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A size exclusion chromatography study of cellulose degradation

A.M. Emsley[a,*], M. Ali[b], R.J. Heywood[b]

[a]*Polymer Research Centre, School of Physical Sciences, University of Surrey, Guildford, Surrey, GU2 7XH, UK*
[b]*National Grid Company, Kelvin Avenue, Leatherhead, Surrey, KT22 7ST, UK*

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Abstract

The degradation of cellulose is an important factor in the life of electrical insulation in power transformers and in the longevity of paper archives. Traditionally, degradation has been studied by following the decrease in the viscometric degree of polymerisation (DP) in a solvent such as copper ethylenediamine (CUEN). In this paper, we report a study of molecular weight distribution (MWD) changes in cotton linters, measured by size exclusion chromatography in dimethylacetamide/lithium chloride (DMAc/LiCl) solvent, during accelerated ageing in the laboratory. The initial mono-modal distribution changes to a multi-modal distribution during ageing, but eventually returns to mono-modal as the DP of the cotton reaches a limiting value of 150–200. Such complex changes in the MWD cannot be reflected truly in any average value such as the DP, nevertheless we show that the number average molecular weight (M_n) changes with time in very much the same way as viscometric DP and the changes can be fitted to the same kinetic model. The general trend is that the polydispersity of the material increases with ageing, as the distribution broadens, but the scatter in the data prevents any accurate trend analysis. The intermediate peak positions indicate preferential scission of molecules near the centre. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Size exclusion chromatography; Viscometric degree of polymerisation; Copper ethylenediamine

1. Introduction

The degradation of cellulose-based paper and hence its life expectancy is important in power transformers, where it is used as electrical insulation [1] and in archives of manuscript material [2], where ageing reduces the value and usefulness of stored papers and books. In order to construct models to predict the life expectancy of paper, we need to understand the kinetics and mechanism of ageing of its main constituent, cellulose, which degrades as a result of the breakage of glycosidic, inter-monomer bonds in the polymer. This reduces the chain-length and ultimately the mechanical strength of the material. Failure occurs when the mechanical strength of the paper decreases to the point where it is brittle and liable to damage by mechanical movement. In a transformer, this might result from load changes, or the flow of oil over the paper and the integrity of the solid insulation ultimately limits the life expectancy of a transformer, although other factors can cause failure to occur early. In stored manuscripts, degradation makes the materials too brittle to handle.

Degradation has been followed traditionally by measuring changes in the viscometric degree of polymerisation (DP) in copper ethylenediamine solution (CUEN). However, the DP is only one of a number of average measures of the polymer molecular weight and does not give detailed information about changes in chain-size distribution during ageing, which are likely to be critical in determining the mechanical strength of the material. Size exclusion chromatography (SEC) provides the molecular weight distribution (MWD) of a polymer and has the potential to give more detailed information about changes in molecular structure during ageing.

Much of the literature on the SEC of cellulose has been based on derivatives of cellulose [3–5], which are soluble more readily than cellulose itself. However, Cosgrove [4], Lawther et al. [6] and Cael [5], have reported that derivatisation degrades the cellulose. In this paper, we compare the use of dimethylacetamide/lithium chloride (DMAc/LiCl) as a solvent for natural cellulose to that of tetrahydrofuran and the tri-carbamate derivative, where the free –OH groups are substituted with phenylisocyanate. DMAc/LiCl is accepted generally as a non-degrading solvent for cellulose; it is also colourless and can be used in the refractive index-based chromatography systems. Cadmium ethylenediamine (Cadoxen) is also a colourless solvent, but is very aggressive, and in our experiments, destroyed the column in a matter of days.

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[*] Corresponding author.

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A method for SEC analysis of cellulose in DMAc/LiCl was first developed by Ekmanis [7] and has been applied by a number of workers since the analysis of cotton-based celluloses (see for instance the work of Timpa et al. [8,9]). However, both transformer insulation and manuscript papers are manufactured normally from wood-based pulp and a wood-based paper would have been the material of choice for our experiments. Westermark et al. [10,11] used SEC to measure the MWD of wood-based Kraft pulps using DMAc/LiCl as the eluent and a method similar to that of Ekmanis. The paper was activated with water, prior to dissolution, to break down hydrogen bonding in the material and swell it sufficiently to allow access to the larger and less polar DMAc molecules. The water was then exchanged for dry DMAc, the paper dissolved in a saturated solution of LiCl in DMAc (6–8% by weight) and finally diluted to 1% LiCl. However, the samples did not dissolve fully and were therefore centrifuged and only the soluble portion, injected into the SEC; the insoluble portion was ignored.

