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The thermal degradation of poly(ethylene glycol)/poly(vinyl alcohol) binder in alumina ceramics

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Abstract

The thermal degradation in air of poly(ethylene) glycol, poly(vinyl alcohol), and a combination of the two polymers in alumina-containing additives has been studied by gas chromatography/mass spectrometry, thermal analysis, and CP-MAS ^{13}C NMR. Both polymers in alumina degraded as previously described for the pure polymers. For the polymer mixture, both polymers degraded independently of each other. Thermal analysis of the various samples showed that the additive, sodium lignosulfonate, required the highest temperature for burnout. Product analysis of the pure and combined polymers along with the respective decomposition mechanisms are summarized.

Keywords: Alumina; Binder; Ceramics; Poly(ethylene glycol); Poly(vinyl alcohol); Thermal degradation

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1. Introduction

A common organic polymeric binder used with aluminum oxide is a mixture of poly(ethylene glycol) (PEG) and poly(vinyl alcohol) (PVA). These polymers serve to hold the raw materials together while the powder is compacted and eventually fired. A twenty-four hour temperature program with a final temperature of approximately 1200°C is commonly used to burn away the binder system. Although the thermal degradation of the two pure polymers has been studied, the effect of the aluminum oxide, the processing additives and the mixing of the polymers on the overall degradation scheme has not been investigated.

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Madorsky and Straus [1] reported in 1959 that the thermal degradation products from PEG were aldehydes, ketones, and ethers and proposed two types of molecular fragmentations to explain the product formations. The first cleavage (Type I) involved homolytic cleavage of the C–O and C–C bonds with an intramolecular transfer of hydrogen. The second proposed cleavage (Type II) did not involve intramolecular transfer of hydrogen, but homolytic cleavage of the polymer backbone to produce radicals. These radicals were then postulated to unzip to form smaller molecules and/or monomer products. The Madorsky–Straus mechanism did not present an adequate discussion of the termination reactions associated with the decomposition.

The thermal decomposition products from poly(vinyl alcohol) have been studied by Tsuchiya and Sumi [2]. The major products of degradation from the initial reaction (up to 240°C) were water, aldehydes, and ketones. The products were explained by the dehydration of the polymer backbone to produce a polyene and then subsequent cleavage of the C–C bonds of the remaining alcohol carbons to form unsaturated aldehydes and ketones. The pyrolysis products from the degradation above 240°C were alkanes, alkenes, and aromatic or unsaturated hydrocarbons [3]. These products resulted from the degradation of the polyene residue and were very similar to those reported for poly(vinyl chloride) (PVC) [4], and poly(vinyl acetate) (PVAc) [5] which also form polyenes on thermal degradation. The product similarity is a strong indication that the degradation mechanism for the residue from the three polymers is very similar.

Research on the thermal degradation of PEG and PVA polymers used in dry-press alumina ceramics has been carried out by Voorhees and coworkers [6,7]. Pure poly(ethylene glycol) and poly(vinyl alcohol) were pyrolyzed in a tube furnace at the temperature of maximum degradation (T_m from thermogravimetric (TG) analysis) with either nitrogen or air as the carrier gas. The volatile and semi-volatile products were analyzed by gas chromatography/mass spectrometry (GC/MS), with both chemical and electron ionizations. Gas chromatography/Fourier transform/infrared spectroscopy (GC/FT/IR) was also used to obtain functional group information to provide further evidence to support proposed product identifications.

Five oligomeric series (the term oligomer will be used to identify low molecular weight compounds that contain repeating units) of compounds (Table 1) for the PEG

Table 1
Characteristic end group masses of the oligomeric series from the thermal degradation of PEG

Label given[a]	Compound name	Molecular weight
A6	CH_3-$O(CH_2$-CH_2-$O)_5$-CH_2-CH_2-OH	296
B6	O=CH-$CH_2(O$-CH_2-$CH_2)_5$-O-CH_2-CH_3	308
C6	CH_3-$O(CH_2$-CH_2-$O)_5$-CH_2-CH_3	280
D6	CH_3-CH_2-$O(CH_2$-CH_2-$O)_5$-CH_2-CH_2-OH	310
E6	CH_3-CH_2-$O(CH_2$-CH_2-$O)_5$-CH_2-CH_3	294

[a] Refers to the different series and the oligomer number.

degradation were identified by GC/MS in conjunction with GC/FT/IR. The primary degradation reactions proposed to support the identified products, involved homolytic cleavage at either the C–O or C–C bonds with disproportionation, hydrogen abstraction, or other reactions involving oxygen. Pyrolysis in a nitrogen atmosphere favored disproportionation and intramolecular reactions, enhancing the product distribution of the oligomeric series of identified compounds. Pyrolysis in oxygen favored oxidation over inter- and intramolecular reactions, thus reducing the amount of detectable degradation products.

This group also investigated the pyrolysis of poly(vinyl alcohol) in air and nitrogen in the temperature range 400–550°C using the same experimental poly(ethylene glycol) protocol [7]. Product identification was done by gas chromatography/mass spectrometry (GC/MS) with electron ionization (EI). Water and acetic acid were the main pyrolysis products. The elemental composition of the residue from a nitrogen atmosphere degradation had an empirical formula of C_6H_6. This suggested that the residue was highly crosslinked and unsaturated.

In the following sections, we discuss the thermal degradation of PEG/PVA binder with processing additives in an alumina body. As previously discussed, the literature has presented data on the decomposition of these polymers individually without the effect of the aluminum oxide. A major part of this investigation will focus on the effect of the aluminum oxide and the presence of both PEG and PVA plus process additives on the degradation mechanisms. Information will be discussed concerning the residues remaining in the ceramic at the late stages of burnout and their effect on processing. The term ‘burnout’ is used by ceramicists to indicate thermal removal of the binder or additives.

2. Experimental

2.1. Description of samples

The polymer binders investigated in this study were PEG 20M (average molecular weight 20000 Daltons) and PVA (average molecular weight 10000 Daltons). The PEG 20M was a double epoxide cross-linked polymer made up of two or three PEG 8M units. The 20000 average molecular weight is based upon the average of the epoxide-linked macromolecules. The PVA used in this study was manufactured by the hydrolysis (99% reported yield) of poly(vinyl acetate). The PEG and PVA samples were obtained from Union Carbide.

Alumina for pressing was prepared by mixing aluminum oxide (Alcoa) with several different additives to aid in processing the powder. These additives were kaolin, talc, sodium lignosulfonate, oleic acid, Triton X-100, callozine green, and methylene blue.

2.2. Sample preparation

Alumina powder containing deflocculent and dyes was ball-milled to ensure uniform mixing and particle size. After the mixture had been milled for 12 h, the aqueous suspension was drained from the ball mill and placed into a stirred 40 gallon container to keep the particles in suspension. The slip (40% solids in water), or mixture, was then divided into 4 batches for the addition of the polymer binders. The first batch was spray-dried directly without addition of binder. In the second batch, 2% poly(vinyl alcohol) (binder weight to the total weight) was combined with the slip and the resulting mixture spray-dried and screened to ~42 mesh. To the third batch, 6% poly(ethylene glycol) was added, and the batch spray-dried and screened. The fourth batch contained 0.5% poly(vinyl alcohol) and 6% poly(ethylene glycol) and was also spray-dried and screened.

Samples were further processed from the spray-dried powders by pressing into bars at 15 Kpsi. The bars of an approximate mass of 10 g were stored in a desiccator to minimize water adsorption before analysis.

2.3. *Thermogravimetric analysis*

All samples were analyzed on a Seiko SSC/5200 TG/DTA 320 thermal analysis system. An air atmosphere with a flow of 300 ml min^{-1} and a heating rate of 20°C min^{-1} were used for all analyses.

2.4. *Pyrolysis*

The decomposition products from the pressed binder–alumina samples were generated in a tube furnace. The furnace temperature was controlled to ±5°C. A diagram of the furnace is shown in Fig. 1.

