues at 700 and 850°C in an inert atmosphere are carbonized.
*: low intensity band. ↑ increase of the band. ↓ decrease of the band.

Figure 5 Infrared spectra of residues at different temperatures and in different atmospheres: a) S1-cycle 1 heated at 500°C under nitrogen, b) S1-cycle 1 heated at 300°C under air, c) S1-cycle 1 heated at 600°C under nitrogen, d) S1-cycle 1 heated at 400°C under air



- the elongation bands of benzaldehyde carbonyls (1760 , 1730 and 1690 cm^{-1}) appear throughout the heat cycle but with low intensity (Figure 5). The intensity of $\nu_{\text{C=O}}$ around 1650 cm^{-1} , attributable to benzophenone, reaches a maximum¹⁸ around 300°C for cycle 1 (around 200°C for cycle 2) (charge of the methylene bridge into hydroxyl then carbonyl and disappearing around 600°C (Figure 3b)). The formation of carbonyls results from auto-oxidation in an inert atmosphere,
- the $\nu_{\text{C-H}}$ vibration bands of aromatic rings disappear between 600 and 700°C . The bands around 1600 cm^{-1} ($\nu_{\text{C-C}}$) disappear from the residue at 700°C (600°C for S2 and S4),
- the lines of the $1300\text{--}1100\text{ cm}^{-1}$ band form a broad band starting at 600°C , proving that the three-dimensional network is degraded, corresponding to the end of the release of aromatic compounds around 620°C , observed by TGA/IR.

Infrared spectroscopy was used to determine the effect of the ratio R on the composition of structures in the residues. At 120 and 200°C at a high ratio R, all the resins exhibited bands around 1355 and $1100\text{--}950\text{ cm}^{-1}$ (CH_2OH , oxymethylene ethers and dimethylene ether), and were more intense than those with a low ratio R, primarily for resins prepared with LiOH and NaOH.

The effect of the catalyst shows that at a low ratio R, the spectra of the residues from each heat cycle exhibited no differences. This confirms that the resins were cross-linked in the same way at a low ratio R. At a high ratio R, several differences were observed, depending on the valence and size of the hydrated cations of the catalyst.

3.1.2 Characterization of residues by solid state ^{13}C NMR (CP/MAS)

The solid state ^{13}C NMR (CP/MAS) spectra of the residues of crosslinked resins reveal some differences in resin structures. All the lines characteristic of oxymethylenes, dimethylene ether bridges, free ortho and para positions disappeared after heat treatment at 300 and 400°C (Figure 6).

The residues treated at 300 and 400°C exhibited an increase in the quantity of methyl groups (around 15 ppm). We suppose that these methyl groups originated from the rupture of dimethylene ether bridges, yielding methyl and carbonyl³.

A weak intensity line was observed around 47 ppm from residues at 300 and 400°C . We suppose that it corresponds to a tertiary carbon between three aromatic rings obtained during the condensation between a phenolic hydroxyl and a methylene bridge.

The low quantity of carbonyl (185 and 195 ppm) and phenoxy ether bridges (156 ppm) was constant for all crosslinked resins, and also for treatments at 300 and 400°C . Solid state ^{13}C NMR (CP/MAS) spectra of residues at 300 and 400°C contained the same lines, whereas the quantities of VOC released up to 300°C are much lower than those released at 400°C (Figure 2). This shows that between 300 and 400°C , the network retains the same qualitative structure and that VOC arises from ruptures of methylene bridges.

3.1.3 Degradation Reaction Mechanisms of Phenolic Resins

The graphic representation in Figure 4 simplifies attribution of reaction mechanisms. The determination of structures of residues and volatile compounds helps to elucidate the mechanisms.

Methanol, formaldehyde and formic acid were released at temperatures lower than those at which the phenolic network degrades (380°C). In addition to these compounds, CO, CO_2 and water were released before degradation of the phenolic network. All these compounds arise from small quantities of polyoxymethylenes, oligomer hemiacetals and oligomer methoxyhemiacetals according to the mechanism shown in Figure 7a.

