Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 501–508

FTIR STUDY OF THE THERMAL DEGRADATION OF POLY(VINYL ALCOHOL)

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Abstract

The degradation of poly(vinyl alcohol) was investigated using TG analysis and Fourier transform infrared spectroscopy to determine the effect of atmosphere on the process of degradation. In the spectra, four vibrational modes were identified that characterised the major steps of the degradation process. These were the O–H, C–H, C=O and C=C stretching modes. The mechanism observed for degradation in an inert atmosphere was in accordance with the accepted mechanism of elimination followed by pyrolisation. Evidence of conjugated polyenes, however, was not observed. For the air atmosphere, oxidation in both steps of the degradation process was observed.

Keywords: infrared spectroscopy, poly(vinyl alcohol), TG, thermal degradation

Introduction

Organic polymers are used extensively as processing aids in the manufacture of ceramic products from ceramic powders. The polymers are added to improve the flow characteristics of the ceramic powders in the dry state, in isotactic pressing. Once the green compacts have been formed, however, the polymer additives must be removed prior to sintering. This is achieved by slowly raising the temperature of the greens to the degradation temperatures of the polymer additives thus volatilising and removing the polymer from the green. In order to optimise the heating program, the characteristics of the degradation process for both inert and oxidative atmospheres must be understood. A comparison of the degradation mechanisms in oxidative and non-oxidative atmospheres may therefore help to elucidate optimised thermal ramping conditions. In this preliminary investigation, the degradation of poly(vinyl alcohol) (PVAl) is investigated using both air and inert atmospheres. Fourier transform infrared (FTIR) spectroscopy is used to investigate the molecular mechanisms of the degradation process in conjunction with thermal gravimetric analysis (TG).

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

PVAl was acquired from the BDH Chemicals Ltd with a mass average molecular mass of 24.000 g mol^{-1}. The PVAl was prepared by alkaline hydrolysis of poly(vinyl acetate) and is quoted to be 99% hydrolysed. This value can be confirmed (approximately) from the FTIR spectra where a small peak is observed at 1718 cm^{-1}. The PVAl was found to be essentially ash free as no residual mass was observed in the TG experiments at 1000°C in air. The purge gases used in this study were supplied by the BOC Group Plc. High purity nitrogen (99.99%<10 ppm oxygen) and instrument grade air were used in the FTIR experiments. For the TG experiments, high purity argon (99.997%<10 ppm oxygen) and instrument grade air were used.

The PVAl was used 'as received' in the TG experiments. To within 0.5 mg, approximately 10 mg of polymer sample was placed in an alumina crucible on the sample stage of a Setaram Setsys 16 TG-DSC. Argon and air were used as the purge gases. The flow rate used for both atmospheres was 20 cm^3 min^{-1}. The atmosphere was stabilised for at least 30 min prior to the beginning of a run. For each experiment the temperature was raised from room temperature to 1000°C at a rate of 1°C min^{-1}. Temperature calibration was attained using the melting transformations of 6 high purity metals (indium, zinc, copper, aluminium, silver and gold) using the DSC facility. A calibration curve for the buoyancy of each gas was also determined for the gas flow and heating rates used. The mass loss measurements were made with a precision of 10 μg and an accuracy of ±100 μg.

For the FTIR spectroscopy experiments, the PVAl was cast from solution in distilled water (1% mass/volume) onto zinc selenide (ZnSe) plates. The plates used had a thickness of 1 mm. The solvent was allowed to evaporate to yield a thin PVAl film. The films were prepared so that the C–H stretch at 2940 cm^{-1} attained an absorbance of 1 (i.e. 10% transmittance). The coated ZnSe plates were placed on the heating element of a Linkam THMS 600 microscope hot stage with the film separated from the hot plate by the ZnSe plate. The hot stage was placed in the micro accessory compartment of a Bomem Ramspec 152 FTIR spectrometer and the sample compartment of the hot stage was purged with either high purity nitrogen or instrument grade air at a flow rate of 20 cm^3 min^{-1}. Prior to collection of the spectra, each sample was annealed at 100°C for 1 h. After the 1 hour annealing process, the temperature was raised at a constant rate of 1°C min^{-1} from 100 to 500°C. Transmittance spectra were acquired at 10°C intervals and were acquired with a resolution of 4 cm^{-1} and averaged over 100 scans. The acquisition time for each spectrum was approximately 3 min.

