T-4272

The Thermal Degradation of Common Binders for Aluminum Oxide Ceramics: Polyethylene Glycol, Methoxy Polyethylene Glycol, Polyvinyl Alcohol, and Polyethylene oxide.

by

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Chemistry).

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ABSTRACT

Common polymers used in alumina ceramics today consist of polyethylene glycol, methoxy polyethylene glycol, polyvinyl alcohol, and high molecular weight polyethylene oxide (polyox). These polymers are typically used in dry press alumina systems where they are used as binders to hold the raw materials together while the powder is compacted and fired. Typically the binders are burned off at temperatures reaching 1200°C over a period of twenty-four hours during the sintering process.

Binder selection has been done to optimize the strength and burnoff characteristics for a particular application. This has been approached by trial and error to achieve the desired characteristics.

The polymer-alumina samples investigated in this study, polyethylene glycol, and polyvinyl alcohol, were analyzed by a variety of techniques. Thermogravimetric and differential thermal analysis were used to establish maximum degradation temperatures, degradation profiles, and total weight loss of the polymer-alumina samples as well as the pure polymers methoxy polyethylene glycol and polyethylene oxide. Solid state ^{13}C cp-mass NMR analysis was done on samples with a range of polymer compositions and weight loss intervals to determine functional group change throughout the degradation process. Pyrolysis followed by GC/MS for both the volatile (C_1-C_6), and semi-volatile (C_6 and up) degradation products was used to identify the degradation compounds.

Polyethylene glycol degrades by oxidation, disproportionation, and hydrogen abstraction. The degradation which is sensitive to oxygen, favors disproportionation and hydrogen abstraction in oxygen depleted environments. The results of this work indicate that PEG binder degrades cleanly and completely without any residue formation. The standard alumina additive sodium lignosulfonate remains stable up to 800°C and is a possible carbon particle source.

Polyethylene glycol-alumina (PEG) samples were analyzed by solid state ^{13}C cp-mass NMR. The results of this work indicate that as the PEG pyrolyzed two functional groups were created from breaking the polymer backbone. They are alkene and aldehyde groups which are consistent with proposed degradation mechanisms for PEG. As the polymer continues to degrade the aldehyde functional groups degrade first. The polymer backbone carbon degrades next and finally the alkene carbon is the last to degrade. The remaining alkene functional group may attributed to the lignosulfonate.

Polyvinyl alcohol first undergoes a dehydration to form a polyene type structure with alkene functional groups. The polymer is observed to produce thermally stable aromatic and unsaturated compounds which may interfere with the sintering process. The polymer degrades by oxidation and intermolecular reactions.

Polyvinyl alcohol-alumina (PVA) samples were analyzed by solid state cp-mass ^{13}C NMR. The results of the analysis indicate that the PVA-alumina has peaks present which correspond to the PVA, deflocculant, and polyvinyl acetate. The polyvinyl acetate is present as remaining starting material from the manufacture of PVA. Thermal degradation of the PVA-alumina system produces a large alkene peak with a reduction in the amount of the original polymer remaining in the sample. Further degradation results in a loss of the remaining PVA with a large alkene peak remaining. The alkene peak is the last to degrade. This peak may be attributed to the lignosulfonate remaining in the sample.

The mixture of the two polymer binders polyethylene glycol and polyvinyl alcohol show the two polymers degrade independently of each other. This is confirmed by solid state ^{13}C cp-mass NMR analysis, and TG/DTA. Polyethylene glycol is dominant for the products produced because of the ratio of the two systems.

Methoxy polyethylene glycol degrades into the same types of products previously observed for the polyethylene glycol but with fewer products. Polyethylene oxide (polyox) also degrades into products that are very similar to those observed for the polyethylene glycol. There are, however, fewer products seen for the degradation of this polymer. Polyox is slightly different than the polyethylene glycol in that instead of being a crosslinked epoxide like the polyethylene glycol, the polyox is a straight chain polymer of 80,000 Daltons.

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ACKNOWLEDGMENTS

I would like to thank my adviser, Dr. Kent J. Voorhees for his long suffering and continued direction during the course of this research. I am also deeply indebted to Coors Ceramic Company, and Bart Hart, for funding this research and for technical assistance that was given me. I would also like to thank my committee members, Dr. Gerald DePoorter and Dr. Scott Cowley, for their direction and instruction provided during classes at Colorado School of Mines.

To my wife MaLinda, and our children Joshua and Katie, I am indeed thankful and grateful for the support and love shown to me. Without you this work would not be complete.

INTRODUCTION

Processing of alumina dry press binder systems poses many problems. The polymers used must be soluble in water to uniformly coat the alumina particles. Initial treatment of pressing the powders into a highly compacted piece also tends to narrow the window of available polymer binder systems. In this stage of processing, there needs to be enough strength for the piece to withstand movement, or machining as well as have the polymer flow under pressure to better match the die from which it is cast.

