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A solid state ^{13}C nuclear magnetic resonance investigation of the thermal degradation of a poly(ethylene glycol) and poly(vinyl alcohol) binder in an alumina ceramic

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Cross polarization and magic angle spinning ^{13}C nuclear magnetic resonance spectroscopy (CP–MAS ^{13}C NMR) has been used to investigate the thermal degradation of poly(ethylene glycol) (PEG)–alumina, poly(vinyl alcohol) (PVA)–alumina, and a mixture of 6% PEG and 0.5% PVA in alumina. Samples were prepared by thermally treating each polymer at 450 °C to remove pre-specified weight losses. The results showed that the polymer chains of both PEG and PVA thermally degraded as postulated in previously published mechanistic studies based on volatile degradation product analyses. The CP–MAS ^{13}C NMR spectra of PEG and PVA in alumina showed that the two polymers thermally decomposed independently of each other.

1. Introduction

Characterization of the volatile products from the thermal degradation of poly(ethylene glycol) (PEG) binder commonly used in dry press alumina ceramics has been conducted by Voorhees and co-workers [1, 2]. In these studies, pure PEG and PEG in pressed alumina were pyrolysed in a tube furnace at temperatures from 450 to 550 °C with either nitrogen or air as the carrier gas. The volatile and semi-volatile products were collected and analysed by gas chromatography/mass spectrometry (GC/MS), using both chemical and electron ionization. Gas chromatography/Fourier transform infrared spectroscopy (GC/FTIR) was also used to obtain functional group information for further evidence in support of the proposed product identifications and degradation mechanism.

Five oligomeric series of compounds (Table I) were identified by GC/MS and GC/FTIR from the PEG degradation. The primary degradation reactions proposed to support the identified products involved homolytic cleavage at either the C–O or C–C bonds with disproportionation, hydrogen abstraction, or other reactions involving oxidation in the presence of air. These reactions are summarized in Fig. 1. Pyrolysis in a nitrogen atmosphere proceeded by disproportionation and intramolecular reactions, enhancing the product distribution of the oligomeric series of identified compounds. Thermal degradation in oxygen favoured oxidation over the inter- and intra-molecular reactions, thus reducing the overall amount of the oligomeric degradation products. A comparison of the volatile products produced from pure binders [1] versus a binder, additive and ceramic system [2] showed the same product distribution. This suggested that the alumina did not have a major effect on the degradation process.

Zhang *et al.* [3] recently applied solid state ^{13}C nuclear magnetic resonance spectroscopy [4–6] to understand the bulk thermal degradation processes of three polymers: poly(vinyl alcohol) (PVA), poly(methacrylic acid) (PMA), and poly(methylmethacrylate) (PMMA) as well as blends of the three. The cross polarization–magic angle spinning (CP–MAS) NMR spectra for pure PVA is of direct interest to this research. As the PVA polymer was heated to different temperatures, the ^{13}C spectra (Fig. 2) showed changes in functional groups occurring in the polymer backbone. Three types of carbon environments were detected (as indicated by an asterisk); (a) *CH–OH, (b) CH–*CH$_2$–CH and (c) *CH=*CH. Of particular importance, was the observation of the C=C peak which became more intense with continued heating. Tsuchiya and Sumi [7] had previously postulated that PVA thermally dehydrates to produce a polyene (a compound with multiple conjugated carbon–carbon double bonds) which can be part of the polymer chain. The application of CP–MAS ^{13}C NMR has allowed direct observation of the polyene structure within the thermally degraded polymer chains.

This paper describes the application of cross polarization–magic angle ^{13}C NMR to the study of the thermal degradation in air of a PEG/PVA binder

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commonly used in alumina ceramics. This technique allowed observation of the functional group changes of the binder polymer chains within the ceramic body. Solid samples can be analysed using magic angle ^{13}C NMR by spinning the sample at kilohertz frequencies at an angle θ of 54.7° relative to the direction of the static magnetic field ($\mathbf{H}_0$). Spinning the sample at this angle removes the line broadening effects of the chemical shift anisotropy as scaled by $3/2(3\cos^2\theta - 1)$, where θ is the angle between $\mathbf{H}_0$ and the sample spinning axis. Line broadening due to the $^1H-^{13}C$ magnetic dipole–dipole interactions was largely removed by high power ^1H decoupling.