A 450°C pyrolysis temperature was chosen, TG/DTA results having shown this to be above the temperatures of maximum degradation for both poly(ethylene glycol) and poly(vinyl alcohol). Air was used as the combustion atmosphere and carrier gas. The pyrolysis products were transferred from the furnace through a heated transfer line

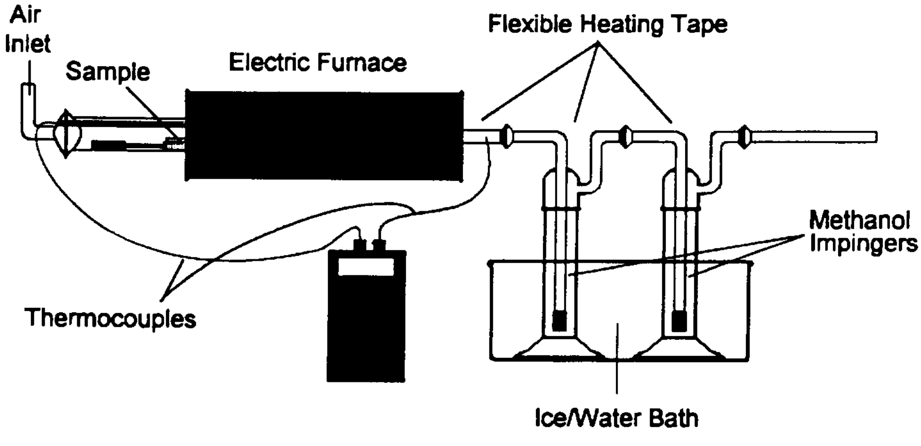


Fig. 1. Diagram of furnace.

maintained at 200°C and trapped in impingers filled with methanol cooled in an ice–water bath.

After cooling the furnace and transfer lines, methanol was used to completely rinse the system. These rinses were combined with the impinger methanol followed by evaporation to concentrate the analytes. After concentrating, the pyrolysis products were analyzed by gas chromatography/mass spectrometry (GC/MS).

Analysis of the C_1 to C_6 volatile products was done by cryotrapping the pyrolysis products in a stainless steel U-tube packed with Tenax GC® cooled in a dry ice–methanol bath. The cryotrap and GC valving interface (Fig. 2) has been previously described [8].

Product analyses over both volatility ranges were conducted with a Varian 3400 gas chromatograph interfaced to an Extrel series 400 triple quadrupole mass spectrometer. The mass spectrometer was utilized in both chemical and electron ionization (EI) modes. The GC conditions included:

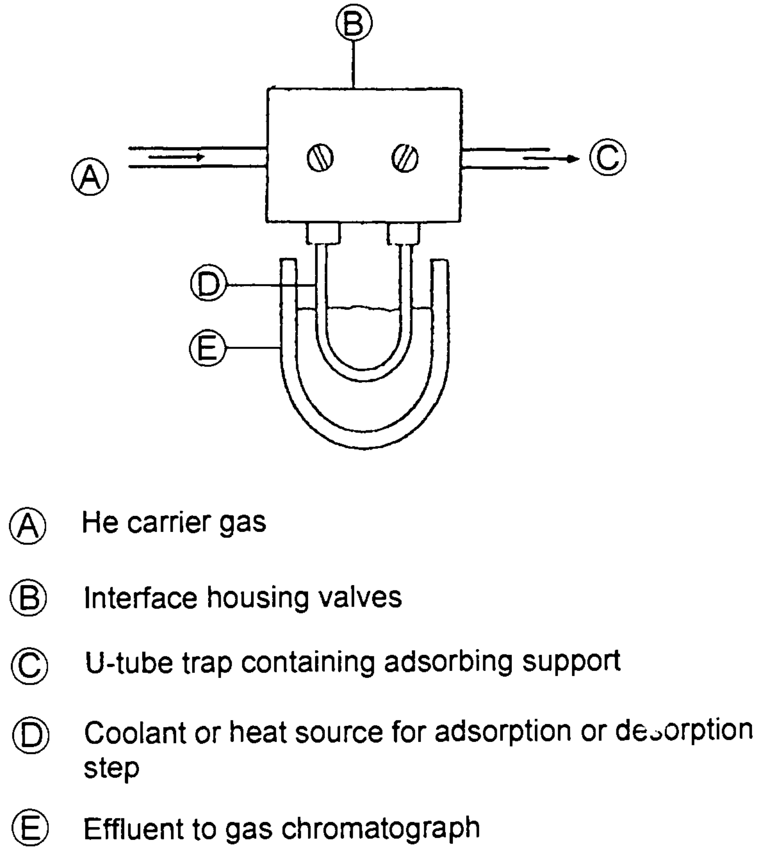


Fig. 2. Cryogenic trapping device.

C_1 to C_6 volatile product analysis: injector, 250°C; column, 1% SP2100 on Carbopak C; flow, 40 ml min^{-1}; temperature program, 30°C for 2 min, 10°C min^{-1} to 230°C, 20 min hold.

C_6 and higher volatile product analysis: injector, 250°C; split, 10:1, 1:30 delay; column, DB5, 0.32 mm i.d. × 30 m; 0.25 μm film thickness; flow, 40 cm s^{-1}; temperature program, 35°C for 2 min, 6°C min^{-1} to 280°C, 5 min hold.

Mass spectrometer conditions: interface, 280°C; ionizer 220°C; electron ionization, 70 eV; filament delay, 3:50 min; start mass, 29; end mass, 501; scan rate, 475 amu s^{-1}; run time, 48 min; CI reagent gases, methane or isobutane.

3. Results and discussion

3.1. Thermal analysis

The thermogravimetric (TG)/differential thermal analysis (DTA) of 6% poly(ethylene glycol) with additives in alumina is shown in Fig. 3. The DTA showed a small endotherm at 90°C possibly associated with the melting point of the polymer. There

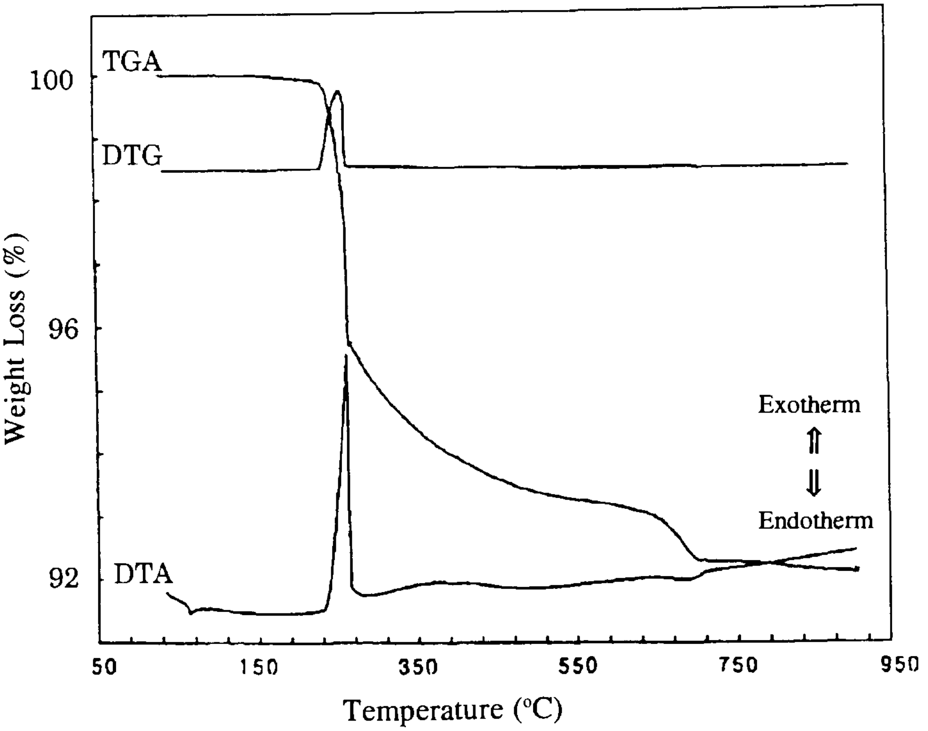


Fig. 3. Thermogravimetric analysis of 6% PEG/additives–alumina in air with a heating rate of 20°C min^{-1}.

was a rapid weight loss beginning at 238°C which marked the initiation of the thermal degradation of the poly(ethylene glycol). The temperature of maximum degradation was at 253°C. There was also a large exotherm in the DTA associated with this weight loss.

