THE THERMAL DEGRADATION OF COPOLYMERS OF VINYL ACETATE AND VINYL ALCOHOL

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A study on the thermal degradation of copolymers of vinyl acetate and vinyl alcohol (V—OAC/V—OH) has been carried out using techniques such as Thermal Volatilization Analysis (TVA), Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA). It has been found that stability to weight loss decreases with the increase of vinyl acetate content in the copolymer. product analysis by Infrared Spectroscopy of the copolymers degraded in steps indicates that there is no interaction between adjacent acetate and alcohol units in the chain and deacetylation of V—OAC units proceeds separately from and at lower temperatures than decomposition of the V—OH units.

INTRODUCTION

The degradation of vinyl acetate/methyl methacrylate (V—OAC/MMA) copolymers has previously been investigated by Daniel and Michel [1] and Gardner [2] who observed the production of acetic acid from the V—OAC units and MMA monomer from the MMA units. In vinylacatate/acrylonitrile (V—OAC/AN), it was observed [3] that elimination of acetic acid was concurrent with the degradation occurring in the AN sequences.

M.A.J. Mohammad [4] in a similar study of vinyl acetate/styrene (V—OAC/S) and vinyl acetate/ethylene (V—OAC/D) copolymers suggested that degradation occurs initially at V—OAC sites which he proposed were weak links in the copolymers.

In V-OAC/E copolymers Gardner [2] and A. Jamieson [5] noted that deacetylation of V-OAC units proceeds separately from and at lower temperatures than decomposition of the E units. In the light of these observations one might expect similar degradation behaviour in V-OAC/V-OH copolymers. Keeping all this in mind a study was undertaken to elucidate the thermal degradation mechanism of V-OAC/V-OH copolymers. This paper describes the results of our experimental investigations.

EXPERIMENTAL

Materials. Poly (Vinylacetate) (PV-OAC) (BDH), molecular weight approximately 45,000 was used as supplied. The solvent, acetone was of A.R. grade. A standard 1M solution of NaOH was used as supplied by Hopkin and Williams.

Preparation of Copolymers of V-OAC and V-OH Copolymers of V-OAC and V-OH were prepared by saponification of PV-OAC. A 2 % solution of PV-OAC in acetone was prepared. An appropriate amount of aqueous NaOH (1M) was added with stirring followed by an addition of sufficient water to bring the solvent composition to acetone/H_2O, 80/20. The ultimate extent of hydrolysis of acetate unit was found to be equivalent to the amount of NaOH used. The reaction mixture was allowed to go to completion at 35° [6] .

Recovery of Copolymers of V-OAC and V-OH. PV-OAC saponified to less than 60 % was in the form of a gel and could not be filtered. To recover the copolymers, the dialysis technique was therefore used. Polymers saponified above 60 % were separated by pouring the reaction mixture into a large amount of water, followed by filtration, washing with acetone/H_2O, 80/20 mixture and drying in a vacuum oven at 60°.

Characterization. Copolymer compositions were calculated from elemental analysis using a Perkin Elmer 240 Elemental Analyser and confirmed by NMR. TVA, was used to obtain TVA traces [7 – 9] . TGA and DTA traces were obtained on a DU Pont 900 thermal analysis apparatus. In the former case an accessory 950 TG Module was also used. Infrared spectra (I R) were recorded using a Perkin Elmer 257 Grating spectrophotometer.

RESULTS AND DISCUSSION

Thermal Volatilization Analysis. TVA traces for V-OAC/V-OH copolymers containing 53.19, 7.72 % and 0.6 % V-OAC are reproduced in Figs. 1 – 4 respectively.

The initial sharp peak of PV-OAC (TVA trace not shown in this paper) is shifted to higher temperature as the acetate content in the copolymer decreases indicating greater stability in the copolymer.