TABLE I Characteristic end groups from the oligomeric series

Compound, where $n < 4$	Group code[a]
$CH_3{-}O(CH_2{-}CH_2{-}O)_n{-}CH_2{-}CH_2{-}OH$	A
$O{=}CH{-}CH_2(O{-}CH_2{-}CH_2)_n{-}O{-}CH_2{-}CH_3$	B
$CH_3{-}O(CH_2{-}CH_2{-}O)_n{-}CH_2{-}CH_3$	C
$CH_3{-}CH_2{-}O(CH_2{-}CH_2{-}O)_n{-}CH_2{-}CH_2{-}OH$	D
$CH_3{-}CH_2{-}O(CH_2{-}CH_2{-}O)_n{-}CH_2{-}CH_3$	E

[a] Group codes are referenced in Fig. 1.

2. Experimental details

2.1. Description of samples

The polymer binders investigated in this study were poly(ethylene glycol) PEG 20 M (average molecular weight 20 000 daltons), PEG 8 M (average molecular weight 8000 daltons), and PVA (average molecular weight 10 000 daltons). The PEG 20 M was a double epoxide cross-linked polymer made up of two or three PEG 8 M units. The 20 000 average molecular weight is therefore an average of the epoxide linked macromolecules. The PVA used in this study was manufactured by the hydrolysis (99% reported yield) of poly(vinyl acetate). The PEG and PVA samples were obtained from Union Carbide.

Alumina for mixing with the polymeric binders was prepared by blending aluminium oxide (Alcoa Corporation) with several different additives to aid in processing the powder. These additives were kaolin, talc, sodium lignosulphonate (deflocculant), oleic acid, Triton X-100, callozine green and methylene blue. The characteristics of the alumina and the composition of the binder system are proprietary and cannot be reported.