Thermal processing is another limiting factor in deciding which binder to use. The optimal characteristics of a thermal binder are that it is strong enough to hold the pressed ceramic piece together before firing and readily degrades into volatile species which can easily escape from the ceramic piece. The binder should also maintain its strength as the polymer degrades. Optimally, the last of the binder should escape from the system as the alumina begins to sinter, or fuse together.

The goal of this research has been to better understand the degradation mechanisms of two classes of polymer binders, polyethylene glycols and polyvinyl alcohol. These polymer classes represent the majority of binders in use with alumina ceramics today.

Previous Research

Polyethylene Glycol

Initial research in 1959 by Madorsky and Straus [1] proposed that the introduction of oxygen into the backbone of an aliphatic polymer would cause a lowering in the thermal stability of a polymer chain because the C-O bond is weaker than the C-C bond. Their study involved the pyrolysis of polyethylene oxide and polypropylene oxide in comparison to previous research on the pyrolysis of non-oxide polymers polyethylene, polymethylene (produced by reacting methylene chloride with sodium), and polypropylene [2, 3, 4].

The Madorsky samples weighing 25-50 mg were heated for 15 minutes at 100°C and then pyrolyzed for 30 minutes at differing temperatures, (T_{pyr}) ranging from 324°C to 363°C. The volatile products were collected in a trap cooled to liquid nitrogen temperatures, and then separated into several fractions (V) by molecular distillation, V_{pyr} (pyrolysis residue), $V_{25°C}$ (volatile from 25°C to T_{pyr}), $V_{-80°C}$ (volatile from -80°C to 25°C), and $V_{-190°C}$ (volatile at -190°C). The volatile products were then analyzed to determine the distribution of products in each fraction which is represented in Table 1.

The $V_{-190°C}$ fraction which accounted for less than 0.1% of the total volatile products and consisted of H_2, CH_4, and CO. The products from the $V_{25°C}$ and $V_{-80°C}$ fractions were analyzed by mass spectrometry and the results are shown in Table 2.

Table 1. Pyrolysis of Polyethylene Oxide.

Experiment No.	Temp., °C.	Volatilization %	Volatile fractions, based on total volatilized. $V_{pyr.}$, %	V_{25}, %	V_{-80}, %
1	324	7.3	89.4	8.5	2.1
2	336	39.6	88.2	9.4	2.4
3	347	51.6	90.8	7.4	1.8
4	347	52.5	88.4	9.3	2.3
5	348	51.4	91.0	7.2	1.8
6	350	58.9	90.8	7.4	1.8
7	354	70.9	91.8	6.6	1.6
8	358	86.1	91.0	7.2	1.8
9	363	98.6	90.8	7.4	1.8
		Average	90.3	7.8	1.9

Table 2. Mass Spectrometer Analysis of Fraction V_{25} + V_{-80} from Pyrolysis of Polyethylene Oxide.

Component	% of total volatiles
Formaldehyde	0.7
Ethanol	0.4
Polyethylene oxide	3.9
Carbon dioxide	1.0
Water	0.2
About 20 saturated and unsaturated compounds, comprising alcohols, acids, aldehydes, ketones, ethers, and esters, in the range of 1 to 7 carbons	3.5
Total	9.7

The V_{pyr} fractions were analyzed by microcryoscopic methods to determine molecular weight and product distribution.

In a comparison of the stability of non-oxide and oxide polymers represented in Figure 1, the oxide polymers are less stabile thermally than the non-oxide polymers. The thermal stability of the polymer is expressed in terms of T_h, the temperature at which the polymer loses half of its weight in 35 minutes, including an initial 5 minute heating time. The thermal stability T_h is represented by the horizontal line at 50% in Figure 1. Temperatures for T_h are 295°, 312°, 345°, 387°, 404°, and 415°C for atactic polypropylene oxide, polyethylene oxide, polypropylene, polyethylene, and polymethylene respectively.