After the initial 4% weight loss (TG% scale) and accompanying thermal events, a gradual 3.8% total weight loss occurred from 267 to 654°C. There was a small endotherm associated with this weight loss. By comparing the TG curves of the additives, this weight loss and endotherm were shown to be primarily related to the degradation of the sodium lignosulfonate. The TG/DTA results for the alumina binder additives are summarized in Table 2. The total weight loss for this sample was 7.9%

The TG/DTA analysis of 2% PVA–alumina is represented in Fig. 4. These data illustrated that the initiation of the thermal degradation of the polymer began at approximately 120°C with the maximum degradation at 290°C. Associated with the maximum weight loss (up to 340°C) was an exotherm indicating the oxidation of the polymer. Following the initial weight loss, a second, more gradual weight loss probably associated with the polyene degradation occurred at 400°C with a corresponding exotherm. The initial weight loss for the PVA–alumina was not as rapid as that observed for the PEG–alumina and is clearly indicative of the difference in the thermal degradation mechanisms for the two polymers.

Thermogravimetric analysis of the 6% PEG–0.5% PVA–alumina binder system illustrated in Fig. 5, shows that thermal degradation started at 242°C. Maximum degradation of the sample was at 255°C with the majority of the binder lost at 268°C. Associated with this weight loss is a large exotherm providing evidence for the oxidation of the polymer. Between 260 and 700°C, there was a gradual weight loss. The weight loss and endotherm at 650°C is associated with the sodium lignosulfonate degradation. The total weight loss for all of the degradations was 7.9%

The thermogravimetric curve for the degradation of the PEG–PVA–alumina binder system (Fig. 5) is very similar to that observed for PEG–alumina (Fig. 3). This is due to the ratio of PEG to PVA in this system. The similarity of the TG/DTA profiles above 400°C for PEG–alumina, PVA–alumina, and PEG–PVA–alumina suggests that the final compounds remaining in the sample after degradation of polymeric binders are from the processing additives. Specifically, the kaolin, talc and sodium lignosulfonate are the final species in the system to degrade.

Table 2
Thermal analysis data in air for the processing additives

Sample	Initial temp./°C	Maximum temp./°C	Final temp./°C
Kaolin		No weight loss	
Talc		No weight loss	
Sodium lignosulfonate	80	327	951
Oleic acid	274	312	350
Triton X-100	235	348	415

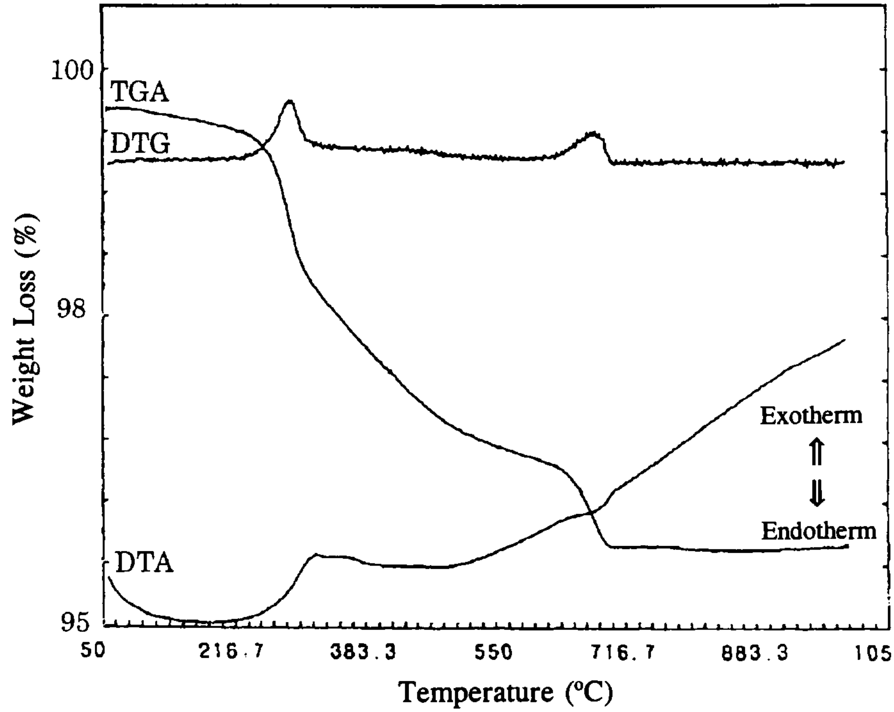


Fig. 4. TG/DTA of 2% PVA/additives-alumina in air with a heating rate of 20°C min^{-1}.

3.2. *Volatile product analysis (C_1–C_6)*

The total ion chromatograms (TIC) of the cryotrapped degradation products from the 6% PEG–alumina, 2% PVA–alumina, and 6% PEG–0.5% PVA–alumina all degraded at 450°C in air are shown in Figs. 6–8, respectively. The product identifications for these chromatograms are summarized in Tables 3–5. The methylene chloride listed in Table 4 was a laboratory artifact.

The major identified degradation products for the PEG–PVA–alumina binder system are very similar to those observed for the degradation of the PEG–alumina system. There are also peaks which correlate to compounds present in the volatile analysis of PVA–alumina. These compounds are 2-propenal, 2-pentanone, benzene, and toluene. Overall, the degradation products of PEG–PVA–alumina appear to be a weighted combination of individual products from the two polymer systems. This would suggest that the polymers degraded independently of each other.

3.3. *Semi-volatile product analysis ($> C_6$)*

The TIC for the products from the 6% PEG–alumina decomposed at 500°C in air is shown in Fig. 9. Table 6 summarizes the observed products. Groupings containing

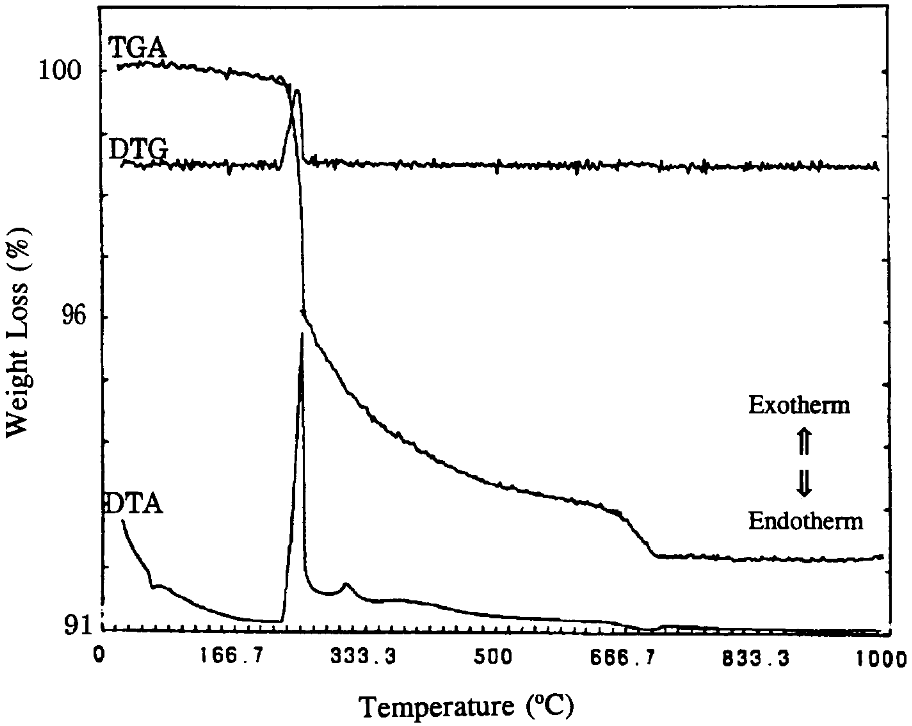


Fig. 5. TG/DTA of 6% PEG/0.5% PVA/additives–alumina in air with a heating rate of 20°C min^{-1}.

from three to seven peaks appear to repeat in a regular sequence along the chromatogram. Each peak within the group has been assigned a compound designator (A, B, C,...), and a group number (3, 4, 5,...). The percent composition (% comp.) is the area percent that each peak in the TIC contributes to the total area of all peaks in the plot. An analyte relative response factor of unity was used for all compounds. The product distribution of the oligomeric series as observed in Fig. 9 is very similar to the results previously reported by Baugh for PEG8M in air and nitrogen atmospheres [7].

Analysis of PVA–alumina pyrolyzed at 450°C in air and analyzed by GC/MS is represented by the TIC in Fig. 10. The number of peaks observed for pyrolysis of PVA–alumina was much less than those observed for PEG–alumina pyrolysis. Table 7 summarizes the products identified for the pyrolysis of PVA–alumina.

