

APPLICATIONS OF DIFFERENTIAL SCANNING CALORIMETRY AND DIELECTRIC THERMAL ANALYSIS TO THE STUDY OF PAPER DETERIORATION *

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ABSTRACT

A preliminary study has been made using differential scanning calorimetry (DSC), IR spectroscopy and dielectric thermal analysis to examine the reaction of recent and old newsprint with ethylene oxide. Data are presented which show that changes occur in the parameters measured and that they do vary with the length of exposure of the paper to ethylene oxide. Indications are that the ethylene oxide treatment improves the thermal stability of the paper, particularly in the case of recent newsprint where the onset of discolouration on heating occurred at higher temperatures for samples with prolonged exposure to ethylene oxide. DSC data also showed that it was possible to distinguish clearly between old (1910) and recent (1989) newsprint.

INTRODUCTION

Paper generally yellows with age and this behaviour has been attributed both to poorly controlled storage conditions and to the presence of a ligneous wood pulp component in the paper [1]. Most recent papers contain lignin in differing amounts and they deteriorate relatively rapidly even under good environmental conditions. Lignin is a reactive material and is readily oxidized to form acidic products which are then able to catalyse the hydrolysis of cellulose. This would cause a decrease in the chain length of

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the cellulosic polymers with accompanying decrease of fibre and paper strength. The aim therefore is to retard this process. Previous methods have used liquid ammonia [2]; the present work describes the use of ethylene oxide vapour. Ethylene oxide is known to react with both lignin and cellulose [3]. Lignin is a complex polymeric material where the basic unit is methoxyphenylpropane [4]. Its structure includes a phenyl ether group which during processing is converted to a phenolic compound. The latter readily oxidises to form aromatic carboxylic acids [5], hence the acidity of degraded lignin containing paper. It is expected that ethylene oxide will form stable ether bonds which will induce resistance to lignin degradation. The reaction between alkylene oxide and hydroxyl groups proceeds rapidly to completion and forms stable ether bonds with no by-products [6].

SAMPLES

The following samples have been investigated before and after treatment with ethylene oxide vapour.

(1) Paper from a periodical printed in 1910. This was made from mixed fibres including mechanical wood which contains lignin. Since lignin is readily oxidized in the presence of light and oxygen there is only a small amount of lignin still present in the paper. The paper itself is badly discoloured and highly deteriorated.

(2) Paper from recent newsprint (1989) which contains mixed fibres including lignin. This sample represents a high lignin containing paper which has as yet not aged.

(3) Recent paper containing alpha cotton cellulose with hardly any lignin (Whatman No. 1 Filter Paper).

SAMPLE TREATMENT

Samples were placed in a Pern fumigation chamber and evacuated. A canister of ethylene oxide gas (26 g) was then introduced into the chamber. Experiments were conducted at both 20°C and 70°C and the paper samples were exposed for different time intervals ranging from 3 h to 94 h. The pressure in the chamber remained just below atmospheric pressure during the course of the experiment. About five samples were treated at the one time and this ensured that an excess of ethylene oxide was present in the system. Samples were weighed before and after the ethylene oxide treatment and the weight gain or loss was recorded.

EXPERIMENTAL PROCEDURE

Differential scanning calorimetry (DSC)

The Perkin–Elmer DSC7 with the TADS7 data station was used for this study. Paper samples in the form of circular discs were taken from the edges to avoid the actual print. They were then placed in either open Al crucibles or pans containing lids which had several perforations to allow access of purge gas and not to inhibit the release of gases on oxidation of the samples. Heating was carried out in oxygen with a flow rate of $60 \text{ cm}^3 \text{ min}^{-1}$, and heating rates of both $10^\circ \text{C min}^{-1}$ and $40^\circ \text{C min}^{-1}$ were used.

Samples were also heated on a Mettler FP-82 stage heater at $5^\circ \text{C min}^{-1}$ to 300°C . The temperature of onset of discolouration and subsequent charring were observed using an Olympus microscope. The ability to observe the initial subtle changes occurring in paper and then to record simultaneously the accompanying temperatures was particularly valuable for studying the effects of ethylene oxide treatment on recent newsprint.

Infrared spectroscopy

The Bruker FTIR (IFS-45) was used for this study. Samples were placed directly on the sample holder of the diffuse reflectance attachment and spectra were recorded. For each sample the spectrum was collected with 200 scans.

Elemental analysis

Samples were analysed using the Perkin–Elmer 2400 automatic C,H analyser in the Chemistry Department, University College of London.

Surface pH measurements

Measurements were made directly on the paper samples using a flat surface combination electrode and pH meter (Corning). The paper samples were placed on Melinex (or any non-ionic support) which rested on a glass plate. The electrode was dipped into a beaker containing deionised water and then transferred to the surface of the paper samples. The pH value was recorded after 20 s.

Care was taken in making the measurements to minimise errors or fluctuations resulting from type of support [7], amount of water transferred from the electrode to the paper, and the different degrees of absorbancy of the paper.

Dielectric thermal analysis (DETA)

The PL dielectric thermal analyser was used for the measurements. Small rectangular samples (thickness 0.1 mm, width 7.5 mm) from the edges of the paper and containing no print were examined with a range of frequencies (0.1 kHz, 1 Hz, and 10 Hz). A plot of $\tan\delta$ was recorded over the temperature range 0°C to 200°C for the degraded paper samples (treated and untreated).

