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The thermal degradation of poly(vinyl alcohol)

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Abstract

This paper is concerned with the thermal degradation of poly(vinyl alcohol), both in the solid and molten state. Initially, thermal degradation in the solid state was considered to be due to the elimination of hydroxyl side groups, but this process should have produced appreciable amounts of isolated and conjugated polyenes in the degradation residue and small amounts of carbonyl group were detected. Side group elimination was followed by a reduction in the melting point and the degree of crystallinity. In the molten state, thermal degradation led to the production of volatile saturated and unsaturated aldehydes and ketones, as well as water. It was considered that the greater flexibility of the polymer chains in the melt facilitated fragmentation of the chain and elimination of chain segments. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl alcohol); Thermal analysis-Fourier transform infrared spectroscopy; Differential scanning calorimetry

1. Introduction

The thermal degradation of poly(vinyl alcohol) (PVOH) has been the subject of several publications [1–4]. Generally, for degradation below 300°C the major pyrolysis product has been reported to be water, produced by the elimination of hydroxyl side-groups [1–2]. A further study [3] at 240°C showed that in addition to water, acetaldehyde, some unsaturated aldehydes and ketones, benzene and benzene derivatives were evolved during thermal degradation. A UV–Vis study [4] showed that the unsaturated double bonds produced by elimination do not lead to the formation of appreciable amounts of conjugation. Furthermore, a molecular weight study by solution viscosity showed that the thermal degradation of PVOH leads to an initial increase in the molecular weight, followed by a decrease. These observations were explained as being due to the combined effects of cross-linking and chain scission.

In this paper, thermal analysis-Fourier transform infrared spectroscopy (TA-FTIR), thermogravimetry (TG) and differential scanning calorimetry (DSC) have been used to study the thermal degradation of PVOH and the structure of the residue produced. TA-FTIR spectroscopy [5] has previously been shown to be extremely useful in the study of the thermal degradation of polymers through kinetic analysis and characterisation of solid residue. A gas cell was also used to characterise the volatile degradation products of PVOH by infrared spectroscopy.

2. Materials

PVOH with a number average molecular weight of 89 kg mol^{-1}, was supplied by BDH. This sample of PVOH was produced from the hydrolysis of PVAc, and was known to contain less than 1 mol% acetate groups.

3. Experimental

3.1. TA-FTIR spectroscopy

The apparatus for TA-FTIR spectroscopy was a combination of a Nicolet 760 IR-Magna infrared spectrometer, and a Linkam 600 microscope hot-stage unit placed in the beam of the spectrometer. The hot-stage unit, was fitted with barium fluoride windows suitable for infrared spectrometry in the range 4000–740 cm^{-1}, and was purged for 30 min with argon (160 cm^3 min^{-1}) prior to each experiment. The same flow of argon was maintained throughout the experiment. The temperature of the hot-stage was calibrated with the melting points of KOH and NaOH. Isothermal degradation temperatures were chosen to study the thermal degradation of each polymer, using an initial heating rate of 90°C min^{-1}, so that the desired degradation

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temperature was reached before significant degradation had occurred.

3.2. Preparation of samples for TA-FTIR

Thin film polymer samples were placed on the surface of 16 mm diameter KBr disks from solutions of dimethyl sulphoxide (hot), and dried in a vacuum oven (80°C). Typically films of about 1 μm were made by this method, which was about the minimum film thickness which could be used whilst still achieving acceptable infrared absorbance. For the purposes of kinetic analysis, sets of 128 or 256 infrared spectra with a resolution of 4 cm^{-1} were taken at intervals of 5 or 10 min, depending on the degradation temperature.

3.3. Analysis of gaseous degradation products by FTIR spectroscopy

The volatile degradation products of PVOH were analysed by degrading 100 mg samples in a furnace under 160 cm^3 min^{-1} flow of argon gas. Isothermal degradation temperatures, between 200 and 300°C were used. The products were swept into a gas cell with KBr windows suitable for FTIR spectroscopy. The volatile products passing through the cell were analysed at two minute intervals using sets of 64 infrared scans.

3.4. Thermogravimetry

Thermogravimetry (TG) was carried out on selected samples at isothermal temperatures, and non-isothermally using a 0.5°C min^{-1} heating rate. A Stanton Redcroft STA 1000 thermogravimetric balance with a type R (platinum–rhodium) thermocouple placed close to a platinum sample crucible was used. A sample size of 30 mg and 40 cm^3 min^{-1} flow of argon gas was chosen. Sample size and gas flow had no measurable effect on the measured isothermal weight loss vs. time plots.

3.5. Thermal analysis-mass spectrometry

Thermal analysis-mass spectrometry (TA-MS) was carried out on a Netzch STA 449 C thermal analyser, connected by means of a heated tube to the inlet of a Fisons Instruments Thermolab quadrupole mass spectrometer. Samples of 30 mg of PVOH were heated at 20°C min^{-1}, under a 40 cm^3 min^{-1} flow of argon gas, and the volatile degradation products detected by mass spectrometry. Mass spectra in the range 1–80 *m/z* were taken at 5 s intervals. The amount of water produced on the degradation of PVOH was calibrated from the accumulated mass spectrometric response from the dehydration of $CuSO_4 \cdot 5H_2O$ in the temperature range 50–150°C.

3.6. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was carried out using a Perkin Elmer DSC-2 at 10°C min^{-1} under nitrogen,

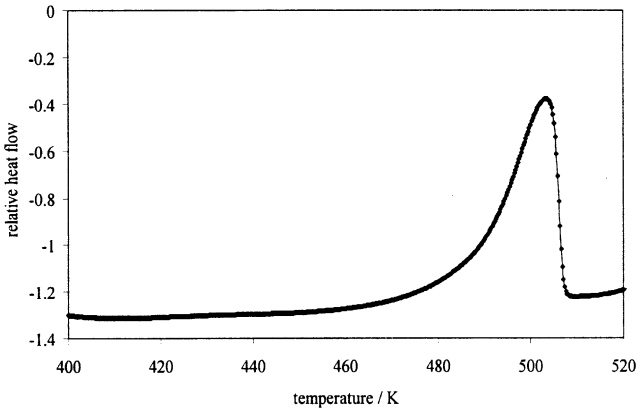

Fig. 1. DSC thermogram of PVOH at 10 K min^{-1}.

to study the changes in thermal properties of PVOH during thermal degradation. 10 mg samples were used.