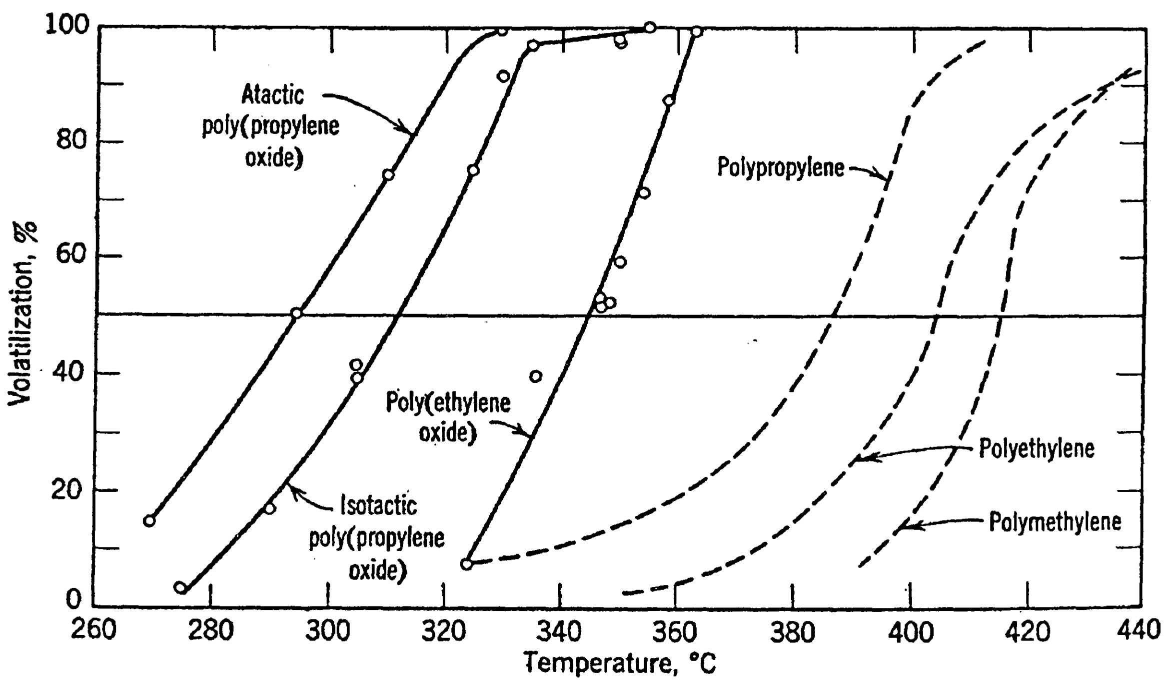


Figure 1. Relative Thermal Stability of Oxide and Non-oxide Polymers.

The products observed by Madorsky such as aldehydes, ketones, and ethers were explained by two types of molecular fragmentations. The first kind of cleavage (Type I) involves homolytic cleavage and an intramolecular transfer of hydrogen.

Type I

$$H{-}\!\left(O{-}C_2H_4\right)_n\!{-}OH \longrightarrow \begin{array}{c} H{-}\!\left(O{-}C_2H_4\right)_n\!{-}O{-}CH{=}CH_2 \\ + \\ H{-}\!\left(O{-}C_2H_4\right)_m\!{-}OH \end{array}$$

or

$$H{-}\!\left(O{-}C_2H_4\right)_n\!{-}OH \longrightarrow \begin{array}{c} H{-}\!\left(O{-}C_2H_4\right)_n\!{-}O{-}CH_2{-}CH{=}O \\ + \\ H{-}\!\left(O{-}C_2H_4\right)_m\!{-}O{-}CH_2{-}CH_3 \end{array} \qquad (1)$$

The second form of chain cleavage discussed (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 type products. The supply of hydrogen in the vicinity of the reaction seemed to be the determining factor for dominance of Type I or Type II chain cleavage.

Type II

$$H\text{-}(O-C_2H_4)_n\text{-}OH \longrightarrow \begin{array}{c} H\text{-}(O-C_2H_4)_n\text{-}O-CH-CH_2\cdot \\ + \\ H\text{-}(O-C_2H_4)_m\text{-}O\cdot \end{array} \qquad (2)$$

The effect of molecular weight on the thermal stability of polyethylene glycol (PEG) was investigated by Ishikawa [5]. The polymer was pyrolyzed in vacuum by heating at 5°C/min up to the point of degradation where the rate was changed to 2°C/min to the final temperature of pyrolysis of 500°C. Pyrolysis products were analyzed by gas chromatography. The one-hundred mg samples were pyrolyzed under vacuum at 500°C both statically and with a temperature program to obtain the activation energy for the thermal degradation of the polymer. The volatile products were analyzed by gas chromatography.

The temperature of degradation increased as the molecular weight of the polymer increased up to a molecular weight of 1000 Daltons (Figure 2). Above this molecular weight, the degradation temperature remained fairly constant. This seems to indicate a change in the weight loss mechanism for the polymer from distillation to degradation. For PEG over 1000 Daltons, the intermolecular force is comparable to the bond dissociation energy. The activation energies for PEG 1000, 4000, and 6000 were 45, 42, and 36 kcal respectively indicating that for molecular weights below 1000 Daltons, evaporation was the dominant form of weight loss, and for PEG polymers with molecular weights greater than 1000 Daltons, pyrolysis caused the weight loss.