Expected products based on previous results from the thermal degradation of PVA–alumina, such as aldehydes and ketones, were identified. However, benzene, a major polyene degradation product, was not observed in this analysis even though it was identified in minor amounts in the volatile product analysis. Benzene was also not reported by Baugh [7] as a degradation product in his investigation of the neat PVA sample.

The TIC of the degradation products from the 6% PEG–0.5% PVA–alumina system pyrolyzed under air at 450°C is represented in Fig. 11 and summarized in Table 8.

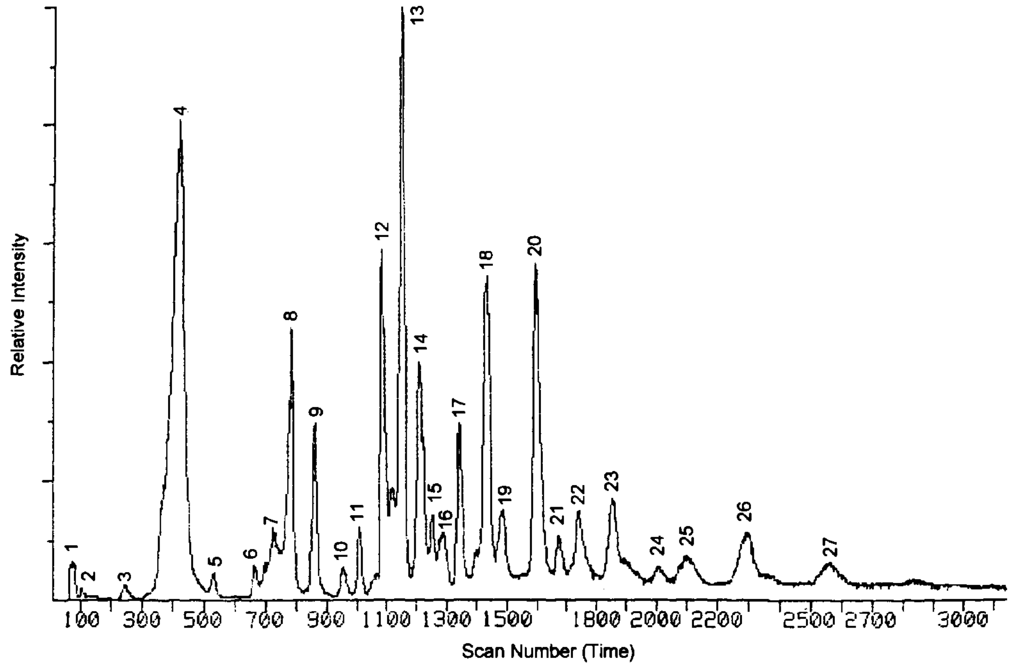


Fig. 6. The TIC of the C_1–C_6 degradation products of 6% PEG/additives–alumina.

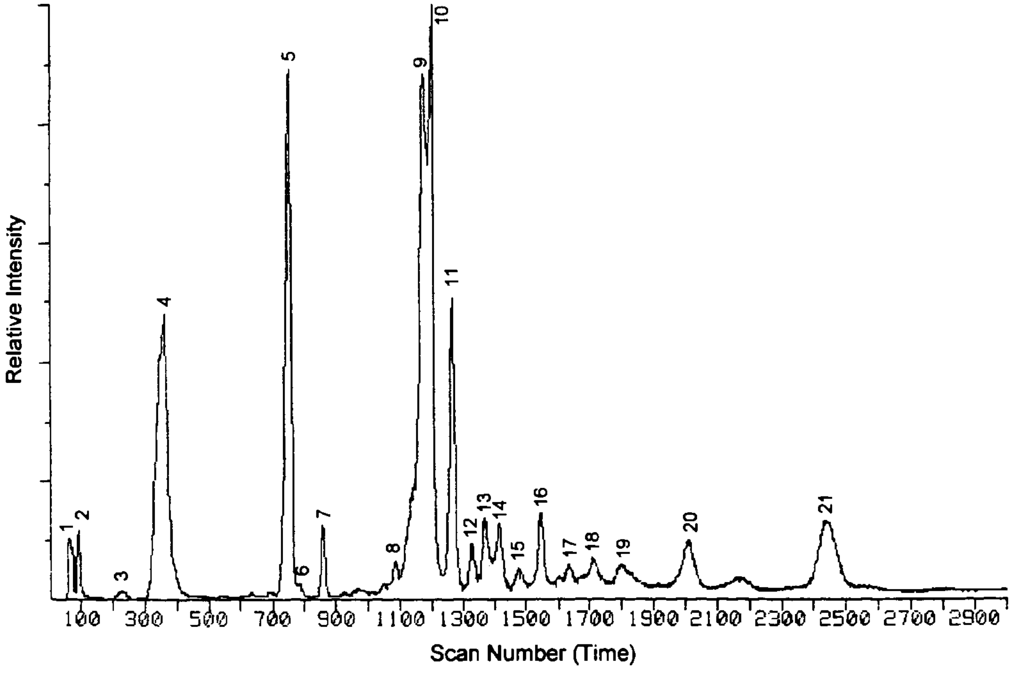


Fig. 7. The TIC of the C_1–C_6 degradation products of 2% PVA/additives–alumina.

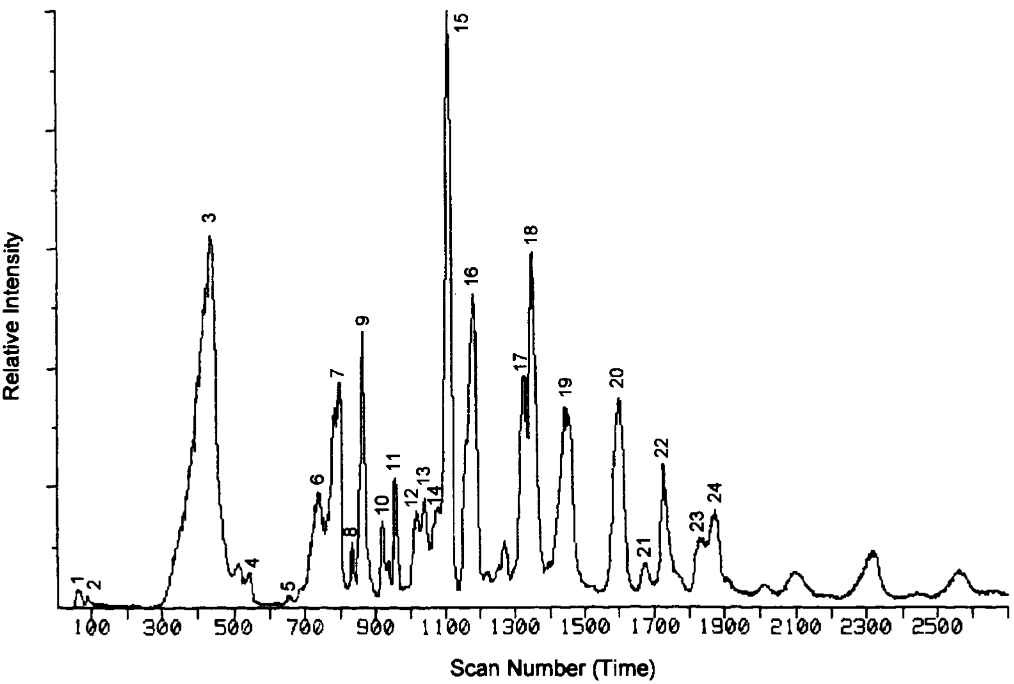


Fig. 8. The cyrotrapped degradation products from 6% PEG/0.5% PVA/additives-alumina.

Comparison of this chromatogram to the TIC in Fig. 9 shows that the products from the PEG-PVA-alumina sample has a distribution which is nearly the same as that observed for the PEG-alumina sample. Single ion plots of the base peaks of the products from PVA-alumina data showed only minor contributions to the overall product array from PVA. This is not surprising considering the 12:1 ratio for PEG to PVA in this system. Importantly, the presence of the PVA did not alter the degradation mechanism of the PEG.

3.4. Degradation mechanisms

Examination of the products produced from the thermal degradation of PEG-alumina and PVA-alumina in air suggests that the major degradation reactions are similar to those described for the pure polymers decomposed in a nitrogen atmosphere [7]. This would suggest that there is not a major effect from the alumina on the product distributions of either binder.

