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APPLICATION OF EVOLVED GAS ANALYSIS TO THE STUDY OF POLY(VINYL BUTYRAL) THERMAL STABILITY

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ABSTRACT

The study of polymer stability can often be aided by the determination of the chemical mechanisms involved in a specific mode of degradation. The technique of evolved gas analysis (EGA) has been combined with kinetic FTIR to identify the reaction products of the thermal and oxidative degradation of poly(vinyl butyral). The data suggests a mechanism involving dehydration of vinyl alcohol functionalities followed by oxidative attack.

INTRODUCTION

The study of polymer stability can often be aided by the determination of the chemical mechanisms involved in a specific mode of degradation. One approach to this determination is the identification of the products of the degradation reaction. In this paper we show how the technique of evolved gas analysis (EGA) was combined with kinetic FTIR to identify the reaction products of the thermal and oxidative degradation of poly(vinyl butyral).

In common with most other vinyl and diene polymers containing reactive functional groups (e.g., polyvinyl chloride and unsaturated rubbers), thermal and oxidative exposure of poly(vinyl butyral) can result in degradation through chemical modification, chain scission, and cross-linking. In degradation processes of this kind, two types of reaction products are generated. One is the degraded polymer itself which may be studied by standard analytical techniques such as FTIR. The second are volatile species which are given off by the polymer as it reacts. EGA is a technique for collecting, separating, and identifying these volatile species.

EXPERIMENTAL AND RESULTS

Polyvinyl butyral (PVB) is a copolymer prepared by the acetalization of polyvinyl alcohol (PVOH) with butyraldehyde. The chemical structure of PVB is shown in Fig. 1. PVOH is, in turn, prepared by hydrolysis of

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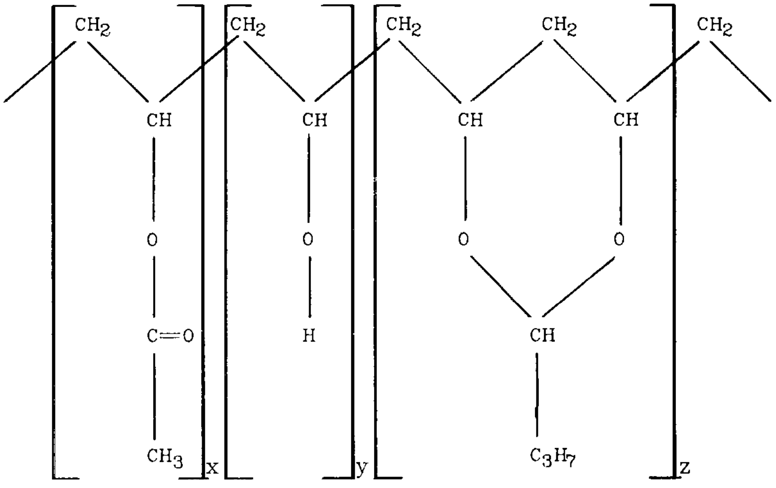

Fig. 1. Chemical structure of poly(vinyl butyral).

polyvinyl acetate. The polyvinyl acetate is typically dissolved in an alcohol and hydrolyzed in the presence of a basic or acidic catalyst. The PVOH is then reacted with butyraldehyde in an acidic medium to effect the acetalization. Following neutralization the PVB is washed and dried [1].

The extent of acetalization can be controlled by the butyraldehyde concentration, since this is an equilibrium reaction. In any case, not all of the hydroxyl groups are able to participate in the reaction. This is because the 1,3-glycol structure along the PVOH chain reacts randomly with the butyraldehyde, and therefore single hydroxyl groups located in between two established acetals will not be able to participate in the formation of a cyclic butyral ring [2]. The level of unreacted hydroxyl in commercial PVB can range from 9–25%. Residual polyvinyl acetate is also present, at a level of less than 2%.

PVB can be prepared over a wide range of molecular weights, and typically has a weight average molecular weight, M_W, between 10000 and 1000000 g mol^{-1}. The polymer is thought to be entirely amorphous, and has a glass transition temperature, T_g, between 60 and 80 °C (as measured by DSC). T_g increases with an increasing level of unreacted hydroxyl [1].

It was known from previous work [3] that PVB could be made to undergo oxidative chain scission is an oxygen containing atmosphere at 200 °C. It was also known from the same work that PVBs of differing stabilities could be prepared and that the relative stability of the polymers could be determined by measuring the reaction induction times and reaction half-times with a DSC used in an isothermal mode. In the present study, this DSC method was extended via a simultaneous thermogravimetry/mass spectrometry (TG/MS) system to provide for the collection of the volatile reaction products, their separation, and their identification.