Results and discussion

The TG curves for the degradation of PVAl in both argon and air atmospheres are shown in Fig. 1. The shape of the mass loss curve for the inert atmosphere is consistent with the generally accepted two-step mechanism for the degradation of PVAl [1–4] and is confirmed to be a two-step process by the differential of mass loss (DTG)

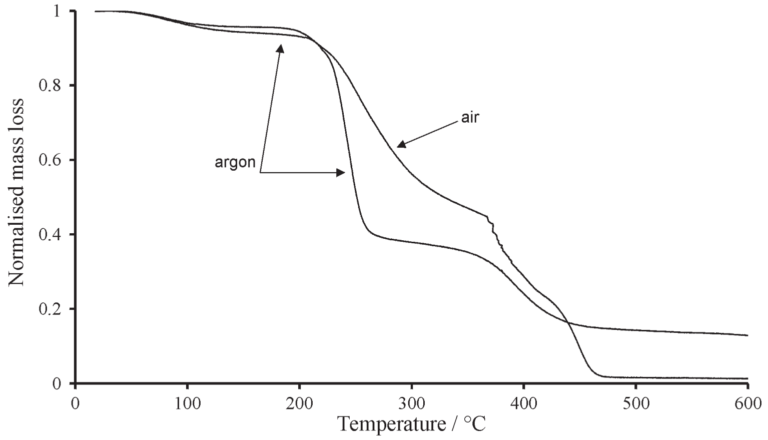

Fig. 1 TG curves for the degradation of PVAl in argon and air atmospheres

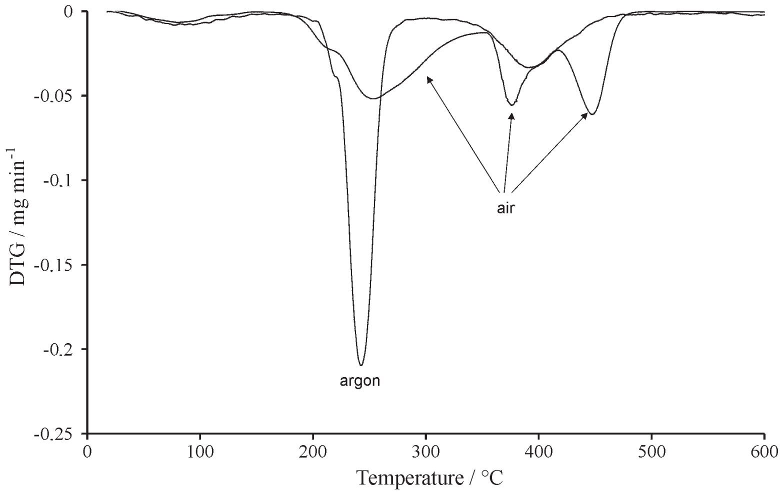

Fig. 2 DTG curves for PVAl degraded in both argon and air atmospheres

curve (Fig. 2). The first step in the mass loss curve results from the elimination of water [1]. In the second step, in the inert atmosphere, pyrolisation occurs producing some organic volatiles resulting in the second mass loss step. The pyrolisation process also leaves a large residue of carbonaceous material which was observed to be oxidisable at 1000°C in air leaving no measurable ash content (Table 1).

The degradation process in an air atmosphere shows some significant differences from that of the inert environment. The first step shows a much reduced rate of mass loss indicating the inclusion of oxygen in the polymer. At 369°C, a sharp change in the rate of mass loss occurs indicating rapid oxidation of the polymer. Similar experiments in oxidising and inert atmospheres have been carried out on poly(vinyl butyral) (PVB), a polymer related to PVAl which also degrades by an elimination mechanism [5]. The mass loss curves reported for PVB are similar to mass loss curves for PVAl observed in Fig. 1 confirming the effect of atmosphere on the degradation mechanism. The second step of the degradation process in air is also observed to differ from the inert environment. Two mass loss steps are observed with maximum rates at 378 and 449°C (Fig. 2).