3.4.1. Poly(ethylene glycol)

Based on the identified compounds listed in Tables 3 and 6, the following reactions were postulated as the major pyrolysis reactions of PEG. Initiation occurs by

Table 3
Cryogenic trapped products from the thermal degradation of 6% PEG-alumina

Peak	Compound name	Formula
1	Air	
2	Carbon dioxide	CO_2
3	Methylene chloride	CH_2Cl_2
4	Ethylene oxide	C_2H_4O
5	1,2-Ethanediol monoformate	$C_3H_6O_3$
6	Ethene methoxy	C_3H_6O
7	Ethane methoxy	C_3H_8O
8	Furan	C_4H_4O
9	1,3-Dioxolane	$C_3H_6O_2$
10	Ethene, 1,1'-oxybis-	C_4H_6O
11	Ethene ethoxy	C_4H_8O
12	Ethane dioic acid (oxalic acid)	$C_2H_2O_4$
13	2-Methyl, 1,3-dioxolane	$C_4H_8O_2$
14	1,4-Dioxane	$C_4H_8O_2$
15	Ethanol 2-methoxy	$C_3H_8O_2$
16	2-Butenal	C_4H_6O
17	Unknown	
18	Unknown	
19	Unknown	
20	1,3-Dioxolane, 2-methoxy-	$C_4H_8O_3$
21	Unknown	
22	Unknown	
23	Diethylene glycol	$C_4H_{10}O_3$
24	Ethanol, 2-(2-methoxyethoxy)	$C_5H_{12}O_3$
25	Unknown	
26	Unknown	
27	Ethanol 2-(2-ethoxyethoxy)-	$C_6H_{14}O_3$

homolytic cleavage (Eqs. (1) and (2)) of the polymer chain at either the C–O or C–C bonds.

$$\begin{aligned} -CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O- \Rightarrow\ & \underset{\textbf{(I)}}{-CH_2\text{-}CH_2\bullet} \\ & + \underset{\textbf{(II)}}{-CH_2\text{-}CH_2\text{-}O\bullet} \end{aligned} \tag{1}$$

$$-CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O- \Rightarrow 2\ \underset{\textbf{(III)}}{-CH_2\text{-}O\text{-}CH_2\bullet} \tag{2}$$

Disproportionation (Eq. (3)) is speculated to be the major radical termination reaction

$$\mathbf{I} + \mathbf{II} \Rightarrow -CH{=}CH_2 + HO\text{-}CH_2- \text{ or } -CH_2\text{-}CH_3 + O{=}CH- \tag{3}$$

Table 4
Cryogenic trapped products from the thermal degradation of 2% PVA-alumina

Peak	Compound name	Formula
1	Air	
2	Carbon dioxide	CO_2
3	Methylene chloride	CH_3Cl
4	Ethylene oxide	C_2H_4O
5	2-Propanone	C_3H_6O
6	Furan	C_4H_4O
7	2-Propanone, 1-hydroxy	$C_3H_6O_2$
8	3-Buten-2-one	C_4H_6O
9	Unknown	
10	Acetic acid	$C_2H_4O_2$
11	2-Butenal	C_4H_6O
12	4-Penten-2-one	C_5H_8O
13	Benzene	C_6H_6
14	3-Penten-2-one	C_5H_8O
15	Cyclopenten-1-one	C_5H_6O
16	3-Penten-2-one,-(E)	C_5H_8O
17	Unknown	
18	2-Cyclohexen-1-one	C_6H_8O
19	Unknown	
20	Phenol	C_6H_6O
21	Benzaldehyde	C_7H_6O

where—represents the continuation of the polymer chain. Reactions (1) and (2) are Type II cleavages as proposed by Madorsky and Straus [1] while Reaction (3) occurs from the radical intermediates rather than from direct intermolecular hydrogen transfer (Type I Madorsky cleavage).

In addition, radicals **I**, **II**, or **III** can abstract hydrogen from any available source

$$—CH_2\text{–}CH_2\bullet + RH \Rightarrow —CH_2\text{–}CH_3 + R\bullet \tag{4}$$

(**I**) (Groups C, D, and E; Table 2)

$$—CH_2\text{–}CH_2\text{–}O\bullet + RH \Rightarrow —CH_2\text{–}CH_2\text{–}OH + R\bullet \tag{5}$$

(**II**) (Groups A and D; Table 2)

$$—CH_2\text{–}O\text{–}CH_2\bullet + RH \Rightarrow —CH_2\text{–}O\text{–}CH_3 + R\bullet \tag{6}$$

(**III**) (Groups A and C; Table 2)

If the source of hydrogen is the polymer backbone, then a long-chain free radical results

$$—CH_2\text{–}CH_2\text{–}O\text{–}\dot{C}H\text{–}CH_2\text{–}O\text{–}CH_2\text{–}CH_2\text{–}O—$$

(**IV**)

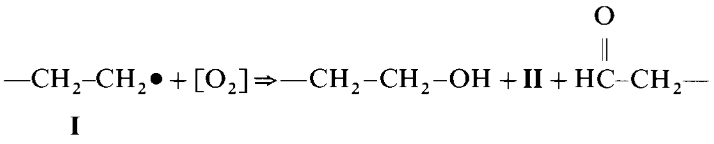
Table 5
Cryotrapped 6% PEG-0.5% PVA thermal degradation products

Peak	Compound name	Formula
1	Air	
2	Carbon dioxide	CO_2
3	Acetaldehyde	C_2H_4O
4	Unknown	
5	Ethene, methoxy	C_3H_6O
6	Unknown	
7	2-Propenal	C_3H_4O
8	Unknown	
9	1,3-Dioxolane	$C_3H_6O_2$
10	Ethene, 1,1′-oxybis-	C_4H_6O
11	Ethene, ethoxy	C_4H_8O
12	Unknown	
13	2-Pentanone	$C_5H_{10}O$
14	Unknown	
15	2-Methyl, 1,3-dioxolane	$C_4H_8O_2$
16	1,4-Dioxane	$C_4H_8O_2$
17	Unknown	
18	Benzene	C_6H_6
19	Unknown	
20	1,2-Ethanediol, diformate	$C_4H_6O_4$
21	Unknown	
22	Unknown	
23	Toluene	C_7H_8
24	Ethanol 2,2′-oxybis-	$C_4H_{10}O_3$

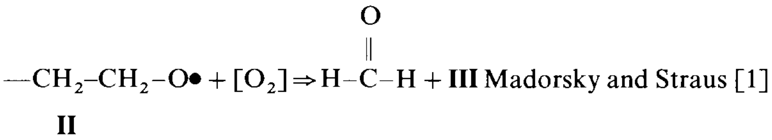
The low temperature decomposition of radicals similar to **IV** has been discussed by Bortel and Lamot [9].

This series of reactions differs from the Madorsky scheme [1] primarily in the fate of the proposed intermediate radicals. Madorsky proposed that the radicals like **II** underwent unzipping reactions to produce ethylene oxide. The observed products from our study clearly suggest that the conventional unzipping of the polymer backbone occurs only to a minor extent.

Structures **I**, **II**, **III**, and **IV** are subject to oxidation reactions with O_2



$$\underset{\textbf{I}}{—CH_2–CH_2\bullet} + [O_2] \Rightarrow —CH_2–CH_2–OH + \textbf{II} + H\overset{\overset{\displaystyle O}{\|}}{C}–CH_2— \qquad (7)$$



$$\underset{\textbf{II}}{—CH_2–CH_2–O\bullet} + [O_2] \Rightarrow H–\overset{\overset{\displaystyle O}{\|}}{C}–H + \textbf{III} \text{ Madorsky and Straus [1]} \qquad (8)$$