RESULTS

Weight change in paper samples during ethylene oxide treatment

The values in Table 1 show that maximum weight gain of the order of 4–5% has occurred in all three samples (Whatman No. 1, recent and old newsprint) after 9 h exposure to ethylene oxide at 70°C.

Variation in surface pH with ethylene oxide treatment (Table 2)

The sample of old untreated newsprint is more acidic than recent newsprint and Whatman No. 1. This is as expected owing to the acidic nature of lignin degradation products. With ethylene oxide treatment a shift in pH of the degraded paper occurs to higher values. It reaches a maximum value of pH 5.7 for the sample treated for 9 h at 70°C. The result is encouraging as this indicates that a reaction has occurred which is reducing the level of acid in the paper. The untreated recent newsprint is less acidic than the old

TABLE 1

Weight change in paper samples during ethylene oxide treatment

Sample No.	Temperature (°C)	Weight gain or loss (%) at ^a						
		3 h	5 h	7 h	9 h	20 h	30 h	94 h
4	20	0.1	0	0.6		-0.4	1.2	1.2
	70	1.3	1.5 1.6 ^b	2.6	4.9			
62	20	0.1	-0.3	0.8		-1.4	1.0	0.7
	70	1.2	1.9 2.5 ^b	2.7	4.7			
63	20	0	-0.3	0.8		-0.9	0.6	0.6
	70	0.9	0.9 1.6 ^b	2.3	4.0			

^a - indicates weight loss.

^b Pre-NH₃ exposure.

TABLE 2
Variation in surface pH with ethylene oxide treatment

Sample No.	Temperature °C	Surface pH at							
		0 h	3 h	5 h	7 h	9 h	20 h	30 h	94 h
4	20	4.3	4.8	4.3	5.5		4.8	4.6	4.8
	70		4.9	5.2 6.0 ^a	5.6	5.7			
62	20	5.8	5.9	6.0	6.2		6.0	6.2	6.2
	70		6.1	6.3 6.3 ^a	6.4	6.6			
63	20	6.7	6.6	6.5	6.4		6.5	6.1	6.1
	70		6.7	6.6 6.6 ^a	6.5	6.6			

^a Pre-NH₃ exposure.

sample and has an initial pH value of 5.8. Treatment with ethylene oxide also gives an increase of the order of 1.2 pH units for the sample treated for 9 h at 70°C. In both cases (recent and old newsprint) the increases are maximum for the samples treated at 70°C.

DSC parameters of untreated samples

The DSC data showed that there was a significant difference between the untreated cellulose, recent and old newsprint samples.

Figures 1 and 2 show the DSC curves obtained on heating the samples at 40°C min⁻¹.

Table 3 contains the calculated values of onset temperature (T_0), peak heights (P), and peak areas (A). The ratios have also been calculated, i.e. (P_r) the peak height of the second exothermic peak/peak height of the first exothermic peak, and similarly for the area ratio (A_r).

TABLE 3
DSC parameters of untreated samples

	Peak 1			Peak 2				
	T_0	P	A	T_0	P	A	A_r	P_r
Heating rate 40°C min ⁻¹								
Whatman No. 1	350.4	49.9	2100	481.0	37.9	1729	0.82	0.76
Recent newsprint	317.8	22.6	1643	463.9	57.9	2275	1.38	2.56
Old newsprint (1910)	305.2	14.8	1163	422.9	19.9	1356	1.16	1.34
Heating rate 10°C min ⁻¹								
Lignin	207.9	2.9	1497	469	27.9	6795	4.5	9.6

DSC Normalization: 62a33
 Sample Weight: 0.529 mg
 Mon Jun 19 22:56:50 1989
 62A36/untreated newsprint 1
 (Normalized)

PERKIN-ELMER
 7 Series Thermal Analysis System

DSC Normalization: 63A36
 Sample Weight: 1.127 mg
 Mon Jun 19 14:16:15 1989
 63A36/Blank untreated 2
 (Normalized)