4. Thermal properties of PVOH

The PVOH used in this study was analysed by DSC and found to be highly crystalline with a crystalline melting point, T_m, of 230°C, see Fig. 1. A glass transition was not observed. The area of the crystalline melting peak was used to deduce the amount of crystallinity in the PVOH sample, and by comparison with literature values for the heat of fusion ($\Delta H_f = 6.87$ kJ mol^{-1}) [6] it was estimated that the sample of PVOH was 65% crystalline. In the remainder of this paper, the thermal degradation of PVOH in the solid state (below 230°C) and molten state (above 230°C) will be considered separately and contrasted.

5. Thermal degradation of molten PVOH

5.1. Non-isothermal TG

Non-isothermal TG of PVOH was carried out at a heating

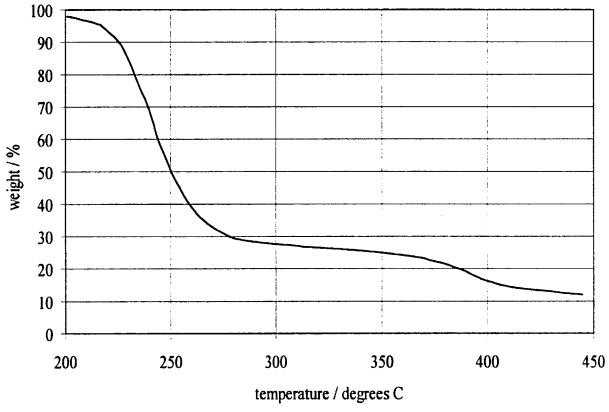

Fig. 2. Non-isothermal TG of PVOH at 0.5 K min^{-1}.

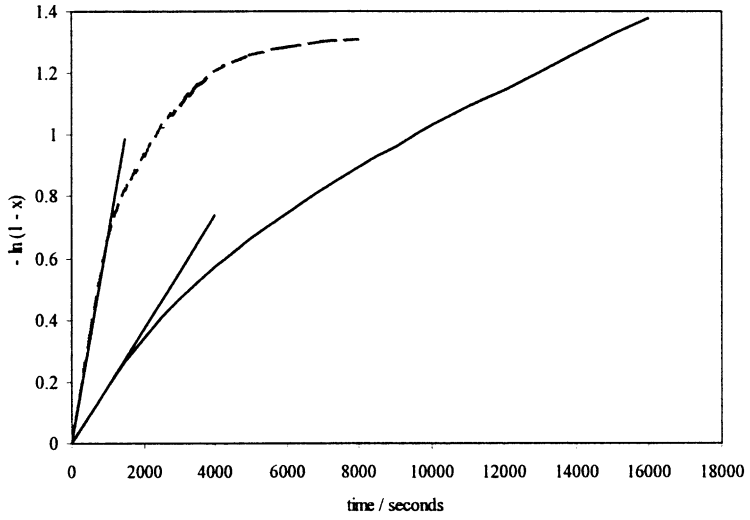

Fig. 3. First order rate plots for the thermal degradation of PVOH at 230 and 280°C (—, 230°C; and - - -, 280°C).

rate of 0.5°C min^{-1}, and the results are shown in Fig. 2. The majority of the weight loss took place between 200 and 300°C, followed by a further weight loss between 350 and 450°C, leaving a residue of approximately 10 wt%. The results were consistent with the elimination of side-groups at lower temperatures, followed by breakdown of the polymer backbone at higher temperatures, as stated in the literature [2]. A sweet smelling odour was present in the TG apparatus, consistent with the production of ketones.

5.2. Isothermal TG

Since the majority of weight loss of PVOH occurred between 200 and 300°C, isothermal TG of PVOH was carried out at temperatures between 230 and 280°C under argon. The weight loss of PVOH was found to follow first order kinetics up to approximately 30 wt%, see Fig. 3. Deviation from linearity at higher conversion was more marked at lower temperatures and was associated with the production of residue at the end of the experiment. A yellow/brown residue was produced in these experiments.

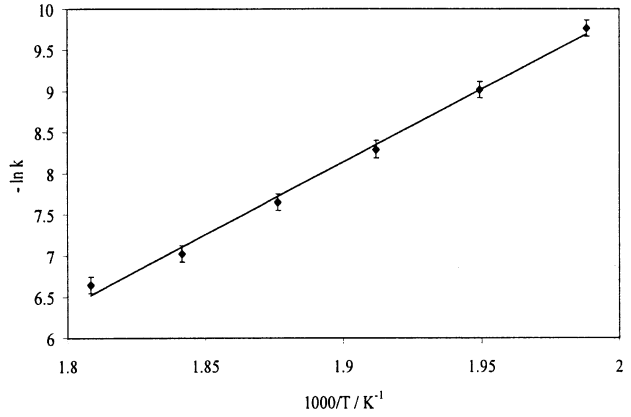

Fig. 4. Arrhenius plot for the thermal degradation of PVOH.

If water elimination was the sole process of thermal degradation of PVOH, a residue of 59.1 wt% of the initial weight would be expected. However, typical residues were in the region of 20–25% of the initial weight, and a sweet smelling odour was detected in the TG apparatus. It was concluded that side-group elimination was not the sole degradation process occurring at these temperatures.

Initial first order rate constants were calculated from the first order rate plots, and from the Arrhenius plot (Fig. 4) an activation energy of 150 ± 10 kJ mol^{-1} and pre-exponential factor of $(1.15 \pm 0.12) \times 10^{11}$ s^{-1} were obtained.