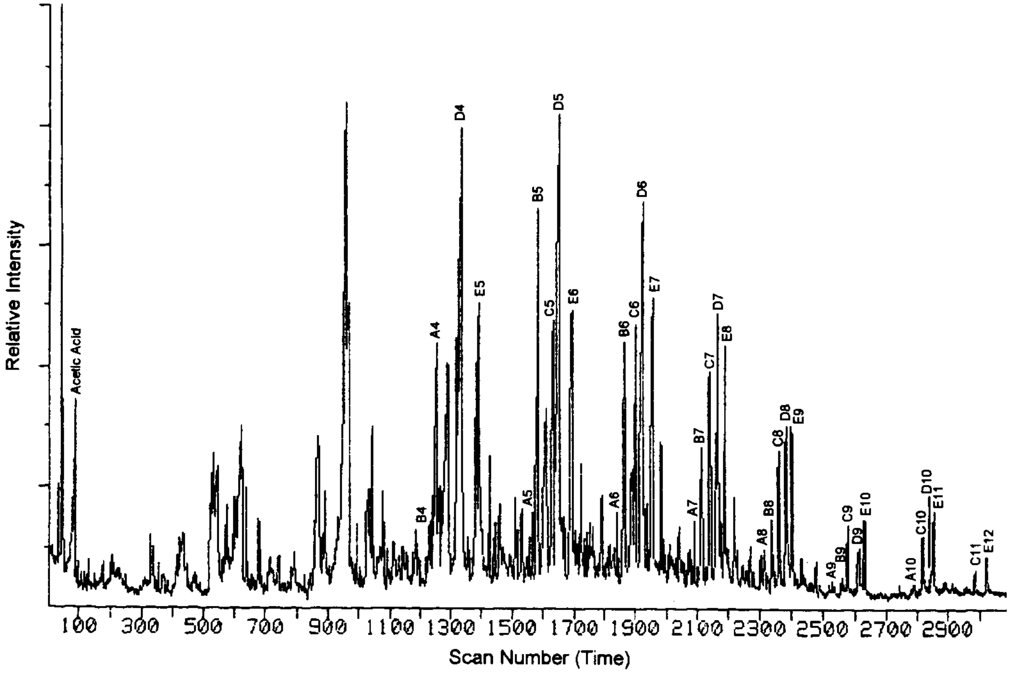
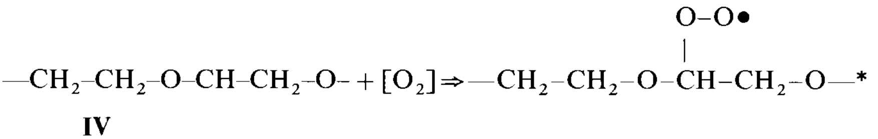


Fig. 9. The TIC of the higher molecular weight degradation products from 6% PEG/additives–alumina.

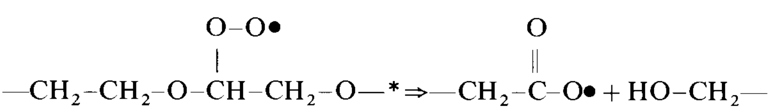
$—CH_2–O–CH_2\bullet + [O_2] \Rightarrow 2H\bullet + CO_2 + \mathbf{II}$ (9)

III



$$—CH_2–CH_2–O–CH–CH_2–O– + [O_2] \Rightarrow —CH_2–CH_2–O–\overset{\overset{\large O–O\bullet}{|}}{C}H–CH_2–O—* \quad (10)$$

IV



$$—CH_2–CH_2–O–\overset{\overset{\large O–O\bullet}{|}}{C}H–CH_2–O—* \Rightarrow —CH_2–\overset{\overset{\large O}{\|}}{C}–O\bullet + HO–CH_2— \quad (11)$$

The oxidation reaction can be used to explain the formation of selected products in Tables 3 and 6 and also the formaldehyde reported by Madorsky and Straus [1].

Based on oxygen availability, it is postulated that the binder within the ceramic body decomposes by disproportionation, hydrogen abstraction and rearrangement with only minor oxidation. Once the primary products distill from the melt, they are subjected to oxidation reactions at the surface of the ceramic and in the gas phase. With an abundant supply of atmospheric oxygen, combustion competes favorably with the polymer inter- and intra-molecular degradation processes. The lower quantities of

Table 6
Poly(ethylene glycol) semi-volatile degradation product analysis summary

Label given	Compound name	Molecular weight	%[a] Comp
PEG 1	Tetrahydro-2, 5-dimethoxy-furan	130	1.5
PEG2	1-Ethoxy-1-methoxy-ethane	104	1.8
A3	$CH_3-O(CH_2-CH_2-O)_2-CH_2-CH_2-OH$	164	2.5
A4	$CH_3-O(CH_2-CH_2-O)_3-CH_2-CH_2-OH$	208	2.0
A5	$CH_3-O(CH_2-CH_2-O)_4-CH_2-CH_2-OH$	252	<0.5
A6	$CH_3-O(CH_2-CH_2-O)_5-CH_2-CH_2-OH$	296	<0.5
A7	$CH_3-O(CH_2-CH_2-O)_6-CH_2-CH_2-OH$	340	<0.5
A8	$CH_3-O(CH_2-CH_2-O)_7-CH_2-CH_2-OH$	384	<0.5
A9	$CH_3-O(CH_2-CH_2-O)_8-CH_2-CH_2-OH$	428	<0.5
A10	$CH_3-O(CH_2-CH_2-O)_9-CH_2-CH_2-OH$	472	<0.5
B3	$O{=}CH-CH_2(O-CH_2-CH_2)_2-O-CH_2-CH_3$	176	<0.5
B4	$O{=}CH-CH_2(O-CH_2-CH_2)_3-O-CH_2-CH_3$	220	0.7
B5	$O{=}CH-CH_2(O-CH_2-CH_2)_4-O-CH_2-CH_3$	264	<0.5
B6	$O{=}CH-CH_2(O-CH_2-CH_2)_5-O-CH_2-CH_3$	308	0.7
B7	$O{=}CH-CH_2(O-CH_2-CH_2)_6-O-CH_2-CH_3$	352	<0.5
B8	$O{=}CH-CH_2(O-CH_2-CH_2)_7-O-CH_2-CH_3$	396	0.7
B9	$O{=}CH-CH_2(O-CH_2-CH_2)_8-O-CH_2-CH_3$	440	<0.5
C2	$CH_3-O(CH_2-CH_2-O)-CH_2-CH_3$	104	2.2
C5	$CH_3-O(CH_2-CH_2-O)_4-CH_2-CH_3$	236	1.2
C6	$CH_3-O(CH_2-CH_2-O)_5-CH_2-CH_3$	280	1.8
C7	$CH_3-O(CH_2-CH_2-O)_6-CH_2-CH_3$	324	3.1
C8	$CH_3-O(CH_2-CH_2-O)_7-CH_2-CH_3$	368	1.6
C9	$CH_3-O(CH_2-CH_2-O)_8-CH_2-CH_3$	412	1.5
C10	$CH_3-O(CH_2-CH_2-O)_9-CH_2-CH_3$	456	1.3
C11	$CH_3-O(CH_2-CH_2-O)_{10}-CH_2-CH_3$	500	1.0
D1	$CH_3-CH_2-O-CH_2-CH_2-OH$	90	1.1
D2	$CH_3-CH_2-O(CH_2-CH_2-O)-CH_2-CH_2-OH$	134	4.4
D3	$CH_3-CH_2-O(CH_2-CH_2-O)_2-CH_2-CH_2-OH$	178	5.4
D4	$CH_3-CH_2-O(CH_2-CH_2-O)_3-CH_2-CH_2-OH$	222	5.6
D5	$CH_3-CH_2-O(CH_2-CH_2-O)_4-CH_2-CH_2-OH$	266	4.2
D6	$CH_3-CH_2-O(CH_2-CH_2-O)_5-CH_2-CH_2-OH$	310	5.1
D7	$CH_3-CH_2-O(CH_2-CH_2-O)_6-CH_2-CH_2-OH$	354	4.8
D8	$CH_3-CH_2-O(CH_2-CH_2-O)_7-CH_2-CH_2-OH$	398	4.3
D9	$CH_3-CH_2-O(CH_2-CH_2-O)_8-CH_2-CH_2-OH$	442	2.8
D10	$CH_3-CH_2-O(CH_2-CH_2-O)_9-CH_2-CH_2-OH$	486	2.2
E3	$CH_3-CH_2-O(CH_2-CH_2-O)_2-CH_2-CH_3$	162	1.3
E4	$CH_3-CH_2-O(CH_2-CH_2-O)_3-CH_2-CH_3$	206	1.4
E5	$CH_3-CH_2-O(CH_2-CH_2-O)_4-CH_2-CH_3$	250	1.6
E6	$CH_3-CH_2-O(CH_2-CH_2-O)_5-CH_2-CH_3$	294	1.9
E7	$CH_3-CH_2-O(CH_2-CH_2-O)_6-CH_2-CH_3$	338	2.0
E8	$CH_3-CH_2-O(CH_2-CH_2-O)_7-CH_2-CH_3$	382	2.0
E9	$CH_3-CH_2-O(CH_2-CH_2-O)_8-CH_2-CH_3$	426	1.7
E10	$CH_3-CH_2-O(CH_2-CH_2-O)_9-CH_2-CH_3$	470	2.2
E11	$CH_3-CH_2-O(CH_2-CH_2-O)_{10}-CH_2-CH_3$	514	1.7
E12	$CH_3-CH_2-O(CH_2-CH_2-O)_{11}-CH_2-CH_3$	558	1.7
	Total = 81.0		

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[a] Percent composition (% comp.) is the area percent of each peak in the TIC based on the total area of all peaks.