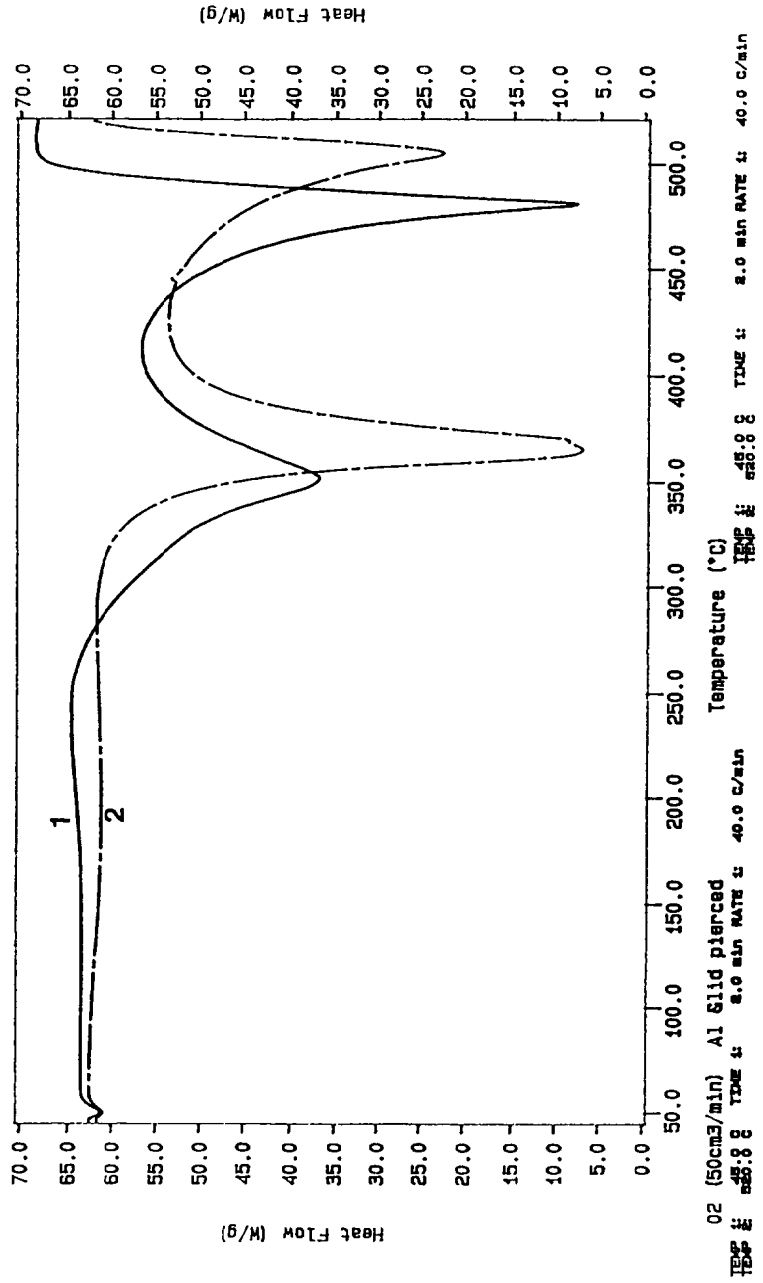


Fig. 1. DSC curves for untreated recent newspaper (1) and cellulose (2) samples.

DSC Normalization: 63a36
 Sample Weight: 1.127 mg
 Mon Jun 19 14:16:15 1989
 63A36/Blank untreated 2
 (Normalized)

PERKIN-ELMER
 7 Series Thermal Analysis System

DSC Normalization: 4a36
 Sample Weight: 0.935 mg
 Sun Jun 18 12:49:52 1989
 4A36/untreated 3
 (Normalized)

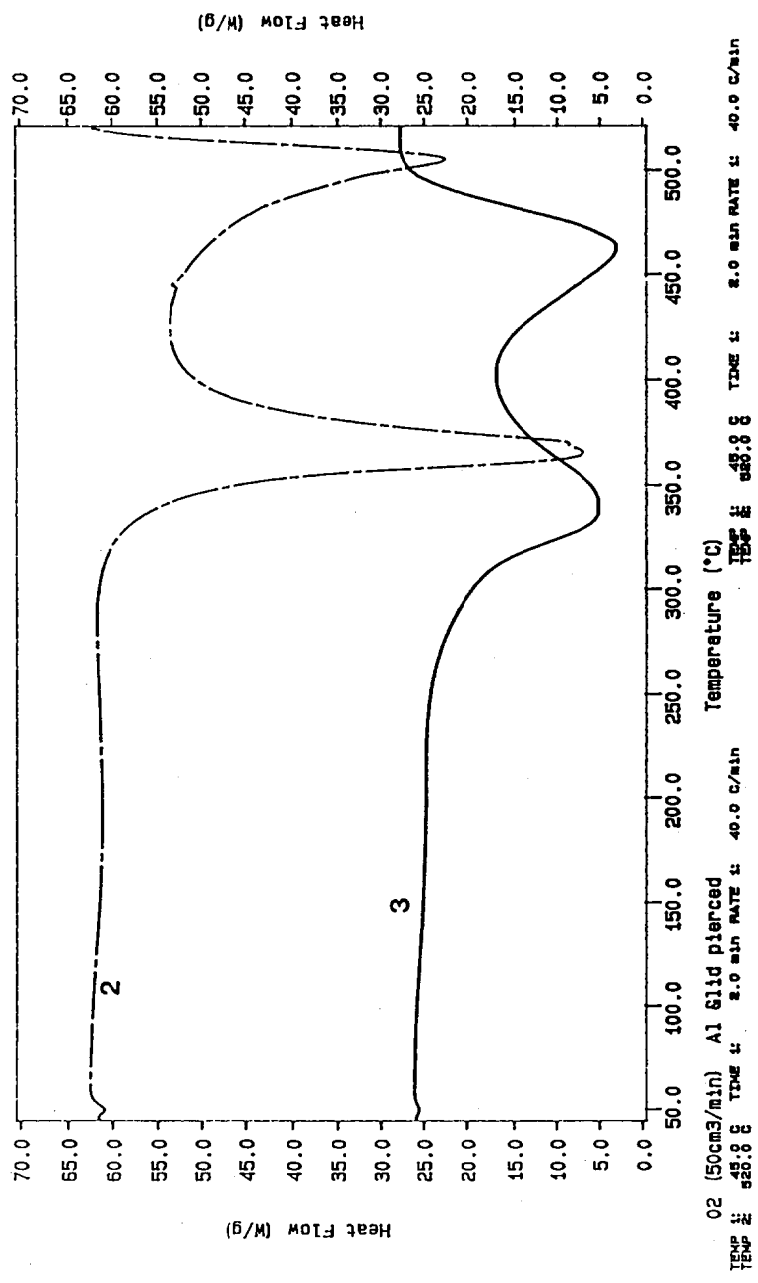


Fig. 2. DSC curves for untreated cellulose (2) and old newspaper (3) samples.

