

Characterization of Flame-retarded Polymer Combustion Chars by Solid-state ^{13}C and ^{29}Si NMR and EPR

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We report here on the results of our continuing effort to study the flame-retardant mechanism of silica gel and potassium carbonate. These additives reduce the flammability of a wide variety of common polymers such as polypropylene, nylon, polymethylmethacrylate, poly(vinyl alcohol), and cellulose. In an effort to determine how these additives reduce polymer flammability, we have used electron paramagnetic resonance spectroscopy and solid-state ^{13}C and ^{29}Si nuclear magnetic resonance spectroscopy to characterize the combustion chars or residues. These data indicate that, in the case of poly(vinyl alcohol), the additives do not change the type of char formed, but they do change the rate of char formation relative to the rate of fuel generation. We also found that, using only CP/MAS ^{13}C NMR, there can be significant intensity distortions which complicate interpretation, if the char is hydrogen depleted and contains paramagnetic centres. © 1998 John Wiley & Sons, Ltd.

INTRODUCTION

Additives that increase the amount of charcoal-like residue or carbonaceous char that forms during polymer combustion are very effective fire retardants.^{1,2} Our research efforts focus on reducing polymer flammability by promoting char formation. Char formation reduces the amount of small, volatile polymer pyrolysis fragments, or fuel, available for burning in the gas phase; this in turn reduces the amount of heat released and fed back to the polymer surface. The char also insulates the underlying polymer, due to its low thermal conductivity, and reradiates externally impinging energy away from the polymer. The char must also function as a mass transport barrier, by physically delaying the volatilization of decomposition products and or trapping decomposition products through chemical reaction. The physical structure of the char is important in this role. Thick, foamy char appears to be more fire resistant than brittle, thin char. This char-enhancing approach is most successful when the polymer chars rapidly and early in the burning process.³ To be useful, the charring process must occur at a temperature above the polymer processing temperature and below or at the temperature where rapid gasification of the polymer to combustible fuel occurs.

BACKGROUND

Elsewhere, we have reported that silica gel⁴ combined with potassium carbonate is an effective fire retardant for a wide variety of common polymers such as polypropylene (PP), nylon-6,6, polymethylmethacrylate (PMMA), poly(vinyl alcohol) (PVA) cellulose, and to a lesser extent polystyrene (PS) and styrene-acrylonitrile (SAN).⁴ Typically, these additives reduce the peak heat release rate by two thirds, without significantly increasing the smoke or carbon monoxide yields during polymer combustion. We found that, for polymers like PP, nylon, PMMA and PS, the silica gel/ K_2CO_3 additives do not significantly affect the heat of combustion. It was proposed that for PP, nylon, PMMA and PS, these additives act primarily in the condensed phase, not in the gas phase, by reducing the mass loss rate. For PVA and cellulose the results indicated a combination of mechanisms of action. In addition to the enhanced char yield and the resulting reduction in mass loss rate, the heat of combustion and the smoke yield were reduced. It was proposed that the additives increase the rate of H_2O elimination from cellulose and PVA. This dilution of the combustible gases may be responsible for the reduction of the specific heat of combustion, and for the reduction of the smoke.

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In this paper, we report on our efforts to determine mechanistically how these additives reduce polymer flammability. Specifically, to determine what, if any, chemical transformations the additives undergo and how the additives enhance char formation and reduce flammability in PVA. We were interested in learning how the additives increased the char yield, and if they formed a char with a different chemical structure.

EXPERIMENTAL

The chars or residues were from combustion of PVA samples burned in the cone calorimeter. The experiments were conducted at an incident heat flux of 35 kW/m^2 . Additional details were published previously.⁴

Nuclear Magnetic Resonance (NMR) spectroscopy: Solid-state ^{13}C NMR characterization utilized techniques of cross polarization⁵ (CP) and magic angle spinning (MAS) (25 MHz, 4 kHz MAS, 1 ms CP time, 3 s rep. time). Single-pulse (SP) MAS ^{13}C NMR utilized 90° carbon pulse with a 60 s delay. In the interrupted decoupling experiments the decoupler was turned off for $40 \mu\text{s}$ prior to acquisition with decoupling.^{6,7} The ^{29}Si NMR characterization used variable amplitude CP/MAS (79 MHz, 2 s delay) and single pulse MAS (79 MHz, 90 s delay) techniques.