Westermark [10] identified two chromatographic peaks and associated the larger, high molecular weight peak with cellulose and the other, at low molecular weight, with the hemi-cellulose in the Kraft pulp. The apparent separation of cellulose and hemi-cellulose has been reported also by Hill et al. [12,13], who analysed Kraft paper from transformers derivatised by carbamation. They also found that the MWD comprised a broad high molecular weight peak and a narrow peak at lower molecular weight, again attributed to hemi-cellulose. They observed a complete loss of the low molecular weight peak during degradation and a corresponding drop in the polydispersity of the sample. However, the low molecular weight peak also could be due to the degradation products from the carbamation.

To avoid the complications identified by Westermark and Hill for wood-based material, the experiments reported here used pure cotton linters. Ageing was carried out in air and oil (to simulate transformer conditions), in the temperature range 120–140°C, which is higher than the operating temperatures (60–80°C in a transformer), but gives significant degradation in a reasonable time scale. The objectives of the work were to investigate macromolecular mechanisms of cellulose degradation and to correlate kinetic models generated from measurements of DP by viscometry [14], with molecular weight averages calculated from the actual MWD.

2. Experimental

2.1. Ageing of linters in air

Cotton linters (3–4 g per sample) were aged in Pyrex petri dishes in fan assisted ovens controlled to ±2°C, at three air ageing temperatures of 120, 140 and 160°C.

2.2. Ageing in oil

Under vacuum, 3 g of cotton linters were dried overnight (115°C). The oven was allowed to cool before the vacuum was released using nitrogen and the sample pot sealed. The sample pot was weighed immediately to calculate the moisture content of the cotton and then placed in a nitrogen glove box. Measurements of viscometric DP showed no discernible ageing effects due to the drying process.

2.2.1. Preparation of the oil

The oil was dried and de-oxygenated by bubbling nitrogen through it (at least 1 h). The conditioned oil contained approximately 400 ppm oxygen and 8 ppm water. A cotton to oil ratio of approximately 0.08 g/ml was used for all ageing experiments.

2.2.2. Ageing of samples in oil

The dried and conditioned oil was added to the dried cellulose samples in a glove box flushed with nitrogen. A small amount (5–10 mm) of overhead space within the pots was permitted to allow the expansion of oil. The sample pots were removed from the glove box and placed in a large flat-bottomed flask to catch any oil spillage. The large flasks were placed in ovens (fan assisted), at pre-set temperatures of 120, 140 and 160°C and a flow of nitrogen passed continuously through the flask, to minimise oxidative degradation effects and avoid a fire in case of a leakage of oil. The temperature was monitored throughout the experiment by thermocouples adjacent to the sample pots. Samples were removed periodically from the oven for analysis. Hexane was used to remove the residual oil prior to dissolution.

2.3. Dissolution in DMAc/LiCl

A method for the SEC of cotton linters, using DMAc/0.5% LiCl, was developed from the original method of Ekmanis [7,15]. The procedure used was as follows:

- the samples were mulched in distilled de-ionised water using a laboratory blender and soaked in water overnight;
- the pulp was passed through a grade 2 sintered filter;
- rinsed thoroughly with methanol and mixed with methanol 2–3 h (sealed container, to avoid evaporation);
- filtered as before and washed with DMAc;
- mixed for 2–3 h with dry DMAc;
- filtered as before;
- the pulp removed from the sintered filter and added to DMAc/8%LiCl (20 ml);
- stirred until a clear solution had formed (2–48 h, depending on the sample).

The removal of all the water during the solvent exchange step is a vital part of the procedure. Water is believed to compete with the hydroxyl groups of the cellulose chain, therefore the DMAc/LiCl molecules cannot complex with the cellulose and dissolution cannot occur. The interference