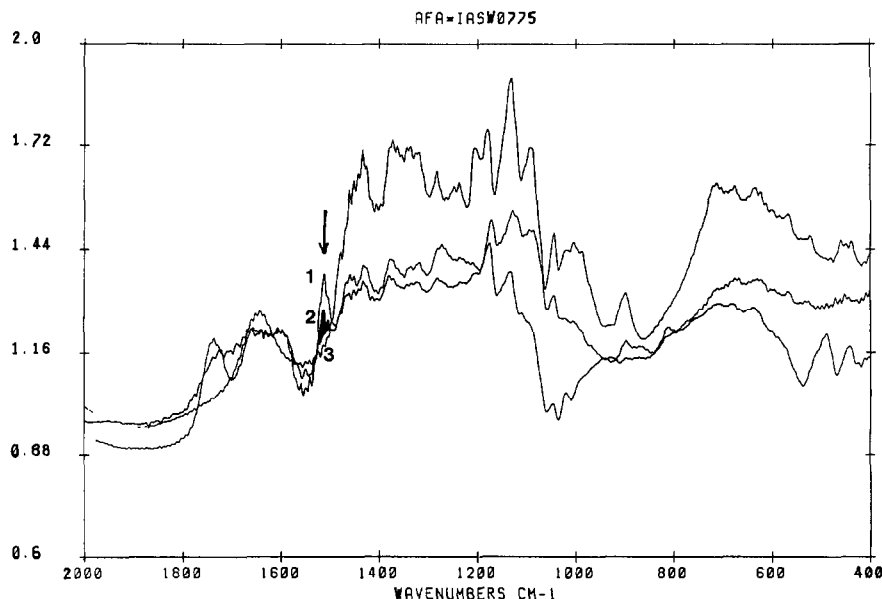


Fig. 3. IR spectra for untreated recent newsprint (1), untreated old newsprint (2) and untreated Whatman No. 1 (3).

Figure 3 shows the IR spectra of the three starting materials. A difference in their spectra occurs at 1512 cm^{-1} . Furthermore the peak is more intense for recent newsprint than it is for old newsprint but is entirely absent in Whatman No. 1. The latter contains mainly cellulose and only about 0.2% lignin. Present information [8] suggests that the peak may be due to the aromatic skeletal vibration in lignin which occurs in the region of $1515\text{--}1510\text{ cm}^{-1}$. Work is in progress to determine more precisely the nature of this peak [9].

Table 4 gives the results of the C,H analysis of the three starting materials. Old newsprint has a significantly lower carbon content and a higher oxygen content than recent newsprint and Whatman No. 1. This results partly from the higher content of carboxylic acids in the sample arising from degradation processes.

TABLE 4

Elemental analysis of untreated samples

	%C	%H	%O
Whatman No. 1	42.40	6.25	51.35
Recent newsprint	46.91	6.44	46.65
Old newsprint	33.55	4.82	61.36
Lignin	58.11	5.45	36.44

TABLE 5

Effect of ethylene oxide treatment at 20 °C on the DSC parameters of recent newsprint (peak 1)

Time (h)	P	A	A_r
Heating rate 40 °C min ⁻¹			
0	23.5	1722	1.4
5	35.1	2010	1.2
30	43.9	2476	1.0
94	64.7	3240	0.8

TABLE 6

Effect of ethylene oxide treatment at 70 °C on the DSC parameters of recent newsprint (peak 1)

Time	P	A	A_r
Heating rate 40 °C min ⁻¹			
0	23.5	1722	1.40
3	23.9	1568	1.42
5	24.1	1670	1.32
7	28.4	1794	1.28

DSC parameters of treated samples (recent newsprint)

The DSC data (Tables 5 and 6) showed two effects. There was an increase in the magnitude of the first exotherm with increased exposure to ethylene oxide which reached a maximum value at 94 h at 20 °C (Fig. 4). This was accompanied by a decrease in the calculated area ratio A_r .

The IR spectra of the treated newspaper samples show a change in intensity of the peak at 1088 cm⁻¹ (Fig. 5). It appears to be a maximum for

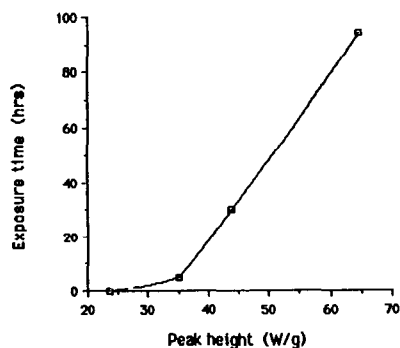


Fig. 4. Exposure time vs. DSC peak height for recent newspaper treated with ethylene oxide.