5.3. TA-FTIR spectroscopic analysis of thermal decomposition

TA-FTIR spectroscopy was used to monitor the thermal degradation of PVOH at temperatures between 260 and 290°C. The evolution of the infrared spectra with time at 260°C is shown in Fig. 5 (for band assignments see Table 1), and the corresponding first order rate plots for loss of intensity of infrared bands at 3450 ($O–H_{(str)}$) and 2930 cm^{-1} ($C–H_{(str)}$) are shown in Fig. 6a and b for 260

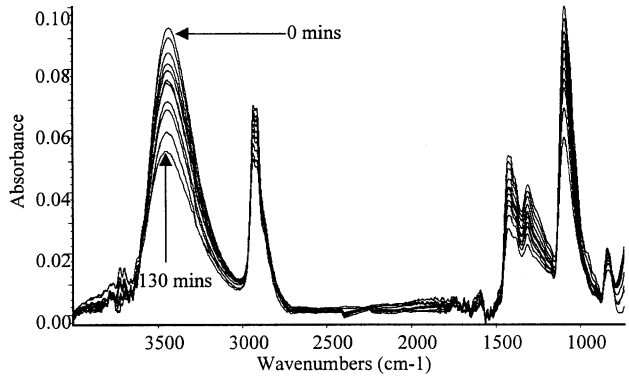

Fig. 5. The thermal degradation of PVOH at 260°C, measured by TA-FTIR spectroscopy.

Table 1
Assignment of infrared bands solid residue of PVOH

Wavenumber (cm^{-1})	Assignment	Intensity
3450	$O–H_{(str)}$	v. strong
2930	$C–H_{(str)}$	strong
2050	$C\equiv C_{(str)}$	weak
1705	Unsaturated aldehyde or ketone	medium
1640	$C=C_{(str)}$	weak
1585	Conjugated $C\equiv C_{(str)}$	strong
1450	$-CH_2-$ $_{(str)}$	strong
1080	$-C-O-H_{(str)}$	v. strong

and 290°C, respectively. Elimination of water was previously considered to be the dominant mechanism of degradation of PVOH, but little or no double bond formation or conjugation was detected by infrared spectroscopy at 260°C. However, at 290°C the residue produced by degradation of PVOH was found to contain infrared bands at 2930, 2050, 1705 and 1585 cm^{-1} (see Fig. 7). The band at 2930 cm^{-1} is clearly associated with saturated $C–H_{(str)}$, which when considered in conjunction with the relatively low intensity of the conjugation band at 1585 cm^{-1}

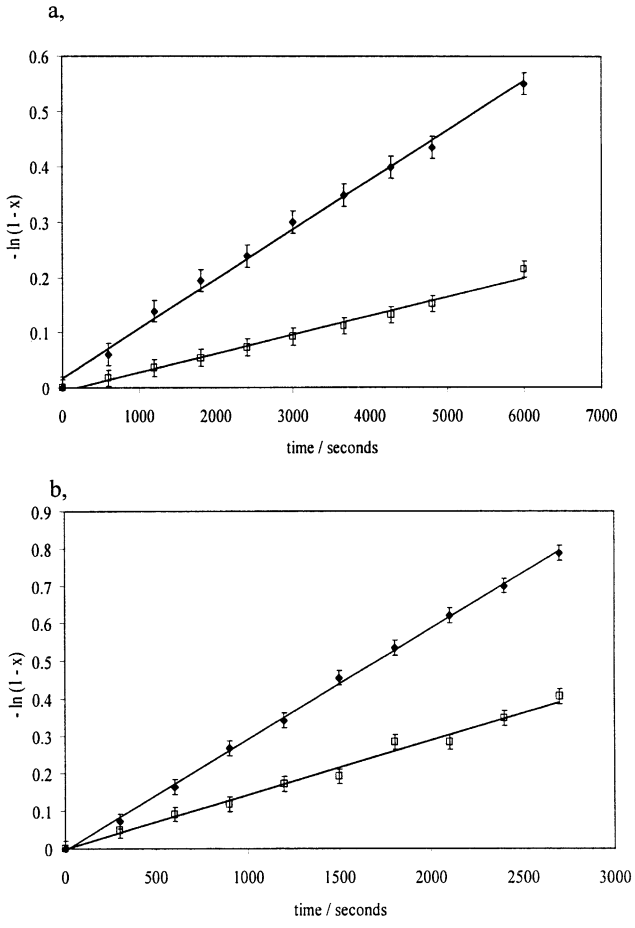

Fig. 6. First order rate plots for the thermal degradation of PVOH at, (a) 260°C, and (b) 290°C (◆, $O–H_{(str)}$; □ $C–H_{(str)}$).

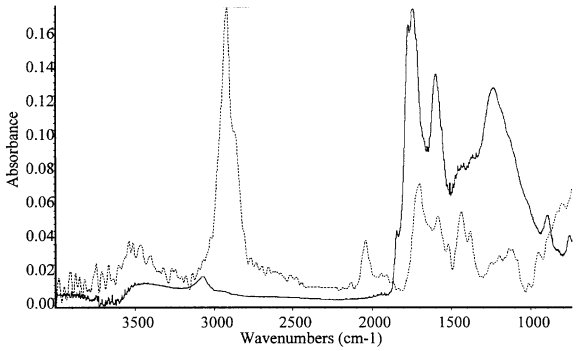

Fig. 7. Infrared spectra of the non-volatile residue of PVOH and PVAc (— PVOH, and - - -, PVAc).

compared to the solid residue of PVAc and the low intensity of the colour of the residue, indicated that the polymer backbone was neither heavily unsaturated nor conjugated. The band at 1705 cm^{-1} was associated with the formation of an unsaturated aldehyde or ketone product due to its low wavenumber. The position of the band was considered to be higher than expected for C=C double bond formation. The infrared band at 2050 cm^{-1} was thought to be associated with the formation of small amounts of alkyne units in the polymer chain. Furthermore it was found that the rate of loss of $C–H_{(str)}$ was lower than that of $O–H_{(str)}$ at the temperatures used, and that there was no evidence of cross-linking through ether formation in the infrared spectra. The C=C double bonds produced by elimination of water must have been used up in other ways.