In view of the fact that elimination of acetic acid from PV-OAC proceeds from unit to unit along the chain, it may be that the greater stability of the copolymer is due to the reaction being blocked by V-OH units which means that each sequence of V-OAC unit requires its own initiation step.

In copolymers at higher V-OH contents water was formed principally in two stages namely, below 120° and above 300°. The water liberated in the first stage was considered to be water trapped in the polymer matrix whereas the liberation of water in the second stage was thought to be the result of a dehydration reaction on the polymer chain.

Two stages of weight loss can be distinguished in the degradation of 53.19 % copolymer (Fig 1). Analysis of the products associated with the first peak showed the presence of carbon dioxide, ketene, acetic acid and water. Products from the second peak were carbon dioxide, with smaller amounts of methane, ethylene and benzene.

From Fig. 2 it is abvious that 7.72 % copolymer degrades in four stages. The first two peaks with Tmax 324° and 368° respectively correspond to acetic acid elimination. The third TVA Pirani response at this peak is mainly due to water and acetaldehyde. Some non-condensable products are also trapped at -196°. The fourth peak gives Tmax at 480°. This high temperature peak results from products, a large proportion of which are non condensable at -196° are formed by break up of the unsaturated polyene chains. Two stage degradation of 2.67 % copolymer is shown in Fig. 3. The first peak due to acetic acid has almost disappeared. In the trace of 0.6 % copolymer shown in Fig. 4, the first low broad peak has a Tmax around 150° and the behaviour in the -75° is characteristic of water in the TVA system [7]. The product analysis of the second peak (Tmax at 295°) showed the presence of water and smaller amount of acetic acid. The pirani responses at the third (Tmax 400°) are mainly due to water and acetadehyde. A very small amount of non-condensable products are also trapped at -100° and -196°. Formaldehyde [10] and hydrogen [11] have also been reported to be formed during the
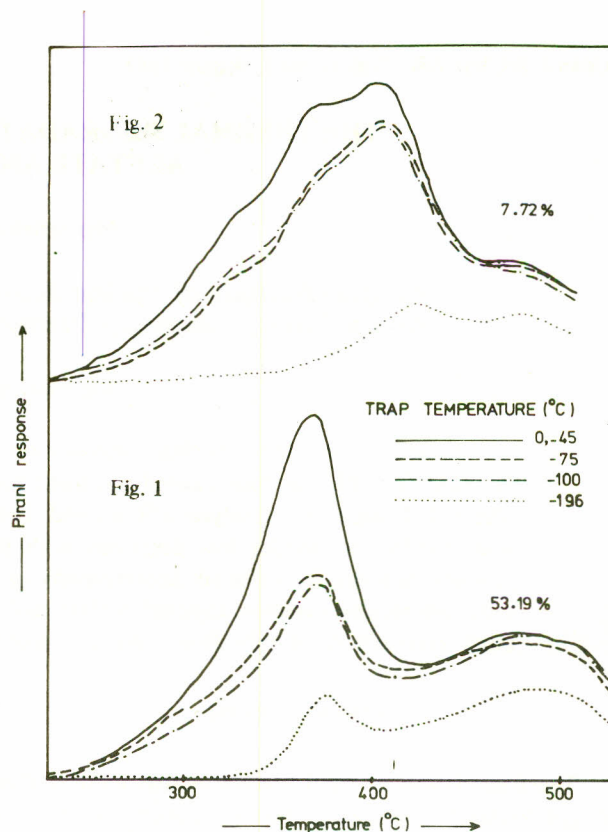

Fig. 1. TVA trace for 53.19 % copolymer.