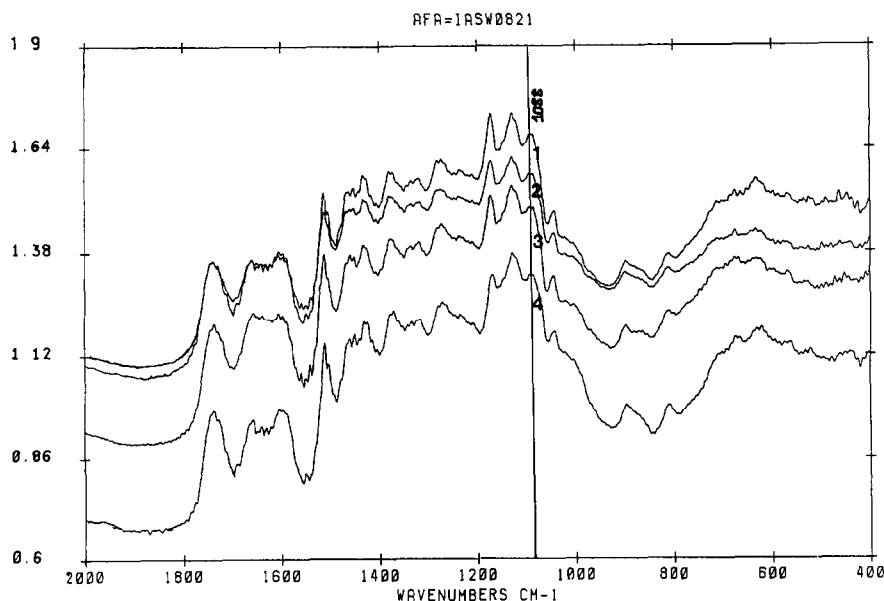


Fig. 5. IR spectra of treated newspaper: 1, recent newsprint treated for 94 h at 20°C; 2, recent newsprint treated for 3 h at 70°C; 3, recent newsprint, untreated; 4, recent newsprint treated for 7 h at 70°C.

the sample exposed to ethylene oxide for 94 h at 20°C. According to Pouchert [10] and Hergert [11] this band falls in the region of C–O–C deformation of aliphatic ethers and C–O deformation in secondary alcohols.

DSC parameters of treated samples (old newsprint)

Figure 6 shows the shift in onset temperature (T_0) to higher values for both exothermic reactions for the sample of degraded paper which has been treated for 7 h at 70°C, and hence the improved thermal stability.

The values for the calculated DSC parameters are shown in Table 7. There is a reduction in the area ratio (A_r) for the sample treated for 5 h at 70°C.

Values for the C,H analysis showed an increase in carbon content of the order of 3% for samples of old newsprint which had been exposed to ethylene oxide for 9 h at 70°C (Table 8). This is in contrast to recent newsprint and Whatman No. 1 where the increases were in the order of 0.2–0.5%.

DETA of treated samples of old newsprint

Figure 7 shows the $\tan \delta$ peak at 45°C at three different frequencies for the untreated degraded paper sample. Figures 8 and 9 show that a new $\tan \delta$

DSC Normalization: 4a36
 Sample Weight: 0.935 mg
 Sun Jun 18 12:49:52 1989
 4A36/untreated 1
 (Normalized)

PERKIN-ELMER
 7 Series Thermal Analysis System

DSC Normalization: 4g7a
 Sample Weight: 0.865 mg
 Sun Jun 18 02:52:52 1989
 4g7a/c2H4O 7 hrs at 70C 2
 (Normalized)

