

Chapter 16

Flammability Properties of Honeycomb Composites and Phenol-Formaldehyde Resins

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The flammability properties of honeycomb composites, which are used in the interior cabin compartments of commercial aircraft, were examined. Analyses of the gases evolved during the thermal degradation of the components indicated that the phenol-formaldehyde resin makes a significant contribution to the flammability of these composites. The possibility that a more fire resistant formulation could be developed was examined by testing a series of resins which differed in the relative amounts of phenol and formaldehyde used in the reaction mixtures. The flammabilities of resins synthesized in excess phenol were measurably less than those synthesized in excess formaldehyde.

The burning of most polymers may be viewed from the perspective of a simple model whereby volatile hydrocarbons, which are formed during the thermal degradation of the condensed phase, are combusted in the gas phase. The basis of this model is the hypothesis that all of the available oxygen is depleted in the flames above the surface of the solid. The cycle must be initiated by heat supplied from an external source, but it is self-sustaining as long as the combustion process generates sufficient energy to further degrade the polymer into fuel. The size of the fire is measured by the net rate-of-heat released (rhr) during this process.

The distinction between the thermal degradation and gas phase combustion steps is blurred in the case of polymers, such as phenol formaldehyde (PF) resins, which contain significant amounts of covalently bound oxygen. This can effect a reduction in flammability because less heat is released during burning if the polymer has already been partially oxidized.

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Furthermore, the oxidation reactions which are responsible for the heat release, are much faster when they occur in the gas phase so that the rhr will be reduced in proportion to the fraction of hydrocarbon which is oxidized in the condensed phase. Finally, the processes involved in condensed phase oxidation also promote the formation of char (1) which provides additional fire resistance by further reducing the amount of fuel available for gas phase combustion (2).

The focus of the present investigation is on PF resins which are known to have a propensity to condensed phase oxidation and char formation. PF resins are found in plywood and other fiber based composites used in the construction of buildings, aircraft and ships. Improvements in the flammability performance of these materials is desirable for certain fire-sensitive applications, such as, in the honeycomb panels used in the sidewalls, ceilings and stowage bins of commercial aircraft.

Experimental

A. Honeycomb Composites

A composite material consisting of nomex honeycomb, fiber backing, and phenol-formaldehyde resin was obtained from the Federal Aviation Administration Technical Center. This material was identified by the code TP4/92. The original square panels were cut into circular disks with an outer diameter of 7.5 cm which was deemed most suitable for the Cone Calorimeter flammability measurements.

B. Synthetic Resins

The method used in synthesizing the PF resins is described in detail in reference 3. Reaction mixtures consisting of 0.5, 1.0 and 2.0 moles of formaldehyde (37% solution, ACS Reagent, Sigma) per mole of phenol (ACS Reagent, Sigma) were refluxed in 15 ml of 5N NaOH (ACS Reagent, Fisher) at 130 °C for approximately 2 hours. The prepolymer was washed in H₂O to remove excess salts and dehydrated by heating at 100 °C. Most of the samples were cured in air at 150 °C for 72 hours. In some cases, the resins were synthesized and cured in a N₂ atmosphere. This precaution, however, did not have an obvious effect on the distribution of products observed during thermal degradation.

C. Measurement Techniques

The NIST Cone Calorimeter was used to make all flammability measurements. This instrument measures a number of combustion-related properties including rhr and is the basis for an ASTM test method (E1354-90a) (4). Samples (~50g) were placed in a Pyrex dish and exposed to a heat flux of 50 kW/m². A high voltage arc was placed above the samples to ignite the off-gases.

Thermogravimetric analyses (TGA) were performed in a N₂ atmosphere using a Perkin-Elmer 7 Series Thermal Analysis System (Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure. Such identification does not imply that the material or equipment identified is necessarily the best available for the purpose.). The samples, which weighed approximately 1 mg at the onset of the experiments, were heated from 30 to 800 °C at a rate of 10 °C/min.

