

# CHAR ENHANCING APPROACHES TO POLYMER FLAMMABILITY

## The Effect of Radicals on Magic Angle Spinning $^{13}\text{C}$ NMR of Chars

Jeffrey Gilman\*<sup>1</sup>, Serge Lomakin†<sup>1</sup>, Takashi Kashiwagi<sup>1</sup>, David L. VanderHart<sup>2</sup>, and Vitaly Nagy†<sup>3</sup>

<sup>1</sup> Fire Sciences Division, <sup>2</sup> Polymers Division, <sup>3</sup> Ionizing Radiation Division

† Guest Researcher from Russian Academy of Sciences

National Institute of Standards and Technology, Gaithersburg, Maryland

**INTRODUCTION.** Additives that increase the amount of charcoal-like residue or carbonaceous char that forms during polymer combustion are very effective fire retardants<sup>1</sup>. However, very little is understood about the detailed structure of char or how it forms. 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 feedback 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. Foamy char structure 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<sup>2</sup>. To be useful the charring process must occur at a temperature above the processing temperature but below the temperature where rapid gasification of the polymer to combustible fuel occurs.

**BACKGROUND.** Elsewhere, we have reported that silica gel combined with potassium carbonate is an effective fire retardant for a wide variety of common polymers such as polypropylene, nylon, polymethylmethacrylate, poly (vinyl alcohol), cellulose, and to a lesser extent polystyrene and styrene-acrylonitrile<sup>3</sup>. Typically, these additives reduce the peak heat release rate (HRR) by up to 68% without significantly increasing the smoke or carbon monoxide levels during polymer combustion. We found that, for polymers like PP, nylon, PMMA and PS, the silica gel / $\text{K}_2\text{CO}_3$  additives do not significantly affect the specific 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. For PVA and cellulose the results indicated a combination of mechanisms of action. In addition to the enhanced charring effect and the resulting reduction in mass loss rate, the specific heat of combustion and the smoke were reduced. It was proposed that the additives may increase the rate of  $\text{H}_2\text{O}$  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. Here we will report on our efforts to determine mechanistically how these additives reduce the flammability of the wide variety of polymers mentioned above.

**MECHANISTIC STUDIES.** 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<sup>4</sup>. Characterization of the chars from combustion in the Cone calorimeter of polyvinylalcohol (PVA) with silica gel / $\text{K}_2\text{CO}_3$  additives (mass ratio, 90:6:4 respectively) using magic angle spinning (MAS)  $^{29}\text{Si}$  NMR shows that the residue may contain some silicate species. However, cross-polarization (CP) MAS  $^{29}\text{Si}$  NMR shows there is still a significant fraction of silanol functionality (Si-OH) present after the combustion. Silanol is also present in the original silica gel structure. This raises the possibility that silica gel itself is affecting the flammability. Therefore, we have attempted to determine the effect of the individual additives on the structure of the char.

We have found that characterization of the intermediate decomposition products of PVA via solid state  $^{13}\text{C}$  NMR can be very useful in exploring the various pathways involved in the pure PVA decomposition<sup>5</sup>. Through application of these  $^{13}\text{C}$  NMR techniques we found that silica gel does not appear to change the structure of the char. We also found evidence that  $\text{K}_2\text{CO}_3$  may increase the fraction of non-protonated carbon in the char. However, several problems potentially interfere with making quantitative measurements of the intensities of  $^{13}\text{C}$  signals in CP/MAS experiments carried out on combustion chars, and therefore with drawing conclusions using these data. First, since these chars are hydrogen-depleted carbon-rich materials, carbons which are more than 0.6 nm from protons will not be properly represented in the CP/MAS  $^{13}\text{C}$  NMR signal. Secondly, these chars may contain significant concentrations of paramagnetic centers (e.g., particles with unpaired electrons, free radicals) which can prevent carbons in the local (1.0-1.5 nm) environment around the radicals from being observed in the  $^{13}\text{C}$  NMR experiment. For these reasons CP/MAS  $^{13}\text{C}$  NMR spectra may only be representative of a fraction of the carbons present in the chars<sup>6</sup>. If this fraction accurately represents the entire sample, i. e. the char is homogeneous, then quantitative analysis of the  $^{13}\text{C}$  NMR spectra will give a proper characterization of the char. However, since these chars may be inhomogeneous, we attempted to determine if the above two factors were affecting our  $^{13}\text{C}$  NMR data.