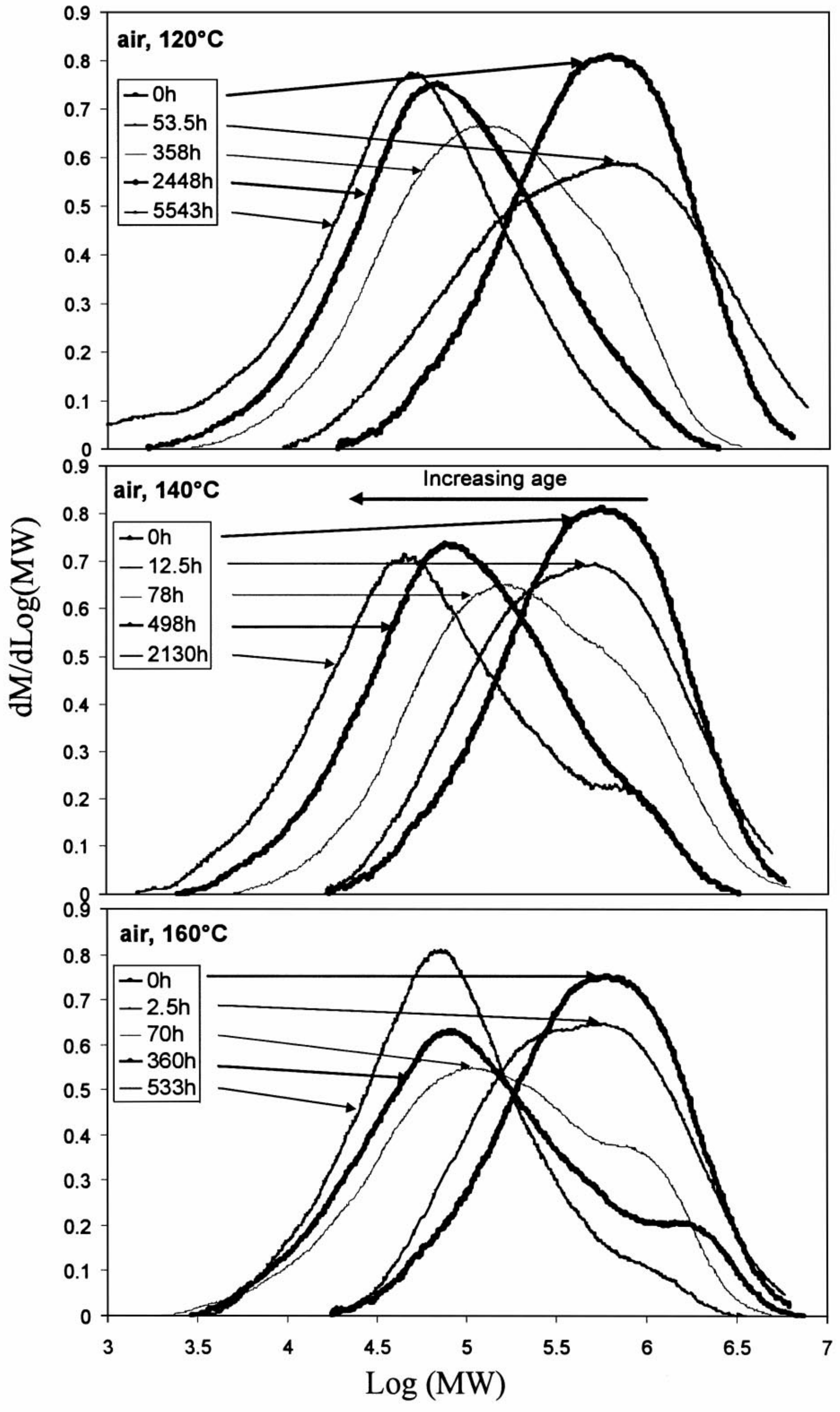

Fig. 1. Cotton linters aged in air.

of water with cellulose dissolution was verified when water was added to clear solutions of cotton paper. The cellulose precipitated as a gel with a similar appearance to 'cloudy solutions' formed during initial experiments, when some residual water may have been left behind.

2.4. SEC of cellulose solutions

The Waters 150-CV (GPCV) incorporates refractive index and viscometer detectors, which allows a universal calibration technique developed by Benoit, to be used to