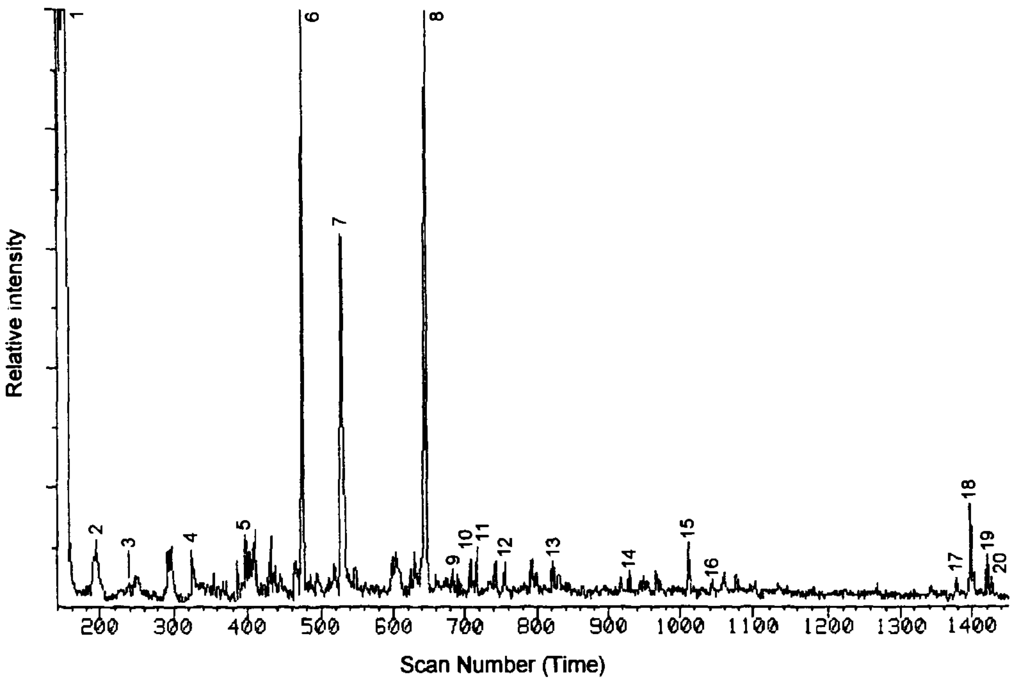


Fig. 10. The chromatogram of the $>C_6$ degradation products from 2% PVA/additive-alumina.

volatile pyrolysis products detected in the oxidation process when compared to nitrogen atmosphere pyrolysis confirms this assumption.

Several samples were partially thermally degraded to varying weight loss percentages (20, 40, 60, and 80%) in order to investigate the residue structure. Using the standard decomposition and analysis procedures, these samples produced chromatograms that were essentially equivalent to Fig. 9. This suggests that the binder remaining in the ceramic piece does not undergo extensive crosslinking and production of char. If this occurred, different products would be expected. The absence of a highly crosslinked residue has been verified by CP-MAS ^{13}C NMR [10].

3.4.2. *Poly(vinyl alcohol)*

The compounds observed from the thermal degradation of PVA as a binder in alumina are similar to those reported by Tsuchiya and Sumi [2]. These authors postulated that the PVA thermal degradation proceeded in two steps, the first being the loss of water and other volatile compounds, and the second involving the breaking of the long chained polyenes (produced from the water loss) to form aromatics. Eq. (12) illustrates the formation of the polyene.

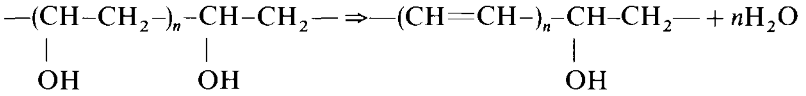
$$-(CH_2\text{-}\underset{\substack{|\\ OH}}{CH})_n\text{-}CH_2\text{-}\underset{\substack{|\\ OH}}{CH}- \xrightarrow{-H_2O} -(CH{=}CH)_n\text{-}CH_2\text{-}\underset{\substack{|\\ OH}}{CH}- \Rightarrow \text{various aromatics} \qquad (12)$$

Table 7
Thermal degradation products from 2% PVA-alumina

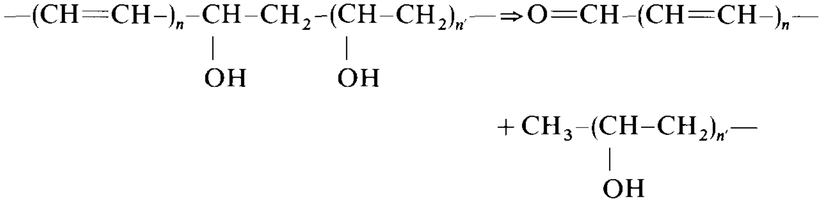
Peak	Compound name	Molecular weight
1	Acetic acid	60
2	3-Penten-2-one	84
3	1,1-Dimethoxy-2-butene	116
4	3-Hexene, 2-5-diol	116
5	2,4-Hexadienal	96
6	Benzaldehyde	106
7	Phenol	94
8	1-Phenyl-ethanone	120
9	Ethanone, 1-(1-cyclohexene)	115
10	Unknown	
11	(1,2-Dimethoxyethyl) benzene	166
12	Unknown	
13	Azulene	128
14	Unknown	
15	Unknown	
16	Unknown	
17	Phenol, 4-(2,2,4-trimethyl)	206
18	Phenol, 4-(1,1,3,3-tetramethyl)	221
19	Benzophenone	317
20	Unknown	

Several substituted aromatics were observed among the products listed in Table 7. The polynuclear aromatics previously observed by Ballistreri et al. [3] were not found in our products.

The homolytic cleavage (Eqs. (13) and (14)) of the polyene chain which contains residual vinyl alcohol repeating units has also been proposed by Tsuchiya and Sumi to explain the unsaturated oxygen-containing species [2].



$$-(\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}-)_n-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}- \Rightarrow -(\mathrm{CH}=\mathrm{CH}-)_n-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}- + n\mathrm{H_2O} \qquad (13)$$



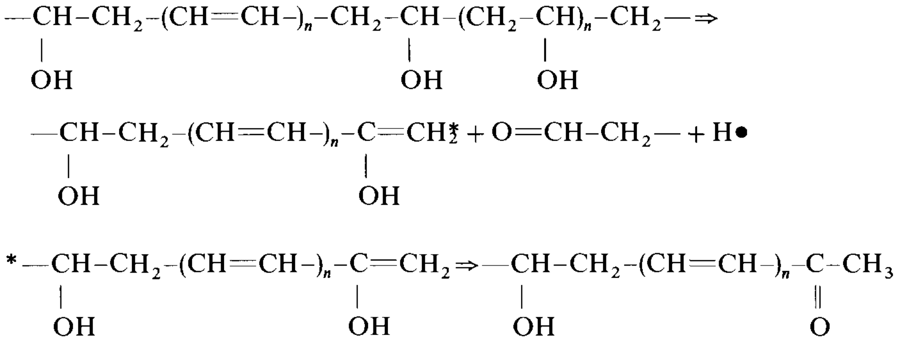
$$-(\mathrm{CH}=\mathrm{CH}-)_n-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}-(\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2})_{n'}- \Rightarrow \mathrm{O}=\mathrm{CH}-(\mathrm{CH}=\mathrm{CH}-)_n- + \mathrm{CH_3}-(\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2})_{n'}- \qquad (14)$$

Several unsaturated ketones and aldehydes listed in Table 7 provide evidence for this type of mechanism. The largest conjugation found in these products was two double bonds. This implies that the cleavages occurred at rather short polyene lengths.

