ELSEVIER

European Polymer Journal 37 (2001) 737–745

EUROPEAN
POLYMER
JOURNAL

High temperature thermal degradation of cellulose in air studied using FTIR and ^{1}H and ^{13}C solid-state NMR

Sandra Soares [a], Nágila M.P.S. Ricardo [a], Steven Jones [b], Frank Heatley [b,*]

[a] Departamento de Quimica Orgânica e Inorgânica, Universidade Federal do Ceará, Campus do PICI, Cx Postal 12200, Fortaleza, Ceará, Brazil

[b] Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

Received 12 January 2000; received in revised form 27 July 2000; accepted 18 August 2000

Abstract

Solid-state NMR spectroscopy and Fourier transform IR (FTIR) spectroscopy have been used to study the degradation of cellulose in the form of transformer insulating paper and Whatman filter paper in air at temperatures from 200°C to 550°C for 1 h with and without 0.01 wt.% NaCl, $ZnCl_2$ and $CuCl_2$. The NMR studies included ^{1}H wide line measurements of the spin-lattice relaxation time (T_1) and spin-lattice relaxation time in the rotating frame ($T_{1\rho}$), and ^{13}C magic-angle spinning experiments. The ^{1}H spectra and relaxation times indicated the presence of absorbed water and oxygen in the papers. On degradation, the ^{1}H intensity and line width decreased, indicating the loss of hydrogen nuclei, and the ^{1}H relaxation times decreased due to the formation of paramagnetic species. The ^{13}C-NMR spectra and FTIR spectra indicated the formation of aromatic structures on degradation above 250°C, the conversion being essentially complete at 450°C. The presence of the salts had little or no effect on the rate or mechanism of degradation.

Keywords: Cellulose; Thermal degradation; ^{1}H-NMR; ^{13}C-NMR

1. Introduction

Cellulose products such as cotton textiles and paper are widely used materials of great commercial importance. An important property of cellulose in these products and others is its deterioration due to ageing and degradation effects. For example, cellulosic materials have been proven to have desirable chemical and physical properties for use as electrical insulators, but the materials degrade as the materials age. The degradation of cellulose at relatively low temperatures (<200°C) has been the subject of a number of studies, two major points of interest being the decrease in the degree of polymerisation and the detection of furanoic compounds for use as specific chemical indicators of degradation [1–13].

Pyrolysis of cellulose at higher temperatures has also been widely studied [14–23], one driving force being understanding the processes involved in the production of activated carbon. The chemistry appears to proceed via the formation first of furanoic then of aromatic structures. Fourier transform IR (FTIR) spectroscopy and high-resolution solid-state ^{13}C-NMR studies [19,20,22] have shown that there is little change in chemical structure up to ≈200°C but degradation is rapid thereafter. ESR studies [23–25] have shown that free radicals are produced during cellulose pyrolysis, the concentration of free radicals increasing for pyrolysis temperatures up to 650–700°C but decreasing thereafter [23]. There is evidence that the process may be affected by the presence of quite small amounts of metal ions [26–31].

---

[*] Corresponding author. Tel.: +44-(0)161-275-4672; fax: +44-(0)161-275-4598.

E-mail address: frank.heatley@man.ac.uk (F. Heatley).

0014-3057/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0014-3057(00)00181-6

In this study, the degradation of cellulose in the form of transformer insulating paper and of Whatman filter paper in air at temperatures up to 550°C with and without metal chlorides has been studied using solid-state NMR spectroscopy and FTIR. The NMR studies included ^1H wide line measurements of the spin-lattice relaxation time (T_1) and spin-lattice relaxation time in the rotating frame ($T_{1\rho}$), and ^{13}C magic-angle spinning (MAS) experiments. Although NMR studies of the high temperature degradation of cellulose have been reported previously [19,20,22,23], none have used all these techniques together on the same materials, nor has such a detailed NMR study using ^1H and ^{13}C-NMR been performed.

2. Experimental

2.1. Materials

The materials studied were

(i) a pulp Kraft paper from Mukyuo, Sweden containing 90% cellulose, the remainder being pentosans and lignin;
(ii) Whatman no. 42 filter paper obtained in Brazil;
(iii) Whatman no. 42 filter paper obtained in Brazil and impregnated with aqueous solutions of the salts NaCl, $ZnCl_2$ and $CuCl_2$ to obtain an increase of metal mass corresponding to approximately 0.01 wt.%. The impregnated papers were dried in air using an oven at a maximum temperature of 50°C;
(iv) Whatman no. 1 filter paper obtained in Manchester.

2.2. Filter paper samples

For reasons explained in Section 3, ^1H-NMR measurements were made on Whatman no. 1 filter paper exposed to the following conditions:

(i) Under ambient conditions exposed to atmospheric oxygen and water vapour. Undried air was used to flush the NMR probe.
(ii) With absorbed water but substantially reduced oxygen. A desorbed sample from (iv) below was exposed to water vapour under N_2 atmosphere in a closed vessel for 24 h, then the NMR tube was sealed.
(iii) With absorbed oxygen but substantially reduced water. A normal sample was placed in air in a dessicator with calcium chloride until the water had been drawn off (24 h) then the NMR tube was sealed.
(iv) Substantially reduced absorbed water and oxygen. The NMR probe was flushed with dry N_2 gas with the sample in an open NMR tube until the NMR spectrum and relaxation times had reached equilibrium (≈24 h).

2.3. Degradation

Thermal degradation was carried out by heating separate samples of papers in air at 200°C, 250°C, 300°C, 350°C, 400°C, 450°C and 550°C for 1 h.