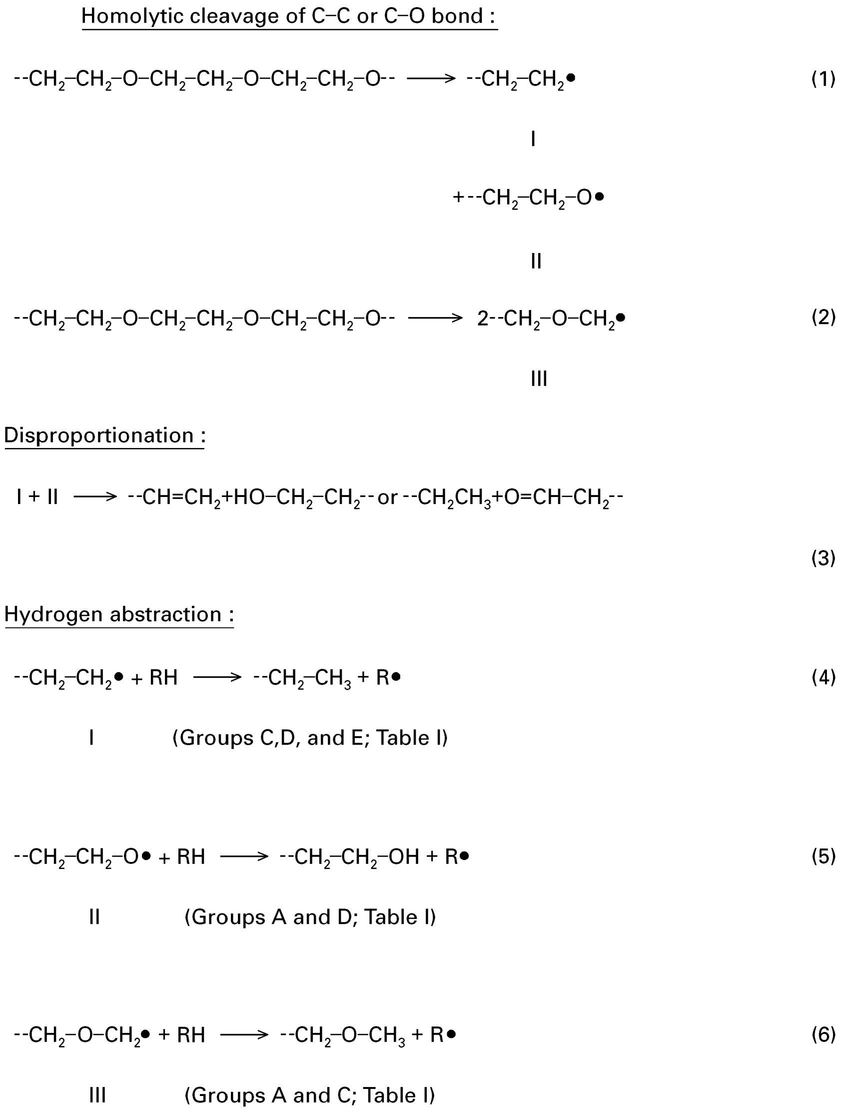

Figure 1 Summary of the reactions occurring during the thermal degradation of PEG (-- represents the continuation of the polymer chain).

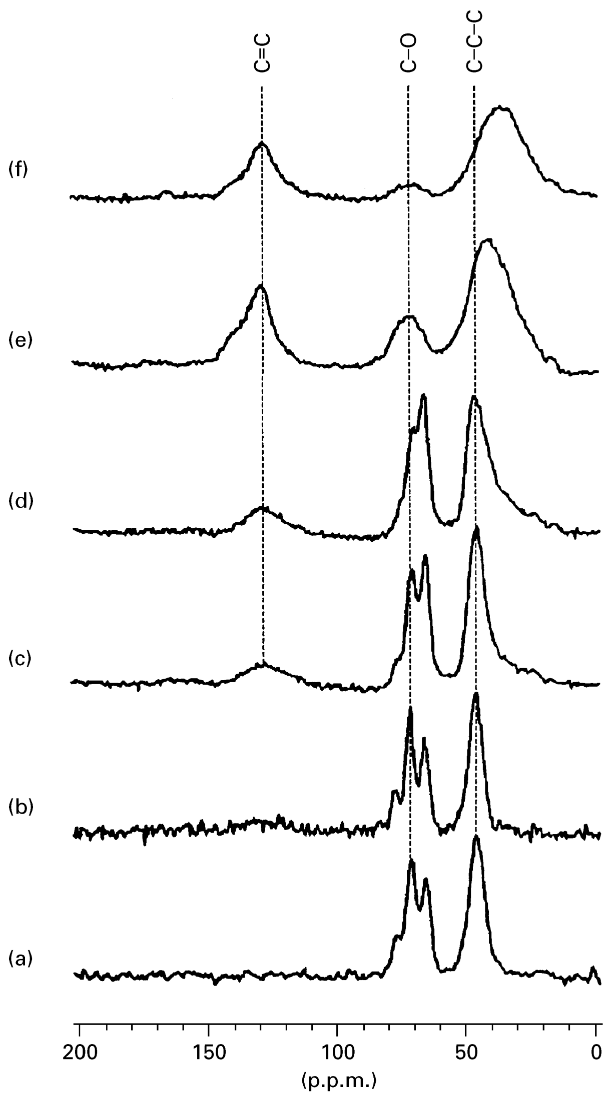

Figure 2 ^{13}C CP–MAS NMR spectra of poly(vinyl alcohol) (a) no heating, (b) 180 °C for 1 h, (c) 215 °C for 1 h, (d) 250 °C for 0.5 h, (e) 250 °C for 1 h, (f) 310 °C for 10 min. (Reprinted from [3] with permission of copyright holder.)