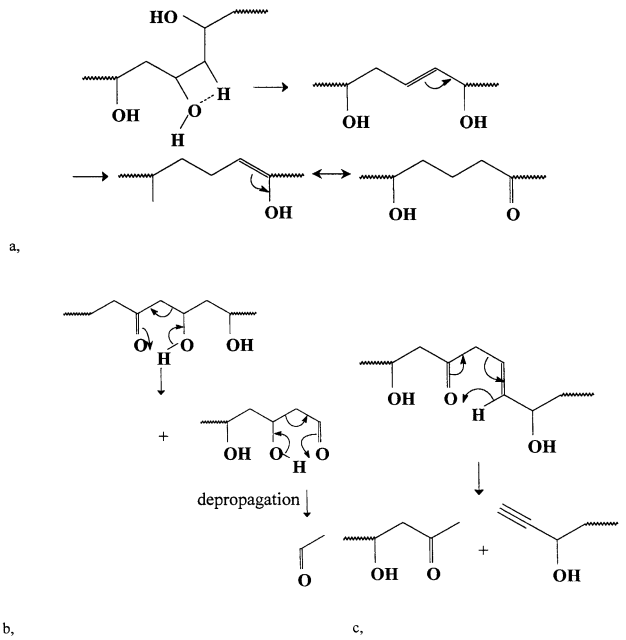

Fig. 8. Thermal degradation processes proposed for molten PVOH, (a) keto–enol tautomerisation, (b) hydrogen transfer leading to depropagation, and (c) hydrogen transfer leading to alkyne end-group.

An isolated double bond produced by the elimination of water can migrate adjacent to the next hydroxyl group along the polymer chain. Keto–enol tautomerisation can then occur, producing the ketone (see Fig. 8a). This would lead to restoration of the saturated C–H bonds lost through water elimination, and would lead to the observed differences in rate of loss of $C–H_{(str)}$ and $O–H_{(str)}$ bands observed. The carbonyl group produced could then form a six-membered transition with an adjacent alcohol side-group (Fig. 8b), leading to chain scission, followed by a depropagation process, which would liberate acetaldehyde (previously observed [3]). This would account for the lower than expected yield of residue. A carbonyl group could also interact with a double bond leading to chain scission (Fig. 8c).

The first order rate constants for loss of $C–H_{(str)}$ and $O–H_{(str)}$ plotted in an Arrhenius form (Fig. 9), gave activation energies for loss of O–H and C–H of 90 ± 10 and 120 ± 10 kJ mol^{-1}, respectively. The pre-exponential factors for loss of O–H and C–H were $(7.32 \pm 0.73) \times 10^5$ and $(3.01 \pm 0.30) \times 10^7$ s^{-1} respectively. It was considered that the rate of loss of $O–H_{(str)}$ was due to elimination of water, formation of ketone groups and production of volatiles. The rate of loss in $C–H_{(str)}$ was also thought to be due to these processes, but some $C–H_{(str)}$ was gained due to migration of a C=C bond, leading to formation of carbonyl groups. For this assumption, the difference between the rate constants for $O–H_{(str)}$ and $C–H_{(str)}$ loss can be regarded as being due to the migration of C=C bonds to form carbonyls. As first order rate constants are additive, the rate constants for loss of $C–H_{(str)}$ were subtracted from those of $O–H_{(str)}$. From an Arrhenius plot (Fig. 9), this process was found to have an activation energy of 70 ± 10 kJ mol^{-1} and a pre-exponential factor of $(1.14 \pm 0.11) \times 10^3$ s^{-1}.

5.4. Analysis of volatile degradation products by FTIR

An attempt was made to analyse the volatile degradation products from the thermal degradation of PVOH at 200, 230 and 300°C, by passing them through an infrared gas cell.

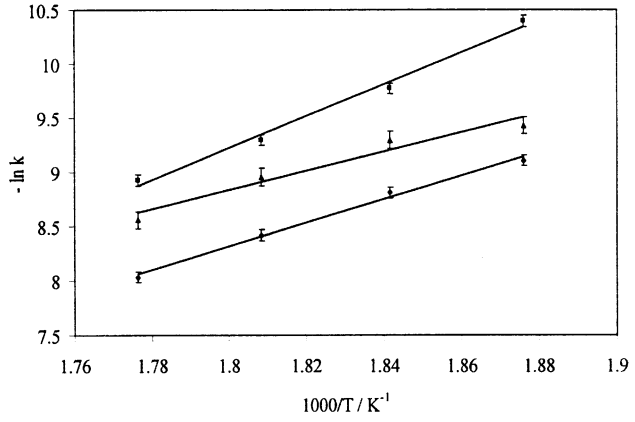

Fig. 9. Arrhenius plot for the thermal degradation of PVOH, measured by TA-FTIR spectroscopy (◆, $O–H_{(str)}$; ■, $C–H_{(str)}$; and ▲, $O–H_{(str)}–C–H_{(str)}$).

The infrared spectra of the volatile degradation products of PVOH at 300°C are shown in Fig. 10, for which the infrared bands are assigned in Table 2. No volatile products were observed up to 230°C, but this may have been due to a very slow rate of volatile evolution.