Table 1 Mass loss data for the degradation of PVAl in both argon and air atmospheres

Atmosphere	Degradation step	DTG peak/°C	Mass loss/%
Argon	Water loss	90	6.0
	Water elimination	247	55.9
	Cracking	396	24.5
	Residue at 600°C	–	13.5
	Residue at 1000°C (in air)	–	0
Air	Water loss	82	4.2
	Water elimination	255	52.4
	Oxidation (2 steps)	378 and 449	41.7
	Residue at 600°C	–	1.6
	Residue at 1000°C	–	0

In both atmospheres a residue is observed at 600°C. For the inert atmosphere the residue is large (13.5%) and expected since pyrolisation results in the formation of amorphous carbon [6]. Although small (1.6%) a residue persists in the air environment. For both atmospheres this residue was observed to oxidise at 1000°C in air. The residue observed in air is indicative of the effect of geometry on the degradation process. It is likely that a proportion, although small, was degraded in the absence of

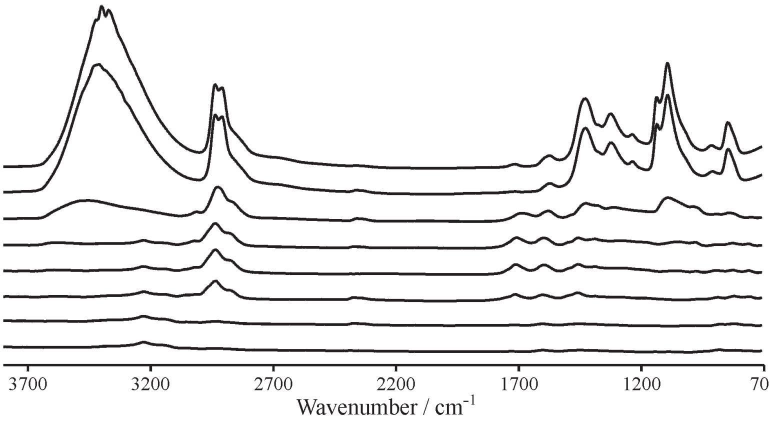

Fig. 3 Transmittance spectra of PVAl degraded in a nitrogen atmosphere. Curves shown are at 50°C intervals from 150°C (top) to 500°C (bottom)

oxygen due to oxygen depletion in the crucible as combustion of the polymer proceeded. Effects of this nature were observed for PVB [5]. This effect is certainly an important consideration in determining optimum heating rates for binder burnout as the diffusion of oxygen will occur at a much lower rate in the pores of a ceramic green.

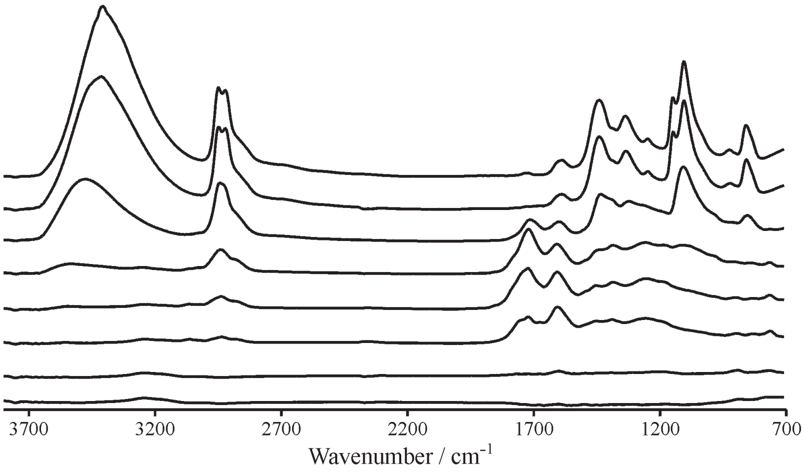

Fig. 4 Transmittance spectra of PVAl degraded in an air atmosphere. Curves shown are at 50°C intervals from 150°C (top) to 500°C (bottom)

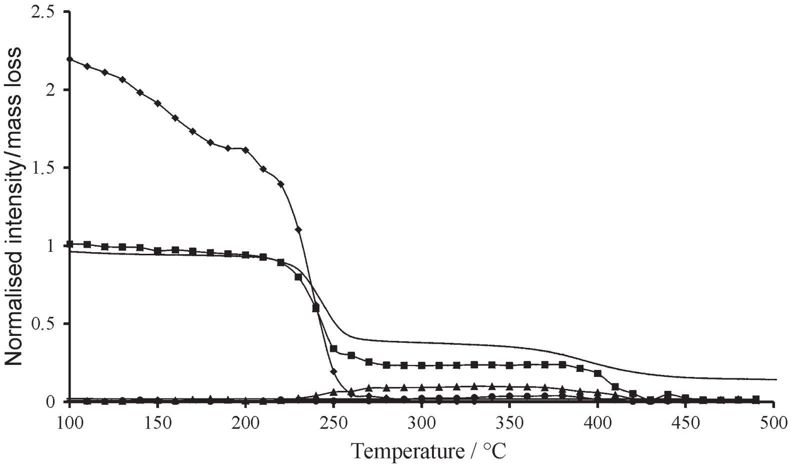

Fig. 5 Intensities of O–H (♦), C–H (■), C=O (▲) and C=C (●) stretching modes at 3370, 2940, 1715 and 1595 cm^{-1} respectively for PVAl in a nitrogen atmosphere. The intensities are normalised to that of the C–H stretch. The mass loss data for the degradation of PVAl in argon atmosphere (—) is also included for comparison