Degradation of the phenolic network starts with the rupture of methylene bridges. Among the compounds formed during this degradation are methylated phenols, substituted benzenes, methane, water, CO_2 and CO (Figure 7b). Carbonyl compounds form from auto-oxidation of hydroxymethyls in the inert atmosphere (structures **17**, **20** and **23**) and of the methylene bridge (structures **33**, **35**, **36** and **39**) (Table 1). Naphthalene compounds (structures **14**, **18**, **27**, **34**, **37**, **38**, **40**, **41**, **42** and **43**) form primarily at temperatures higher than 400°C according to the mechanism in Figure 7c. Release of H_2 has been reported in prior work^{3,7,8}. Intramolecular rearrangements may occur, forming certain compounds containing ether bridges by the release of one molecule of dihydrogen (Figure 7d) (structures **25**, **28**, **30**, **36**, **39**, **42** and **43**).

Figure 6 Solid state ^{13}C NMR (CP/MAS) spectra of resins treated at different temperatures in an inert atmosphere: (a) S1-cycle 2, (b) S1-cycle 2 heated at 300°C ($5^\circ\text{C}.\text{min}^{-1}$), (c) S1-cycle 2 heated at 400°C ($5^\circ\text{C}.\text{min}^{-1}$), Rot: lateral rotation band

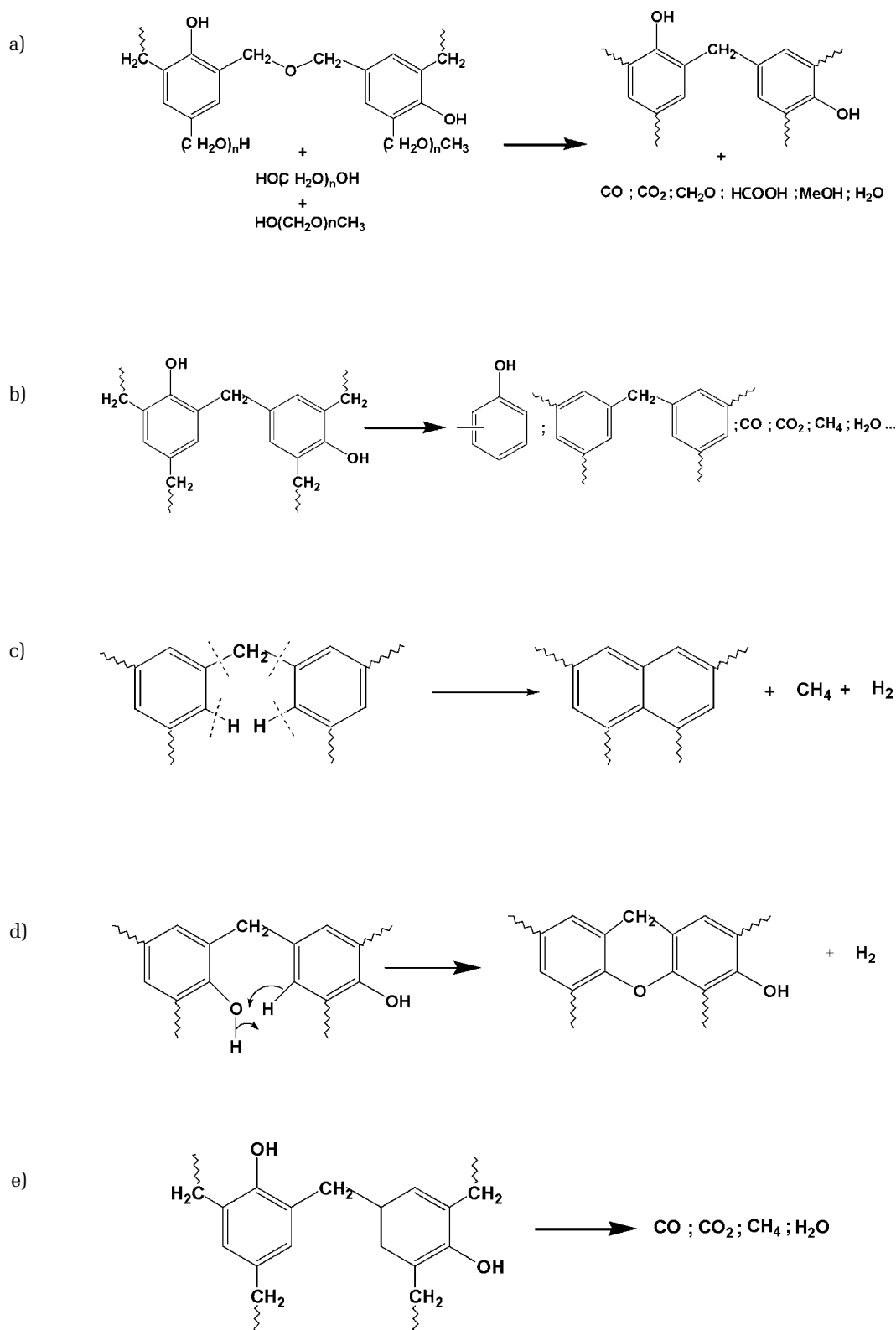
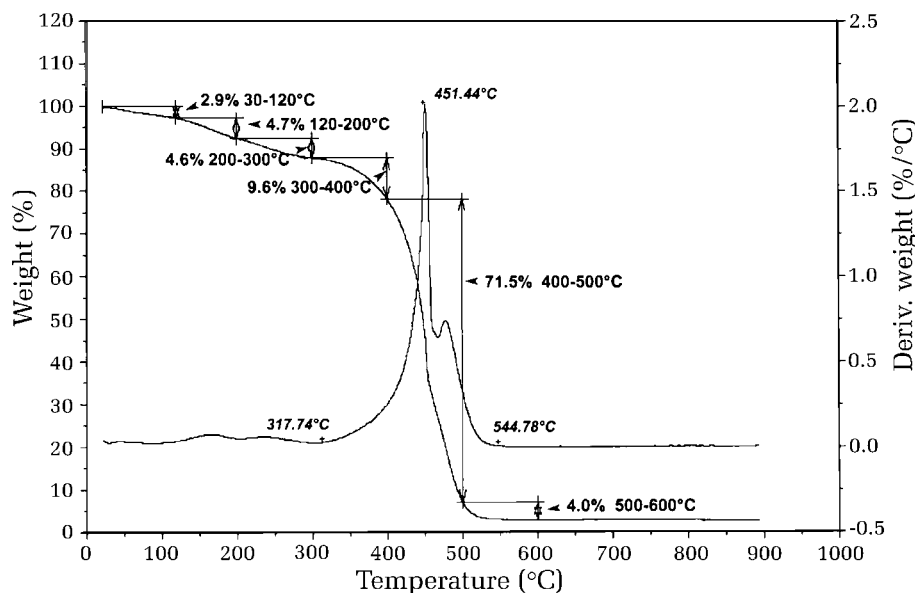