Infrared analyses of the evolved gases (FTIR-EGA) were performed using a gas cell with a 10 cm path length and programmable paralyzer manufactured by Chemical Data Systems Instruments. Samples, ranging from about 10-20 mg in mass, were placed in a quartz tube which was surrounded by a resistance heating element. This assembly was inserted into the IR cell which was purged with N₂ and heated either isothermally at a series of temperatures between 800 and 850 °C or dynamically from 25 to 1000 °C at a rate of 50 °C/min. The progress of the pyrolysis was monitored every 5 seconds for the kinetics measurements and every 20 seconds in the dynamic heating experiments. The spectra were collected on a Mattson Galaxy 7000 Series FTIR at a resolution of 2 cm⁻¹.

The ^{13}C nuclear magnetic resonance (NMR) spectra were measured using the cross polarization (CP)/magic angle spinning (MAS) technique (5) at 25.193 MHz in a static field of 2.354 T. The spectra were acquired at a spinning rate of 4 kHz with contact and repetition times of 1 ms and 3 s, respectively.

Results and Discussion

A. Honeycomb Composites

The rhr from a sample of honeycomb composite exposed to an incident flux of 50 kW/m^2 is displayed as a function of burn time in Figure 1 (upper curve). Initially, these composites burn with a yellow luminous flame indicative of the presence of soot. This appears as a distinct peak in the rhr curve centered at about 45 seconds. The luminosity disappears about 15 seconds later giving way to an unstable blue flame which is associated with fluorescent emissions accompanying the oxidation of CO. The composites usually continue to smolder long after the flame disappears. This effect is indicated by the tail in the rhr curve which extends from about 70 seconds. The lower curve in Figure 1 is the rhr from a sample taken from the same panel which was heated in an oven overnight at 250°C before it was burned. The thermograms of the resin taken before (Figure 2) and after (Figure 3) the heat treatment exhibit differences in the region between 500 and 575°C . A comparison of the FTIR-EGA spectra of these resins is even more revealing (Figure 4). The peaks centered at about 1300 and 3000 cm^{-1} , which are most prominent in the spectrum of the untreated resin, are due to CH_4 . The FTIR-EGA spectra obtained from the components of treated (Figure 5) and untreated (Figure 6) composites indicate that much higher levels of CH_4 are generated from the degradation of the resin than from the fiber backing or honeycomb.

Thus, there is a correlation between the amount of CH_4 produced in the thermal degradation of the resin and the rhr of the composite. On this basis, it seems clear that any attempt to improve the fire resistance of honeycomb composites should begin with an examination of the flammability properties of PF resins.

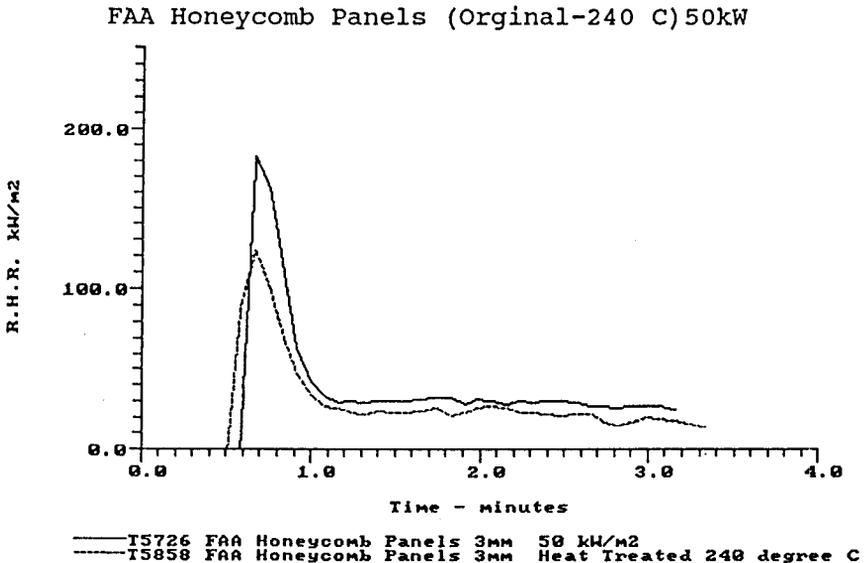


Figure 1. Comparison of rhr curves obtained by burning honeycomb composite material before (upper) and after the heat treatment.