2.4. FTIR spectroscopy

Degradation residues in the form of KBr discs were analysed by transmittance IR spectroscopy using a Perkin Elmer Spectrum 1000 FTIR spectrometer.

2.5. NMR spectroscopy

Residues from thermal degradation were studied by ^1H wide line (300 MHz) and ^{13}C-NMR (75.5 MHz) spectroscopy, using a Varian Associates Unity 300 spectrometer equipped with Doty Scientific Inc. probes. All ^{13}C spectra and most ^1H spectra were run under ambient atmosphere at ≈22°C. ^1H spectra of some samples were also run using dry N_2 gas to flush the probe. For ^1H spectra, the samples were packed into short lengths of 5 mm OD glass NMR tubes. T_1 and $T_{1\rho}$ were measured using standard techniques [18]; the RF field for $T_{1\rho}$ was 45 kHz and the 90° pulse width was 1.6 μs. For ^{13}C spectra, the samples were packed into 7 mm OD alumina or zirconia rotors. Spectra were acquired using CP/MAS cross-polarisation (CP) at a spin rate of 4–4.5 kHz. The RF field strengths were 36 kHz for CP and 45 kHz for dipolar decoupling. Other relevant spectrometer conditions are given in the text or figure captions.

3. Results and discussion

3.1. ^1H-NMR line shape

Fig. 1 shows ^1H wide line NMR spectra run in ambient atmosphere for Kraft paper in its original state and after degradation at various temperatures. All spectra clearly showed relatively broad and narrow components. The broad component was attributed to rigid cellulose molecules. The narrow component disappeared after a few hours when dry N_2 gas was used to flush the NMR sample (see Fig. 2) but re-appeared when air was restored, and it was therefore attributed to relatively mobile absorbed water. It is noteworthy that water was absorbed even by highly degraded samples which appeared highly carbonaceous: compare for example the spectra of the sample degraded at 350°C run in air (Fig. 1(e)) and in N_2 (Fig. 2(b)).

As the degradation temperature increased, there were two noticeable changes in the character of the ^1H spectrum. The first change was that the total ^1H intensity decreased significantly. Although it is recognised that it is difficult to compare the NMR intensity of different

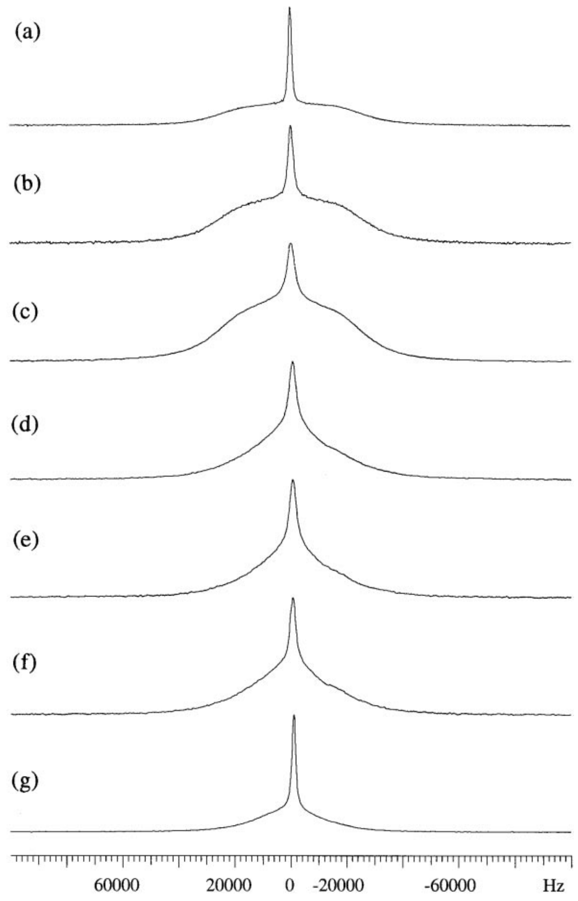

Fig. 1. Wide line ^{1}H-NMR spectra run in ambient air for Whatman no. 42 filter paper degraded at different temperatures: (a) original; (b) 200°C; (c) 250°C; (d) 300°C; (e) 350°C; (f) 400°C; (g) 450°C.

samples because of variations in such instrumental influences as the sample tube filling factor and probe tuning, nevertheless every effort was made to keep these conditions constant as far as possible, and it is believed that the intensities of different samples were comparable to better than a factor of 2. In fact a difference of a factor of 5 in absolute integrated intensity was observed between the original cellulose and that degraded at 450°C. This difference was therefore significant, and pointed to a substantial loss of hydrogen nuclei during degradation. This is consistent with elemental analysis results of Julien et al. [17] who reported that the H/C ratio decreased from a value of 1.8 in cellulose to a value of ≈0.4 on pyrolysis at 500°C for 3 h. The second change was that the ^{1}H line shape narrowed significantly on degradation. In principle, a reduction in line width could arise from either an increase in molecular mobility or from a decrease in the magnitude of ^{1}H–^{1}H dipole–dipole coupling arising from more widely separated ^{1}H nuclei. In view of the brittle character of the degraded materials and the loss of ^{1}H nuclei, the second interpretation is undoubtedly correct.