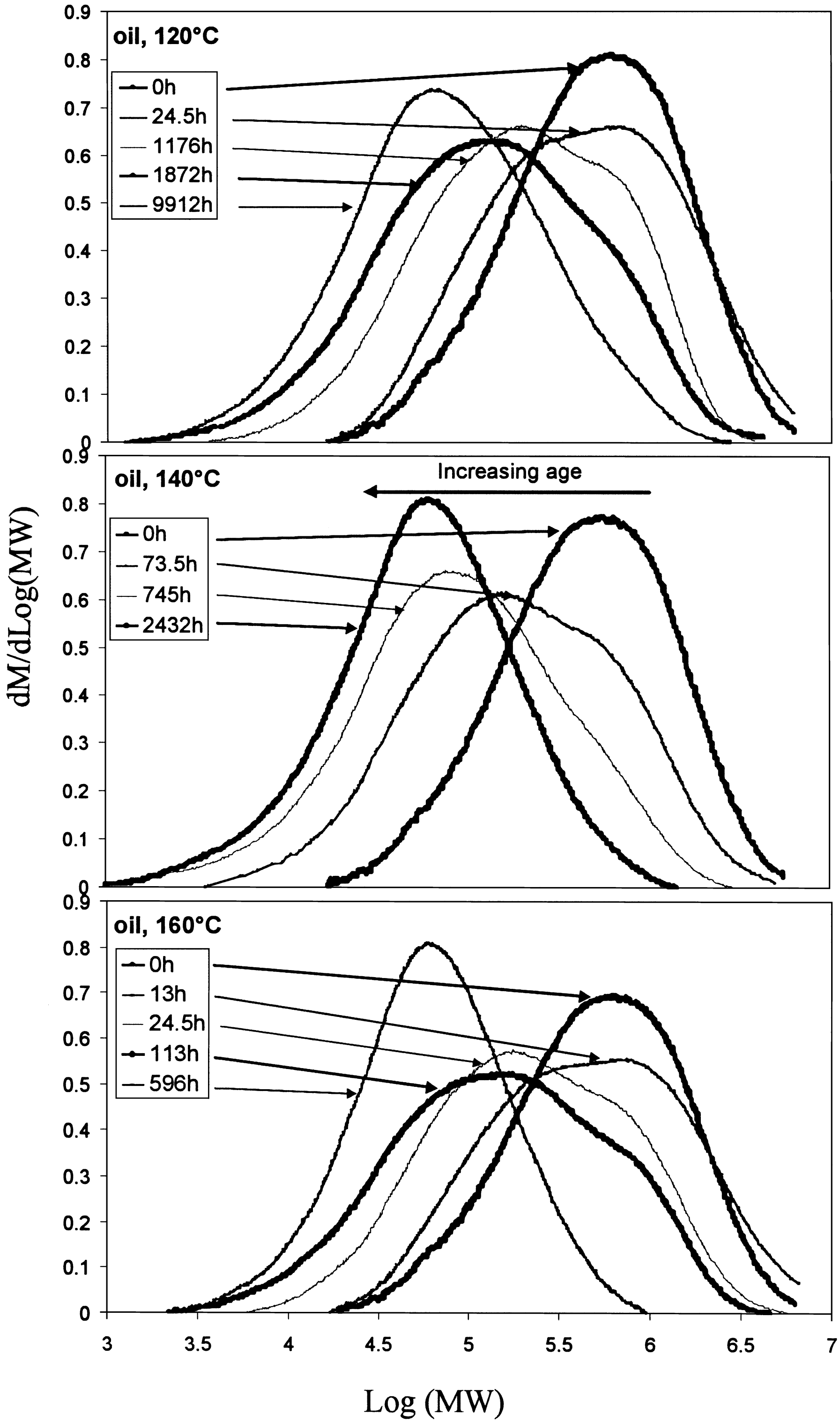

Fig. 2. Cotton linters aged in oil.

calculate the absolute molecular weights [16]. Eight narrow molecular weight polysaccharide standards (chosen because of their structural similarity to cellulose) in the range 8500–853 000 Da (Polymer Laboratories) were used to calibrate the columns. There are no broad molecular weight cellulose or polysaccharide standards available against which the calibration can be checked, so the NBS 706 polystyrene broad standard was used. The calculated average molecular weight agreed within 5% with the published data.