At 300°C, volatile products were observed (see Fig. 10a), bands above 3500 cm^{-1} attributed to the presence of water were observed, whilst at 3450 cm^{-1} a broad band was detected, consistent with the presence of hydroxyl containing products. This was consistent with literature findings [3]. The $C–H_{(str)}$ region of the spectrum was complicated, but there was evidence for the presence of unsaturated C–H groups (3000–3100 cm^{-1}), saturated C–H groups (2960 and 2820 cm^{-1}), and aldehyde C–H groups (2730 cm^{-1}). Five bands in the region 1800–1700 cm^{-1} were detected (see Fig. 10b). These bands are associated with different types of carbonyl group. The band at 1715 cm^{-1} was considered to be due to unsaturated aldehyde groups, whilst the band at 1725 cm^{-1} was due to the presence of saturated aldehyde groups (e.g. acetaldehyde). The bands at 1745 and 1760 cm^{-1} were due to the formation of products containing unsaturated and saturated ketones, respectively. The origin

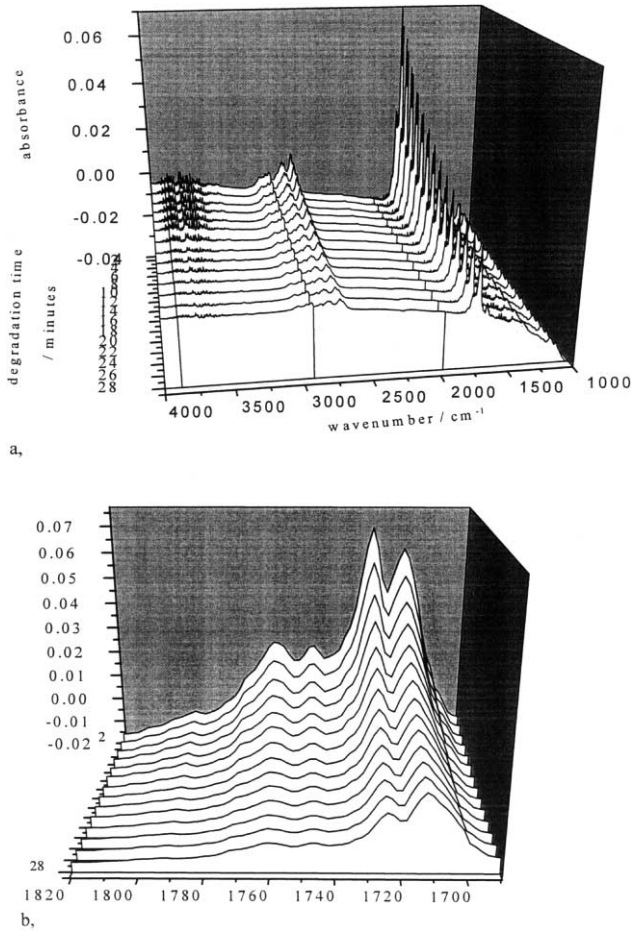

Fig. 10. Evolution of volatile degradation products of PVOH at 300°C, measured by FTIR, (a) in the range 4000–1000 cm^{-1}, and (b) in the range 1820–1690 cm^{-1}.

Table 2
Assignment of infrared bands of volatile degradation products of PVOH

Wavenumber (cm^{-1})	Assignment	Intensity
Narrow bands above 3500	Water vapour $O-H_{(str)}$	weak
3100–3000	Unsaturated $C=C_{(str)}$	weak
2960–2820	Saturated $C-H_{(str)}$	weak
1790	Vinyl ester	weak
1760	Saturated ketone	medium
1745	Unsaturated ketone	medium
1725	Saturated aldehyde	strong
1715	Unsaturated aldehyde	strong

of the band at 1790 cm^{-1} is not clear, but may be due to the formation of a vinyl ester product through a rearrangement process. The evolution of bands at 1680 and 1650 cm^{-1} was further evidence for the formation of unsaturated products.

The above analysis was consistent with the results of Tsuchiya and Sumi [3], which indicated the formation of water, acetaldehyde, acetone, ethanol, unsaturated aldehydes (from crotonaldeyde to 2,4,6-octatriene-1-al), unsaturated ketones (from 3-pentene-2-one to 3,5,7-nonatriene-2-one) and aromatic products at 240°C. It was considered that acetaldehyde was produced by the depropagation mechanism proposed in Fig. 8a. However, in cases where considerable elimination of hydroxyl groups has already occurred, such a reaction may only lead to random scission, and liberate unsaturated aldehydes and ketones. The reaction of a hydroxyl group with a C=C bond may also lead to chain scission (see Fig. 11a). A degradation fragment with a ketone groups and an aldehyde end-group could have lead to the formation of a vinyl ester by the rearrangement shown in Fig. 11b. The change in peak height of selected carbonyl bands evolved at 300°C is shown in Fig. 12, and it is clear that the rate of evolution of unsaturated aldehydes was slower than that of the other three materials.

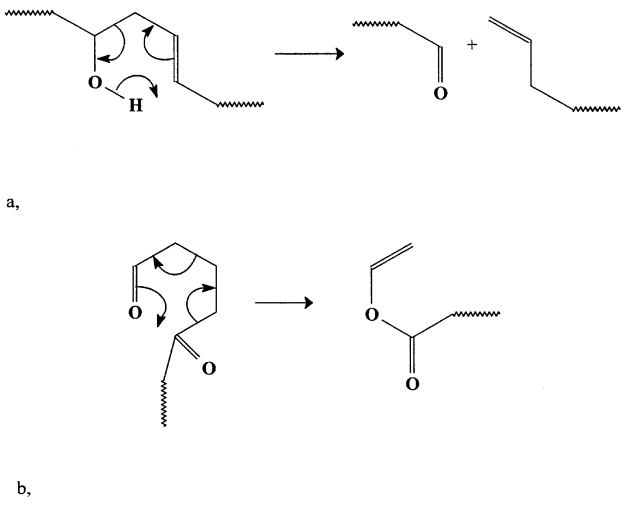

Fig. 11. Thermal degradation processed proposed for molten PVOH, (a) leading to aldehyde and alkene end-groups, and (b) leading to vinyl ester.