Electron Paramagnetic Resonance (EPR) spectroscopy: EPR quantifications (measurements of concentration of spins/g in char samples) were performed at room temperature on Bruker ECS106 and ESP300 X-band spectrometers at 50 and 100 kHz field modulation, respectively. TMH-type cavities were used. For EPR spectrum recording, a sufficient amount of the ground sample was placed into a 3 mm quartz tube to fill it to a level above the cavity height; the sample mass and height were measured for normalizing the EPR signal intensity to sample density. The depth of the sample tube insertion into the cavity was selected so that the sample would run along the entire active zone of the cavity. This depth, as well as the rotational orientation of the sample tube with respect to its axis were kept constant during the entire measurement sessions. The spectra were recorded at microwave power 1 mW, which provided no statistically significant indications of signal saturation, and the modulation amplitude 1 G. The standard requirement to the speed of spectrum recording (10 time constants between the extrema of the derivative of the spectrum line) was observed. The spectra were integrated over a range of 20–50 linewidths depending on the line shape. The concentration of the paramagnetic centres was determined against a reference sample (toluene solution of 4,4,6,6-tetramethylpiperidine-1-oxyl) placed into the same sample tube. The concentration of free radicals in the paramagnetic material used to prepare the reference sample was determined by precise titrimetry. An adjacent ruby standard was used in all the measurements to normalize the signals to Q -factor; in some cases its intersample variations were very large. Due to sample inhomogeneity, uncertainties for these radical concentrations are $\pm 10\%$ of the reported value, unless indicated otherwise. For each material, five replicate determinations were done from different portions.

The pulse EPR was done by Dr Ralph Weber at Bruker in Billerica, MA. A Bruker ESP380E FT-EPR spectrometer was used to collect the EPR spectra as well as to measure the relaxation times of the samples. All EPR experiments were performed at room temperature (about 22°C). EPR spectra were acquired by detecting the echo as the magnetic field was swept. In order to minimize power-broadening effects, the area underneath the echo was integrated with an integrator gate of 256 ns. Echoes were excited by two 12 ns microwave pulses with a separation of 128 ns. TM (phase memory time) was determined by measuring the two pulse echo decay as the two pulses were moved apart from each other. Both pulses were 12 ns microwave pulses. T1 (spin-lattice relaxation time) was measured by an echo-detected inversion recovery. A 20 ns inversion pulse was used in conjunction with two 12 ns microwave pulses to detect the magnetization.

CHAR CHARACTERIZATION: ^{29}Si NMR

One possible mechanism of action for these additives is through the formation of a potassium silicate glass during the combustion. In earlier work on fire retardants, silicates were claimed to be quite effective.⁸ We characterized the char from the combustion in the Cone calorimeter of PVA with silica gel/ K_2CO_3 additives (mass ratio, 90:6:4, respectively) using single pulse magic angle spinning (SP/MAS) ^{29}Si NMR. The SP/MAS ^{29}Si spectrum (Fig. 1) shows a broad resonance from -130 ppm to -90 ppm, which indicates that the residue may contain some silicate species. Comparison of this spectra to the SP/MAS ^{29}Si NMR spectra of the char from combustion of PVA with sodium silicate (mass ratio 90:10) (Fig. 2) confirms this, since both spectra show the majority of the silicons are of the Q^3 [$(\text{SiO})_3\text{SiO}^-$] (100–110 ppm) and Q^4 [$(\text{SiO})_4\text{Si}$] (110–120 ppm) type.

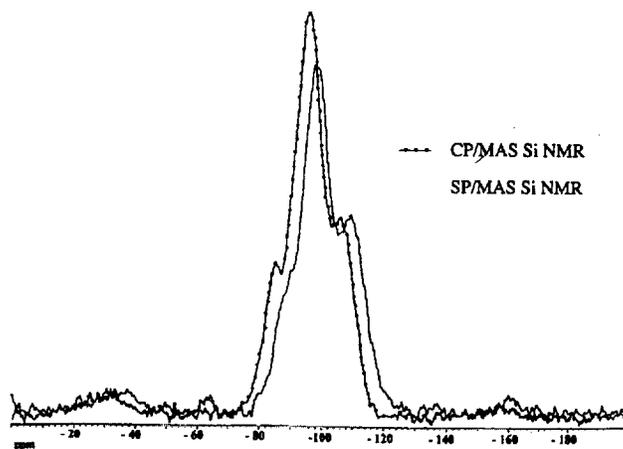


Figure 1. The CP/MAS ^{29}Si NMR and the SP/MAS ^{29}Si NMR of the char from the combustion in the Cone calorimeter of poly(vinyl alcohol) with silica gel/ K_2CO_3 additives (mass ratio, 90:6:4, respectively). The selective enhancement of the SiOH silicons, in the CP spectrum, indicates that not all the silanols have been converted to silicates during the combustion.