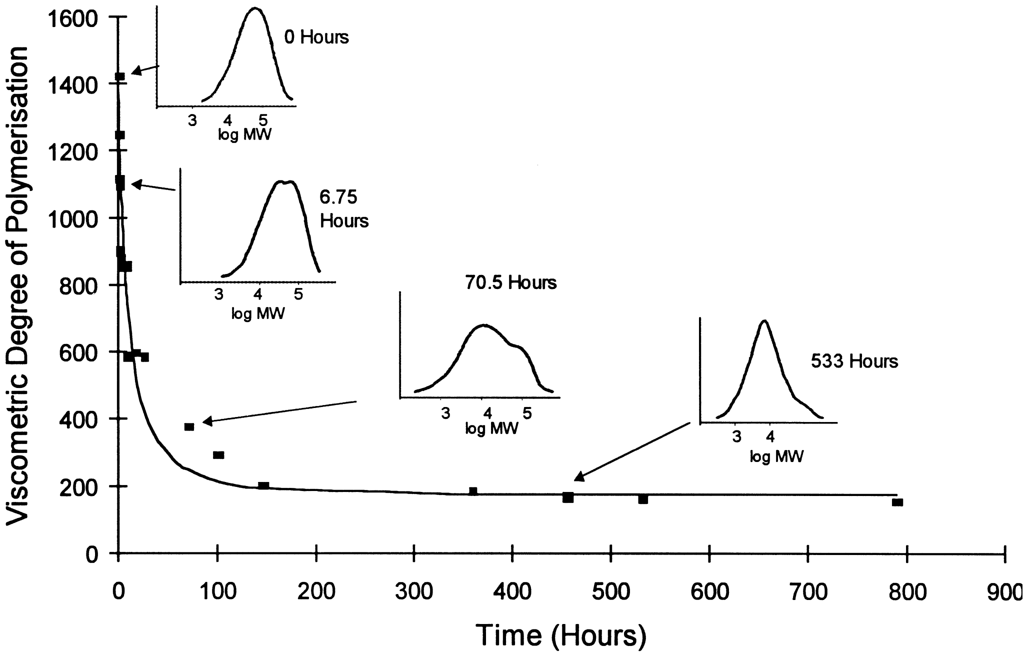

Fig. 3. Relationship of MWD changes to the ageing curve measured in terms of the viscometric DP.

The cellulose samples dissolved in DMAc/1% LiCl were analysed using DMAc/0.5% LiCl as eluent as follows:

Four columns were used in series—Waters μstyragel HT 10^3, 10^4, 10^5 Å and a Waters ultrasytragel 10^6 Å.
Column compartment temperature 60°C, Injector 60°C, Pump 50°C.
Eluent—0.5% LiCl in DMAc.
Density of solvent—0.9453 g/ml.
Flow rate—(set at 0.8 ml/min on 150 GPCV instrument), measured as 0.72 ml/min.
Run time—90 min.
Injection volume—(set as 400 μl), measured as 405.5 μl.
Refractive index detector—sensitivity −256 for the cellulose solutions. The sensitivity was −64 for the narrow calibration standards, both at Scale factor 4.
Viscometer detector—capillary length (8 cm).
Viscometer offset—26 mV.

3. Results and discussion

One of the problems of using a two-detector system and an important source of error in quantifying the SECs arises from the estimation of the inter-detector volume. Mixing of the analyte, as it passes from one detector to the other, can alter significantly the calculated average molecular weights (Balke et al. [17]). An inter-detector volume of 17 s was calculated for the system using a known broad molecular weight standard (NBS 706, polystyrene) and the peak heights of the narrow molecular weight standards used to calibrate the instrument.

3.1. Molecular weight distributions

Figs. 1 and 2 show MWDs for cotton linters aged in air and oil, respectively, as a function of age. Up to 8 samples were analysed at each temperature, but only 4 or 5 are displayed for clarity, using different line thickness to

Table 1
Peak/shoulder positions in the MWD during ageing of cotton linters averaged across all samples

Peak number	Air			Oil			Average	Standard deviation
	120	140	160	120	140	160		
1	630 960	630 960	630 960	630 960	630 960	630 960	630 960	
2	295 120	338 840	316 230	309 030	275 420	331 130	310 965	17 420
3				208 930		192 750	200 840	11 440
4	139 640	169 820	125 890	147 910	158 490		148 350	13 090
5	87 095	87 095	87 095		91 200	96 830	89 865	16 300
6	72 445		74 130			71 45	72 240	3490
7	63 095	57 545		66 070	64 565	61 660	62 590	3025
8	53 090	47 860					50 475	3695