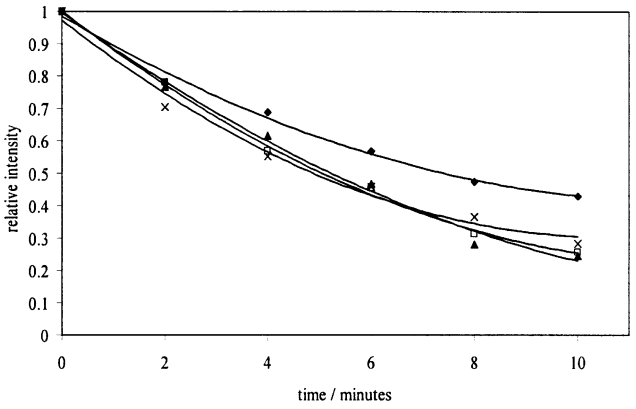

Fig. 12. Change in intensity of carbonyl bands associated with the volatile degradation products of PVOH at 300°C (◆, unsaturated aldehyde; □, saturated aldehyde; ▲, unsaturated ketone, and × saturated ketone).

5.5. TA-MS of PVOH

TA-MS was carried out on PVOH at a heating rate of 20°C min^{-1} in an attempt to detect water produced by the elimination of hydroxyl side-groups. In the range 1–80 *m/z*, seven ions were detected from the volatile degradation products of PVOH, see Fig. 13. The ion at 18 *m/z* was confirmed as being due to water by comparison with the dehydration product of $CuSO_4 \cdot H_2O$. Water began to evolve at lower temperatures than the other degradation products, probably due to the low energy of activation of the dehydration process, although it was necessary for PVOH to melt before significant amounts of water were observed. The ion at 28 *m/z* was thought to be due to carbon monoxide. The ions at 29, 41, 43 and 69 *m/z* were thought to be due to fragments of formaldehyde, ketene, acetaldehyde and crotonaldehyde respectively. The ion at 77 *m/z* was thought

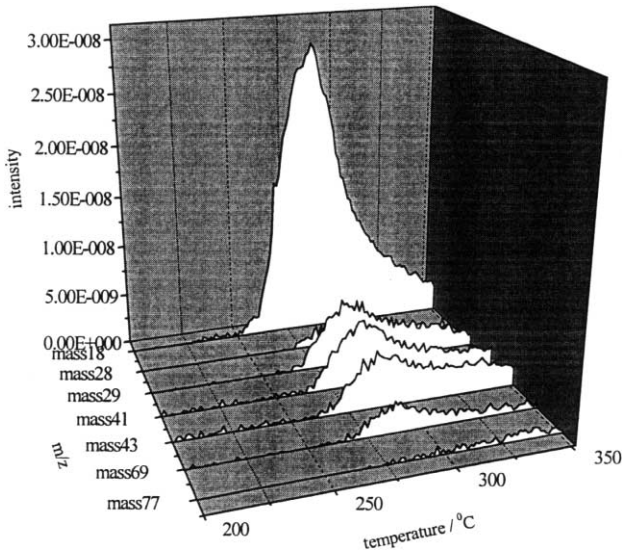

Fig. 13. Mass spectrometric response from volatile degradation products evolved during the thermal degradation of PVOH at 20°C min^{-1}.

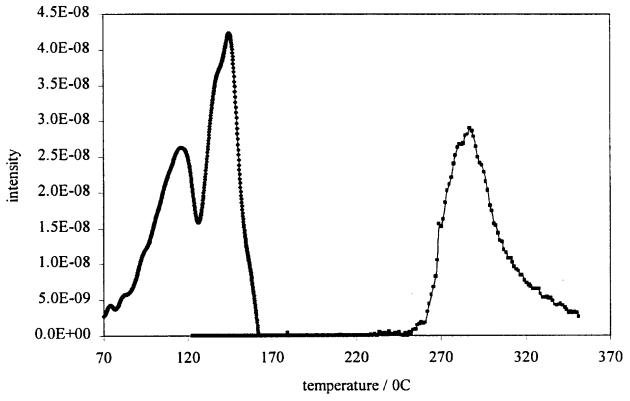

Fig. 14. Mass spectrometric response at 18 *m/z* from dehydration of $CuSO_4{\cdot}5H_2O$ and the thermal degradation of PVOH (◆ $CuSO_4$ and ■ PVOH).

to be due to the fragment of benzene, and was found to occur at a higher temperature than the other fragments, consistent with it being a product of the breakdown of the polymer chain.

The accumulated signal of the mass spectrometric measurements of evolved water from PVOH (32.2 mg) was compared to that of the dehydration of $CuSO_4{\cdot}5H_2O$ (25.7 mg), see Fig. 14. It was found that the dehydration of $CuSO_4{\cdot}5H_2O$ lead to the production of 7.2 mg of water, and by comparison of the area under the curves for dehydration of $CuSO_4{\cdot}5H_2O$ and degradation of PVOH, it was found that 32.2 mg of PVOH yielded 5.5 mg of water (17 wt%). This was approximately half the amount of water expected if PVOH underwent elimination alone (41%).

No water was detected while PVOH remained in the solid state. This may have been because the rate of elimination of water in the solid state was too slow to be measured.

6. Discussion of thermal degradation in the molten state

From the results presented in Section 5, it was concluded that random chain scission leading to volatile products was a major degradation process in the molten state. Acetaldehyde was thought to be a major degradation product, but several saturated and unsaturated aldehydes and ketones were also produced. It was considered that random scission of the polymer occurred by a six-membered transition state involving a hydroxyl group and an adjacent carbonyl group. The carbonyl groups were produced by migration of a double bond after water elimination, followed by keto–enol tautomerisation. Very little carbonyl was detected in the degraded polymer residue, which was probably due to the low stability of the carbonyl structure to further degradation. In contrast, large quantities of carbonyl products were observed amongst the gaseous degradation products.