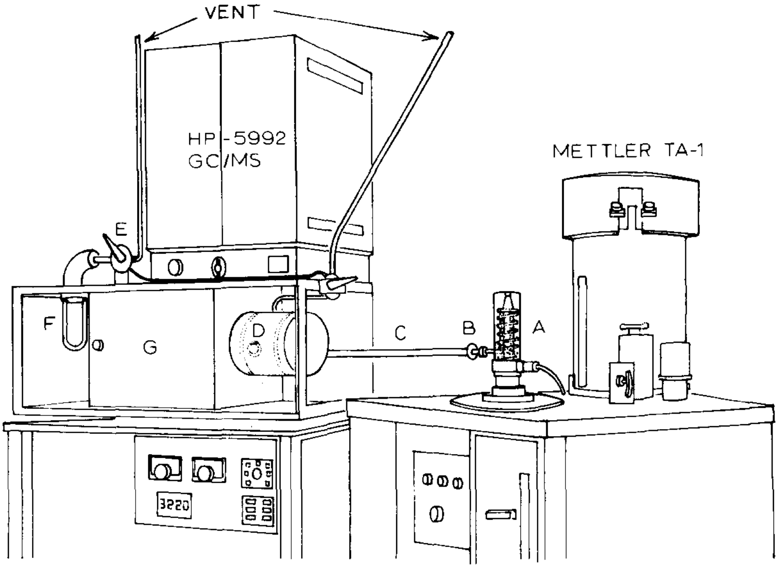

Fig. 2. A schematic drawing of the tandem instrument consisting of a Mettler TA-1 thermoanalyzer and a HP-5992 mass spectrometer: A. quartz furnace; B. 3/8–1/4 in stainless steel swagelock union; C. volatile transfer tube; D. Varian leak valve; E. Valco valve; F. liquid N_2 trap; G. GC oven.

The instrument used has been described in detail in previous publications [4,5]. In brief, it consists of a Mettler Thermoanalyzer, model TA-1 in tandem with a Hewlett-Packard 5992 GC/MS (Fig. 2). The sample (~ 400 mg) was loaded into the thermoanalyzer in a 16 mm alumina crucible and was quickly heated at 25°C min^{-1} under a helium atmosphere to 200°C, where it was held isothermally and the helium was replaced with an oxygen : helium (20 : 80) mixture. The experiment was continued until the derivative thermogravimetric (DTG) peak due to oxidative degradation was completed. The volatiles evolved from the sample were monitored in real time by the HP mass spectrometer after passing through a Varian 951-5100 leak valve. Only a minute portion of the volatiles was permitted to enter the mass spectrometer in real time. The majority was diverted to a liquid nitrogen trap where it was preserved for subsequent GC/MS analysis to provide the separation needed for interpretation of the real time mass spectral data.

Three samples of poly(vinyl butyral) were synthesized and tested by the above evolved gas analysis method. The samples were of equivalent molecular weight and residual PVOH content, and were chosen to represent resin of low (A), moderate (B), and high (C) stability towards oxidative degradation as measured by DSC reaction half-time in oxygen.

Figures 3–5 illustrate the TG/DTG curves obtained from samples A, B, and C, respectively. In each, three episodes of strong evolution of volatile