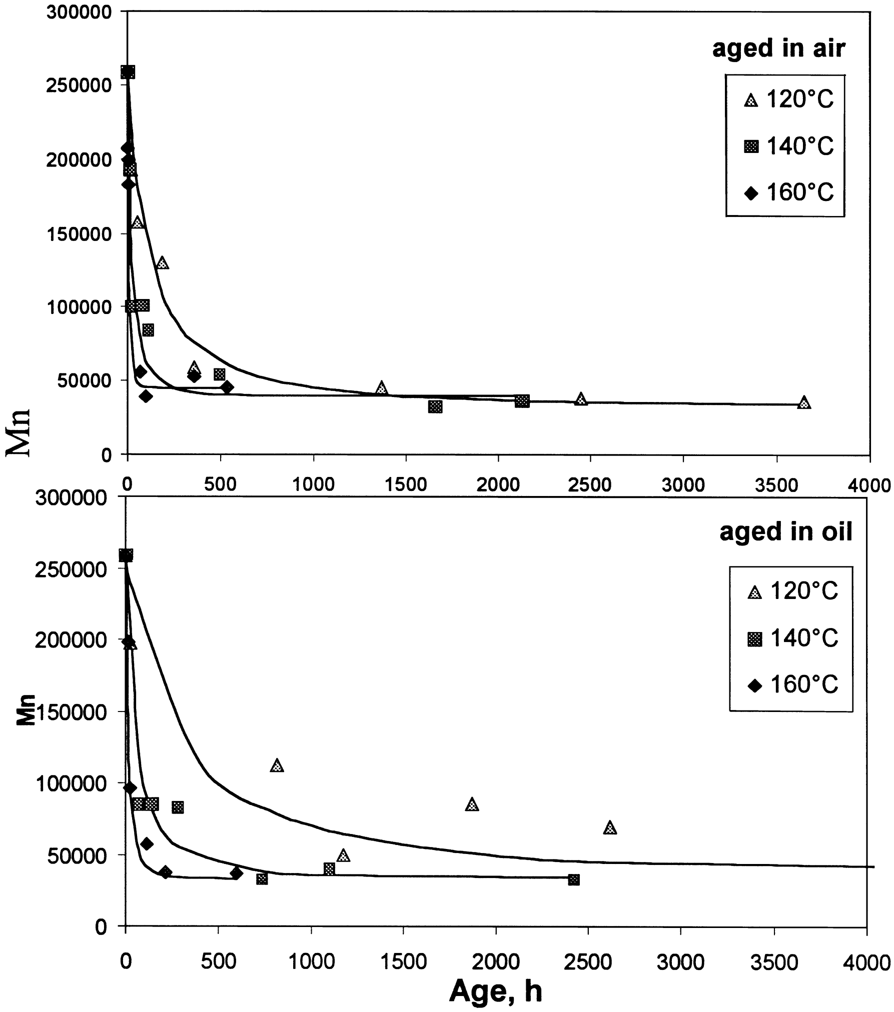

Fig. 4. Decrease in number average molecular weight age, according the Emsley–Heywood model.

distinguish between them. The primary differences between ageing environments are the retention of high molecular weight material in samples aged in air and the broader tails to the aged peaks to high and low molecular weight.

Some distributions appear to show an increase in high molecular weight materials in the earliest stages of ageing. This may just indicate changes in column interactions in lightly aged material, but if real, we could interpret it as an increase in the molecular weight at the start of ageing caused by cross-linking of the cellulose chains. This would correlate with small increases in tensile strength, which we have observed previously in the early stages of ageing [18]. Further ageing then proceeds via a series of complex distributions before returning to a mono-modal distribution, when the cellulose is aged fully at a DP of 200 or below (Fig. 3). Similar observations have been reported during GPC studies of chitosan degradation [19]. Table 1 lists the approximate positions of the 8 peaks and shoulders and it is interesting to note that the peaks can be identified in similar positions at each temperature. The peak numbers do not refer to any specific distribution in Figs. 1 or 2 but are averaged across all the distributions. Peaks 1, 2, 4 and 6 roughly follow a geometric progression, halving in length each time; peak 3 is roughly one third of peak 1; peaks 5 and 8 are again roughly half and peak 7 is roughly one third of peak 3. This may indicate preferential scission towards the centre or one end of the molecules.