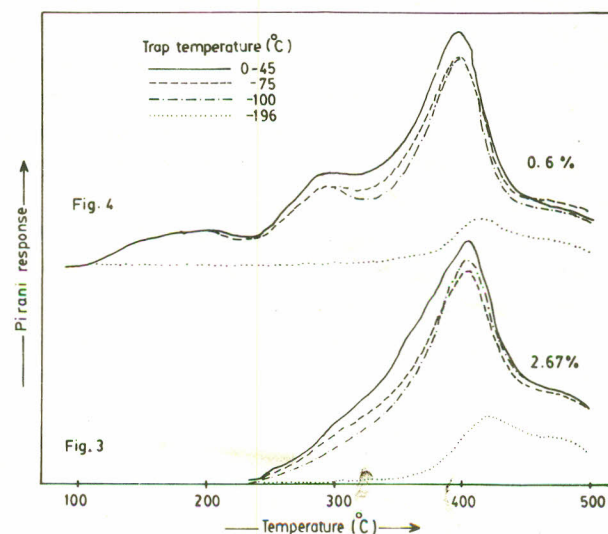Fig. 2. TVA trace for 7.72 % copolymer.

Fig. 3. TVA trace for 2.67 % copolymer.

Fig. 4. TVA trace for 0.6 % copolymer.

degradation but they were not observed in the present study. The high temperature peak (Tmax at 475°) is accounted for the breakdown of the polyene structures.

Thermal Gravimetric Analysis. TG traces for four V-OAC/V-OH copolymers containing 53.19 %, 19.9 % 7.72 % and 0.6 % V-OAC in the chain are reproduced in Fig. 5. For the copolymer there are two regions of weight loss corresponding to the breakdown of V-OAC and V-OH units, the latter breakdown occuring at slightly higher temperatures; also as the V-OAC content of the copolymers increases the stability to weight loss decreases. Weight loss from the alcohol rich polymers at lower temperatures is considered to be the result of the elimination of water trapped in the copolymer matrix.

The loss in weight of the 53.19 % copolymer which occurs during isothermal heating under nitrogen was investigated at different temperatures and the results are presented in Fig. 6. The energy of activation of the thermal decomposition of the copolymer calculated from the initial slopes of the curves in Fig. 6 was found to be 30.3 Kclas/mole.

Differential Thermal Analysis. DTA traces for V-OAC/V-OH copolymers containing 53.19 %, 19.9 %, 7.72 % and 0.6 % V-OAC are shown in Fig. 7. The endotherms in the region $172 - 231^O$ are associated with melting. The sharpening of the endotherms with increasing alcohol contents reflects the greater crystallinity of PV-OH compared with high content V-OAC copolymer. Degradation is reflected by the endotherms and exotherms at higher temperatures where the endotherms are probably associated with the breakdown of acetate and alcohol units while the exotherms are probably associated with cyclisation processes.

Product Analysis. I.R. Spectra of the volatiles from the various copolymers are almost indentical differing only in the relative amounts of individual products. Typical IR spectrum of the volatile products obtained from the degradation of 53.19 % copolymer (Fig. 8) shows absorptions due to carbon dioxide, ketene, acetic acid (vapour), acetaldelyde, unsaturated hydrocarbons and water. Fig. 9 shows the spectra of cold ring fraction (C.R.F.) and residue for 53.19 % copolymer degraded to 500°. This also includes the spectrum of the undegraded copolymer. The CRF spectrum is broadly similar to that of undegraded copolymer, the only real difference being the appearance of peak above 3000 cm^{-1} bands around 1600cm^{-1} and in the 800-990cm^{-1} regions associated with conjugation.