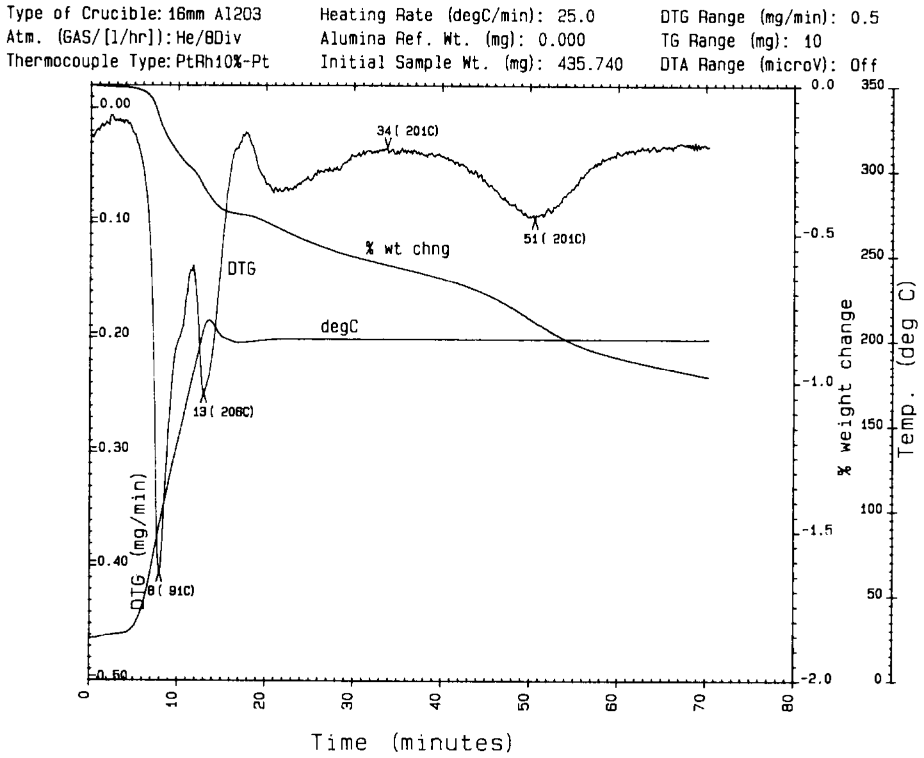

Fig. 3. TG and DTG thermograms of poly(vinyl butyral), sample A.

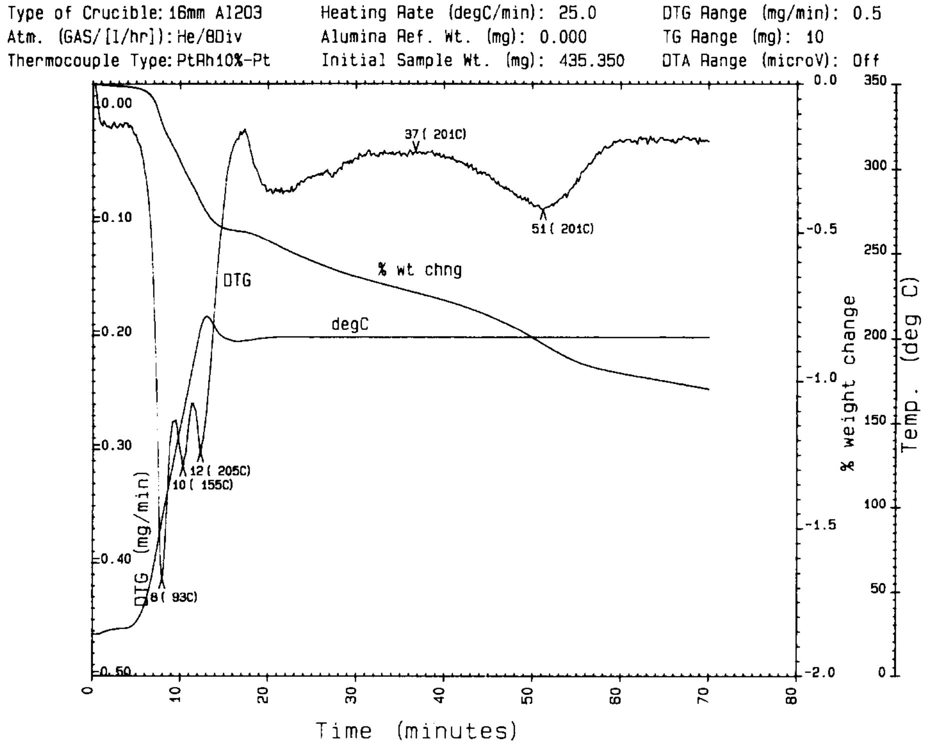

Fig. 4. TG and DTG thermograms of poly(vinyl butyral), sample B.