2.2. Sample preparation

An aqueous suspension of alumina powder with deflocculant and dyes was ball milled to ensure uniform mixing and particle size. After 12 h, the aqueous suspension was removed from the ball mill, placed into a 40 gallon container, and then stirred to keep the particles in suspension. The slip, or mixture (40% solids in water), was then divided into 4 batches before the addition of the polymer binders. In the first batch, a quantity of poly(vinyl alcohol) corresponding to a 2% PVA/alumina dry weight was combined with the slip and the resulting mixture spray dried and screened to approximately 42 mesh. A second batch was prepared to produce a 6% poly(ethylene glycol)/alumina ratio followed by spray drying and screening. The third batch was mixed to contain 0.5% poly(vinyl alcohol) and 6% poly(ethylene glycol). The fourth batch was spray dried directly without addition of a binder. Samples for the study were prepared from the spray dried powders by pressing 1×10^7 kg m^{-2} into 10 cm × 50 cm × 5 cm bars. The bars were stored in a desiccator to minimize water adsorption before analysis.

The pressed bars were subjected to partial thermal degradation in a muffle furnace at 450 $\mp$ 25 °C in air to varying weight loss percentages prior to ^{13}C NMR analysis. The total burnout sample (100%) was prepared by heating at a temperature of 800 °C for 4 h. The thermal degradation percentages were calculated by taking the ratio of the weight loss from each partial thermal degradation to the total weight loss. The various samples were ground into fine powders for ^{13}C NMR analysis.

2.3. Thermogravimetric analysis

The thermogravimetric (TG) analyses were conducted with a Seiko SSC/5200 TG/DTA 320 thermal analysis system using approximately 30 mg samples of powdered binder and alumina. A heating rate of 20 °C min^{-1} was used between 20 and 1000 °C with air as the decomposition atmosphere.

2.4. ^{13}C NMR spectroscopy

^{13}C CP–MAS spectra were obtained at 22.7 MHz on a modified Chemagnetics M-90S spectrometer, using a home-built probe employing a large volume (2.5 cm^3) MAS system [8]. MAS speeds of $\sim$ 3.5 kHz were used.

3. Results and discussion

The CP–MAS ^{13}C NMR spectrum (Fig. 3, bottom spectrum) of a thermally untreated 6% PEG–alumina sample has a strong peak at approximately 72 p.p.m. corresponding to the C–O–carbon in the polymer backbone. Peaks at 30 and 130 p.p.m. were assigned to the deflocculant used in dry pressing the powder. These same peaks were observed in the spectrum of the deflocculant–alumina system without binder.

Spectra from a series of PEG–alumina samples that had been partially thermally degraded to varying percentages are also shown in Fig. 3. At a 20% weight loss, the 72 p.p.m. peak due to the C–O–carbon is still present; however, new peaks, assigned to an alkene carbon (130 p.p.m) and a carbonyl carbon (175 p.p.m), have appeared. The 40% weight loss sample spectrum contains the alkene carbon peak (130 p.p.m) at a slightly higher relative intensity, the carbonyl carbon peak which has remained roughly constant (perhaps a small decrease), and the C–O–carbon peak of somewhat decreased intensity. For the sample thermally degraded to 55% weight loss, there was a significant decrease in the relative intensities of both the C–O– and carbonyl carbon peaks, while the alkene peak became more pronounced. This trend continues for the C–O– and C=O peaks as the thermal pre-treatment weight loss was increased to 80%. It is speculated that a major portion of the alkene carbon remaining in the 55 and 80% weight loss samples was associated with the deflocculant. The 100% weight loss sample had no detectable carbon NMR signal (not shown).

These results are consistent with the published PEG thermal degradation mechanism [1, 2, 9]. A ^{13}C