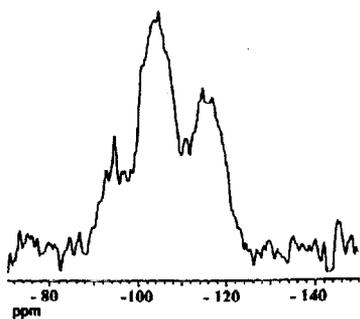


Figure 2. The SP/MAS ^{29}Si NMR spectra of the char from combustion of PVA with sodium silicate (mass ratio 90:10).

However, SP/MAS ^{29}Si NMR cannot distinguish between silicate ($\text{SiO}^{(-)}$) and silanol (SiOH) silicons. Cross-polarization (CP)/MAS ^{29}Si NMR, which selectively enhances the signal intensities of Si nuclei near protons, can accomplish this, but only in a qualitative manner. The CP/MAS ^{29}Si spectrum of the PVA with silica gel/ K_2CO_3 char (shown in Fig. 1) exhibits enhanced signal intensities of the silicons in the Q^2 [$-(\text{SiO})_2-\text{Si}(\text{OH})_2$] (85–95 ppm) and Q^3 [$-(\text{SiO})_3-\text{Si}-\text{OH}$] (95–105 ppm) region. This indicates that there is still a significant fraction of Q^2 [$-(\text{SiO})_2-\text{Si}(\text{OH})_2$] (85–95 ppm) and Q^3 [$-(\text{SiO})_3-\text{Si}-\text{OH}$] (95–105 ppm) silanol functionality present after the combustion. Silanol is also present in the original silica gel structure. SP/MAS and CP/MAS ^{29}Si spectra, similar to those discussed above, are reported in the literature for silica gel.^{9,10} Specifically, the results of these studies showed, as we have observed here, significant intensity from Q^2 and Q^3 structures between 80 and 100 ppm. Thus, this ^{29}Si NMR data indicate that the majority of the silica gel original structure remains intact during the combustion. This raises the possibility that silica gel itself is directly affecting the flammability, either chemically, in a catalytic process, or physically.

MAS ^{13}C NMR and EPR char characterization

Influence of unpaired electrons on ^{13}C NMR signals. We have attempted to determine the effect of the individual additives on the carbonaceous structure of the char by characterizing the char using MAS ^{13}C NMR techniques. Other research groups, as well as our own, have used these techniques to study polymer degradation processes.^{11–18} Previously, we found that these techniques, when used to characterize the intermediate decomposition products of pure PVA (formed at 250 to 400°C, 30 min in N_2), were very useful in exploring the various pathways involved in the PVA pyrolysis.¹⁹ However, several problems potentially interfere with making quantitative measurements of the intensities of ^{13}C NMR signals in experiments carried out on combustion chars, hence, with drawing conclusions using these data. First, since these combustion chars are hydrogen-depleted carbon-rich materials, there may be a significant fraction of carbons which, are more than ~ 0.5 nm from protons and, therefore, will not readily cross polarize, and will not be properly represented in the CP/MAS ^{13}C signal.²⁰ Secondly, these chars may

contain significant concentrations of paramagnetic centers (e.g. particles with unpaired electrons, free radicals). Paramagnetic centres can potentially broaden or shift resonances of ^{13}C carbons in the local (0.5–1.5 nm) environment around the radicals, preventing these carbons from being observed in either CP/MAS or SP(90°)/MAS ^{13}C NMR experiments.