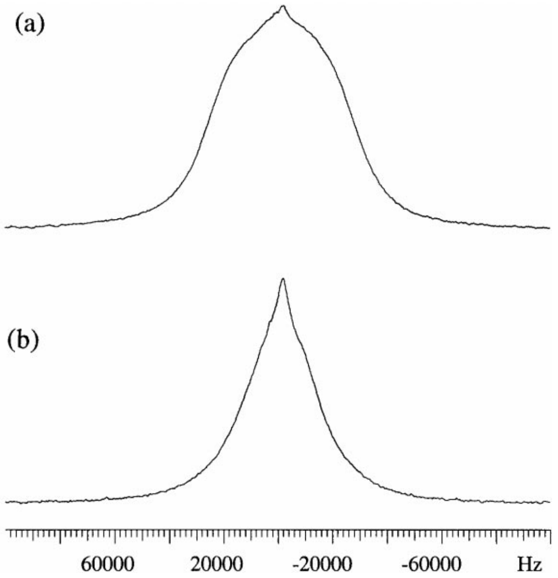

Fig. 2. Wide line ^{1}H-NMR spectra of Whatman no. 42 filter paper run under N_2 gas. (a) original; (b) degraded at 350°C.

To examine magnetic relaxation in the presence of absorbed water in more detail, the ^{1}H line shape was separated by integration into broad and narrow components, the latter being defined somewhat arbitrarily as the central 10 kHz region. This separation was not carried out for dried samples.

3.2. ^1H T_1 *relaxation times*

For a particular sample, the T_1 relaxation curves of both broad and narrow components were very closely exponential (standard deviations of an exponential fit of 1% or less) with similar time constants, suggesting efficient coupling of broad and narrow spin populations by spin diffusion. We consider first data for the original materials and for the filter paper with and without water or oxygen. Under ambient air conditions, the relaxation times of the original materials were very similar, but there were substantial changes when water and/or oxygen was removed. It was observed that for unsealed samples, the use of N_2 gas for probe cooling had two effects, first the narrow component disappeared as noted above and second the value of T_1 increased markedly. The increase in T_1 could arise from two factors, antiplasticisation of the cellulose due to loss of absorbed water, and/or loss of absorbed paramagnetic oxygen. In order to elucidate the relative importance of these factors, measurements were made on filter paper treated as described in Section 2 so as to have (i) ambient absorbed

Table 1
^{1}H T_1 relaxation times for Whatman filter paper under various conditions

Material	Conditions	% Narrow component	T_1 (s)	
			Broad	Narrow
Kraft paper	Ambient O_2, H_2O	8.4	1.51	1.27
Whatman no. 42	Ambient O_2, H_2O		1.40	1.42
Whatman no. 1	(i) Ambient O_2, H_2O		2.00	1.91
	(ii) Absorbed H_2O, no O_2		1.09	0.99
	(iii) Absorbed O_2, no H_2O		3.36	–
	(iv) No O_2, no H_2O		6.73	–

oxygen and water, (ii) absorbed water but substantially reduced oxygen, (iii) absorbed oxygen but substantially reduced water, and (iv) substantially reduced water and oxygen; results are given in Table 1. Comparing samples (iii) and (iv) first, the slightly greater value of T_1 for sample (iv) clearly indicates that cellulose is capable of absorbing O_2, although the extent of absorption cannot be determined from these data. Attempts to detect absorbed oxygen using X-band ESR [32] were unsuccessful because of low concentration and/or broad lines. The presence of absorbed oxygen could have implications for the mechanism of cellulose degradation under aerobic or anaerobic conditions. Large effects of absorbed oxygen on longitudinal relaxation have been reported for other polymers [33] though these contained aromatic groups which are more capable of interacting with oxygen molecules. Comparing samples (ii) and (iv), it is also evident that the presence of absorbed water provides an important longitudinal relaxation mechanism. The fact that T_1 of sample (ii) was *shorter* than that of sample (i) even though (ii) contains no O_2 is explained by the fact that sample (ii) actually contained more absorbed water than (i) because it was exposed to water vapour at its saturated vapour pressure in a sealed container rather than water vapour under ambient air conditions. The higher water content was clearly manifest in a higher relative intensity for the narrow component in sample (ii). The narrow line width for the absorbed water indicates that compared to the cellulose chains, the water is relatively free motionally and capable of acting as a longitudinal relaxation sink. The coupling of longitudinal relaxation of the cellulose and the water is suggested by the near equality of the T_1 values of the broad and narrow components and proven by a Goldman–Shen experiment [34] illustrated in Fig. 3 which clearly shows the features of two spin populations undergoing rapid spin diffusion viz initially a rapid fall in the narrow intensity and a rapid rise in the broad intensity until their spin temperatures are equalised, followed by a common relaxation to thermal equilibrium.

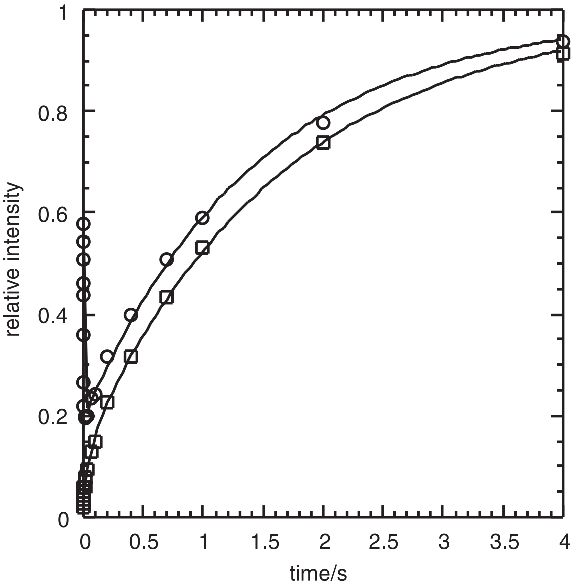

Fig. 3. Example of a Goldman–Shen spin diffusion experiment for Whatman no. 1 filter paper under ambient atmosphere. The ordinate is the integral as a fraction of its equilibrium value. (□): broad component; (○): narrow component.