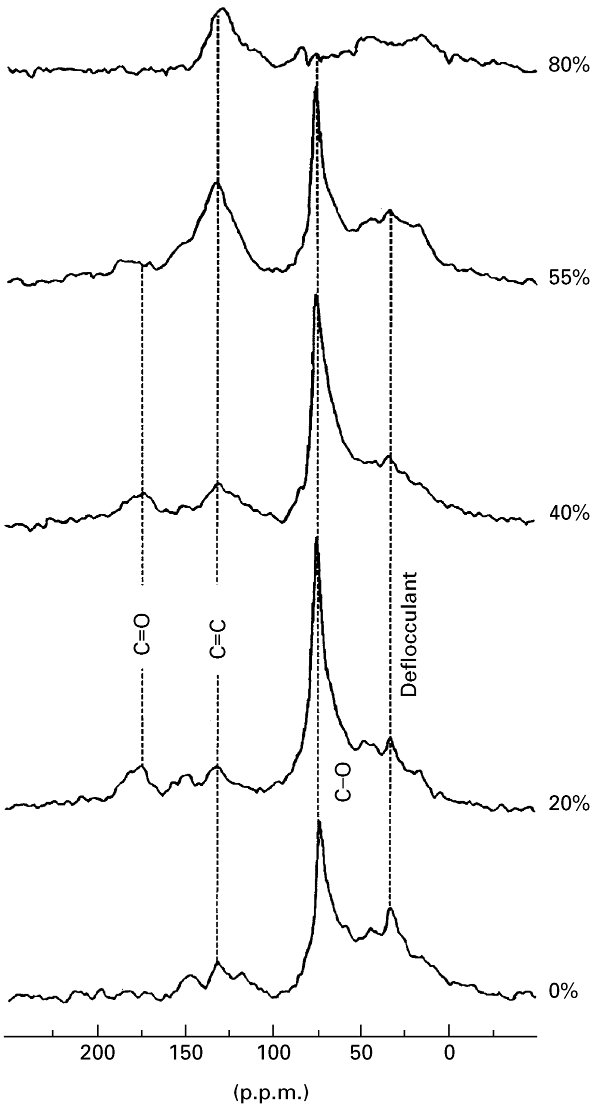

Figure 3 The CP–MAS ^{13}C NMR spectra of 6% PEG in alumina exposed to various degrees of burnout. The percentages listed with each spectrum indicate the thermal weight loss.

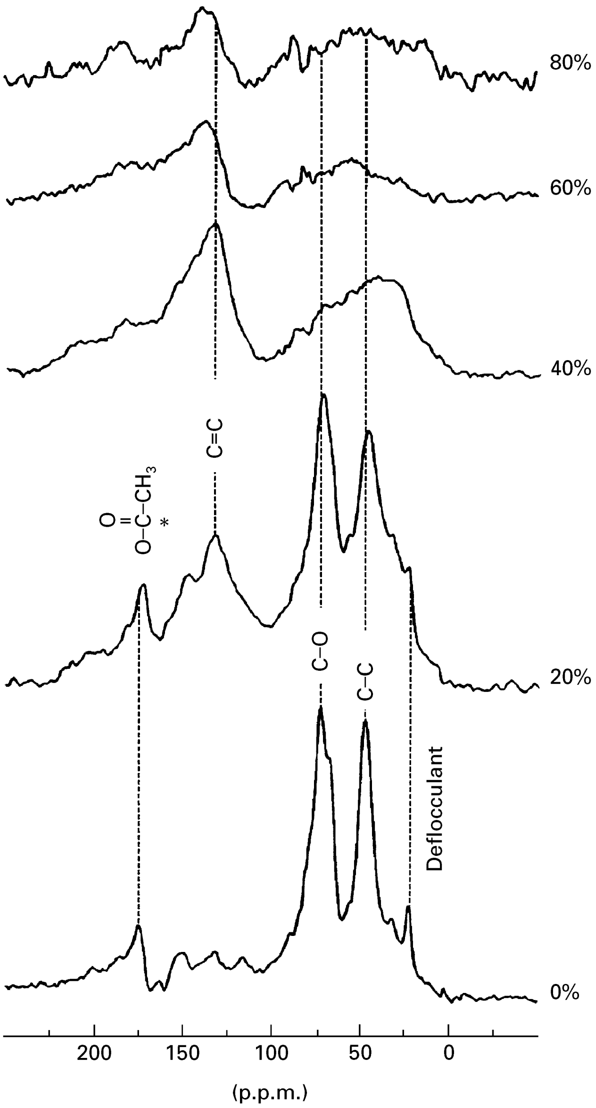

Figure 4 ^{13}C CP–MAS NMR spectra of 2% PVA in alumina thermally degraded to differing weights. The percentages listed with each spectrum indicate the thermal weight loss.