The range and nature of the influence of an unpaired electron on the ^{13}C signals depends on the spin lifetime (T_1^e) of the electron. When $T_1^e \leq 10^{-8}$ s, fewer spins are perturbed directly and it is mainly the ^1H spin-lattice relaxation time (T_1^H) and the ^{13}C spin-lattice relaxation time (T_1^C) which are shortened. On the other hand, when $T_1^e \geq 10^{-6}$ s, many more nuclear spins are strongly perturbed and the rotating frame relaxation time ($T_{1\rho}$) is shortened much more than T_1^H . With short $T_{1\rho}$'s, the CP intensities will be weaker and more distorted with respect to protonated and non-protonated carbons. Aside from the influence of unpaired electrons, a proton-depleted solid can also possess carbons with very long T_1^C 's. Thus, single-pulse MAS ^{13}C NMR experiments may also under represent the carbons, in combustion char samples, if scans are repeated too frequently.²¹ For these reasons, CP/MAS and SP/MAS ^{13}C spectra may only be representative of a fraction of the carbons present in combustion chars. Bourbigot *et al.*¹³ have observed these type of effects in CP/MAS ^{13}C NMR studies of a commercial polymer flame-retardant system. Bourbigot observed, in the CP/MAS ^{13}C spectrum of the polymer flame-retardant additive char, prepared at 430°C, a disappearance of the aromatic band. This was attributed to the presence of free radicals 'trapped' in the material. Indeed, subsequent electron paramagnetic resonance (EPR) analysis showed a radical concentration of $\sim 10^{19}$ spins/g.¹² Several quantitative studies have been done on these effects on CP/MAS and SP/MAS ^{13}C measurements in coals, coal chars and biomass chars.^{16,22,23} Single-pulse (90°)/MAS ^{13}C spectra of coal samples containing high concentrations of paramagnetic centres ($\sim 10^{19}$ spins/g) were found to have greater percent carbon observed in the sample ($\%C_{\text{obs}}$, 43–70%) than CP/MAS ^{13}C spectra, which showed $\%C_{\text{obs}}$ from 26 to 55%.²³ For both the coal chars and the biomass chars CP/MAS ^{13}C techniques were found to underestimate the aromaticity by 10% as compared to that obtained from SP/MAS ^{13}C experiments.²³

Quantitative EPR and pulse EPR measurements

Quantitative EPR analysis of PVA combustion chars, of PVA N_2 -flow-pyrolysis chars and of N_2 flow pyrolysis chars of epoxy and cyanate ester resins, reveals moderate to high concentrations of paramagnetic centres for all chars, whether produced under combustion or pyrolysis (see Tables 1 and 2). A calculation based on the EPR

Table 1. Radical concentration in PVA combustion chars

PVA/additive char	Radical concentration ($\times 10^{19}$, spins/g)
PVA	8.2 ± 0.2
PVA/10% silica gel	1.00 ± 0.04
PVA/6% silica gel/4% K_2CO_3	3.5 ± 0.2

Table 2. Radical concentration in combustion and N₂ flow pyrolysis residues

Entry	Residue (char)	Radical concentration (N × 10 ¹⁸ spin/g)	Residue yield (mass %)
1 [†]	PVA/10% silica gel	1.0	29
2 ^{‡350}	PVA/10% silica gel	2.9	16
3 [†]	PVA/6% silica gel/4% K ₂ CO ₃	3.5	43
4 ^{‡350}	PVA/6% silica gel/4% K ₂ CO ₃	4.3	30
5 [†]	PVA/6% silica gel/4% K ₂ CO ₃	6.7	—
	Control (HCl wash only)		
6 [†]	PVA/6% silica gel/4% K ₂ CO ₃ Sm I ₂ treated 12 h w/HCl wash	5.5	—
7 [†]	PVA/6% silica gel/4% K ₂ CO ₃ Sm I ₂ treated 96 h w/ HCl wash	4.4	—
8 ^{‡400}	Epoxy	33.0	9
9 ^{‡450}	Epoxy	37.0	4
10 ^{‡450}	Cyanate ester	20.0	67

[†]Cone combustion residue; All residue yields are corrected for mass of additive.

^{‡350} = residue from 350°C N₂ flow pyrolysis, 0.5 h.

^{‡400} = residue from 400°C N₂ flow pyrolysis, 0.5 h.

^{‡450} = residue from 450°C N₂ flow pyrolysis, 0.5 h.

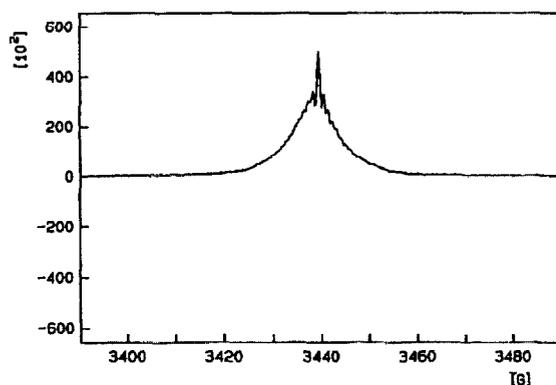


Figure 3. Pulse EPR spectrum of the combustion char of PVA with silica gel and K₂CO₃ (mass ratio: 90:6:4) entry 3, Table 2.