Degradation occurs predominantly at chain centres, which would account for the sharp initial drop in the DP measured by viscosity (Fig. 3). The MWD shifts towards lower molecular weight as ageing proceeds, as it approaches its limiting distribution, the rate of change of the DP decreases towards zero. Computer modelling of MWD changes has indicated that movement of the peak to lower

Table 2
Comparison of kinetic parameters of cotton linters aged in air and oil

	$A(k_{1_0})$	$A(k_2)$	$E(k_{1_0})$	$E(k_2)$
Linters aged in air	3.4307×10^7	4.40×10^{13}	113	124
Linters aged in oil	1.44×10^7	1.74×10^{11}	113	109

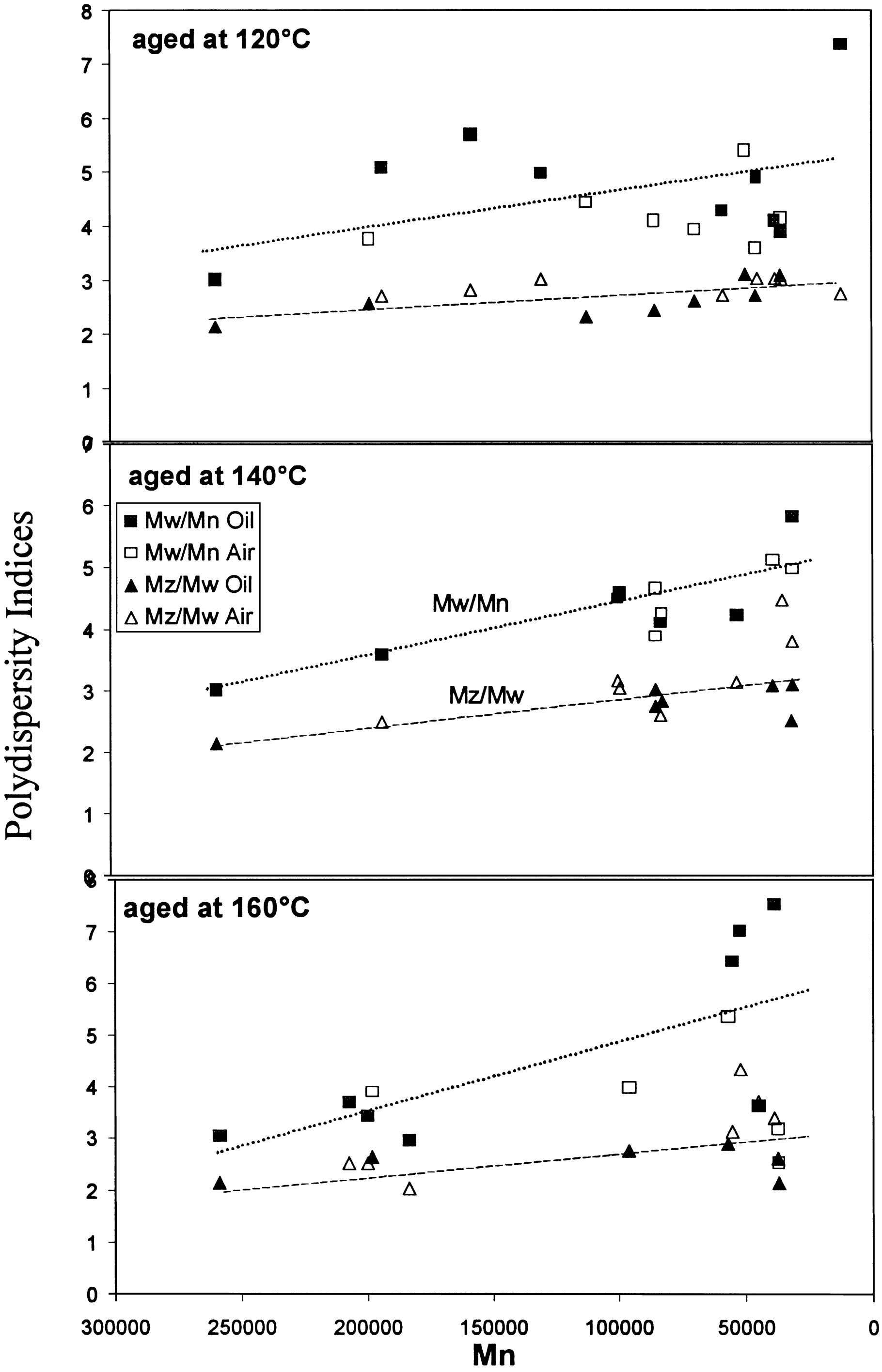

Fig. 5. Changes in dispersity indices of cotton linters with age.

molecular weight and bi-modal distributions are most likely to arise from systematic scission of bonds towards the centre of the molecule [20]. The tendency towards scission in the centre of the chain was also proposed by Plaumann et al. [21] for the degradation of isoprene, where molecules below a certain threshold molecular weight would not undergo further scission. A similar effect would explain observations in the cellulose literature of a so-called 'limiting DP', which is generally reported to be in the region of 200–150.