NMR signal was observed for each of the major functional groups listed in Table I. The C–O and C=O peaks decreased much earlier in the burnout sequence than the C=C peak. The deflocculant was the most difficult component in the ceramic system to thermally degrade, as noted by the presence of the C–C peak at 130 p.p.m. and the second peak identified as deflocculant at 30 p.p.m. Thermogravimetric analysis showed that temperatures in excess of 500 °C were required to totally degrade the sodium lignosulphonate. The fact that this compound required high burnout temperatures and was observed in late stages of the burnout of the PEG–alumina samples suggests that other deflocculants should be considered as a replacement for more effective thermal removal.

The CP–MAS ^{13}C NMR spectrum of thermally untreated 2% PVA–alumina is presented as the bottom spectrum in Fig. 4. Although there are gross similarities between this spectrum and some of those in Fig. 2, there are substantial differences including the signal-to-noise ratio. The spectra in Fig. 2 were obtained from pure polymer residues, while spectra in Fig. 4 were from samples containing a maximum of 2% PVA in alumina with additives. Peaks in Fig. 4 due to the carbons in the polymer backbone are present at 45 p.p.m. (CH_2 carbon) and 72 p.p.m. (CH–OH carbon). The smaller peaks at 110, 130, 155, and 175 p.p.m. are probably from unhydrolysed poly(vinyl acetate) and deflocculant. It is clear from this spectrum that the manufacturer's claim of 99% hydrolysis was not correct. At 20% weight loss, the spectrum (Fig. 4) showed a large increase in the relative intensity of the alkene carbon peak (130 p.p.m.). Based upon the literature, the alkene carbon is produced from the dehydration of the PVA polymer chain to produce a polyene [7]. For the 40% weight loss, thermally pre-treated sample, the PVA backbone carbons (signals at 45 and 72 p.p.m.) were substantially attenuated. The dominant peak at 130 p.p.m. is indicative of the buildup of the postulated polyene (alkene carbons) in the polymer residue. The sample thermally degraded to 60% weight loss showed the C=C carbon residue at 130 p.p.m. and a small broad peak at about 30 p.p.m. This pattern is similar to that observed in the 80% burnout PEG spectrum in Fig. 3, where only deflocculant residue remained. With a thermal pretreatment to 80% weight loss, there was a reduction in the relative intensity of both peaks remaining in the system. As the polymer was further degraded to beyond 80% weight loss, the residue that remained contained no new peaks. Complete absence of a carbon signal was observed in the 100% burnout spectrum.

The ^{13}C CP–MAS NMR spectra of a series of samples containing a mixture of 6% PEG and 0.5% PVA in alumina thermally degraded in 20% weight-loss intervals is shown in Fig. 5. The spectrum of the untreated PEG–PVA–alumina sample is dominated by the PEG peak at 72 p.p.m., with smaller peaks due to the PVA present at 45 and 89 p.p.m., and at 30 p.p.m. due to the deflocculant. In the spectrum of the 20% weight loss thermally pre-treated sample, the small peak at 45 p.p.m. has decreased showing the relative loss of PVA in the sample. The dominant form of carbon present at this weight loss is the C–O carbon from the PEG and PVA. At 40% thermal pre-treatment weight loss, peaks for the alkene at 130 p.p.m., and carbonyl carbon at 175 p.p.m. have increased in relative intensity, while the signal intensity corresponding to the sp^3 C–O carbon decreased. The spectrum of the 60% weight loss sample had comparable signals for the alkene carbon (130 p.p.m.) and the C–O carbon (72 p.p.m.). The appearance of this spectrum is similar to the 55% weight loss PEG spectrum in Fig. 3. When the thermal pre-treatment weight loss was 80%, only the alkene carbon signal and a small peak at about 30 p.p.m. associated with the deflocculant were present.