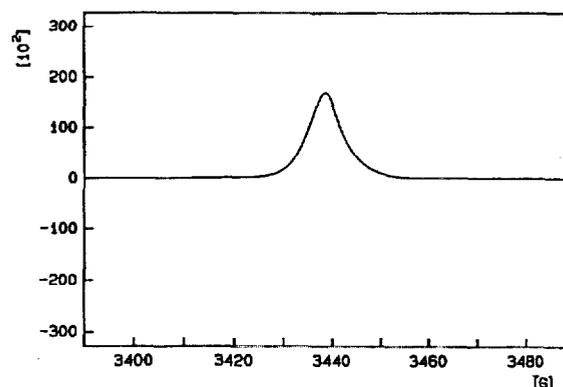


Figure 4. Pulse EPR spectrum of the combustion char of PVA with silica gel (mass ratio: 90:10) entry 1, Table 2.

data, which assumes that each radical obscures all ¹³C nuclei within a spherical volume with a radius of 1 nm, reveals, if the radicals are assumed to be distributed uniformly in the char, that 1%, to as much as 10%, of the carbons might be obscured at these radical concentrations (10¹⁸–10¹⁹ spins/g). A similar analysis by Muntean *et al.* is in agreement with this calculation.²⁵

The pulse EPR spectrum of the combustion char of PVA with silica gel and K₂CO₃, shown in Fig. 3, reveals that the char may contain two radical species. One relatively broad signal and the other a narrow signal. The pulse EPR spectrum of the combustion char of PVA with silica gel (Fig. 4) exhibits only the broad signal. This signal may be from the same species that gives the broad signal in Fig. 3. The difference between these two spectra indicate that the presence of K₂CO₃ may cause different types of radicals to be formed during the combustion, or the K₂CO₃ may prevent the reaction of a radical species, hence allowing it to be observed in the EPR spectrum.

When we washed the PVA/silica gel/K₂CO₃ char with aqueous HCl, which neutralizes the K₂CO₃, produces CO₂, and effectively removes the K₂CO₃ from the char (see entry 5, Table 2) the EPR spectrum still showed two

signals. Furthermore the radical concentration *increased* (compare entry 3 to entry 5, Table 2) indicating that the K₂CO₃ was a diluent which did not contain significant concentrations of radicals.

Samarium (II) iodide reduction of radicals. Muntean *et al.*²⁴ have published a method for chemically reducing the radical concentrations in coals, for the purpose of improving the fraction of observable carbon in the coal when using ¹³C MAS techniques. For Muntean, this resulted in a factor of 4 reduction in the radical concentration in the coal sample, and an increase in the fraction of observable carbon in the ¹³C CP/MAS spectrum from 58 to 85%.²⁴ We applied this approach to the combustion char of PVA with silica gel and K₂CO₃ (mass ratio: 90:6:4). The method involves stirring a slurry of the char in a solution of THF containing samarium (II) iodide, SmI₂, under a N₂ atmosphere for 96 h, followed by removal of the SmI₂ by treatment of the solution with aqueous HCl.

As the data, entries 5, 6 and 7, in Table 2 show the radical concentration was reduced by 30%, from 6.7 × 10¹⁸ spins/g (control sample) to 5.5 × 10¹⁸ spins/g

after 12 h, and to 4.4×10^{18} spins/g after treatment for 96 h. Only slight changes are seen in the pulse EPR spectrum after the treatment (Fig. 5), as compared to before the SmI_2 treatment (Fig. 3). The analysis of the effectiveness of this reaction using CP/MAS ^{13}C is shown in Fig. 6. The spectrum of the control sample is shown on the top. The spectrum of the SmI_2 -treated char is shown in the middle. The difference spectrum (bottom, SmI_2 -treated char—control sample) reveals little improvement. A comparison of the fraction of observable carbon in the ^{13}C CP/MAS spectrum of the samples ($\%C_{\text{obs}}$, done by spin counting using an estimated carbon concentration, vide infra) also showed little improvement. The minimal effect of the SmI_2 /THF treatment on the char may be due to the fact that although THF is an effective solvent for swelling coal, it does not appreciably swell the char. Therefore, the SmI_2 may not have had access to the radical sites in the char, and hence could not react with them.