The pre-exponential factors for thermal degradation calculated from the rate of loss of $C{-}H_{(str)}$ and $O{-}H_{(str)}$ were relatively low. For a first order reaction, a low pre-exponential is indicative of a large decrease in entropy in achieving the transition state required for thermal degradation. The large decrease in entropy was attributed to the four membered transition state associated with water elimination. However, the pre-exponential factor was probably increased by the volatile degradation processes, which were thought to occur through six membered transition states, and as such did not require such a large decrease in entropy.

7. Degradation of PVOH in the solid state

7.1. Isothermal TG

An isothermal TG experiment was carried out at 195°C under argon. A weight loss of 33% was recorded after four days, consistent with thermal degradation occurring by water elimination only. The solid residue was in the same fine powder form as the sample before thermal degradation, but was slightly discoloured (light brown). It was concluded that elimination took place in the solid state, and an infrared spectrum of the degraded sample (Fig. 15) was similar to that of undegraded PVOH, except for two new infrared bands at 1705 and 1640 cm^{-1}. The band at 1705 cm^{-1} was probably associated with the formation of unsaturated aldehyde or ketone groups, and the band at 1640 cm^{-1} with formation of C=C double bonds in the polymer backbone.

7.2. TA-FTIR spectroscopy

TA-FTIR spectroscopy was carried out on PVOH at temperatures of 210–231°C. It was found that thermal degradation at these temperatures lead to an equal rate of loss of the $O{-}H_{(str)}$ and $C{-}H_{(str)}$ bands (see Fig. 16). Due to the slow rates of thermal degradation (10^{-6} s^{-1}), degradation was only allowed to proceed to 30 mol% in each case. At which point no evidence for the formation of carbonyl groups or C=C double bands was observed.

First order rate plots for the loss of the $O{-}H_{(str)}$ band in the

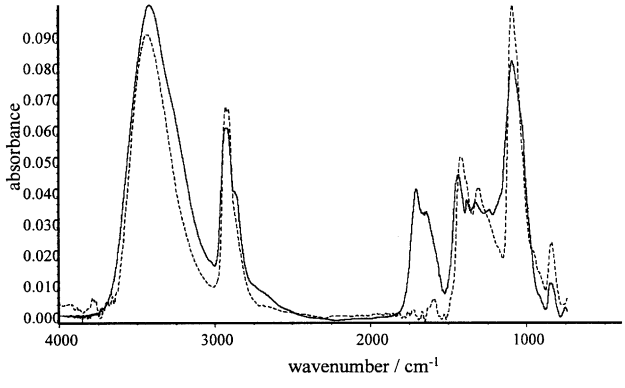

Fig. 15. Infrared spectra of PVOH degraded at 195°C for four days, and undegraded material (—, degraded PVOH and - - -, PVOH).

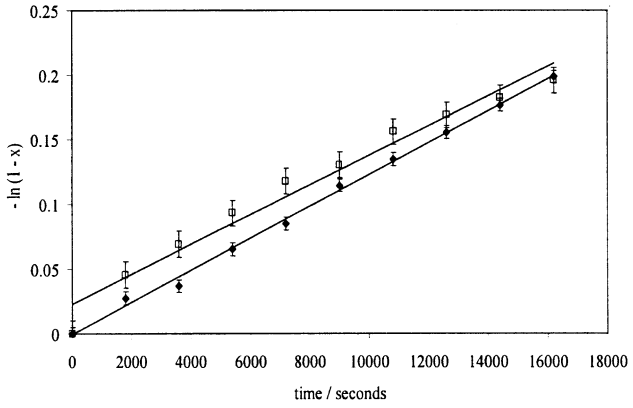

Fig. 16. First order rate plot for the thermal degradation of PVOH at 220°C, measured by TA-FTIR spectroscopy (◆, O–$H_{(str)}$ and □, C–$H_{(str)}$).

solid state were used to produce an Arrhenius plot, and compared to the data collected in the molten state (see Fig. 17). A distinct change in the Arrhenius relationship for the thermal degradation of PVOH was observed between 225 and 231°C, due to a sudden increase in the rate constant. It was considered that a significant amount of PVOH melted between these temperatures. The activation energy for loss of the O–$H_{(str)}$ band in the solid state was 70 ± 10 kJ mol^{-1}, and the pre-exponential factor was 45 ± 5 s^{-1}.

Given that the rate of thermal degradation of the O–$H_{(str)}$ and C–$H_{(str)}$ bands was equal, and that no aldehydes or ketones were observed in the volatile product array, it was considered that the mechanism of thermal degradation operating in the solid state was that of elimination of water. The lack of motion in the chain segments in the solid state was thought to prevent formation of the six-membered transition state required to achieve chain scission. The lack of motion in the polymer chain and the low number of conformations that water elimination can occur through a four membered transition state, were probably responsible for the very low pre-exponential factor for thermal degradation obtained.

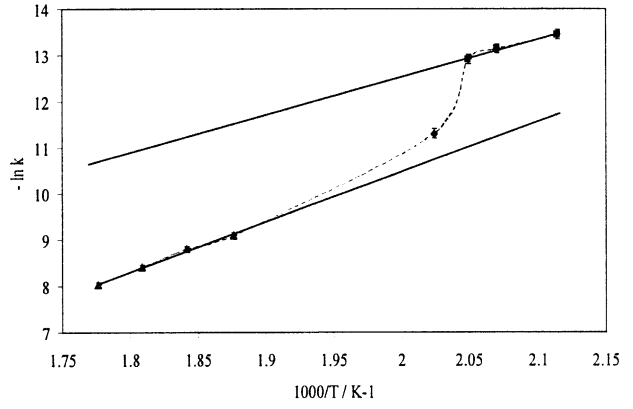

Fig. 17. Arrhenius plot for the loss of O–$H_{(str)}$ during the thermal degradation of PVOH in the molten and solid states.