3.2. Modelling the degradation kinetics

We have demonstrated previously [14] that the degradation of cellulose can be modelled by an equation of the form:

$$\frac{1}{\mathrm{DP}_t} - \frac{1}{\mathrm{DP}_0} = \frac{k_{1_0}}{k_2}(1 - \mathrm{e}^{-k_2 t})$$

Kinetics of the DP change in Kraft papers have been reported elsewhere [14,22]. This equation was used to plot the solid line in Fig. 3 and Fig. 4 shows that M_n calculated from the MWD also fits the same type of model. k_{1_0} and k_2 are assumed to obey the Arrhenius function for temperature change. The activation energy and pre-exponential for each constant were estimated using a commercial modelling package (ModelMaker, Cherwell Electronics) and are tabulated in Table 2. The model fits are not ideal, because we did not have sufficient data to refine the models adequately, but it is interesting to note that the higher figures for ageing in air are consistent with more rapid rates of degradation in the oxidising environment. (Note that the activation energy for k_{1_0} was set at 113 kJ/mol, the figure quoted by Emsley and Stevens [1] for the ageing of cellulose, using a simple zero-order model, in order to reduce the number of variables in the optimisation.) In Fig. 3, deviations from the model occur only where the MWD breaks down into a distinctly bi-modal pattern. The viscometric measurement averages out such changes and would tend to yield a slightly higher value, due to the influence of the residual, high molecular weight shoulder.

4. Discussion of the changes in MWD

Zou et al. [2] studied the ageing of Whatman filter paper by SEC analysis and suggested that the ratio of $\mathrm{DP}_\mathrm{z}/\mathrm{DP}_\mathrm{w}$ was good guide to the homogeneity of the degradation process. The ratio in their data remained fairly constant, indicating that degradation proceeded randomly without any preferential breakdown of the longest cellulose chains. Guita et al. [23] modelled polymer degradation in a computer and predicted that when scissions are purely random the dispersity index ($\mathrm{DP}_\mathrm{w}/\mathrm{DP}_\mathrm{n}$) approaches a value of two and remains constant independent of any fragments coupling during the degradation process. They predicted that dispersity would fall below 2 if the scission were primarily in the centre of the chains.

Polydispersity ratios from our experiments are shown in Fig. 5, where both $M_\mathrm{w}/M_\mathrm{n}$ (solid points) and $M_\mathrm{z}/M_\mathrm{w}$ (open points) are presented. The ratios generally increase with age, as the average molecular weight decreases, initially from about 3 to about 5 in heavily aged samples. The scatter in the data is so large that it is impossible to derive realistic trends and straight line fits have been added merely to demonstrate the upward drift in the data. There is no evidence for the ratio decreasing towards 2, which confirms that the degradation of cotton linters is not random and that there may be preferential breakdown of the longest cellulose chains. Further work is continuing to clarify this issue.

Cosgrove et al. [4] aged cellulose in acid and alkali media and studied the degradation by gel permeation chromatography, using Cadoxen as the eluent. They showed a bi-modal distribution and suggested that this was an intermediate stage of degradation, where only a fraction of the cellulose had become accessible to the degrading reagent. They described bond scission not at random, but with smaller molecules having a higher tendency to rupture than larger ones. Accessibility increased with time and therefore the rate of degradation changed with time. A continually changing rate of degradation during ageing, either due to accessibility effects or differences in the reactivity of the cellulose chains, is assumed implicitly in models we have developed and used here [14].

5. Conclusions

The MWD changes of the cellulose samples (cotton linters) follow the same degradation trend independent of the ageing temperature and conditions. The MWDs of air aged samples tend to be broader than those of oil aged material and show retention of high molecular weight materials. The degradation appears to occur preferentially at chain centres, such that an initially mono-modal distribution becomes multi-modal during ageing, before returning to a mono-modal distribution at low molecular weight. A slight increase in the polydispersity with ageing confirms that degradation is not purely random, but occurs preferentially in the high molecular weight part of the MWD. The number average molecular weight of aged cellulose can be fitted to the same kinetic model as that developed previously for the change of the viscometric DP with ageing. Deviations from the model occur where the MWD still retains a significant proportion of high molecular weight material, which skew the viscosity determination to higher molecular weight.

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