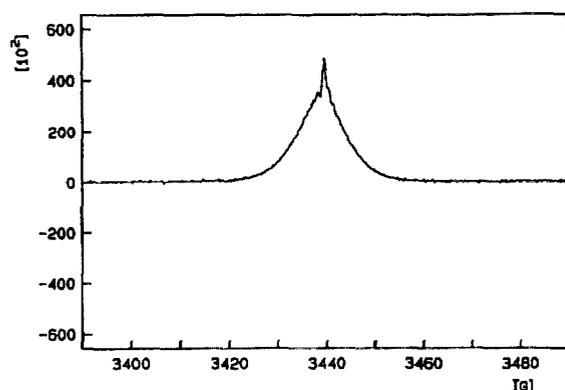


Figure 5. Pulse EPR spectrum of combustion char of PVA with silica gel and K_2CO_3 (mass ratio: 90:6:4) after treatment with SmI_2 -THF solution and aqueous HCL wash.

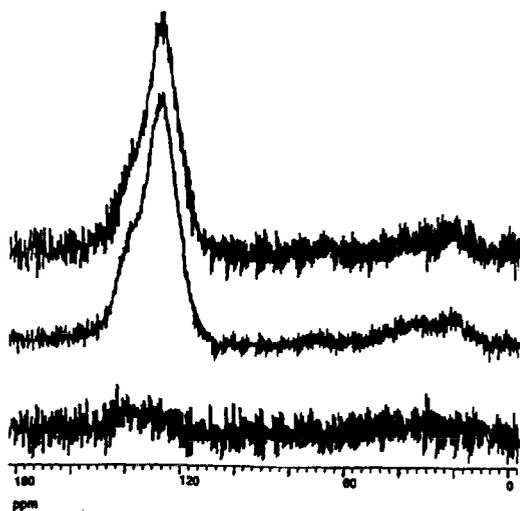


Figure 6. The CP/MAS ^{13}C spectra of the char of PVA with silica gel and K_2CO_3 (mass ratio: 90:6:4). The spectrum of the control sample is shown on the top. The spectrum of the SmI_2 -treated char is shown in the middle. The difference spectrum (SmI_2 -treated char—control sample) reveals little improvement.

SP/MAS ^{13}C char characterization

The ratio of the $\%C_{\text{obs}}$ in the SP/MAS spectrum versus the $\%C_{\text{obs}}$ in the CP/MAS spectrum, for the combustion char of PVA with silica gel and K_2CO_3 , was found to be 4.5 to 1.0, that is the SP/MAS technique is capable of allowing characterization of a greater fraction of the carbon in the char sample than the CP/MAS method. As was mentioned above, this was also the case for characterization of coal chars and biomass chars, although the ratio (SP $\%C_{\text{obs}}$ to CP $\%C_{\text{obs}}$) was not so large.

Therefore, we choose to use SP(90°)/MAS ^{13}C NMR to attempt to obtain as quantitative a characterization of the chars as possible. The SP/MAS ^{13}C spectra of the chars of: PVA with silica gel and K_2CO_3 (mass ratio: 90:6:4), PVA with silica gel only (mass ratio: 90:10), and of pure PVA, are shown in Fig. 7. A variable pulse width series of SP/MAS experiments were done; these confirmed that no intensity was lost due to saturation.

The major feature of the SP/MAS spectra for these chars is a broad resonance in the aromatic-olefinic region from 110 to 150 ppm. The absence of any strong signal in the aliphatic region indicates that these materials consist mostly of aromatic-olefinic-type carbon, although poor signal-to-noise, in the spectra of the chars with additives, prevents making a quantitative conclusion about the exact aromatic to aliphatic carbon ratio.

To determine the observable percentage of carbon nuclei ($\%C_{\text{obs}}$) in these SP/MAS spectra, by spin counting measurements,²¹ and to determine the carbon-to-hydrogen ratio, elemental analysis was done on each PVA char sample. For the pure PVA char the CP/MAS $\%C_{\text{obs}}$ was $30 \pm 4\%$ and the SP/MAS was $70 \pm 9\%$. However, inconsistencies between the elemental analysis data, X-ray photoelectron spectroscopy (XPS) data and calculations based on the char yields, made it difficult to determine the fraction of ^{13}C nuclei observed in the samples containing silica gel, or to determine the carbon-to-hydrogen ratio. In terms of carbon analysis, this may be because some of the carbon is not readily oxidized during the $\geq 600^\circ\text{C}$ oxidation performed for