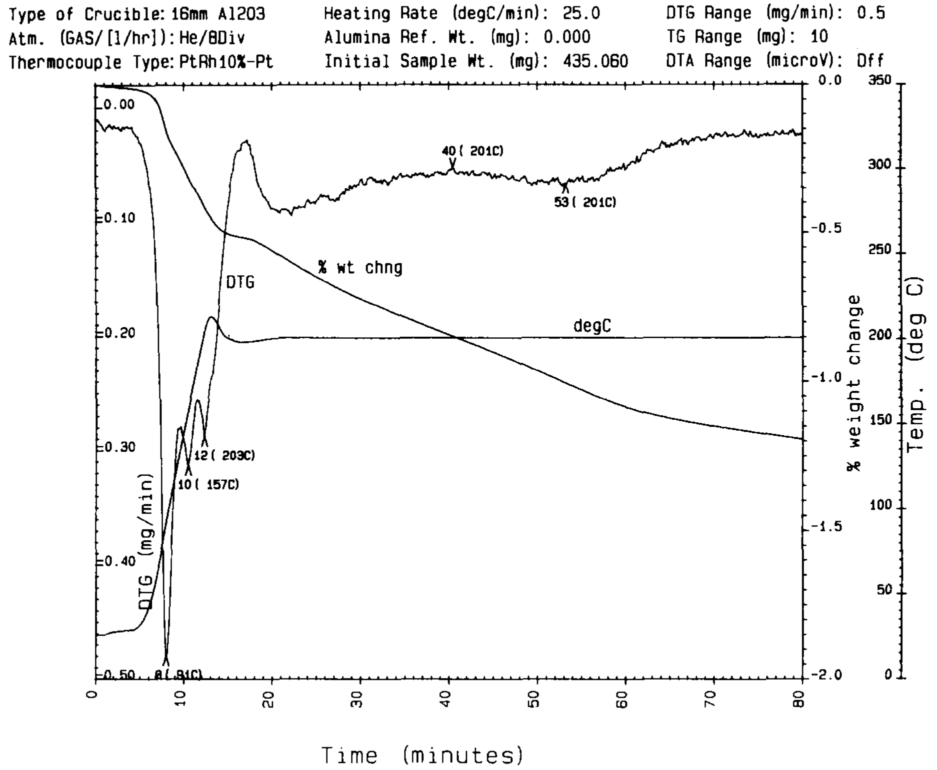

Fig. 5. TG and DTG thermograms of poly(vinyl butyral), sample C.

products were observed: (1) an initial evolution of free volatiles from 91 to 180°C; (2) a second evolution or an initial degradation upon introduction of 20% oxygen at 200°C; and (3) an evolution associated with chain scission and degradation around 38 min into the oxidative portion of the run. Each weight loss had a characteristic group of volatiles associated with it.

The major volatile species generated during the analysis were identified as water, butenal (crotonaldehyde), butanal (butyraldehyde), butanoic acid, acetone, 2-ethyl hexenal.

Figures 6–7, 8–9, and 10–11 show the evolution profiles of these volatiles from each of the three samples, respectively.

The degradation peak, in particular, is associated with the evolution of water, butyraldehyde, butanoic acid, crotonaldehyde, and acetone, indicating that these are the primary volatile products of chain scission. The butyraldehyde and crotonaldehyde would be expected to be produced simultaneously upon degradation of a vinyl butyral ring, whereas the butanoic acid would result from an alternative detachment of the butyral ring or from the oxidation of the butyraldehyde. The water arises in part from the dehydration of the polyvinyl alcohol.

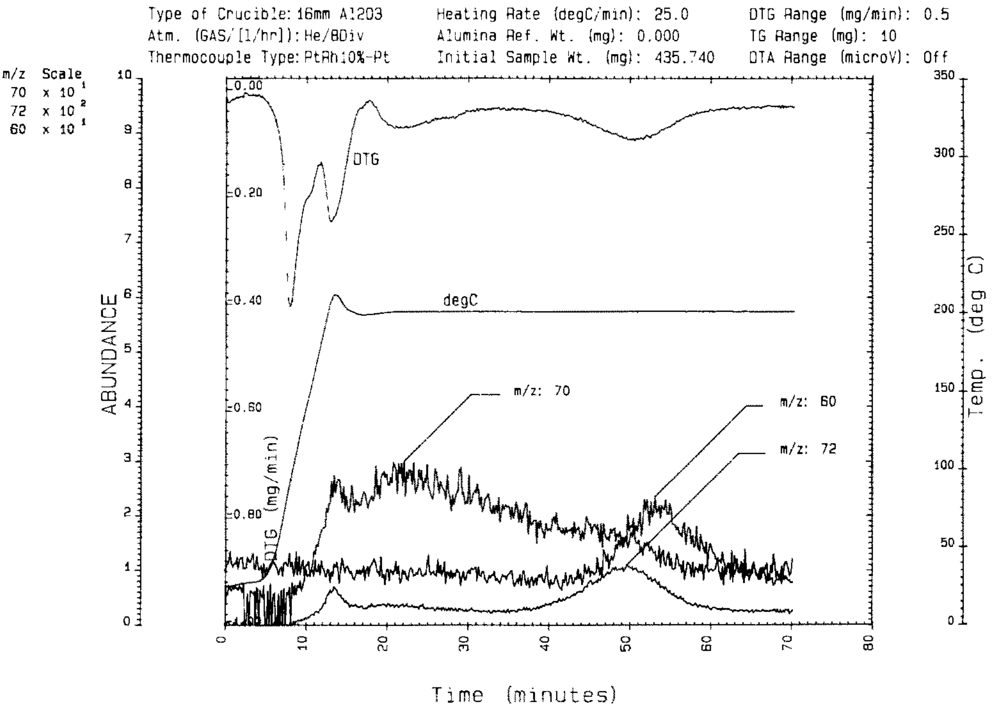

Fig. 6. DTG thermogram and MS profiles of poly(vinyl butyral) sample A showing evolution of butenal ($m/z = 70$), butanal ($m/z = 72$), and butanoic acid ($m/z = 60$).

The DTG data for the three samples analyzed agreed with the independently collected DSC data in ranking the inherent stability of the samples towards oxidative degradation, as explained in a previous paper [3]. The types of volatiles evolved by all three samples were the same, except that acetone was not evolved from the least stable sample. On the other hand, stability correlated directly with the evolution of butanoic acid by the degrading resin with the least stable resin evolving the most butanoic acid.