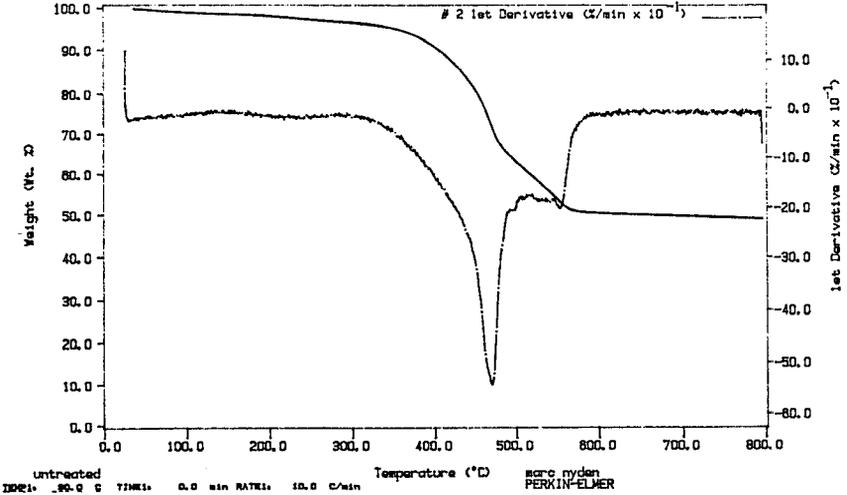


Figure 2. Thermograms of resin taken from an untreated panel.

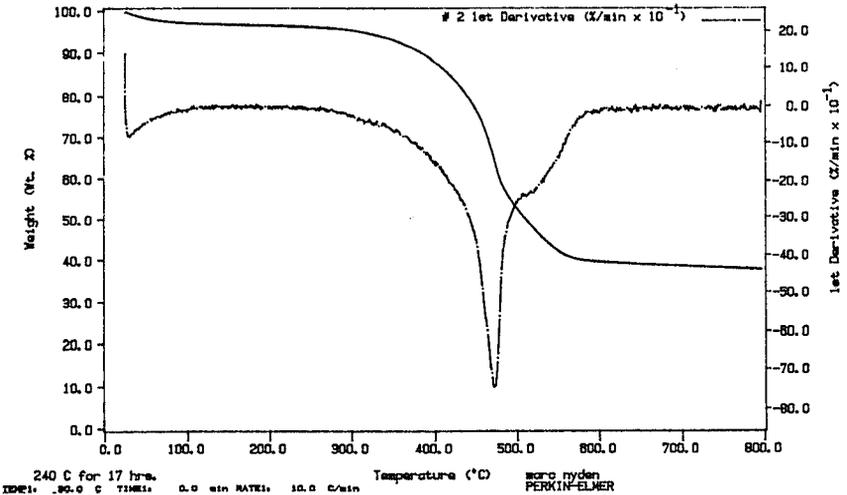


Figure 3. Thermograms of resin taken from a heat treated panel.

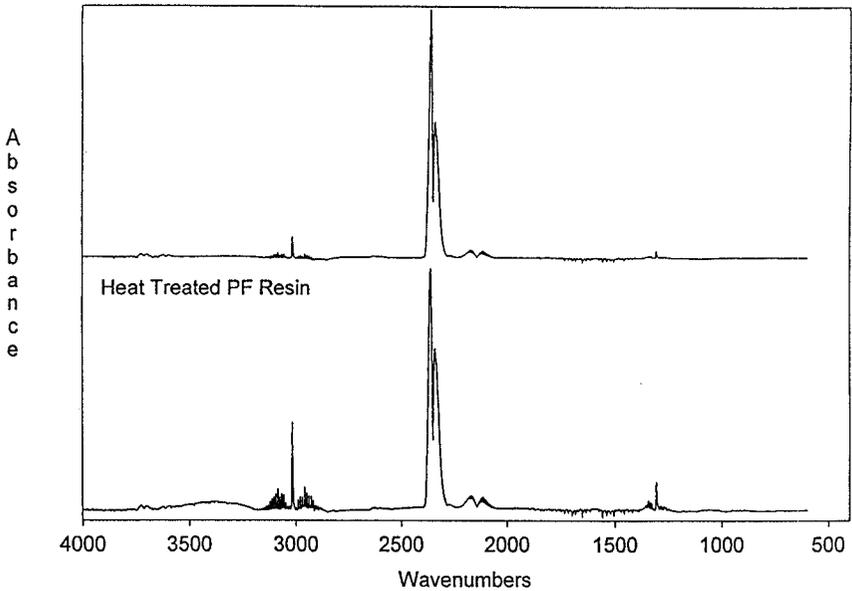


Figure 4. Comparison of FTIR-EGA spectra taken from heat treated (upper) and untreated panels.