Figure 7 Mechanism of degradation of phenolic resins; (a) in both atmospheres before degradation of the phenolic network, (b) in an inert atmosphere after degradation of the phenolic network, (c) in an inert atmosphere with release of hydrogen and PAH, composed of naphthalene, (d) formation of the ether bridge according to an intramolecular mechanism, (e) in an oxidizing atmosphere after degradation of the phenolic network



The structures of degradation residues identified by infrared spectroscopy and solid state ^{13}C NMR (CP/MAS) confirm that degradation of the three-dimensional network starts by the rupture of methylene bridges, followed by breaks in phenolic functions and finally the formation of the polyaromatic network (Figure 5).

3.2 Degradation of Resins in an Oxidizing Atmosphere

3.2.1 Characterization of Volatile Compounds

3.2.1.1 Degradation of Phenolic Resins Determined by TG/TCT/GC/MS

The major pathway for thermal decomposition of the material is oxidation in air, leading to the total and rapid destruction of the phenolic and polyaromatic networks. According to the shape of the TGA thermograms, the onset of degradation occurs around 380°C and the loss of mass is total at 600°C (Figure 8). The greatest loss ($\approx 70\%$) occurs between 400 and 500°C. Before this total destruction, mass losses are low until 300°C, proving that the resin is rigid up to this temperature in either atmosphere. TG/TCT/GC/MS analysis of samples from degradation in air in the

selected temperature ranges shows only several compounds in small quantities (traces). This shows that degradation in air yields primarily low molecular weight compounds.