As measured from the GC/MS analysis, the level of butanoic acid per unit of butyraldehyde from samples A and B was found to be in the ratio 21 : 2. The butanoic acid evolved from sample C was much less than that evolved from sample B and the peak area could not be determined accurately by integration.

The evolution of acetone is particularly interesting. It has already been noted that it is not evolved by the least stable resin. When it is evolved, the acetone is given off primarily during the degradation, indicating that it is a product of the oxidative reactions in some form. In particular, acetone is given off strongly upon the first introduction of oxygen, then again strongly during the degradation peak. Acetone can be generated by the detachment of aldehydic end groups from the chain and its evolution is evidence for

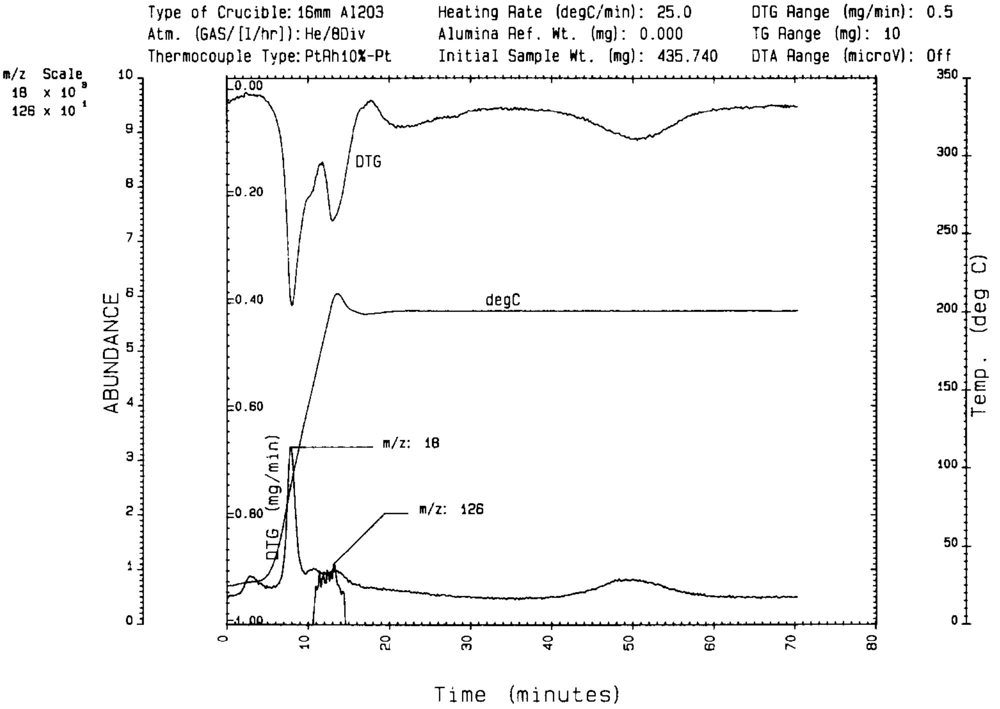

Fig. 7. DTG thermogram and MS profiles of poly(vinyl butyral) sample A showing evolution of water (*m*/*z* = 18) and 2-ethyl hexenal (*m*/*z* = 126).

some level of unzipping of the polymer chain. The correlation of acetone generation with resin stability may indicate that in unstable PVB the degradation reaction is dominated by chain scission while in the more stable resins it is dominated by loss of low molecular weight species from the chain ends. Loss of chain end groups will, in general, result in less measured viscosity loss than scission near the end of the chain [6].

In an independent experiment, kinetic FTIR measurements were taken on a sample of PVB as it degraded in the presence of oxygen at elevated temperature. This experiment identified loss of OH, severe loss of the butyral ring, an increase in carbon–carbon unsaturation, and the formation of keto–enol structures as the key changes in the nonvolatile portion of the resin during degradation. A typical set of FTIR curves is shown in Fig. 12.

The FTIR data agrees with the EGA data in that the evolution of C_4-aldehydes results from the loss of butyral rings, the loss of OH by dehydration of the polyol results in the evolution of water, and the keto–enol structures are conjugated aldehydic end groups which result from mid-chain scission and correspond to the evolution of acetone from chain-end unzipping.