B. Synthetic Resins

The base catalyzed reaction of phenol with formaldehyde produces stable hydroxymethylphenol intermediates which condense into branched polymers (resoles) at temperatures of between 60 and 100 °C (6). Further condensation of methylol groups occur during the curing process resulting in the formation of highly crosslinked network polymers. Methylene bridges, which are produced in head-to-tail interactions between methylphenols, are thermodynamically favored over ether linkages (7) which form when methylphenols are aligned in a head-to-head configuration or from condensation of methylphenols with phenol itself. An investigation of the degradation properties of PF resins was conducted by Conley and coworkers (7-10). They concluded that the primary degradation pathway for PF resins is oxidative in nature even in an oxygen deficient atmosphere and that thermal processes only begin to compete at higher temperatures. The spectra obtained in dynamic FTIR-EGA experiments indicate that H₂O, CO₂ and CH₃OH are evolved in the degradation of PF resins in N₂ at temperatures as low as 250 °C (Figure 7). The presence of CO is first detected at about 350 °C, while CH₄, which is the major volatile product from the thermal degradation of the resin, is evident only at temperatures above 550 °C.

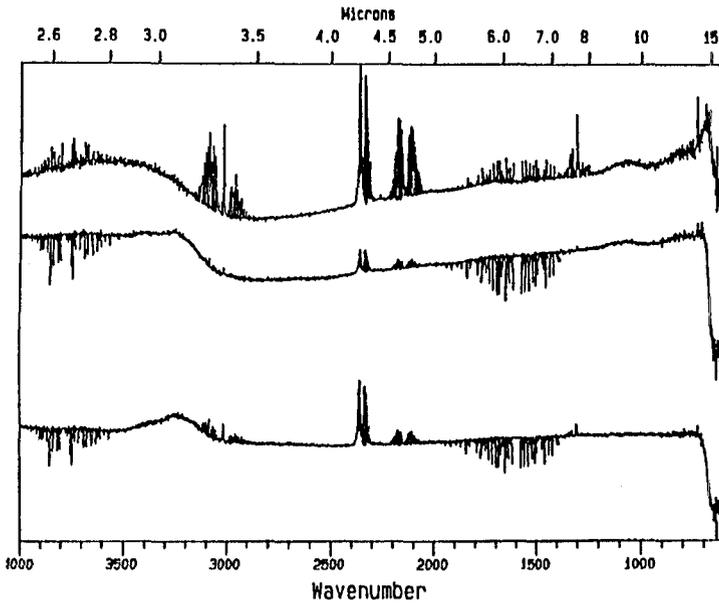


Figure 5. Comparison of FTIR-EGA spectra (1000 °C) of the honeycomb (lower), fiber backing (middle), and resin (upper) taken from an untreated panel.

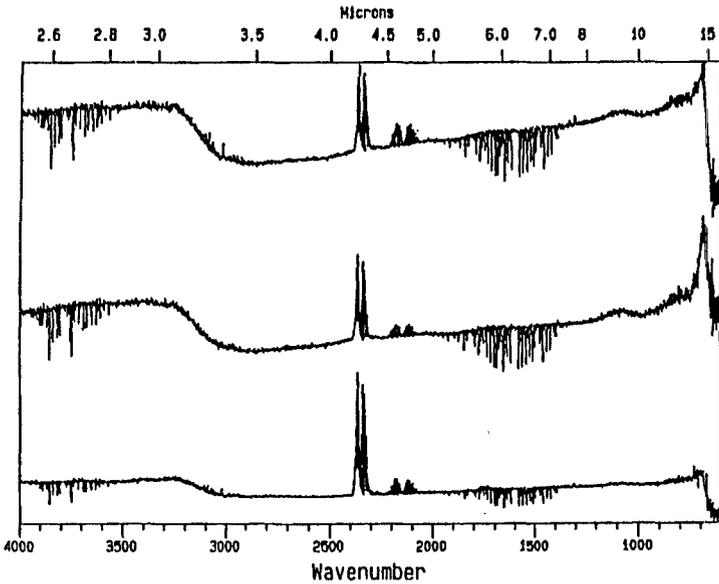


Figure 6. Comparison of FTIR-EGA spectra (1000 °C) of the honeycomb (lower), fiber backing (middle), and resin (upper) taken from a treated panel.