3.2.1.2 Degradation of phenolic resins determined by TGA/IR

Changes in each volatile compound were followed by TGA/IR during degradation of all resins in air (Figure 4). Water was released between room temperature and 530°C (Figure 4) and the quantity released depends on the cross-linking cycle of the resin. All resins release water in two steps. The first, between room temperature and 130°C, corresponds to small quantities of chemically bound or adsorbed water. The second step, between 130 and 530°C, is the departure of compounds of the condensation residue ($130^\circ\text{C} < T < 180^\circ\text{C}$), followed by the degradation of polyoxymethylenes, oligomer hemiacetals and the phenolic network ($T > 180^\circ\text{C}$). In the case of cycle 2 resins, the departure of water is very low between 130 and 180°C in comparison to cycle 1 resins. This confirms the influence of cross-linking advancement on the departure of water in the course of degradation.

The loss of formaldehyde depends on the polymerization heat cycle (Figure 9). It occurs in two steps for cycle 1 resins: 80-200°C and 200-310°C. Resins from cycle 2 exhibit a small loss of formaldehyde between 120 and 200°C, increasing between 200 and 310°C (Figure 9). The origin of formaldehyde is the same as that occurring in the inert atmosphere.

Formic acid was released in only very small quantities between 70 and 190°C for S3-cycle 1 and S1-cycle resins². Its presence was not constant and its formation may have been due to the oxidation of formaldehyde trapped in the resin.

Figure 8 TGA thermogram of resin S1-cycle 1 obtained in an oxidizing atmosphere (air)

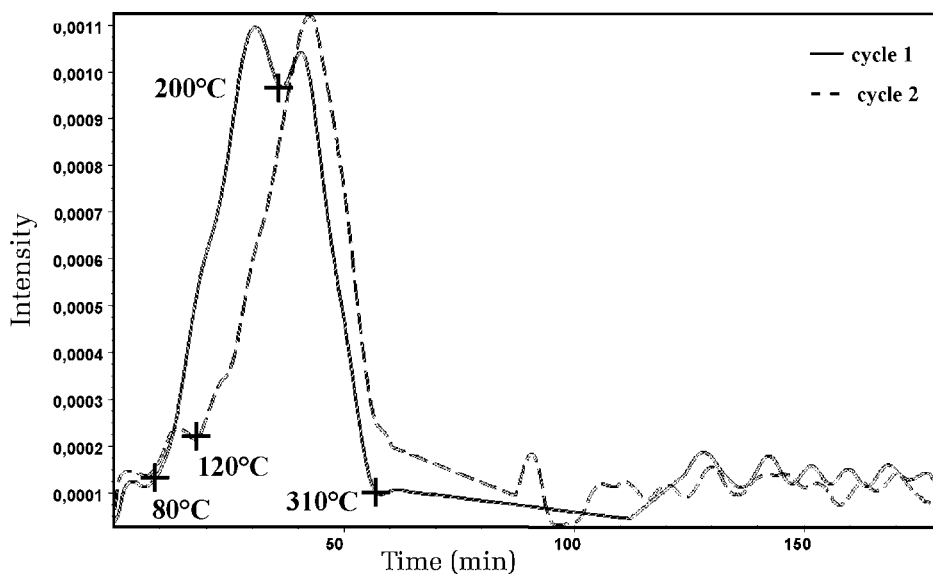


Figure 9 Infrared chemigrams at 1744 cm⁻¹ (TGA/IR) of formaldehyde release during the degradation of resins S1-cycle 1 and S1-cycle 2 in an oxidizing atmosphere (air)