The percent carbon observed (%  $\text{C}_{\text{obs}}$ ) in the CP/MAS (and single pulse (SP) MAS)  $^{13}\text{C}$  NMR was calculated via spin-counting techniques for Cone combustion chars and for  $\text{N}_2$  pyrolysis residues. These data are shown in Table 1 along with the carbon-to-hydrogen ratio and the radical concentrations from electron paramagnetic resonance (EPR) measurements for each residue. The %  $\text{C}_{\text{obs}}$  in the CP/MAS  $^{13}\text{C}$  NMR of the PVA/ 6% silica gel (SG) / 4%  $\text{K}_2\text{CO}_3$  (PC) cone char was surprisingly low, only 20% (see Row 1 in Table 1). The %  $\text{C}_{\text{obs}}$  in the SP/MAS  $^{13}\text{C}$  NMR was higher, but still only 87%<sup>7</sup>. From the EPR data we see that the concentration of paramagnetic centers is very high, comparable to the

concentrations found in some coal samples. We propose that, since C/H ratios around 1.0 : 1.0 usually yield reliable CP/MAS  $^{13}\text{C}$  spectral intensities, the low %  $\text{C}_{\text{obs}}$  is due primarily to the presence of carbon radicals in the char. We attempted to reduce the concentration of radicals by chemical reduction with  $\text{SmI}_2$  so as to improve the %  $\text{C}_{\text{obs}}$ . Muntean and coworkers had some success with  $\text{SmI}_2$  reduction of radicals found in coals<sup>8</sup>. Our attempts to treat the PVA/ 6% silica gel / 4%  $\text{K}_2\text{CO}_3$  cone char with  $\text{SmI}_2$  in refluxing tetrahydrofuran (thf) for 24h and 72h are shown in rows 3 and 4, respectively, in Table 1. Row 2 shows that the radical concentration following the "control" reaction (24h in refluxing thf, with no  $\text{SmI}_2$ , 1%  $\text{HCL}_{\text{aq}}$  wash) is nearly twice the concentration of the original cone char (Row 1). This apparent increase is due to loss of the  $\text{K}_2\text{CO}_3$  in the char through reaction with the 1%  $\text{HCL}_{\text{aq}}$  wash. This indicates that the carbon radicals are not carbonate radicals. Comparison of row 2 to row 3 and to row 4 shows that the  $\text{SmI}_2$  treatment reduced the radical concentration by 18% after 24h and by 34% after 72 h. However, the %  $\text{C}_{\text{obs}}$  (21%) in the CP/MAS  $^{13}\text{C}$  spectra of these  $\text{SmI}_2$  treated samples was essentially unaffected by this reduction in the radical concentration. The characterization data of a pyrolysis sample of PVA/ 6% silica gel / 4%  $\text{K}_2\text{CO}_3$  ( $\text{N}_2$  at 350°C for 30 min) is shown in row 5. This residue has the same C/H ratio as the Cone char but the radical concentration is almost two orders-of-magnitude lower and, presumably due to this low concentration, the %  $\text{C}_{\text{obs}}$  in the CP/MAS  $^{13}\text{C}$  NMR spectrum is higher, 74%.

**CONCLUSIONS.** From the above NMR and EPR data it appears that loss of observable carbon in the NMR signals is primarily due to the high radical concentrations. There are several mechanisms by which the radicals directly effect the NMR signal, and we are looking into these issue further. The possibility remains that if these materials are sufficiently inhomogeneous, regions of the char may be more hydrogen-depleted than the elemental analysis indicates, and these domains might not be fully represented in the CP/MAS  $^{13}\text{C}$  NMR signal.

**Table 1.**

Row no.	PVA/ 6% SG/ 4% PC	C/H Ratio	Radical Concentration ( $\times 10^{18}$ 1/g)	Residue Yield (%)	% Carbon observed (CP/MAS)	% Carbon observed (SP/MAS)
1	Cone Char	1.0 : 1.4	3.5	43	20	87
2	Cone Char <u>control</u> treated 24 h	1.0 : 1.0	6.7	-	21	-
3	Cone Char $\text{SmI}_2$ treated 24 h	1.0 : 1.1	5.5	-	21	-
4	Cone Char $\text{SmI}_2$ treated 72 h	-	4.4	-	21	-
5	Flow pyrolysis Residue 350°C/30min/ $\text{N}_2$	1.0 : 1.4	0.043	30	74	-

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