Table 2 gives T_1 data for degraded samples. There was a substantial difference between the degraded samples of the Kraft and filter papers. For the filter paper, T_1 initially increased slightly for temperatures of 200°C and 250°C but thereafter decreased significantly as the degradation temperature increased. The initial increase is qualitatively consistent with data reported by Ali et al. [22] for Kraft insulating paper degraded at 160°C, though their values of T_1 were shorter than those found here by a factors of 3 or 4, even though measurements were made at the same resonance frequency. In this work, no increase in T_1 for the Kraft paper samples was observed, and the values were significantly less than those of the filter paper samples. Possibly the difference in T_1 between celluloses from different sources is due to variations in morphology or molar mass, and a detailed study of the variation in T_1 for cellulose samples of different origins and histories would seem desirable. In two cases (filter paper at 200°C and 400°C), the values of T_1 increases substantially when N_2 was used to flush an unsealed sample tube. It is thus likely that the char products continue to be able to absorb water and oxygen.

Table 2
^{1}H T_1 relaxation times for degraded cellulose

Material	Degradation temperature (°C)	NMR atmosphere	Salt	% Narrow component	T_1 (s)	
					Broad	Narrow
Kraft paper	200	Air	–	6.4	0.39	0.38
	250	Air	–	10	0.23	0.22
	300	Air	–	6.5	0.12	0.12
	350	Air	–	8.6	0.069	0.042
Whatman no. 42	200	Air	–	5.7	2.14	2.05
	200	N_2		–	7.6	–
	250	Air	–	4.9	2.14	2.09
	300	Air	–	10	0.39	0.36
	350	Air	–	11	0.19	0.20
	400	Air	–	8.2	0.093	0.088
	400	N_2	–	–	0.38	–
	450	Air	–	22	0.077	0.069
Whatman no. 42	Original	Air	$CuCl_2$	7.8	0.11	0.14
	350	Air	$CuCl_2$	12	0.077	0.076
	350	Air	$ZnCl_2$	12	0.22	0.21
	350	Air	NaCl	8.2	0.23	0.21

As the degradation temperature increased up to 450°C, the value of T_1 decreased significantly. In view of the brittle character of the residues, this decrease in T_1 is unlikely to be due to an increase in chain mobility but rather enhancement of relaxation efficiency by paramagnetic species whose presence in degraded cellulose was mentioned by Zawadzki [16] and by Price et al. [18] and which have been observed directly by ESR [23,24]. Wind et al. [23] have reported values of ^{1}H T_1 at resonance frequencies of 64 and 187 MHz in cellulose degraded under N_2 at up to 1000°C for 6 h, measured on samples sealed in vacuo. As well as the differences in degradation and experimental NMR conditions, their data were reported graphically so it is difficult to compare results in detail. As an example, we estimate their T_1 at 187 MHz for a sample degraded at 450°C to be 0.12 s. This is of the same order of magnitude to the value of 0.069 s reported here for a sample degraded for only 1 h run at 300 MHz in air.

For the filter paper samples, the presence of NaCl and $ZnCl_2$ had little or no effect on T_1 of either degraded or undegraded materials (Table 1), but the presence of $CuCl_2$ led to a significant decrease, due presumably to enhanced relaxation by the paramagnetic Cu^{2+} ions.

3.3. ^{1}H $T_{1\rho}$ relaxation times

The $T_{1\rho}$ relaxation curves of both broad and narrow components for the filter paper samples were found to be non-exponential in character as shown by the non-linearity of the example plot of log (intensity) vs. time in Fig. 4. The $T_{1\rho}$ curves were accordingly fitted with a biexponential function with fast and slow contributions, $T_{1\rho f}$ and $T_{1\rho s}$. The quality of this analysis is shown in Fig. 4, where the biexponential fit (solid line) is compared with a single exponential fit (dashed line); it is clear that the former is an acceptable representation. Biexponential fit parameters for all samples are given in Table 3. As for T_1, the values of $T_{1\rho}$ decrease on degradation, again presumably due to the contribution from paramagnetic degradation products, but in general the magnitude of the decrease in $T_{1\rho}$ is somewhat less than that in T_1. Also the decrease in $T_{1\rho}$ appears to occur as a rather sudden step at a degradation temperature of ≈300°C, its value remaining relatively constant below and above that temperature. Thus unlike T_1, $T_{1\rho}$ appears insensitive to the increasing concentration of unpaired electrons produced [23] as the degradation temperature increases. Both T_1 and $T_{1\rho}$ are controlled by ^{1}H–^{1}H dipole–dipole interactions and by ^{1}H–electron dipole–dipole and scalar interactions, but it is well-known that $T_{1\rho}$ is more sensitive than T_1 to slow molecular motions and that it is much less susceptible than T_1 to averaging by spin diffusion because of its much lower value [35]. It is suggested therefore that $T_{1\rho}$ is controlled principally by the relaxation contribution from ^{1}H–^{1}H dipole–dipole interactions operating on a slower timescale than that of the ^{1}H–unpaired electron interactions. $T_{1\rho}$ therefore changes to a smaller extent on degradation. For the same reason, the values of $T_{1\rho}$ changed very little when N_2 was used for probe cooling. The relative constancy of $T_{1\rho}$ for degradation temperatures above 300°C suggests a heterogeneous structure for the char in which the protons remain localised in small groups separated by carbon-rich domains. Further clarification of the relaxation mechanism could shed light on the structure of the degradation products, but an