IR Spectrum of the black residue is similar to the spectrum of the C.R.F. (Fig. 9). No residual carbonyl and hydroxyl absorptions are observed in the residue which must therefore be largely composed of the long
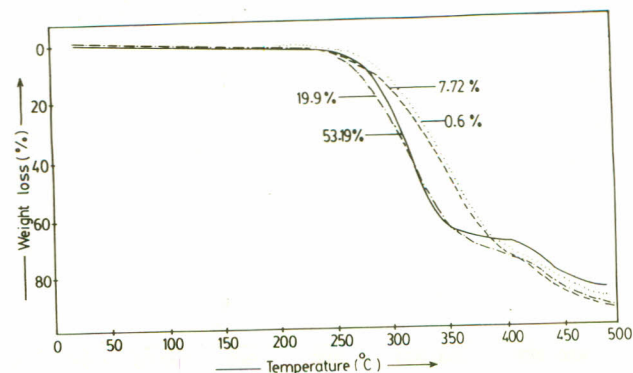
Fig. 5. TG traces for V-OAC/V-OH copolymers, sample size 5 mg, dynamic N atmosphere, heating rate 10°/ min.
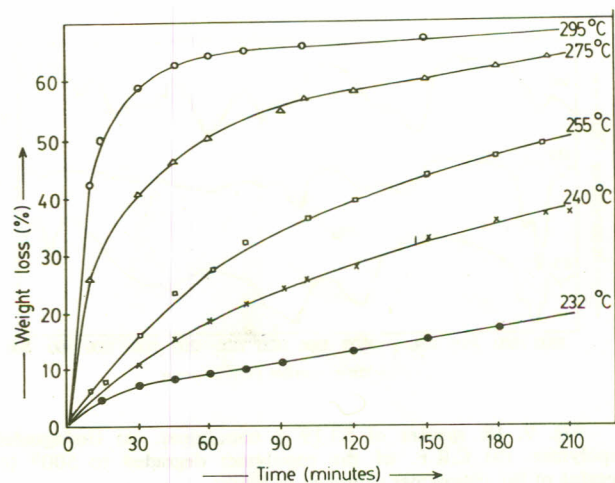
Fig. 6. Weight loss of 53.19 % copolymer as a function of time at various temperatures.

Fig. 7. DTA traces for V-OAC/V-OH copolymers, sample size 10/mg, dynamic N atmosphere heating rate 10°/ min.

conjugated sequences resulting from complete elimination of water and acetic acid.

Quantitative Estimation of Acetic Acid and Water. 50 mg sample of 53.19 % copolymer was degraded under

Fig. 8. IR spectrum of condensable degradation products from 53.19 % copolymer.

Fig. 9. IR spectra of 53.19 % copolymer. (a) Undegraded copolymer. (b) C.R.F. of the copolymer degraded to 500⁰ (c) Residue of the copolymer degraded to 500⁰.

Fig. 10.IR spectra of 53.19 % copolymer. (a) Undegraded copolymer. (b) Copolymer heated to 367⁰. (c) Copolymer heated to 500⁰.

isothermal conditions at different temperatures in a closed evacuated system for various lengths of time; a liquid nitrogen trap was used to collect acid and water as they were formed and the acid was titrated against 0.01 M NaOH using phenolphthalein as an indicator. The results of this investigation are shown in Table 1.

Structural Changes During Degradation. Before dis-

Fig. 11.IR spectra of the condensable degradation products of 53.19 % copolymer. (a) Copolymer heated to 370⁰. (b) Copolymer heated from 414 to 500⁰.

cussing the detailed mechanism of the degradation of the copolymer system it is of interest to consider the possibility of interaction between adjacent acetate and alcohol units in the chain. In particular it was considered that a reaction sequence of the following type might be possible, which would be revealed by the indentification of the cyclic ether structure as an intermediate product. Strong IR absorption by such a structure should occur in the region $970 - 980$ cm^{-1}.

50 mg samples of the copolymers were degraded in steps by programmed heating. Copolymers of various V-OAC contents seemed to follow a similar course of degradation and therefore a detailed account of only 53.19 % copolymer is given.

Fig. 10 illustrates the IR region of primary interest in (a) undegraded copolymer, (b) copolymer heated to 367⁰ at 10⁰/min (the first peak max), (c) copolymer heated to 500⁰, (d) CRF of the copolymer heated to 500⁰. Fig. 10 (b) shows only the bands of the undegraded 53.19 % copolymer except for a new absorption around 3000 cm^{-1} associated with conjugation. Fig. 10 (c) reveals new absorptions that arise from conjugation. CRF of the copolymer degraded to 500⁰ (Fig. 10 (d)) shows residual V-OAC units in the copolymer. Acetic acid,

Table 1. Acetic acid and water evolution per 50 mg sample degraded in vaccum under isothermal conditions.