The rate constants (k) for the formation of CO_2 and CH_4 are reported in Table I. These values were determined by integrating characteristic peaks in the FTIR-EGA spectra measured under isothermal conditions for temperatures between 800 and 850 °C in accordance with the following model for first order thermal degradation of the polymer:

$$\ln\left(1 - \frac{[\alpha]_t}{[\alpha]_\infty}\right) = -kt.$$

In this equation, $[\alpha]_t$ denotes the integrated absorbance of either product at time t and $[\alpha]_\infty$ is the asymptotic value which is attained in the limit as $t \rightarrow \infty$. The global activation energies for CO_2 and CH_4 are 59 ± 13 and 180 ± 33 kJ/mol, respectively.

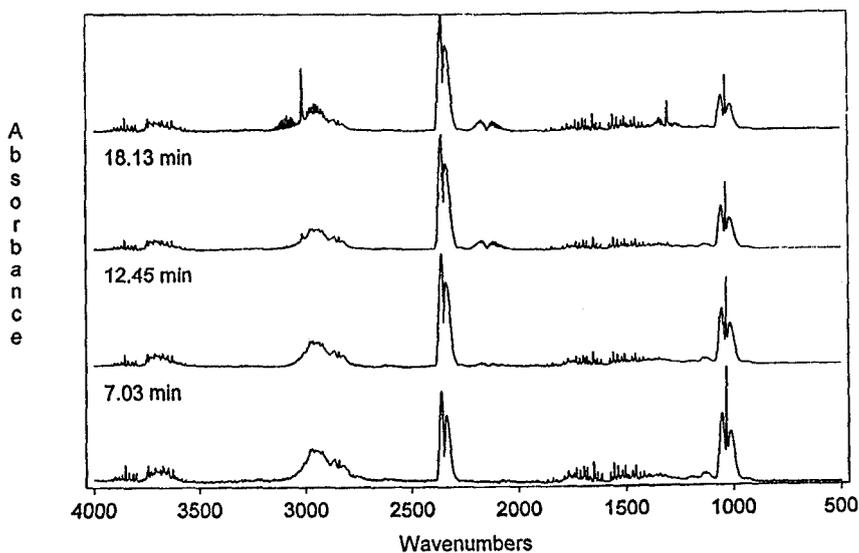


Figure 7. FTIR-EGA spectra of PF resin at 250 (bottom), 375 (7.03 min), 650 (12.45 min) and 930 °C (18.13 min).

Compound	Rate Constants (s^{-1}) for the Formation of CO_2 and CH_4		
	Temperature (°C)		
	800	825	850
CO_2	0.090 ± 0.005	0.093 ± 0.030	0.095 ± 0.012
CH_4	0.058 ± 0.003	0.068 ± 0.003	0.073 ± 0.008

A mechanism has been advanced for the formation of CO and CO₂ during the oxidative degradation of PF resins. According to Conley (7), the first step is the conversion of methylene bridges into carbonyl linkages. The resulting benzophenones can either undergo thermal scission to produce CO or further oxidation resulting in the formation of benzoates which then release CO₂ in decarboxylation reactions. The evidence for this mechanism is compelling, however, the extension to oxygen deficient atmospheres, which will be the prevailing condition at the surface of burning polymers, is questionable. The postulate that the CH₄ comes from the thermal scission of methylene bridges is also suspect since this bond is known to be exceptionally strong. The bond dissociation enthalpy, based on the difference between the measured heats of formation of diphenylmethane (11) and the benzyl (12) and phenyl (13) radicals, is 389 kJ/mol. In fact, a simple mechanism whereby the methylphenol condensation process is reversed at elevated temperatures in the presence of residual H₂O can account for the evolution of all of the major volatile products. The CH₂O, which is released during the depolymerization of the resin, is known to produce CH₃OH and CO₂ via the Cannizzaro reaction, while the formation of CH₄ from rearrangement of hemiacetal intermediates also seems likely; at least at the elevated temperatures considered in this study.