The DTG curves also highlight the effect of crystal melting on the degradation process. The melt temperature for the PVAl used in this study was measured to be

223°C at peak. Shoulders around 220°C are observed in the DTG curves for both atmospheres. This would indicate that the melting of the crystallites inhibits the degradation process. It is likely that the endothermic nature of the melting reduces the temperature of the polymer thus reducing the rate of degradation. It is, however, possible that the change in rate is associated with a morphological dependence of the degradation mechanism where degradation is initiated in the amorphous regions and does not extend to the crystalline regions before melting.

The FTIR spectra for the degradation of PVAl in nitrogen and air atmospheres are shown in Figs 3 and 4, respectively. In both atmospheres there is a marked reduction in the intensities of all the absorption bands in the PVAl spectrum as the degradation process proceeds. Two new bands at 1715 and 1595 cm^{-1}, attributed to carbonyl (C=O) and carbon–carbon double bond (C=C) stretching, respectively, are also evident particularly in the air atmosphere and to a lesser extent in the inert atmosphere. The normalised intensities (ratioed to the intensity of the carbon–hydrogen (C–H) stretching mode at 2940 cm^{-1} in the spectrum acquired at 100°C) of four vibrational modes at 3370, 2940, 1715 and 1595 cm^{-1} are plotted as a function of the temperature for both atmospheres in Figs 4 and 5. These modes were chosen as they represent the reactants and products of the important chemical species of the accepted degradation mechanism of PVAl [1–4]. Also included in these figures are the respective mass loss curves.

For the degradation in nitrogen, both the hydroxyl (O–H) and the C–H stretching modes reduce sharply in intensity with an onset at approximately 220 and a maximum rate at approximately 240°C. The decline in the intensities of both of these modes correlates extremely well with the mass loss curve for the inert environment. The sharp decline in the intensity of the O–H peak is indicative of the mechanism for

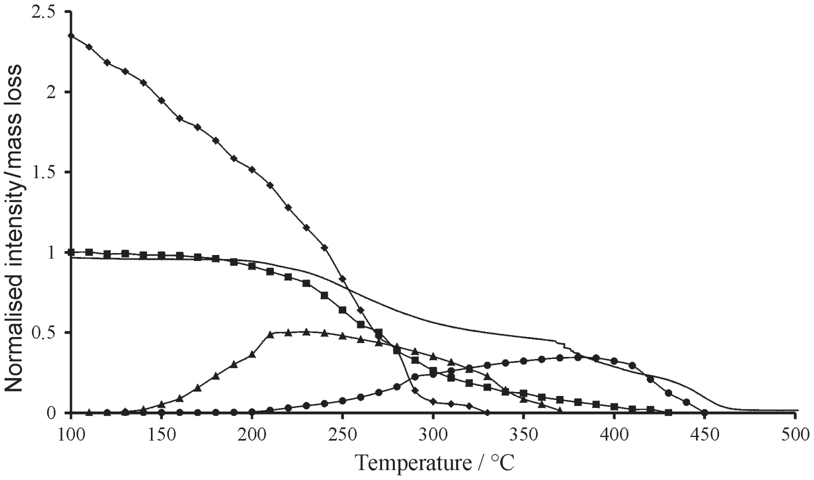

Fig. 6 Intensities of O–H (♦), C–H (■), C=O (▲) and C=C (●) stretching modes at 3370, 2940, 1715 and 1595 cm^{-1} respectively for PVAl in an air atmosphere. The intensities are normalised to that of the C–H stretch. The mass loss data for the degradation of PVAl in air atmosphere (—) is also included for comparison