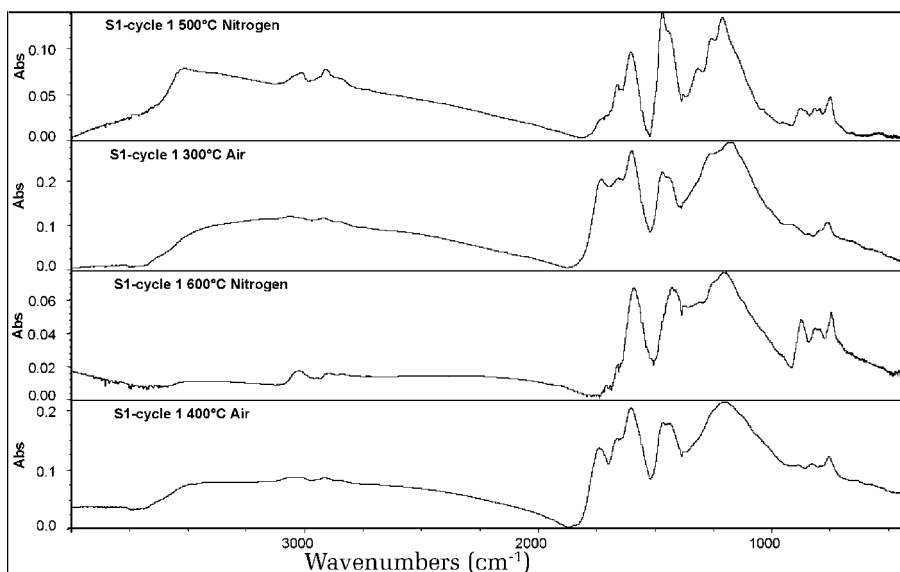


Table 3

Attribution of infrared frequencies observed in residues of thermal degradation in an oxidizing atmosphere.

*: low intensity band. ↑ increase of the band. ↓ decrease of the band

Methanol was released between 60 and 310°C (Figure 4). Between 60 and 160°C, the small quantities corresponded to residual methanol of the formaldehyde solution in the resin. The second loss was between 140 and 310°C (Figure 4) and had the same origin as in the inert atmosphere (methoxyhemiacetals of phenol and oligomers).

Carbon monoxide was lost between 200 and 600°C (100% of mass lost) (Figure 4), with small quantities between 200 and 320°C. The formation of this compound is activated by the oxidizing atmosphere. Between 320 and 600°C, CO formation increased. It arises from the decomposition of the phenolic network.

Carbon dioxide was the compound formed in the largest quantity in the oxidizing atmosphere, with release occurring between 140 and 660°C (Figure 4). A little CO₂ was released in the 140-350°C range, and then increased rapidly up to 600°C. It arises primarily from the oxidation of the phenolic network by atmospheric oxygen.

Aromatic compounds were not detected in the oxidizing atmosphere because of their decomposition. Nevertheless, the more sensitive TG/TCT/GC/MS analysis enabled traces of aromatic compounds to be identified.

Methane was released in a lower temperature range than in the inert atmosphere. Release started around 440°C and terminate around 570°C.

3.2.2 Characterization of Solid Residues by Fourier Transform Infrared Absorption Spectroscopy (FTIR)

FTIR was used to analyze solid residues (120, 200, 300 and 400°C) in the oxidizing atmosphere (Table 3). Degradation was more rapid than in the inert atmosphere (Figure 5).

The intensity of elongation (3500 cm⁻¹) and deformation bands (around 1355 cm⁻¹) of hydroxyl of

primary alcohols decreased as the temperature increased, disappearing between 200 and 300°C.

The bands around 2950-2820 cm⁻¹ (aliphatic ν_{CH_2}) and around 1100-950 cm⁻¹ (ν_{C-O} of primary alcohols and ν_{C-O-C} of ethers) disappeared between 300 and 400°C. This confirms the activation of network degradation by atmospheric oxygen.

Lines of the broad band between 1300 and 1100 cm⁻¹ lost their resolution after 300°C, showing the transformation of the network into a polyaromatic system (Figure 5). Aromatic ν_{C-H} (3005 cm⁻¹) disappeared beyond 400°C.

The formation and disappearance of carbonyls in the oxidizing atmosphere is activated by atmospheric oxygen. Larger quantities of carbonyls are formed in air than in nitrogen (Figure 5).