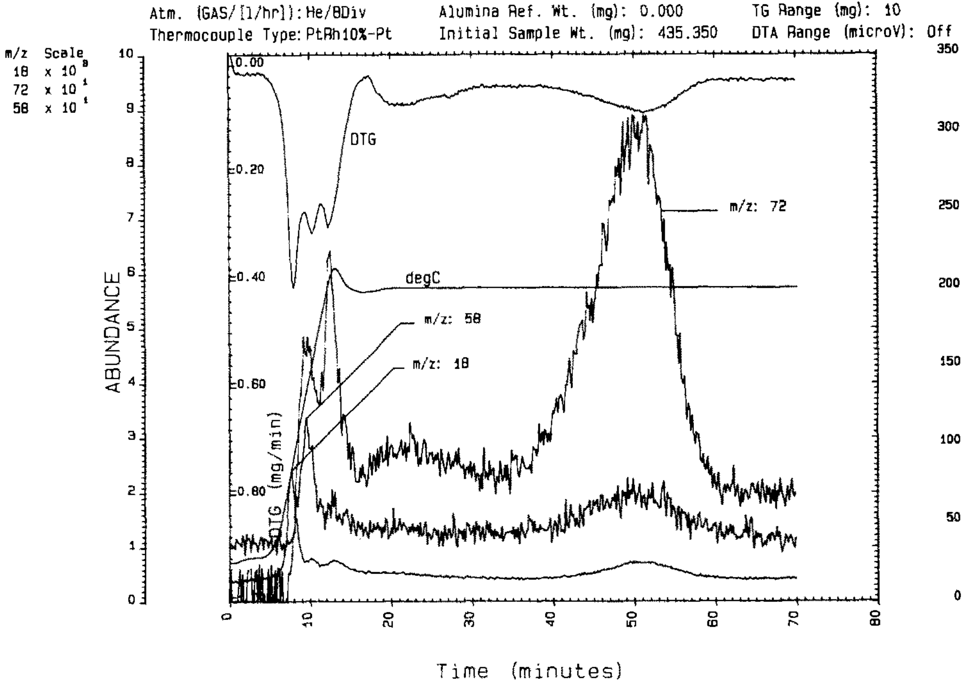

Fig. 8. DTG and MS profiles of poly(vinyl butyral) sample B showing evolution of water ($m/z = 18$), butanal ($m/z = 72$), and acetone ($m/z = 58$).

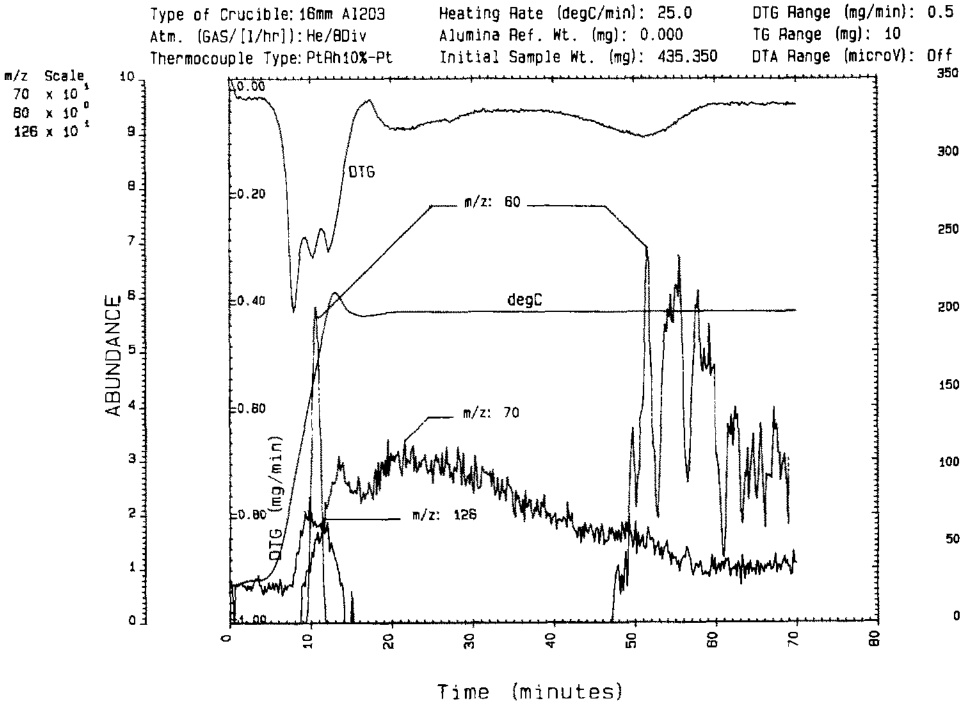

Fig. 9. DTG and MS profiles of poly(vinyl butyral) sample B showing evolution of butenal ($m/z = 70$), butanoic acid ($m/z = 60$), and 2-ethyl hexenal ($m/z = 126$).