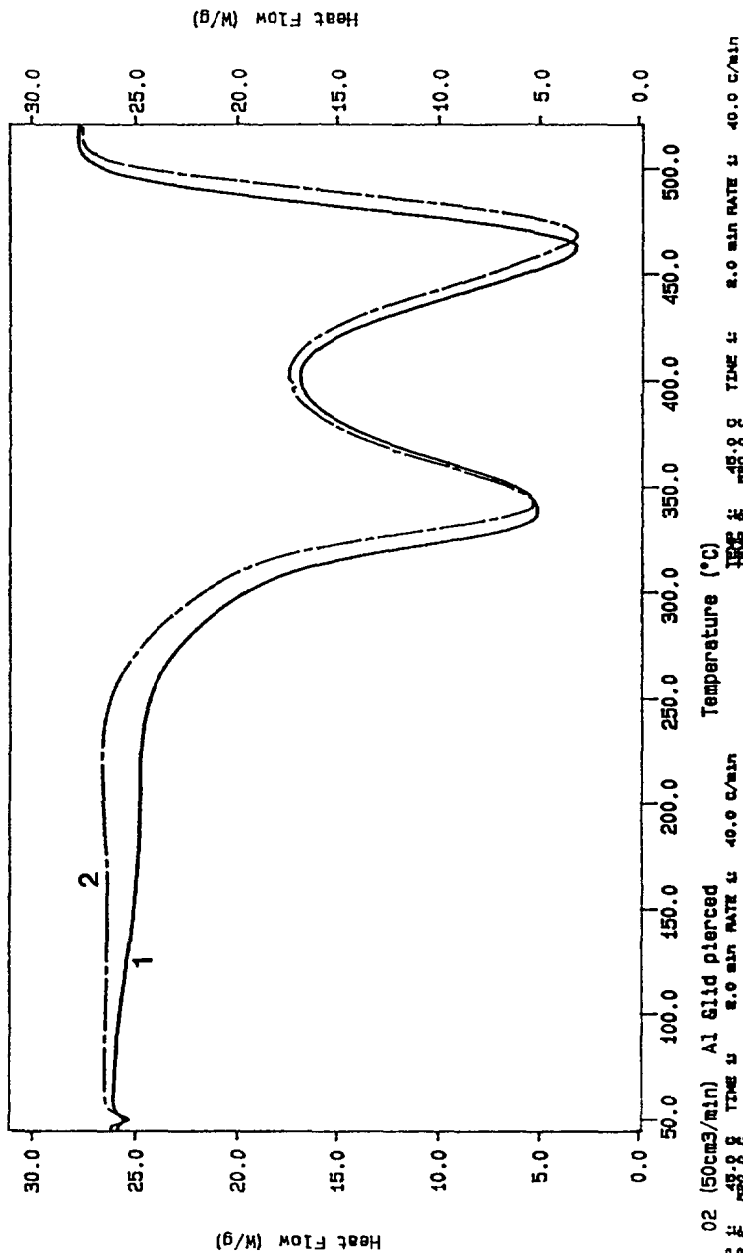


Fig. 6. DSC curves for degraded untreated paper (1) and degraded paper treated for 7 h at 70 °C (2).

TABLE 7

Effect of ethylene oxide treatment on the DSC parameters of old newsprint

Time (h)	T_0	P	A	T_0	P	A	A_r	P_r
Temperature 70 ° C								
0	279.3	6.9	1880	398.6	6.5	1781	0.95	0.94
5	281.3	8.1	1963	392.5	5.2	1538	0.78	0.64
7	283.3	8.4	1777	383.9	5.9	1716	0.96	0.7
9	271.4	5.3	1749	396.6	5.9	1646	0.94	1.1
Temperature 20 ° C								
94	284.3	8.2	1957	394.2	6.0	1590	0.81	0.7

TABLE 8

Elemental analysis of treated samples (old newsprint)

Time (h)	%C	%H	%O
Temperature 70 ° C			
0	33.55	4.82	61.36
3	35.16	4.96	59.88
5	34.26	4.90	60.84
5 (+ 30 min NH ₃)	34.44	4.84	60.72
7	35.78	5.16	59.06
9	36.73	5.30	57.97
Temperature 20 ° C			
94	35.11	5.04	59.85

peak appears at a higher temperature: 55.5 ° C for the sample treated for 94 h at 20 ° C, and 56.5 ° C for the sample treated for 9 h at 70 ° C.

DISCUSSION

An examination of the values of area (or peak) ratios in the previous tables of DSC data show an interesting trend: cellulose-only material has an area ratio which is less than 1; lignin-only material (milled wood lignin from pine) has a ratio much larger than 1; recent newsprint gives a ratio which is much lower than that of the lignin-only sample but is higher than the cellulose ratio; old newsprint has a value which is lower than that for recent newsprint.

This variation in area (or peak) ratios in the presence of fresh and degraded lignin was used as a starting point for monitoring the effect of ethylene oxide, i.e. whether it changed the lignin in any way. For recent newsprint there was a definite decrease in the area ratio with prolonged

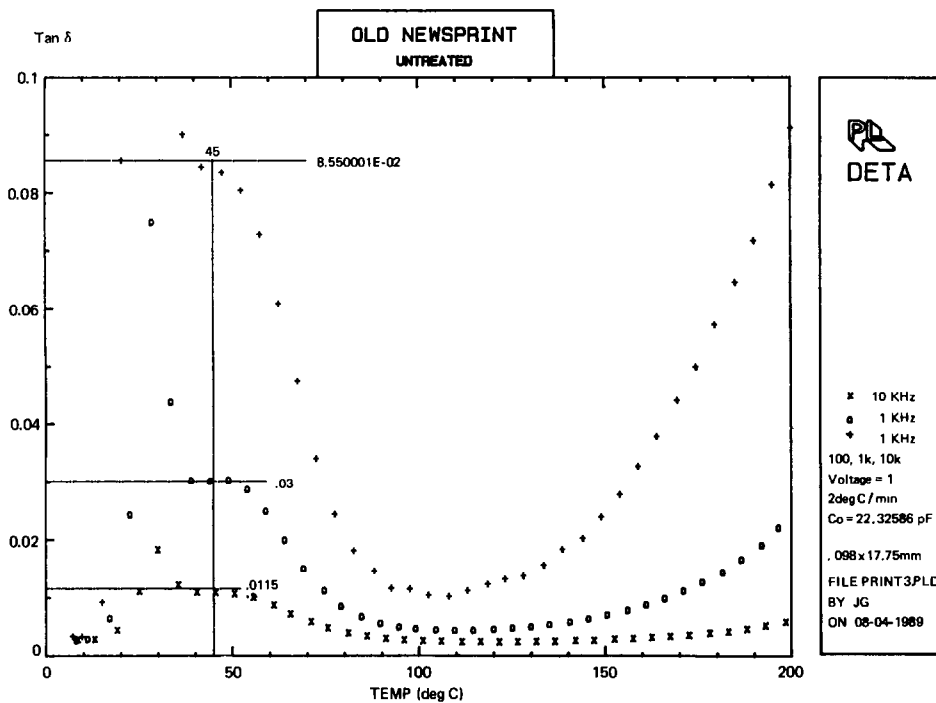


Fig. 7. $\text{Tan } \delta$ for untreated degraded paper; \times , 10 kHz; \circ , 1 kHz; $+$, 0.1 kHz.