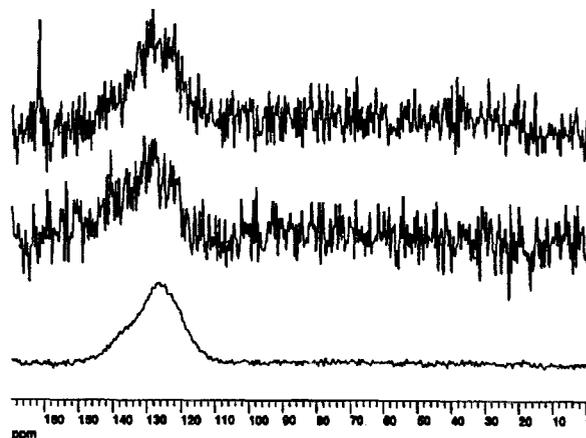


Figure 7. The SP/MAS ^{13}C spectra of the chars of: (top) PVA with silica gel and K_2CO_3 (mass ratio: 90:6:4), (middle) PVA with silica gel only (mass ratio: 90:10), and of pure PVA (bottom). The major feature of these SP/MAS spectra is the broad resonance in the aromatic-olefinic region from 110 to 150 ppm.

carbon elemental analysis. Indeed, in our lab, these silica-containing samples remained black even after exposure to 1100°C in air for 1 h. As for the hydrogen elemental analysis, the PVA char samples showed mass %H levels that were close to the typical detectability threshold of $\sim 0.5\%$. However, even with these uncertainties we were able to determine, as stated above, that the SP/MAS technique is capable of allowing characterization of a greater fraction of the carbon in the char samples than the CP/MAS method. We are in the process of evaluating other methods of quantitatively determining the composition of these chars.

Characterization of non-protonated carbon versus protonated carbon. One of the goals of this work is to determine the role that non-protonated carbon, present in the char, plays in controlling char performance, and flammability. Since these type of carbons should be part of cross-links and or graphitic type structures, their presence may improve the performance of the char by increasing thermal stability and improving mechanical strength. A particularly useful ^{13}C NMR experiment for characterizing chars, which allows observation of the non-protonated carbons in the char is the interrupted decoupling (ID) experiment.⁷ However, due to signal-to-noise limitations we have not been able to obtain suitable ID SP/MAS ^{13}C spectra. Since the CP/MAS spectra should give a good representation of protonated carbons in the char, by virtue of their ease of cross polarization, we felt the ID CP/MAS ^{13}C data would provide the best characteristic lineshape of the protonated carbon of the chars. This approach gives a suitable method for partitioning the SP/MAS signal into its non-protonated carbon (C_{NP}) and protonated carbon (C_{P}) components.

An example of our method of obtaining the C_{P} lineshape for the char of PVA with silica gel (mass ratio: 90:10) using CP/MAS ^{13}C NMR and ID-CP/MAS ^{13}C NMR techniques is described below. The CP/MAS ^{13}C and ID-CP/MAS ^{13}C spectra of the char of PVA with silica gel is shown in Fig. 8. The normal CP/MAS ^{13}C NMR, shown in the middle of the figure, contains a broad resonance in the aromatic-olefinic region from 110 to 150 ppm and two weaker broad signals in the aliphatic region, one centred at 20 ppm and the other at 35 ppm. This spectrum shows that, $\sim 10\%$ of the carbons that cross polarize are aliphatic (sp^3) carbons in this char. The ID-CP/MAS spectrum, the bottom spectrum in Fig. 9, reveals only the non-protonated carbons which have cross-polarized. Comparison of the ID-CP/MAS spectra (bottom) to the normal CP/MAS spectra (middle) shows that the downfield shoulder in the CP/MAS spectra, at 135 ppm, is due to non-protonated aromatic-olefinic carbons. The result of subtracting the appropriate intensity of the ID-CP/MAS spectrum from the CP/MAS spectrum, so that the downfield shoulder is removed, is shown in the top of the figure. This is our best estimate of the lineshape for the protonated carbons in the PVA with silica gel char.

Comparison of the intensity of the non-protonated to protonated aromatic-olefinic carbon spectra gives a C_{NP} to C_{P} ratio of ~ 1.5 to 1.0 for this sample. Using this same method for the other two chars (PVA with silica gel and K_2CO_3 (mass ratio: 90:6:4), and pure

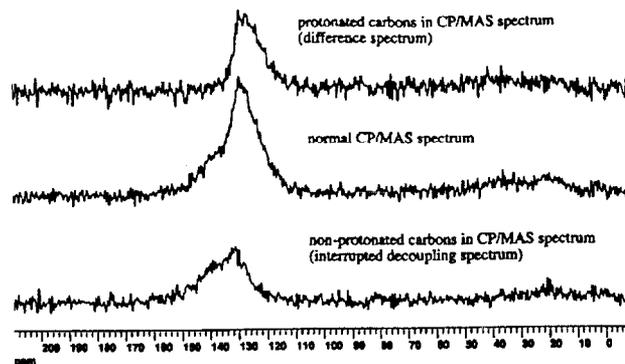


Figure 8. The CP/MAS ^{13}C spectra of the char of PVA with silica gel. The normal CP/MAS ^{13}C spectrum is shown in the middle. The ID-CP/MAS spectrum (bottom) reveals only the non-protonated carbons which have cross-polarized. The difference spectrum (top), obtained by subtracting the appropriate intensity of the ID-CP/MAS spectrum from the CP/MAS spectrum, gives the spectrum of the protonated carbons that cross-polarized.