Degradation temp.($^{\circ}$C)	Degradation time (Min)	53.19% Saponified copolymer			
		CH_3COOH (moles x 10^{-5})	H_2O (moles x 10^{-5})	Copolymer (Molar ratio)	CH_3COOH,H_2O (Molar ratio)
	50	2.9	11.44	1.14	0.253
225	200	8.9	24.33	"	0.365
	300	11.1	33.55	"	0.330
	60	17.60	21.88	1.14	0.804
273	120	27.4	33.11	"	0.827
	200	31.3	42.33	"	0.739
	60	33.2	41.11	1.14	0.807
	100	36.5	45.00	"	0.811
301	200	37.3	42.77	"	0.872
	300	37.4	42.00	"	0.890

ketone, CO_2 and water were identified as degradation products from copolymer degraded upto 370° (Fig. 11 (a)). Unsaturated hydrocarbons and water are the degradation products from the copolymer degraded to the second peak (Fig. 11 (b)).

There is no positive indication, either in the residue or products of the formation of intermediate cyclic ether structure although thorough investigation would be necessary to eliminate the possibility completely.

Proposed Reaction Mechanism. From the shift in values of the initiation of breakdown towards lower temperatures and the similar shift in values of Tmax with increasing acetate content it would appear that the acetate units are the weak links in the V-OAC/V-OH copolymer chain.

The fact that ketene is produced from the V-OAC/ V-OH copolymer degradation seems to agree with Grassie's hypothesis [12] that ketene is a result of the pyrolysis of acetic acid which also leads to the production of methane and carbon dioxide as indicated by our results.

Scotney [13] has observed decomposition of acetic acid to ketene at 380°. He also observed the production of ketene resulting from the vacuum degradation of cellulose acetate at 322°. There is no evidence to suggest that the decomposition of acetic acid proceeds by either a free radical or molecular mechanism.

The residual copolymer after degradation is highly coloured, the colour being attributed to conjugated structures which may be described as polyacetylene.

TVA investigations have shown that acetic acid and water are produced in two separate steps during degradation, suggesting that the units in the copolymer decompose quite separately.

The following reaction mechanism is suggested to account for the major degradation products evolved from the copolymer.
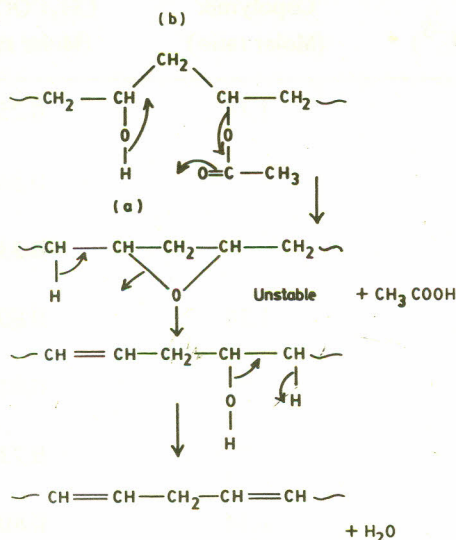
Since in the copolymer chain hydrogen (a) is more acidic than hydrogen (b), interaction between acetate and hydroxyl groups seems possible and the following degradation mechanism may also be possible.

Acetic acid elimination in the first step of the degradation mechanism leads to the formation of a four member ring which is not detected during the examination of degradation products and the cold ring fractions of the copolymers. This would appear to rule out the possibility of any interaction between acetate and hydroxyl groups in the copolymer chain in such a way as to initiate degradation but the four membered cyclic ether ring would be fairly unstable and presumably difficult to detect.

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