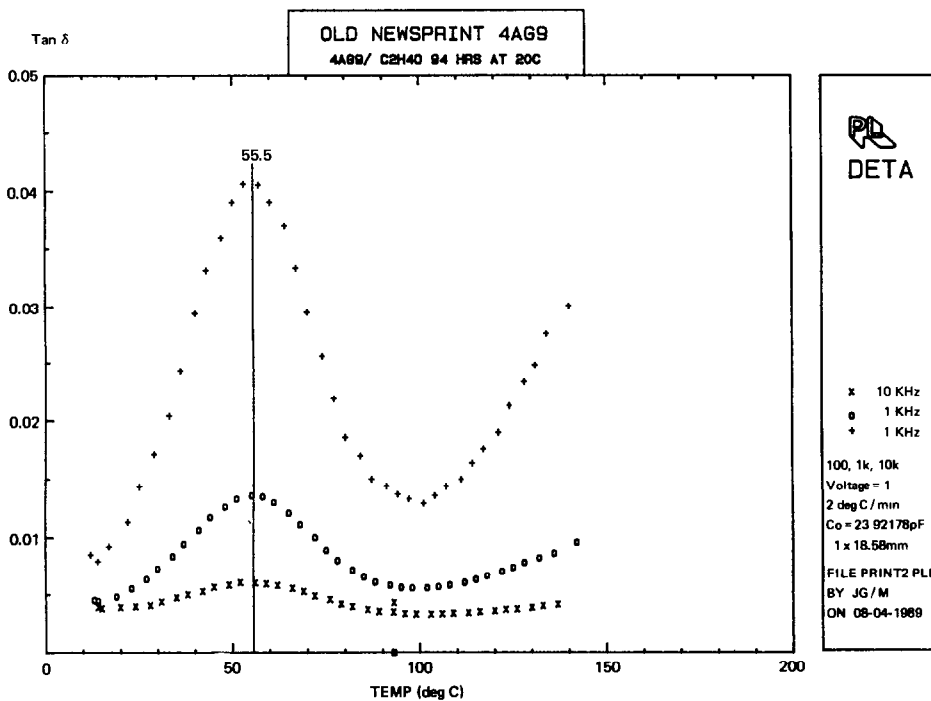


Fig. 8. $\text{Tan } \delta$ for degraded paper treated for 94 h at 20°C; \times , 10 kHz; \circ , 1 kHz; $+$, 0.1 kHz.

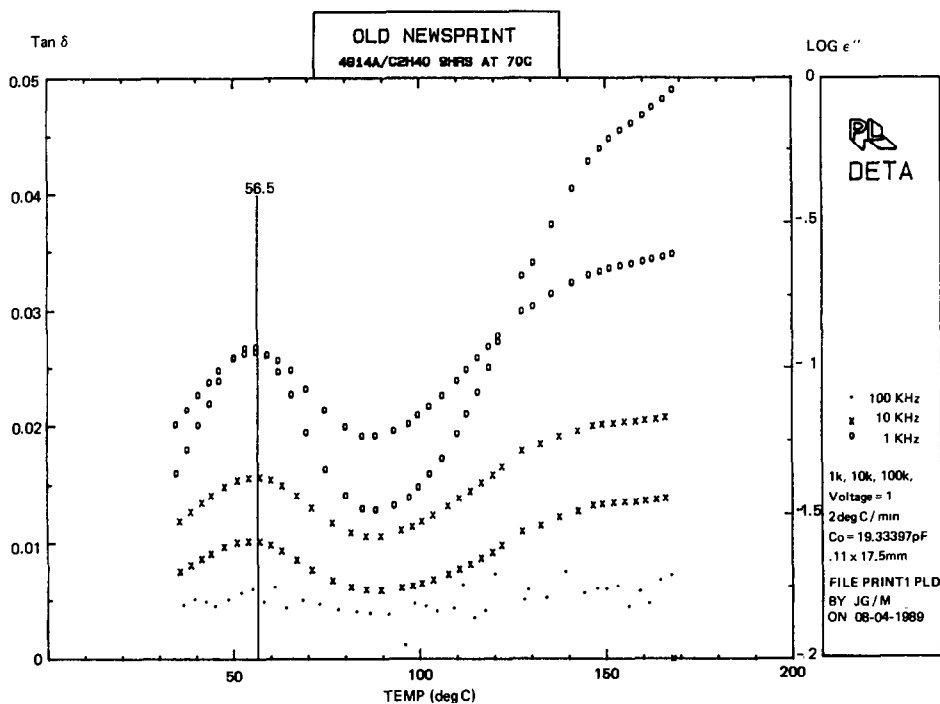


Fig. 9. $\text{Tan } \delta$ for degraded paper treated for 9 h at 70°C .

exposure to ethylene oxide in the direction of a more “cellulose”-type value. In the case of degraded newsprint there was also a trend in this direction but not as clearly defined.