3.2.3 Degradation Reaction Mechanisms of Phenolic Resins

In the same way as in the inert atmosphere, reaction mechanisms are proposed before and after degradation of the phenolic network. Between room temperature and 300°C, results in the oxidizing atmosphere show that the general mechanism is the same as in the inert atmosphere (Figure 7-a). Only the quantities of compounds released could differ between the two atmospheres.

When the phenolic network degrades, CH₄, CO, CO₂ and H₂O are released. The degradation mechanism of the phenolic network leads primarily to the formation of CO₂ (Figure 7e) in the absence of cyclic compounds.

4. CONCLUSIONS

In order to determine the stability of resins, we examined their thermal degradation in controlled atmospheres. The structures of gaseous products released and of degradation residues show that they depend on the degradation atmosphere, temperature

and the conditions in which the crosslinked resins were prepared.

In the case of thermal degradation in an inert atmosphere, cyclic compounds (aromatic, PAH, etc.) and low molecular weight compounds (CO₂, CO, H₂O, HCOOH and MeOH) form. In the case of degradation in an oxidizing atmosphere, cyclic compounds are negligible, while large quantities of low molecular weight compounds are released. Formaldehyde is released in both atmospheres. Less formaldehyde is released by resins prepared with cycle 2.

The analysis of degradation residues proves that these resins exhibit good thermal stability up to 300°C in an oxidizing atmosphere and up to 380°C in an inert atmosphere.

REFERENCES

1. Knop A. and Pilato L.A., "Phenolic Resins", Springer-Verlag Berlin Heidelberg, New York (1985)
2. Gardziella A., Pilato L.A. and Knop A., "Phenolic Resins", Springer-Verlag Berlin Heidelberg, New York (1999)
3. Costa L., Montelera L.R.D., Camino G., Weil E.D. and Pearce E.M., *Polymer Degradation and Stability*, **56**, (1997) 23
4. Trick K. A. and Saliba T.E., *Carbon* **33**, **11**, (1995) 1509
5. Shafizadeh J.E., Guionnet S., Tillman M.S. and Seferis J.C., *Journal of Applied Polymer Science*, **73**, (1999), 505
6. Ozaki J.I., Ohizumi W. and Oya A., *Letters to the editor/carbon*, **38**, (2000), 1499
7. Morterra C. and Low M.J.D., *Carbon*, **23**, (1985) 525
8. Blazso M., *Journal of Analytical and Applied Pyrolysis*, **25**, (1993), 25
9. Grenier-Loustalot, M.F., Raffin G., Salino B. and Païssé O., *Polymer*, **41**, (2000), 7123
10. Campbell J.H., *Fuel*, **57**, (1978), April 217
11. Blazso M. and Toth T., *Journal of Analytical and Applied Pyrolysis*, **19**, (1991) 251-263
12. Rama Rao M., Alwan S., Scariah K.J. and Sastri K.S., *Journal of Thermal Analysis*, **49**, (1997), 261
13. Alajbeg Andja., *Journal of Analytical and Applied Pyrolysis*, **9**, (1986), 255
14. Blazso M., *Journal of Analytical and Applied Pyrolysis*, **10**, (1986), 41
15. Lenghaus K.; Qiao G.G. and Solomon D.H., *Polymer*, **42**, (2001), 3355
16. Bouajila J., Raffin G., Waton H., Sanglar C., Païsse O. and Grenier-Loustalot M.F., *Polymers & Polymer Composites*, **10**, **5** (2002), 341
17. Bouajila J., Raffin G., Waton H., Sanglar C., Païsse O. and Grenier-Loustalot M.F., *Polymers & Polymer Composites*, 2002 (accepted)
18. Bouajila J., Raffin G., Waton H., Sanglar C., Alamerçery S. and Grenier-Loustalot M.F., *Polymers & Polymer Composites*, 2002 (submitted for publication)
19. Larroque S., Thèse « Mécanismes et cinétiques de polymérisation de systèmes Phénol/Formaldéhyde – Etudes spectroscopique et chromatographique ». Université de Pau et des Pays de l'Adour, Septembre, (1994) France
20. Socrates G., *Infrared Characteristic Group Frequencies*, John Wiley & Sons, Chichester, New York, Brisbane, Toronto (1980)