7.3. DSC study of the thermal degradation of PVOH in the solid state

Samples of PVOH were degraded at 195°C under a flow of argon for up to four days. The weight loss was used to estimate the amount of water elimination that had occurred in each sample. DSC was carried out at 10°C min^{-1} on each sample to study the effect of elimination on the crystallinity of the samples. DSC thermograms of the degraded samples are shown in Fig. 18. It was found that in the first 30 mol% of elimination that the amount of crystallinity did not vary (Fig. 19a), but the crystalline melting point decreased with increasing elimination (Fig. 19b).

It was considered that the decrease in T_m was due the evolution of degradation products in the amorphous phase, as a result of water elimination. This would reduce T_m by changing the free energy of the molten state. The decrease in crystallinity accelerated above 30 mol% elimination after what was thought of as having effectively eliminated all side groups from the amorphous region, that elimination began to occur in the crystalline region, thus disrupting the crystallinity. Once the crystalline regions start to decompose the measured crystallinity fell of rapidly.

8. Discussion of thermal degradation in the solid state

The thermal degradation of PVOH in the solid state was found to involve predominantly elimination of water through a four membered transition state, although due to the slow rate of elimination, it was not possible to detect the

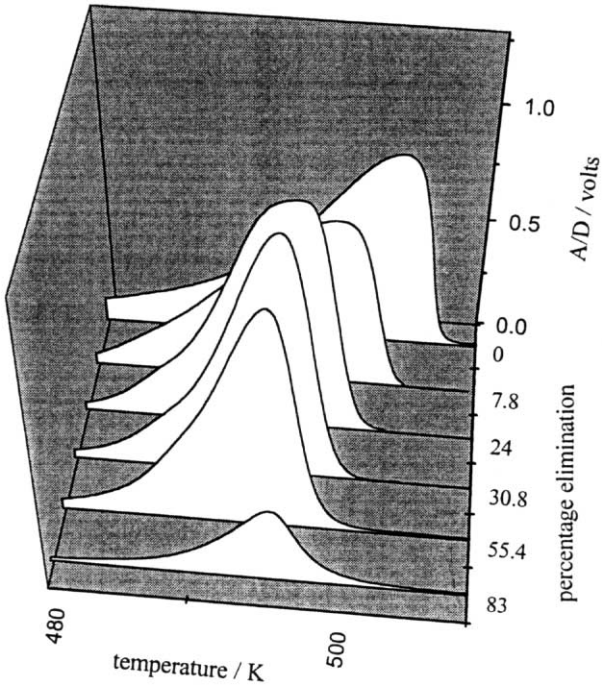

Fig. 18. DSC thermograms of PVOH degraded at 195°C.

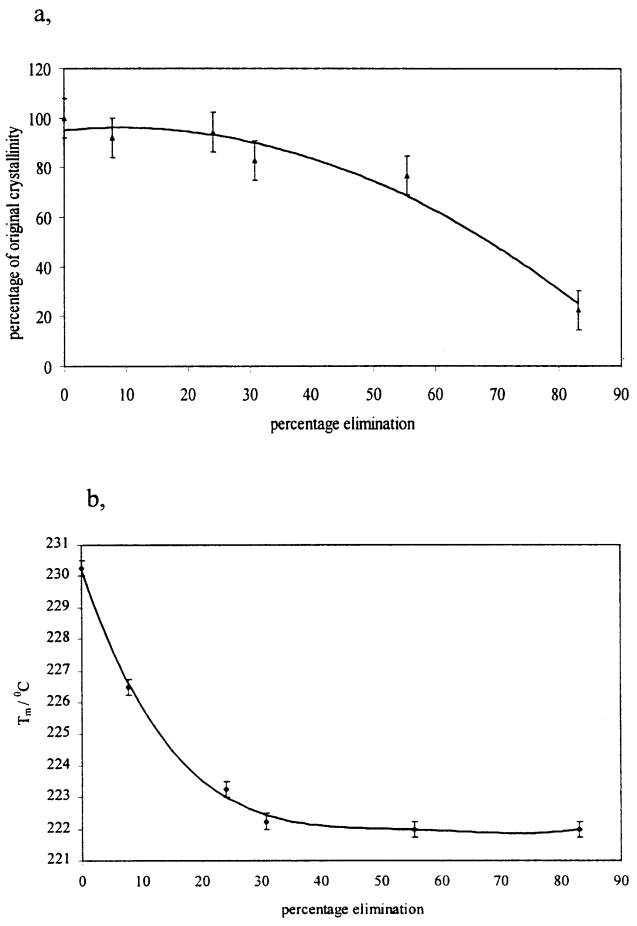

Fig. 19. Effect of percentage water elimination on, (a) crystallinity, and (b) melting point, of PVOH.

water evolved. Carbonyl groups were also formed, presumably by the double bond migration process proposed for degradation in the molten state. However, due to the low mobility of PVOH polymer chains in the solid state, the six-membered transition state required for chain scission was difficult to achieve, and no volatile aldehydes or ketones were observed. Furthermore the maximum observed weight loss was less than 40 wt% of the initial polymer weight, indicative that water elimination was the only weight loss process.

Thermal degradation in the solid state also lead to a reduction in the crystalline melting point and amount of crystallinity due to production of degradation products and the disruption of the crystalline regions. The evidence suggests that the crystalline regions were more stable than the amorphous regions.

9. Conclusions

The thermal degradation of PVOH in the molten state consisted of water elimination and chain scission, via a six-membered transition state, leading to the formation of volatile products including saturated and unsaturated aldehydes and ketones.

In the solid state, thermal degradation of PVOH was exclusively by elimination of water. Due to the lack of conjugation observed, it was considered that elimination in both solid and molten states was random, and C=C bond formation did not activate elimination of adjacent hydroxyl units, contrary to the case of PVAc [7]. Elimination of water decreased the amount of hydrogen bonding in PVOH, and hence reduced the T_m. Above 30 mol% elimination, double bonds disrupt the crystalline regions of the polymer.

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