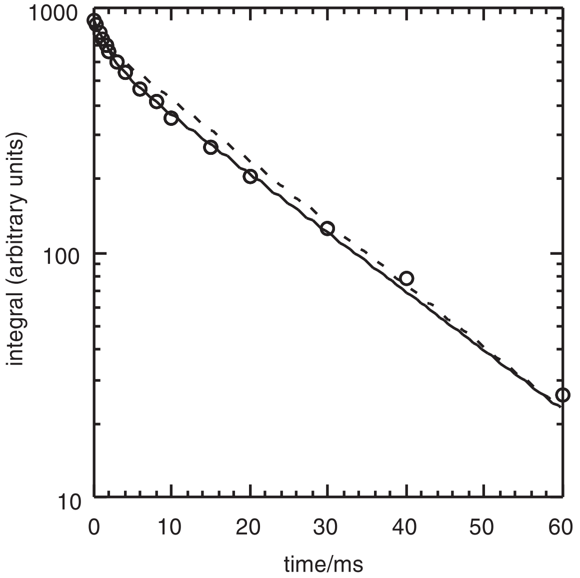

Fig. 4. Example of the analysis of a $T_{1\rho}$ decay curve. The data is for the broad component of Whatman no. 42 filter paper degraded at 200°C run under ambient atmosphere. (□): experimental points, (—): biexponential best fit and (- - -): exponential best fit.

extensive investigation of the temperature and frequency dependence of relaxation times would be required.

3.4. ^{13}C-NMR

Fig. 5 shows ^{13}C-CP/MAS-NMR spectra of Kraft paper in its original state and after degradation for 1 h at various temperatures. Up to a degradation temperature of 250°C, the ^{13}C spectra remained relatively unchanged and fairly well resolved with peaks in the region of 60–100 ppm corresponding to carbons bonded to oxygen in the cellulose polysaccharide structure [22]. However there was a dramatic change at 300°C and above. The spectra became much less well resolved and new peaks developed. The most significant new peak was an intense, broad unsaturated carbon peak spanning the region 100–160 ppm which was present for all degradation temperatures. The second new peak was a broad saturated carbon peak spanning the region 0–60 ppm which developed rapidly in intensity at a degradation temperature of 300°C but which thereafter declined and became barely detectable at 450°C. There were large chemical shielding anisotropy spinning sidebands (ssb) of the unsaturated carbon peak as indicated on the spectra. Unfortunately the low frequency sidebands completely obscured the original cellulose peaks and partially overlapped the saturated carbon resonance at 0–60 ppm. To quantify the saturated/unsaturated carbon ratio, it was necessary to estimate the contribution of the low frequency unsaturated carbon sidebands to this saturated carbon resonance. To do this, it was assumed that degradation at 450°C eliminated all saturated carbons, an assumption justified by the very low intensity at 30–50 ppm in Fig. 5(f). This spectrum then gave the relative intensities of the aromatic sidebands and centreband, which were then used to estimate the aromatic sideband contribution to the saturated carbon region in the lower temperature samples. It was found that at 300°C, about 30% of the carbon intensity lay in the aliphatic region, and at 350°C, about 10%. These values are consistent with those reported previously [20] for similar samples where ^{13}C spectra were recorded using a lower resonance frequency at which spinning sidebands were not a problem.

In order to obtain additional information on the constitution of the degraded cellulose, additional ^{13}C-

Table 3
^{1}H $T_{1\rho}$ relaxation times for degraded Whatman no. 42 filter paper

Degradation temperature (°C)	NMR atmosphere	Salt	$T_{1\rho}$ (ms)					
			Broad			Narrow		
			$T_{1\rho f}$	$T_{1\rho s}$	% Fast	$T_{1\rho f}$	$T_{1\rho s}$	% Fast
Original	Air	–	3.8	25	37	1.0	58	84
200	Air	–	2.5	19	33	0.54	23	93
200	N_2	–	2.5	20	28	–	–	–
250	Air	–	2.4	17	37	0.38	16	84
300	Air	–	0.76	5.8	33	0.29	7.6	85
350	Air	–	0.54	4.0	51	0.24	3.9	82
400	Air	–	0.75	5.6	54	0.50	4.5	82
400	N_2	–	0.52	6.6	73	–	–	–
450	Air	–	0.67	4.4	47	0.86	4.3	77
Original	Air	$CuCl_2$	2.9	19	41	0.71	12	86
350	Air	NaCl	0.53	4.6	57	0.21	8.6	81
350	Air	$ZnCl_2$	0.57	4.3	57	0.18	9.4	73
350	Air	$CuCl_2$	0.59	4.4	55	0.27	9.7	86