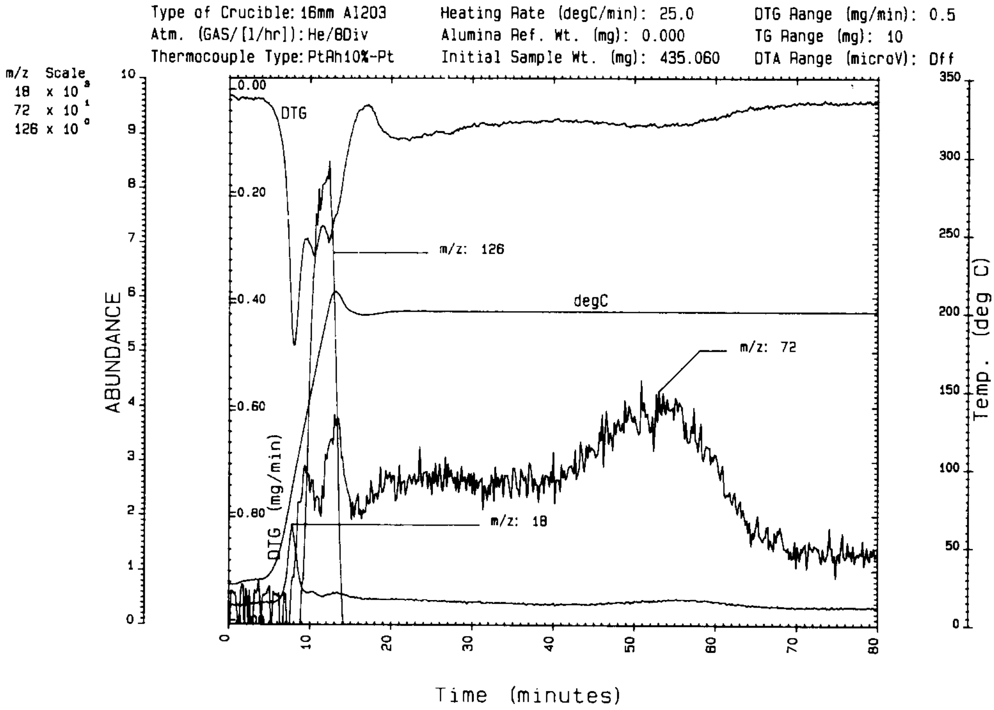

Fig. 10. DTG and MS profiles of poly(vinyl butyral) sample C showing evolution of water ($m/z = 18$), butanal ($m/z = 72$), and 2-ethyl hexenal ($m/z = 126$).

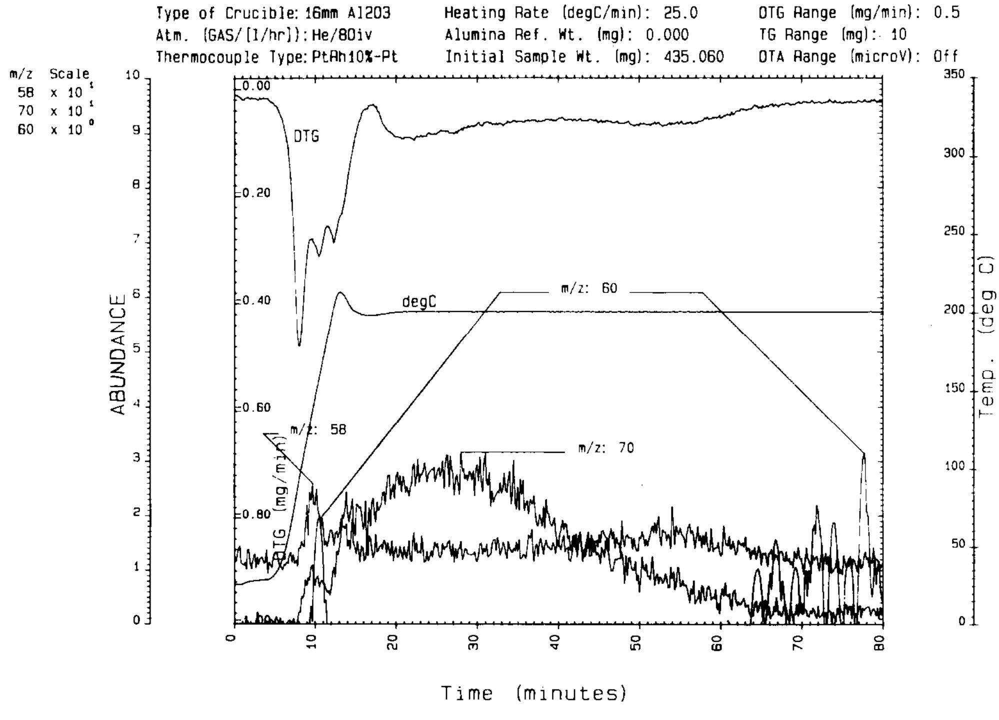

Fig. 11. DTG and MS profiles of poly(vinyl butyral) sample C showing evolution of acetone ($m/z = 58$), butenal ($m/z = 70$), and butanoic acid ($m/z = 60$).