Table 8
6 % PEG-0.5% PVA-alumina binder thermal degradation products

Label given	Compound name or structure	Formula
A1	$CH_3-O-(CH_2-CH_2-O)-CH_2-CH_2-OH$	$C_5H_{12}O_3$
A2	$CH_3-O-(CH_2-CH_2-O)_2-CH_2-CH_2-OH$	$C_7H_{16}O_4$
A4	$CH_3-O-(CH_2-CH_2-O)_3-CH_2-CH_2-OH$	$C_9H_{20}O_5$
A5	$CH_3-O-(CH_2-CH_2-O)_4-CH_2-CH_2-OH$	$C_{11}H_{24}O_6$
B4	$O=CH-CH_2-(O-CH_2-CH_2)_3-O-CH_2-CH_3$	$C_{10}H_{20}O_5$
B5	$O=CH-CH_2-(O-CH_2-CH_2)_4-O-CH_2-CH_3$	$C_{12}H_{24}O_6$
B6	$O=CH-CH_2-(O-CH_2-CH_2)_5-O-CH_2-CH_3$	$C_{14}H_{28}O_7$
C4	$CH_3-O-(CH_2-CH_2-O)_3-CH_2-CH_3$	$C_9H_{20}O_4$
D2	$CH_3-CH_2-O-(CH_2-CH_2-O)-CH_2-CH_2-OH$	$C_6H_{14}O_3$
D3	$CH_3-CH_2-O-(CH_2-CH_2-O)_2-CH_2-CH_2-OH$	$C_8H_{18}O_4$
D4	$CH_3-CH_2-O-(CH_2-CH_2-O)_3-CH_2-CH_2-OH$	$C_{10}H_{22}O_5$
D5	$CH_3-CH_2-O-(CH_2-CH_2-O)_4-CH_2-CH_2-OH$	$C_{12}H_{26}O_6$
D6	$CH_3-CH_2-O-(CH_2-CH_2-O)_5-CH_2-CH_2-OH$	$C_{14}H_{30}O_7$
E4	$CH_3-CH_2-O-(CH_2-CH_2-O)_3-CH_2-CH_3$	$C_{10}H_{22}O_4$
E5	$CH_3-CH_2-O-(CH_2-CH_2-O)_4-CH_2-CH_3$	$C_{12}H_{26}O_5$
E6	$CH_3-CH_2-O-(CH_2-CH_2-O)_5-CH_2-CH_3$	$C_{14}H_{30}O_6$
E7	$CH_3-CH_2-O-(CH_2-CH_2-O)_6-CH_2-CH_3$	$C_{16}H_{34}O_7$
O1	1,3-Dioxolane, 2-methyl	$C_4H_8O_2$
O2	1,4-Dioxane	$C_4H_8O_2$
O3	Triethylene glycol	$C_6H_{14}O_4$
TX1	Phenol	C_6H_6O
TX2	Phenol, 4-(1,1,3,3-tetramethylbutyl)-	$C_{14}H_{22}O$
TX3	Ethanol, 2-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-	$C_{16}H_{30}O_2$

Although Tsuchiya and Sumi did not mention radical formation, a radical contribution would be a logical extension to the above mechanism [11]:



$$-\underset{\mathrm{OH}}{\mathrm{CH}}-CH_2-(CH=CH-)_n-CH_2-\underset{\mathrm{OH}}{\mathrm{CH}}-(CH_2-\underset{\mathrm{OH}}{\mathrm{CH}})_n-CH_2- \Rightarrow \qquad (15)$$

$$-\underset{\mathrm{OH}}{\mathrm{CH}}-CH_2-(CH=CH-)_n-\underset{\mathrm{OH}}{\mathrm{C}}=CH_2^{*} + O=CH-CH_2- + H\bullet$$

$$^{*}-\underset{\mathrm{OH}}{\mathrm{CH}}-CH_2-(CH=CH-)_n-\underset{\mathrm{OH}}{\mathrm{C}}=CH_2 \Rightarrow -\underset{\mathrm{OH}}{\mathrm{CH}}-CH_2-(CH=CH-)_n-\underset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-CH_3$$

* denotes an unstable compound which rapidly undergoes the subsequent reactions. Initiation of radicals would result from the homolytic cleavage of a C–C bond followed by hydrogen abstraction.

The proposed polyene structure in poly(vinyl chloride) has been postulated to undergo Diels–Alder-type reactions to form network chars [12]. This type of structure

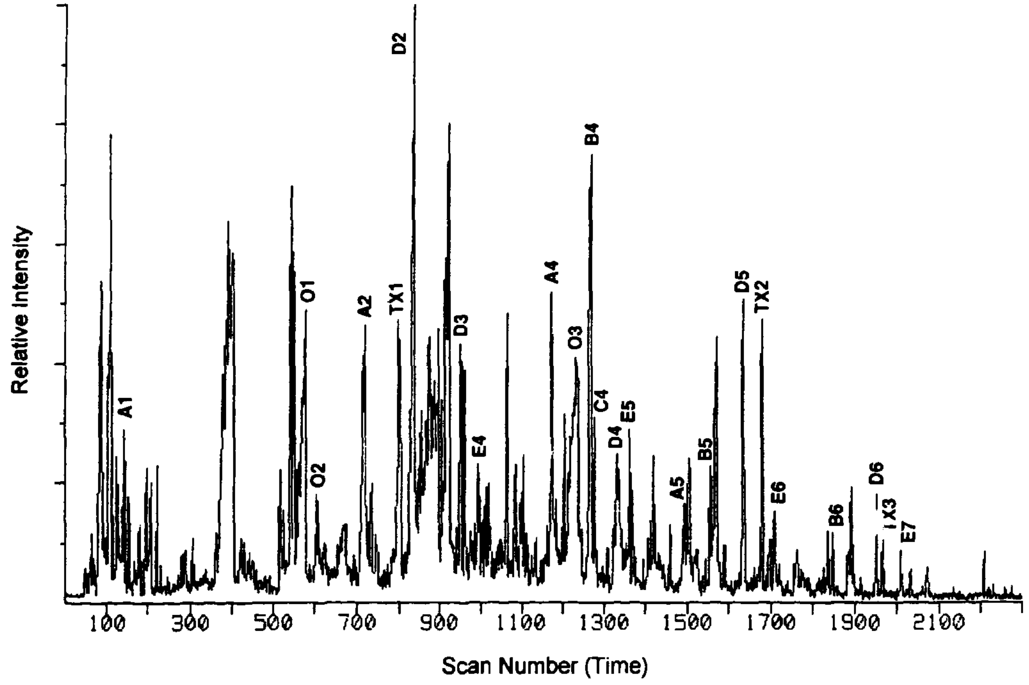


Fig. 11. TIC of the $>C_6$ degradation products from 6% PEG/0.5% PVA/additives-alumina.

could be a precursor for carbon particles in the ceramic. CP-MAS ^{13}C NMR [10] was used to investigate the production of the polyene and its possible transformation to a crosslinked residue. In samples that were partially thermally decomposed, the alkene carbons associated with the polyene were observed to appear primarily during the early stages of the burnout. However, as the degradation process continued, no crosslinked residue from the polyene could be detected in the sensitivity range of the NMR.

4. Conclusions

Analysis of the degradation products from the 6% PEG-0.5% PVA binder system indicated that the product array was a mixture of the individual products from PEG and PVA. This observation suggests that the two polymers degraded independently of each other. The PVA at the 0.5% level did not show a significant tendency to form a crosslinked residue which would form carbon particles in the final ceramic product. However, the process additives remained in the system after the binders were degraded. Specifically, the sodium lignosulfonate was stable at temperatures up to 850°C and because of its aromatic structure, could contribute to the formation of char particles. No effect from the alumina on the degradation of the two polymers was detected.

Analysis of the PEG–PVA–alumina system by CP-MAS ^{13}C NMR indicated that the 6% PEG–0.5% PVA binder degraded similarly to that observed for the PEG–alumina system. The PVA was identifiable in the NMR spectra by the C–COH peak, but did not change the degradation products from those observed from the PEG–alumina. A thermally treated sample to 80% weight loss showed that the only remaining peak was a C=C carbon peak associated with the sodium lignosulfonate.

Acknowledgements

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