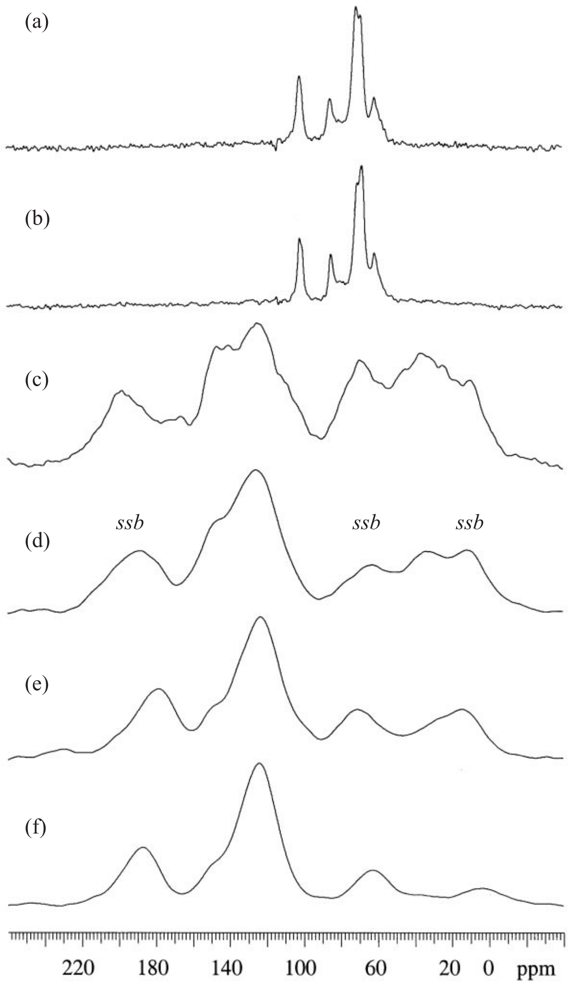

Fig. 5. ^{13}C-CP/MAS spectra for Whatman no. 42 filter paper degraded at different temperatures. (a) original; (b) 250°C; (c) 300°C; (d) 350°C; (e) 400°C; (f) 450°C. The labels ssb on (d) indicate a CSA ssb.

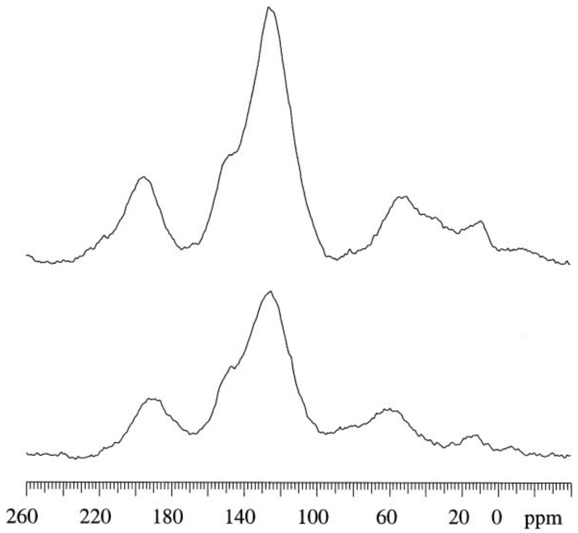

Fig. 6. ^{13}C-CP/MAS spectra for Whatman no. 42 filter paper degraded at 350°C. (a) standard spectrum; (b) spectrum after allowing the ^{13}C-FID to dephase under the influence of ^{13}C–^{1}H dipolar coupling for 30 μs.

NMR experiments were carried out. Fig. 6 compares the standard CP/MAS spectrum of the Whatman paper no. 42 degraded at 350°C with that obtained after allowing the ^{13}C-FID to dephase under the influence of ^{13}C–^{1}H dipolar coupling for 30 μs. The dipolar dephasing technique discriminates against protonated carbons compared to non-protonated carbons because of the greater ^{13}C–^{1}H dipole–dipole coupling for the former. It is apparent that dipolar dephasing results in a much greater loss in intensity for the saturated carbon degradation peak at 0–60 ppm than for the unsaturated peak at 100–160 ppm. Thus the unsaturated peak has a substantial contribution from unprotonated carbons. This is also revealed by variable contact time experiments in which the intensity of a ^{13}C peak is monitored as a function of the time for which the Hartmann–Hahn contact is maintained to transfer magnetisation from ^{1}H to ^{13}C nuclei. Typically the ^{13}C intensity first increases rapidly for ≈100 μs due to fast CP with a time constant T_{CH} and then decreases more slowly due to ^{1}H relaxation in the rotating frame with relaxation time $T_{1\rho\mathrm{H}}$, according to the equation [34]

$$S_t = S_0\left(1 - \mathrm{e}^{-t/T_{\mathrm{CH}}}\right)\mathrm{e}^{-t/T_{1\rho\mathrm{H}}} \tag{1}$$

where S_0 is the equilibrium ^{13}C-CP intensity in the absence of ^{1}H or ^{13}C rotating frame relaxation. Using peak heights as a measure of peak intensity, the intensities of the unsaturated and saturated degradation peaks for the Whatman no. 42 paper degraded at 350°C are shown as a function of contact time in Fig. 7, together with the best-fit curves according to Eq. (1). The best-fit relaxation times were:

unsaturated peak: $T_{\mathrm{CH}} = 0.14$ ms and $T_{1\rho\mathrm{H}} = 3.4$ ms,
saturated peak: $T_{\mathrm{CH}} = 0.05$ ms and $T_{1\rho\mathrm{H}} = 2.7$ ms.

The value of T_{CH} for the saturated peak was a factor of 3 shorter than that of the unsaturated peak, indicating a very much higher proportion of protonated carbon content. The values of $T_{1\rho\mathrm{H}}$ were not significantly different, indicating that the ^{13}C intensity of both saturated and unsaturated peaks in CP experiments was generated from the same ^{1}H population.

CP/MAS spectra for cellulose degraded at 350°C with added NaCl, $ZnCl_2$ or $CuCl_2$ are shown in Fig. 8; these were little different from each other or from cellulose degraded alone, indicating that these salts had

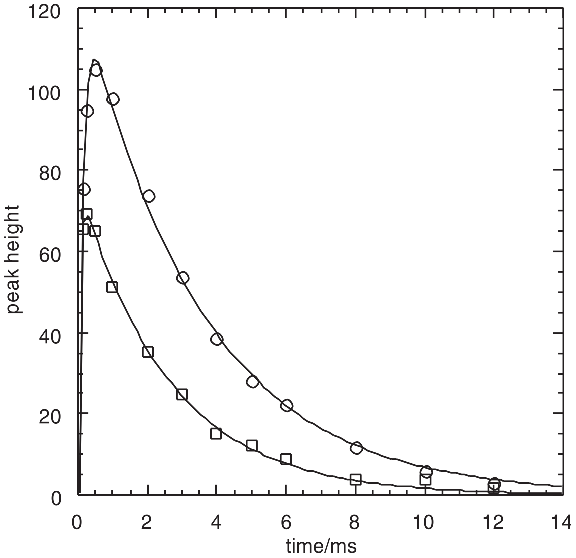

Fig. 7. ^{13}C-CP/MAS intensity as a function of contact time for Whatman no. 42 filter paper degraded at 350°C. (○): unsaturated carbon peak at 125 ppm; (□): saturated carbon peak at 20 ppm. The curves are best fits using Eq. (1).