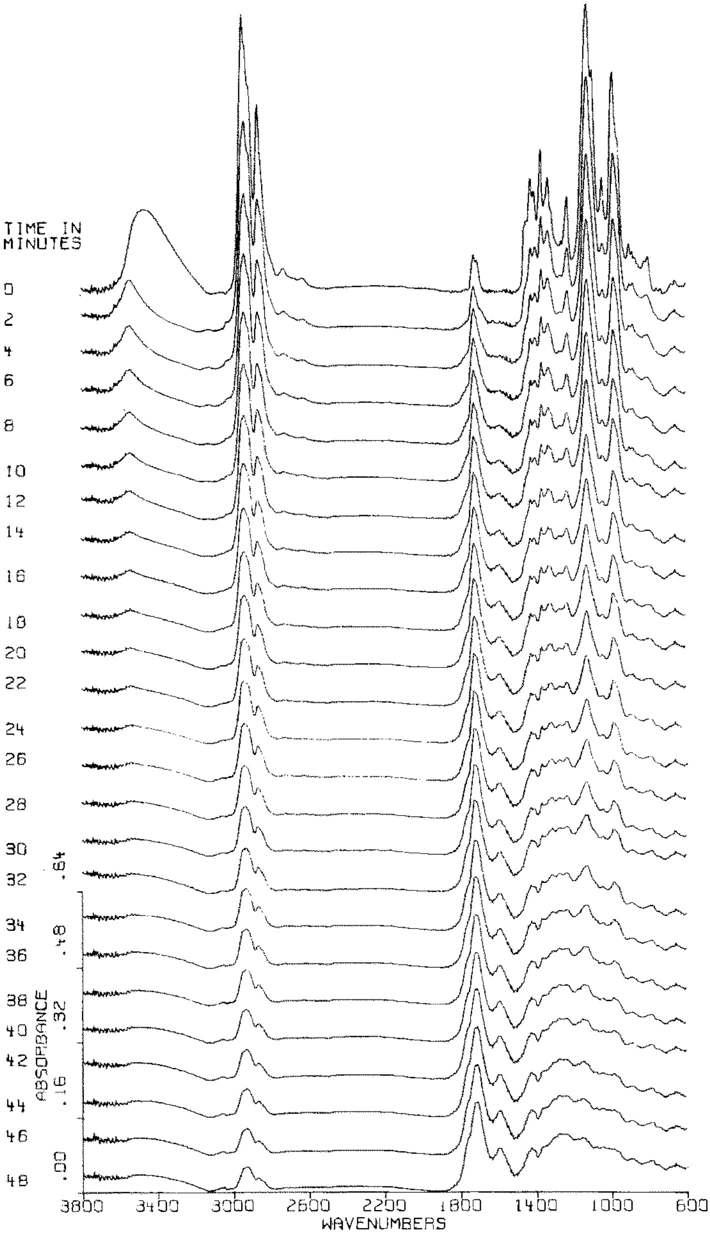

Fig. 12. A typical set of FTIR curves on poly(vinyl butyral).

DISCUSSION

The experiments and results described above demonstrate the usefulness of thermal analytical methods for characterizing the oxidative degradation of PVB. A study of the underlying chemistry is in progress, and some preliminary remarks will now be given.

We believe that the oxygen is attacking weak links in the chain brought about by the dehydration of the vinyl alcohol. The PVOH used in these studies was prepared by acid hydrolysis of polyvinyl acetate. Residual acid groups may well be present in the PVB that catalyze the removal of hydroxyl groups and adjacent hydrogen to form water. This would leave a carbon–carbon double bond in the chain. From the study of the oxidation of rubbers it is well known that oxygen can attack the tertiary carbon adjacent to the double bond and cleave the chain [6]. This mechanism is consistent with all of the data given above.

Loss of the butyral ring, as evidenced by the generation of the C_4-aldehydes and the FTIR data would also result in unsaturation in the backbone. This loss may be helped by oxygen attack on the carbon attached to one of the di-ether oxygens in the ring. The formation of the aldehydes clearly indicates that degradation of the ring is the result of elimination of at least one of the acetal oxygens and the presence of butanoic acid indicates that in at least some cases, both oxygens may be lost.

As mentioned above, evolution of acetone is evidence for unzipping of the chain, and its prevalence in the more stable resins may indicate the absence of other sites for oxygen attack away from the chain ends.

CONCLUSIONS

The use of a combination of EGA and FTIR can be a valuable technique for the identification of mechanisms of degradation. Either technique in isolation can identify the volatile or nonvolatile reaction products, but together they can identify the source of the volatiles in the polymer structure and point towards the chemistry involved in the degradation.

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