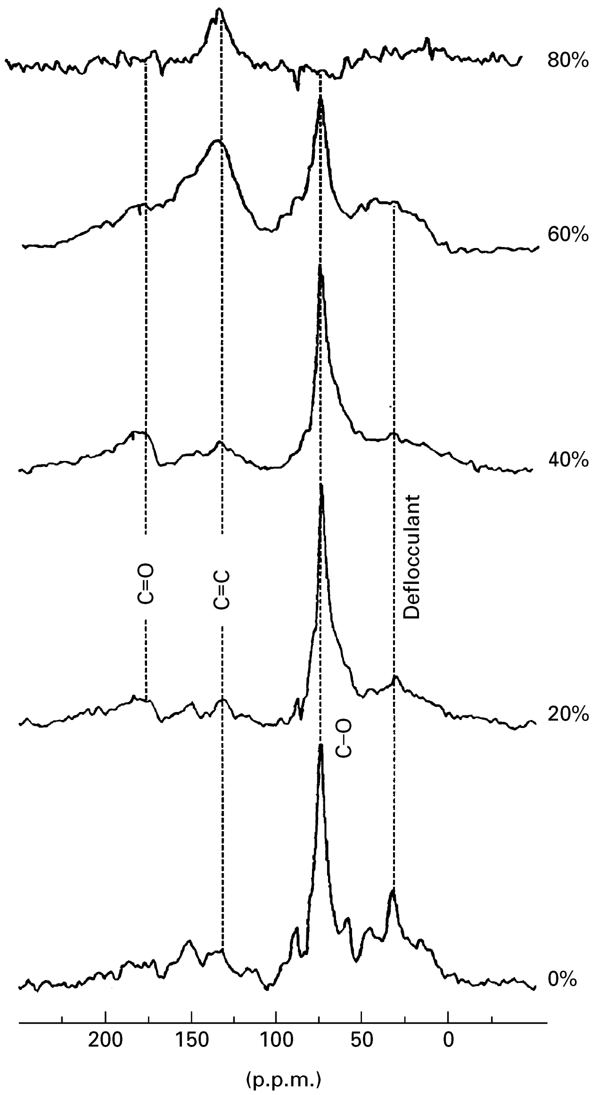

Figure 5 The CP–MAS ^{13}C NMR spectra of controlled thermal degradation products from 6% PEG/0.5% PVA in alumina. The percentages listed with each spectrum indicate the thermal weight loss.

4. Conclusions

The NMR spectra of the PEG samples showed the expected decrease in the relative intensity of the backbone (C–O) carbon upon thermal degradation. An accompanying increase in the relative intensities of carbonyl and alkene peaks compared to the C–O peak in the various thermally treated samples also occurred (see Fig. 1, Equation 3). As the thermal pre-treatment weight loss increased, the C=O and C–O carbons eventually were totally degraded. However, at 80% weight loss, there remained a significant alkene carbon peak that was attributed to the deflocculant. The trends observed for the samples with varying degrees of burnout support the radical based mechanism previously postulated for the PEG thermal degradation [1, 2, 9].

CP–MAS ^{13}C NMR analysis of PVA-alumina and controlled degradation residues indicated that as the polymer degraded; an increase in the alkene carbon signal was observed. This continued as the PVA–alumina decomposed to about 40%, at which point the C=C peak became dominant. The results of the ^{13}C NMR analysis from this study agree with the results reported by Zhang *et al.* [3] for the thermal degradation of neat PVA polymer. Based on our results and the Zhang paper, we postulate that the PVA degraded independently of alumina and copolymers.

Analysis of the PEG–PVA–alumina system by CP–MAS ^{13}C NMR indicated that the mixed binder degradation is very similar to that previously observed for the PEG–alumina and PVA–alumina systems. Weak signals for the CH_2 carbon at 45 p.p.m. for the PVA are identifiable in the ^{13}C NMR spectra. In general, the binders degrade independently of each other. At 80% thermal pre-treatment weight loss, the only observable functional group was the alkene carbon associated with the sodium lignosulphonate deflocculant. The NMR data agreed with the mechanism previously postulated from analysis of the volatile thermal degradation products [1, 2].

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