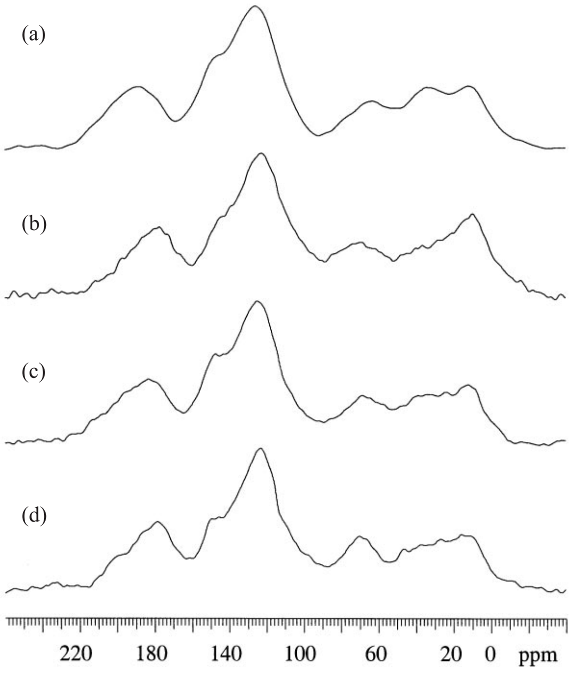

Fig. 8. ^{13}C-CP/MAS spectra for Whatman no. 42 filter paper degraded at 350°C with and without added salt. (a) no salt; (b) with NaCl; (c) with ZnCl$_2$; (d) with CuCl$_2$.

little or no effect on the kinetics or mechanism of formation of the char product.

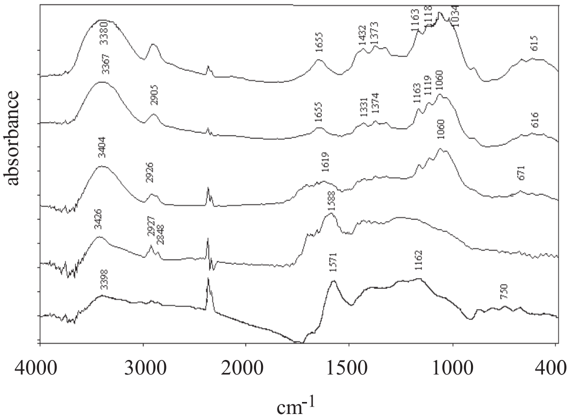

Fig. 9. FTIR spectra of Kraft paper samples degraded at different temperatures: (a) original; (b) 250°C; (c) 350°C; (d) 450°C; (e) 550°C. The feature at ≈2300 cm^{-1} is an instrumental artefact.

3.5. FTIR spectroscopy

Fig. 9 compares the FTIR spectra of Kraft paper residues at various temperatures, while Fig. 10 compares the spectra of the 350°C residues of the different papers and of Whatman no. 42 paper impregnated with salts. There were no significant differences between the FTIR spectra of the different samples, indicating that neither the pentosans and lignin in the Kraft paper nor the salts in the impregnated Whatman paper had any significant effect. The spectra are unfortunately rather poorly resolved, presumably because of complex changes in chemical structure and morphology. Detailed examination of the spectra in Fig. 9 reveals the following changes in functional groups:

(a) Above 250°C, decomposition of the glycopyranose ring was shown by the disappearance of bands at 3400–3300 cm^{-1} (OH stretch), 2900 cm^{-1} (CH stretch), 1430 cm^{-1} (CH$_2$ deformation), 1370–1320 cm^{-1} (CH and C–OH deformation), 1160 cm^{-1} (C–O–C stretching) and 1058 cm^{-1} (skeletal vibration involving C–O stretching).
(b) A band at ≈1600 cm^{-1} due to aromatic C=C stretching modes grew during degradation. An aromatic structure was also indicated by aromatic C–H out-of-plane deformation vibrations at 870, 800 and 750 cm^{-1} for the sample degraded at 550°C.
(c) A band at ≈1700 cm^{-1} attributable to a carbonyl stretch was observed on degradation at 350°C and 450°C. This declined sharply for the sample degraded at 550°C. Although a characteristic carbonyl peak would be expected at 170–200 ppm in the ^{13}C-CP/MAS spectra, this would be obscured by the high frequency ssb of the unsaturated carbons. In the absence of a better resolved spectrum, and further information