As is the case with many polymers, the flammability properties of PF resins will depend on how they are prepared and cured. The range of possibilities was explored by comparing flammability performance of cured and uncured resins synthesized from reaction mixtures containing different proportions of the two monomers. The results of the Cone Calorimeter measurements, which are reported in Table II, indicate that flammability increases with increasing mole fraction of formaldehyde in the reaction mixture and that the cured resins are significantly less flammable than the uncured resins. The difficulties involved in preparing large samples with uniform properties precluded the possibility of performing a rigorous uncertainty analysis based on duplicate measurements. The trends, however, are unambiguous. Indeed, the high levels of char and low heat release rates exhibited by the 2:1 resins are remarkable, considering the high flux of incident radiation used in these tests.

The relative amounts of CO₂, CH₃OH and CH₄ produced in the thermal degradation of the resins in N₂ were estimated from characteristic peaks in the steady-state FTIR-EGA spectra measured at 800 °C. The values obtained by dividing the integrated absorbance of the characteristic peak by the initial mass of the sample are listed in Table III. The CH₃OH data follow the trends observed in the flammability performance of the resins in that the highest levels were observed in the most flammable resins. This is not true in the case of CO₂. Although the concentration of CO₂ decreases with increasing phenol content, the highest levels were observed in the thermal degradation of the less flammable cured resins. There is some indication that the evolution of CH₄ may follow a similar trend. Unfortunately, the uncertainty in these measurements is too large to make a definitive statement. The variations between different samples of the same resin, which approached 50% of the measured values, were of the same order of magnitude as were the variations between the samples taken from different resins.

The ¹³C CP/MAS spectra of the cured resins are displayed in Figure (8). The peak assignments, which were made using a computer program (14), were consistent with previously published data on phenol-formaldehyde resins (15,16). The integrated intensity of each peak, which is proportional to the number of carbon atoms corresponding to the specified assignment, is listed in Table IV. Not all of the peaks were well resolved. In some cases, the contribution of the components had to be estimated by inspection. These values are indicated by an asterisks.

These spectra indicate structural differences between the resins which are consistent with the Cone Calorimeter data. In particular, the ratio of aromatic to aliphatic carbons is highest in the least flammable (2:1) resin. The two weak resonances centered at about 57 and 75 ppm, which are discernible in the spectra of both the 1:2 and the 1:1 resins, are indicative of the presence of aliphatic OH. This is a likely source of the CH₃OH which was detected during pyrolysis of these resins. Indeed, the 2:1 resin also appears to contain significantly less aromatic OH as evinced by a reduction in the intensity of the resonance due to phenolic OH at 152 ppm.

Moles of P:F	Mass of Sample (g)	Time to Ignition (s)	Peak RHR (kW/m ²)	Total Heat (MJ/m ²)	Residue (%)
1:2 (uncured)	45.2	124	213	113	49.8
1:2 (cured)	66.3	102	174	23	76.6
1:1 (uncured)	42.2	422	164	148	44.8
2:1 (uncured)	45.0	44	116	10	93.9
2:1 (cured)	66.3	59	79	5	95.1

Moles of P:F	Uncured	Cured
CH ₄ (1295-1310 cm ⁻¹)		
1:2	14	29
1:1	26	27
2:1	14	20
CH ₃ OH (970-1085 cm ⁻¹)		
1:2	373	149
1:1	157	44
2:1	71	12
CO ₂ (2285-2390 cm ⁻¹)		
1:2	1278	2143
1:1	1053	1489
2:1	232	326

* Values normalized by dividing by the initial mass of the sample.