elimination of water as the first step of the degradation process. The O–H peak declines to zero intensity by the end of the first step indicating that complete elimination of the alcohol groups has occurred. The product of the elimination is olefinic resulting in the production of C=C in the polymer residue. As a consequence, the C–H peak also declines in intensity as olefinic C–H stretching occurs at greater than 3000 cm^{-1} and an olefinic C–H stretch at 3020 cm^{-1} does indeed appear above 230°C. If the elimination occurs at adjacent OH groups the formation of a polyene results [2–3] yielding conjugated unsaturation in the backbone chain. A peak around 1600 cm^{-1} is therefore expected. Only a weak peak in this region is observed. This is consistent with a Diels–Alder type cyclisation process which has been proposed to occur as the elimination of water proceeds isolating C=C in cyclic ring structures [2–3]. This deduction is based on the relative intensities of unconjugated and conjugated C=C being relatively weak and strong, respectively [7]. This result is also consistent with the average length of polyene segments which has been reported to be of the order of 1.1C=Cs [4]. Evidence of the presence of a weak carbonyl peak is also apparent for the first step of the degradation and is consistent with a mechanism of chain scission and rearrangement yielding the carbonyl group [6].

In the second degradation step, the change in the intensity of the C–H stretch correlates well with the mass loss data. The aliphatic hydrocarbons produced in the first degradation step degrade to form the carbonaceous residue observed in the TG curves. For the FTIR, little remains of the spectrum at 500°C. However, a peak at 3220 cm^{-1} does appear and may be associated with the carbonaceous residue.

The degradation of the PVAl in an air atmosphere produces a similar reduction in the intensities of the O–H and the C–H stretching modes. The decline in the intensities of these modes compares well with the mass loss as a steady decline in the intensities of each mode is observed. The O–H mode persists to higher temperatures in the air atmosphere (relative to the inert atmosphere) indicating the inclusion of atmospheric oxygen in the polymer during degradation. The reduction in intensity of the O–H stretching mode correlates well with the first step of the degradation process indicating that elimination may be an important mechanism in the first step. However, in the oxidative degradation of polymers, the inclusion of oxygen commonly results in hydroxyl groups in the oxidation products. A number of mechanisms could therefore be attributed to the decline in the O–H peak particularly as it is delayed to much higher temperatures than is the case for degradation in an inert atmosphere.

A large carbonyl peak around 1715 cm^{-1} appears in the spectrum is observed to coincide with the first degradation step of the mass loss curves. This is indicative of the inclusion of atmospheric oxygen in the polymer. This peak has a centre of mass at about 250°C and corresponds with the maximum rate of degradation in the first step in the TG experiments (255°C). The carbonyl peak remains important in the degradation throughout the first degradation step and diminishes towards the end of this step. Towards the end of the first step and throughout the second stage of the degradation a C=C peak appears around 1595 cm^{-1}. Peaks at 3055, 3020, 890 and 760 cm^{-1} also appear in the same temperature range as the 1595 cm^{-1} peak and are also consistent with the presence of C=C. High intensity of the C=C peak indicates conjugation and, given the low intensity of the C–H stretch at 2940 cm^{-1}, it is possible that this unsaturation is associated with aromatic species. As observed for the inert atmosphere, a peak at 3220 cm^{-1} also appears in the spectrum and is present at 500°C. The peak is weaker and less well defined than its counterpart in the inert atmosphere which is consistent with oxidative degradation leaving little (1.6%) residue at 500°C. The peak may therefore be attributed to any carbonaceous residue species remaining.

Conclusions

The data presented in this paper correlates well with the established mechanism for the degradation of PVAl in an inert environment. Elimination of water is the predominant mechanism of the first step of the degradation process. This is followed by pyrolysis of the residue into a carbonaceous product which is stable to high temperature in an inert atmosphere. In air, the degradation of the PVAl is oxidative. The first degradation step in air also results in the reduction in O–H species, but is not solely due to the elimination of water as oxidation of the polymer is also occurring. The final stage of the oxidation process results in a small residue.

In the context of ceramic processing and binder burnout, it is the desirable goal to minimise the residue content. The economics of a commercial sintering process also require the optimisation of the heating rates in order to maximise throughput and reduce energy costs. A knowledge of the degradation mechanisms of the binder can aid such optimisation through the use of more then one atmospheric environment and heating rate. For the case of PVA1 the degradation mechanism indicate that the initial burnout process should be carried out in an inert atmosphere as the mass loss is more rapid for the elimination mechanism. The residue from this process may then be removed by oxidation. Optimisation of the binder burnout process may therefore include the optimisation of the heating rates as well as modification of the atmosphere.

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