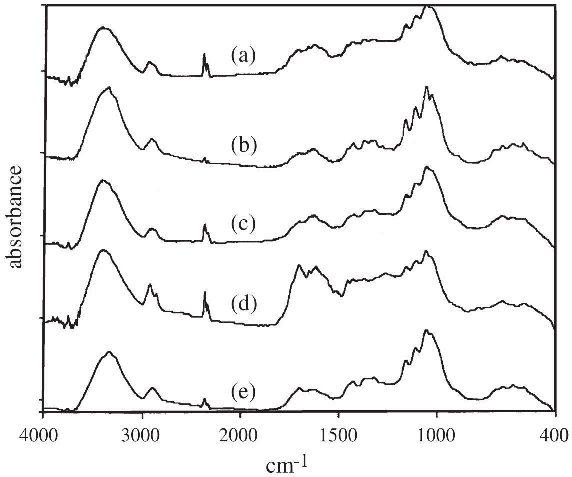

Fig. 10. FTIR spectra of cellulose samples degraded at 350°C. (a) Kraft paper; (b) Whatman no. 42 filter paper; (c) Whatman no. 42 paper with NaCl; (d) Whatman no. 42 paper with $ZnCl_2$; (e) Whatman no. 42 paper with $CuCl_2$. The feature at $\approx$2300 cm^{-1} is an instrumental artefact.

on the influence of degradation conditions on the FTIR spectrum, the question of why the carbonyl peak decreases after 450°C remains unclear.

4. Conclusions

This work has shown in more detail than previously the extent to which ^1H and ^{13}C-NMR spectra and relaxation times are affected by high temperature degradation of cellulose. Major changes occur rather suddenly at temperatures higher than 250°C resulting in the loss of protons and the development of new saturated and unsaturated structures. Unfortunately the ^{13}C-CP/MAS spectra showed insufficient resolution to give detailed information on the chemical structure of the degradation char product. ^1H spectra relaxation times are affected by the presence of adsorbed oxygen and water. Since both of these may influence the degradation process, NMR offers a possible method of investigating their effects.

Acknowledgements

The authors would like to express their gratitude to Dr. G. Camino and Dr. S. Levchik who originally stimulated this field of research.

References

[1] Shafizadeh F, Bradbury AGW. J Appl Polym Sci 1979;23:1431.
[2] Emsley AM, Stevens GC. Cellulose 1994;1:26.
[3] Hill DJT, Le TT, Darveniza M, Saha T. Polym Degrad Stab 1995;48:79.
[4] Hill DJT, Le TT, Darveniza M, Saha T. Polym Degrad Stab 1995;49:429.
[5] Emsley AM, Stevens GC. Polym Degrad Stab 1994;44: 324.
[6] Emsley AM. Polym Degrad Stab 1994;44:343.
[7] Emsley AM, Stevens GC. IEE Proc-Sci Meas Technol 1994;141B:324.
[8] Burton PJ, Graham J, Hall AC, Laver JA, Oliver AJ. Paper 12-09. Int Conf Large High-Voltage Electron Syst (CIGRE), 1984.
[9] Hill DJT, Le TT, Darveniza M, Saha T. Polym Degrad Stab 1996;51:211.
[10] Scheirs J, Camino G, Tumiatti W, Avidano M. Angew Makromol Chem 1998;259:19.
[11] Levchik S, Scheirs J, Camino G, Tumiatti W, Avidano M. Polym Degrad Stab 1998;61:507.
[12] Biggar SW, Scheirs J, Camino G. Polym Degrad Stab 1998;62:33.
[13] Scheirs J, Camino G, Avidano M, Tumiatti W. J Appl Polym Sci 1998;69:2541.
[14] Sekiguchi Y, Frye JS, Shafizadeh F. J Appl Polym Sci 1983;28:3513.
[15] Sekiguchi Y, Shafizadeh F. J Appl Polym Sci 1984;29:1267.
[16] Zawadzki J. Chem Phys Carbon 1989;21:147.
[17] Julien S, Chornet E, Tiwari PK, Overend RP. J Anal Appl Pyrolysis 1991;19:81.
[18] Price D, Coleman GV, Horrocks AR. J Therm Anal 1993;40:649.
[19] Pastrova I, Botto RE, Arisz PE, Boon JJ. Carbohydrate Res 1994;262:27.
[20] Norton FJ, Love GD, Mackinnon AJ, Hall J. J Mater Sci 1995;30:596.
[21] Milosavljevic I, Vahur O, Suuberg EM. Ind Eng Chem Res 1996;35:653.
[22] Ali M, Apperley DC, Eley CD, Emsley AM, Harris RK. Cellulose 1996;3:77.
[23] Wind RA, Maciel GE, Wooten JB. Appl Mag Reson 1993;5:161.
[24] Singh R, Arora S, Lal K. Therm Acta 1996;289:9.
[25] Czechowski F, Jezierski A. Energy and Fuels 1997;11:951.
[26] Essig M, Lowary T, Richards GN, Schenck E. Res. Thermochem biomass convers. In: Bridgwater AV, Kuester JL, editors. Ed Rev Pap Int Conf, vol. 143. London: Elsevier, 1988.
[27] Pan WP, Richards GN. J Anal Appl Pyrolysis 1989;16:117.
[28] Pan WP, Richards GN. J Anal Appl Pyrolysis 1990;17:261.
[29] Richards GN, Zheng G. J Anal Appl Pyrolysis 1991;21:133.
[30] Edye LA, Richards GN, Zheng G. Prepr Pap – Am Chem Soc Div Fuel Chem 1991;36:1715.
[31] Lerdkanchanaporn S, Dollimore D, Alexander KS. Thermochim Acta 1998;324:25.
[32] Mabbs FE. University of Manchester, personal communication.
[33] Capitani D, Segre AL, Pentimalli M, Ragni P, Ferrando A, Castellani L, Blicharski JS. Macromolecules 1998;31:3088.
[34] Goldman M, Shen L. Phys Rev 1966;144:321.
[35] McBrierty VJ, Packer KJ. Nuclear magnetic resonance in solid polymers. Cambridge University Press, 1993.