Assignment/ P:F Ratio	C(ar)-O-C(ar) 160-180 ppm	C(ar)-OH 152 ppm	C(ar) 130 ppm	-OCH ₂ 55-80 ppm	CH ₂ 15 ppm	ar:al Ratio
1:2	3.0	11.2	60.5	4.1	4.3	3.0
1:1	2.3*	9.1*	61.6	3.0	2.4	3.1
2:1	8.7*	8.7*	58.8	0.0	2.6	3.4

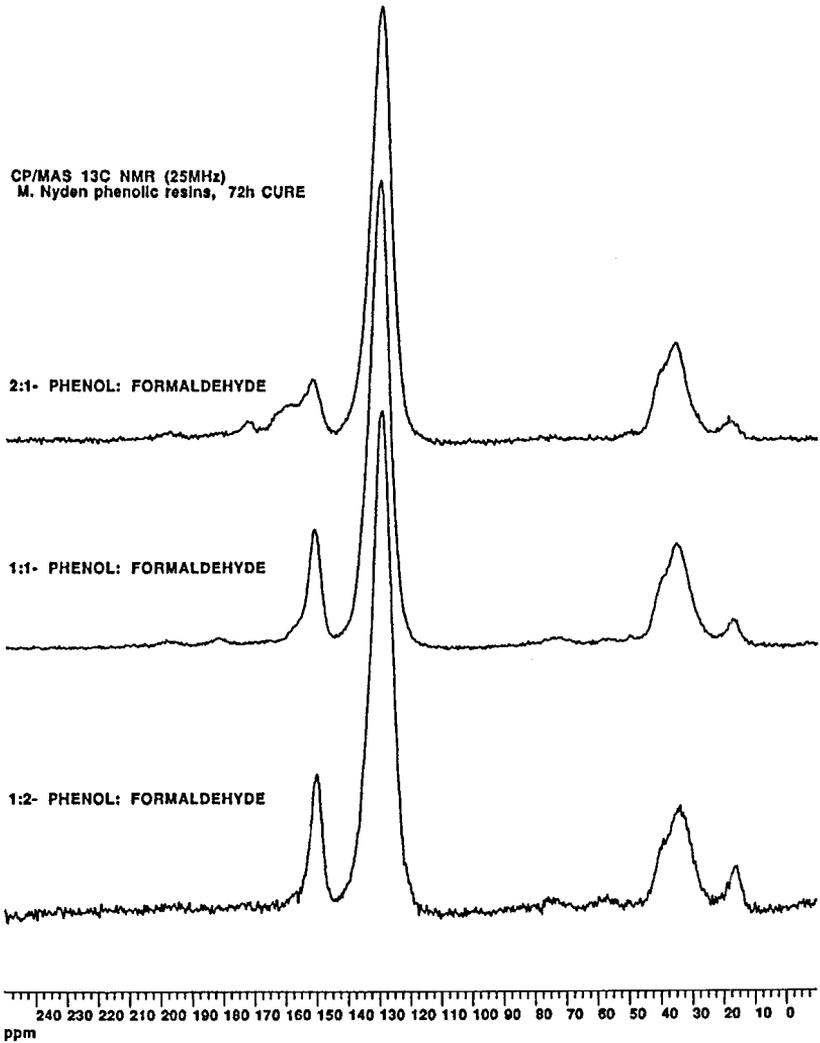


Figure 8. ^{13}C CP/MAS NMR spectra of the 1:2 (bottom), 1:1 (middle) and 2:1 PF resins(top).

This oxygen is accounted for in the spectrum of the 2:1 resin by the broad resonance extending from about 155-180 ppm which is characteristic of the presence of biphenyl ethers (15). Presumably, these ether linkages are formed as a result of self-condensation of the phenol. Thus, it is not surprising that they are more prevalent in those resins which were synthesized in an excess of this reactant. Likewise, resins synthesized in excess formaldehyde might be expected to contain significant amounts of the formaldehyde homopolymer. Pure polyoxymethylene is known to be thermally labile. Depolymerization is thought to be initiated at the chain ends at about 200 °C (17) which is consistent with the temperature at which CH₃OH and CO₂ first appear. The presence of polyoxymethylene in the 1:1 and 1:2 resins would account for the high levels of CO₂ which are evolved during curing; even when this process is carried out in N₂, as well as, providing a simple explanation for the reduced flammability of the cured resins.

Conclusions

Combustible products, particularly CH₄ and CH₃OH which are released during the thermal degradation of the PF resin, make a significant contribution to the flammability of the honeycomb composites considered in this investigation. A reduction in flammability was demonstrated in the case of resins which were synthesized from reaction mixtures containing an excess of phenol. The fire resistance of these resins is also affected by the curing process. The levels of combustible products released in thermal degradation and the peak rate-of-heat-release were significantly higher in the uncured resins than they were in the cured resins.

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