The DSC curve of recent newsprint was found to be very similar to that of unbleached refined mechanical pulp (Fig. 10). This pulp according to a recent reference [12] contains 4.4% lignin. Elemental analysis showed that there was a difference in carbon content between Whatman No. 1 and recent newsprint of the order of 4.5%. This indicates that the samples of recent newsprint studied contained about 4.5% lignin, which is a relatively small amount and may explain why the observed changes on treatment were small, though larger than those occurring in the cellulose-only samples. The latter points to the fact that the ethylene oxide is reacting with the ligneous component in the paper and not to any extent with the cellulose.

Solid state NMR has been used successfully to monitor the chemical transformations of lignin during fungal degradation processes [13], and so further work is in progress, which includes solid state NMR, to determine what is happening to the ligneous component in paper during ethylene oxide treatment on a mechanistic level.

As far as the DETA curves are concerned, it is as yet too soon to attempt an explanation of the observed effect. However, if DETA is able to dis-

DSC Normalization: prtn4
 Sample Weight: 1.316 mg
 Wed Aug 09 15:26:07 1989
 Unbleached refined mechanical pulp 1
 (Normalized)

DSC Normalization: inssw
 Sample Weight: 1.382 mg
 Sat Jul 29 19:40:34 1989
 Paper 62a36/ Recent newsprint untreated 2
 (Normalized)

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 7 Series Thermal Analysis System
 Paper 62a36/ Recent newsprint untreated 2

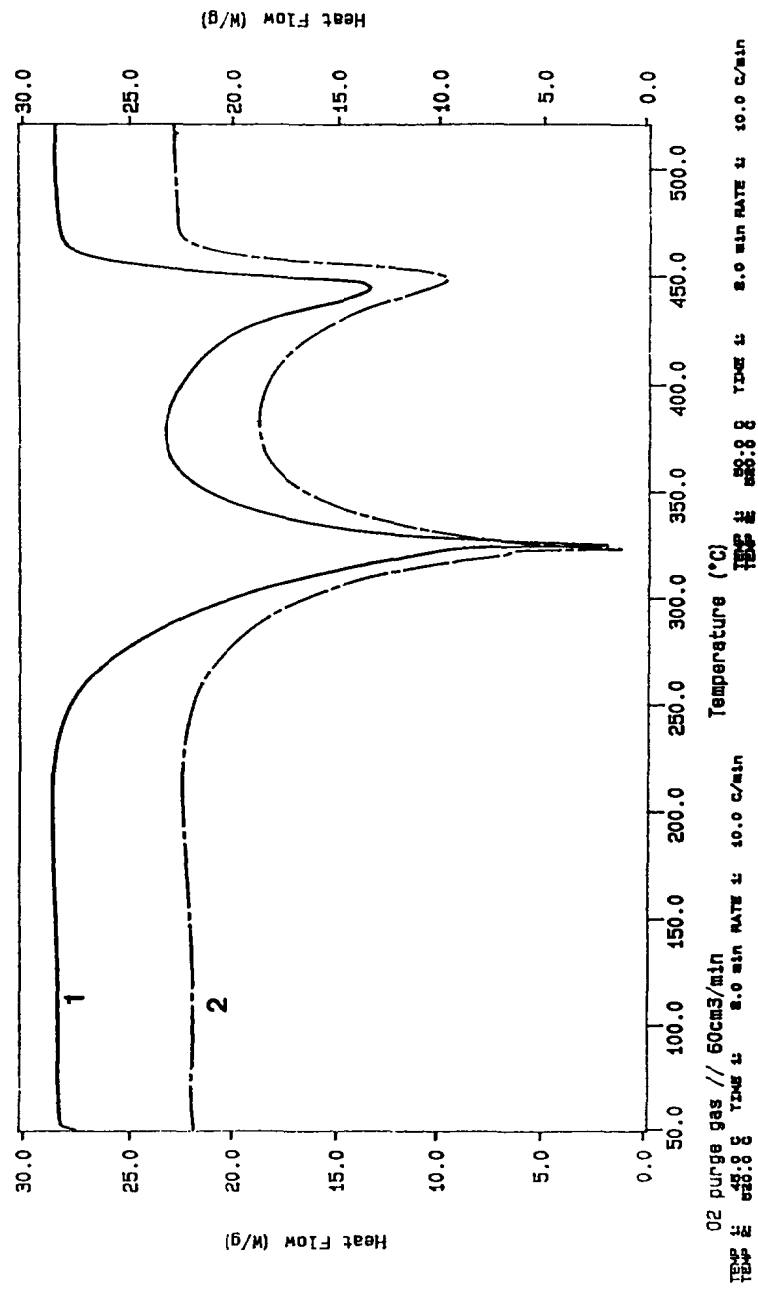


Fig. 10. DSC curves for unbleached mechanical pulp (1) and recent untreated newsprint (2).

tinguish so well between treated and untreated samples it may be a more sensitive method for monitoring paper treatment.

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