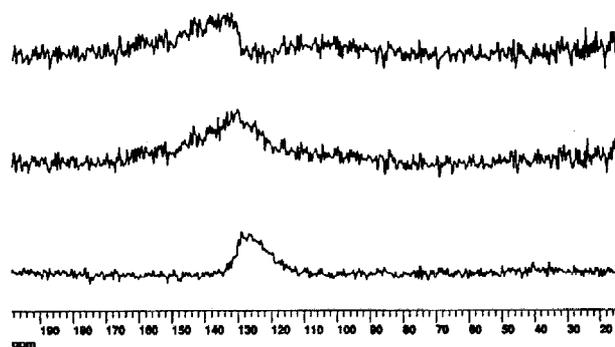


Figure 9. Spectra of the char of PVA with silica gel. By subtracting the appropriate intensity of the protonated carbon (difference) spectrum (bottom) from the normal SP/MAS spectrum (middle), so that the upfield portion of the line is removed, we generated the non-protonated carbon (difference) spectrum (top). The rationale for complete removal of the upfield portion of the aromatic-olefinic resonance is based on the belief that this region of the spectrum is usually dominated by protonated aromatic-olefinic carbons.

PVA), i.e. subtracting the protonated carbon (difference) spectra, obtained from the respective CP/MAS spectra, from the SP/MAS spectra for these chars, we are able to make the best estimate of the ratio of C_{NP} to C_{P} . This ratio is also ~ 1.5 to 1.0 for these chars. That is, all three chars have the same C_{NP} to C_{P} ratio (1.5:1.0).

It should be noted that, when only the CP/MAS ^{13}C data were used to characterize these chars different results and conclusions were found, especially for the pure PVA char and the PVA with silica gel char.⁴ The C_{NP} to C_{P} ratio, from the CP/MAS data, for these chars are: 1.5:1.8 for the pure PVA char, 1.5:1.8 for the PVA with silica gel char, and 1.5:1.0 for the char from PVA with silica gel and K_2CO_3 .¹⁹ A comparison of the C_{NP} to C_{P} ratios using the two different approaches is shown in Table 3.

These substantially different results, for the ratio of C_{NP} to C_{P} , illustrate, for some systems, that there can be

Table 3. Comparison of the C_{NP} to C_P ratios found using SP and CP/MAS ^{13}C NMR

Carbonaceous char yield (%)	PVA/additive char	C_{NP} to C_P ratios from SP and CP/MAS data	C_{NP} to C_P ratios from CP/MAS data only
5	PVA	1.5:1.0	1.5:1.8
29	PVA/10% silica gel	1.5:1.0	1.5:1.8
43	PVA/6% silica gel/ 4% K_2CO_3	1.5:1.0	1.5:1.0

uncertainties associated with attempting to quantitatively characterize hydrogen depleted materials that contain paramagnetic centres, using *only* CP/MAS ^{13}C NMR. Such results may also point to more clustering of protonated carbons in the pure PVA char, and the PVA with silica gel char.

CONCLUSIONS

To the extent that this combined SP and CP/MAS ^{13}C NMR approach to characterizing these materials

accurately reflects the sample-wide chemistry, these data indicates that, even though the char yields are very different for these three systems (carbonaceous char yield: 5% for pure PVA; 29% for PVA with silica gel; and 43% for PVA with silica gel and K_2CO_3) the carbon structure of the chars are quite similar. It appears that the additives do not change the type of char formed, in terms of the C_{NP} to C_P ratio. Furthermore, in this study we did find evidence that K_2CO_3 may be responsible for formation, or stabilization, of an additional type of radical in the char. It appears that the additives act primarily by changing the *rate of char formation* relative to the *rate of fuel generation*, since the char yield is higher and the flammability (due to a lower fuel generation rate) is reduced. Elsewhere, we will report on our study of the effect of silica gel material properties on the flammability of polypropylene.²⁸

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