Conder *et. al.* [6] investigated the thermal decomposition of polyethylene glycol 20M, and its sensitivity to oxygen, as a stationary phase in gas chromatography. They proposed three factors influencing the thermal degradation of PEG: 1) The amount of oxygen present in the carrier gas, 2) catalytic action of the support and 3) catalysis by acidic products of decomposition. The major products of the thermal decomposition were acetaldehyde and acetic acid. The thermal degradation of PEG was strongly influenced by the amount of oxygen present in the carrier gas. After reducing the amount of oxygen present from 10^{-5} to 10^{-8} parts, the rate of decomposition decreased to 20% of its previous level. The corresponding minimum decomposition temperature was also increased from

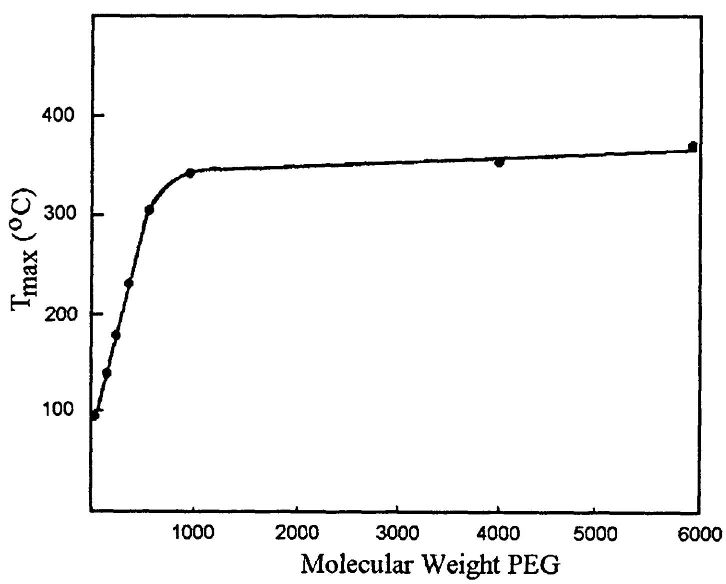


Figure 2. Degradation Temperature of PEG as a Function of Molecular Weight.

160°C to 200°C. The acidic decomposition of products can also act as catalysts in the non-oxidative decomposition of the polymer. Reported decomposition products of PEG are acetaldehyde and the acid-catalyzed depolymerization of PEG to carbonyls [7].

Mikheyev *et. al.* [8] investigated the chain degradation of polyethylene oxide and polypropylene hydroperoxides (HP) at the moderate temperature of 100°C. The hydroperoxide of PEG was investigated because of the selective attack on the C-O bond by the peroxide radical. Intermediate products of polymer oxidation such as hydroperoxide are formed with yields dependent on the amount of oxygen present. The degradation of the HP polymer chain is inhibited by the oxygen present in the system. Experiments were done by producing high concentrations of HP which allowed IR spectroscopy to be used for analysis of the functional groups present during the reaction. High concentrations of HP were produced by oxidizing PEG 20M, T_{melt} = 60°C, at 100°C on the surface of a fluorite window in a drying cabinet. The concentration of HP was determined by UV absorption of I_3^- ions produced by the peroxide from KI. Degradation of the polymer was done in ampoules at 1 Pa, with and without 10% or 15% stabilizer.

Thermal degradation of the PEG HP under vacuum was first order below 90°C, and at higher temperatures the rate was too fast to determine. The rate was independent of the amount of aldehyde present (up to 10 mole/kg) from the oxidation of the polymer. Chain degradation of HP was inhibited by the presence of oxygen.

Oxidation of PEG, at 99°C for 2.5 hr with a concentration of HP of 1.3 mole/kg, shows a decrease in the amount of IR absorption of C-H bonds (2850 cm^{-1}) and the appearance of bands at 330 (HP), 1745 (esters), 1720 (aldehydes), and 1600 cm^{-1} (groups with conjugated double bonds. The product believed to correspond with the 1600 cm^{-1} band is the oxidized product of an aldol condensation. The HP can also form epoxides with elimination of OH radicals. Their conclusion was that consecutive conversion of peroxide radicals through an epoxide ring stage explains the products of oxidation.

Research on the thermal degradation of polymers used in dry press alumina ceramics by Baugh [9], investigated the pure polymer polyethylene glycol. Pure polymers were studied to elucidate their individual thermal decomposition pathways independent of aluminum oxide.

Polyethylene glycol was analyzed by thermogravimetric and differential thermal analysis to optimize pyrolysis conditions, or find the optimal maximum temperature (T_m) for pyrolysis. The polymer was pyrolyzed in a tube furnace at T_m with either nitrogen or air as the carrier gas. The volatile and semivolatile products were collected in ice cooled methanol impingers. The products were then analyzed by gas chromatography/mass spectrometry (GC/MS), using both chemical ionization and electron ionization. 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 and degradation mechanisms.

Five series of homologous compounds (Table 3) were identified by GC/MS in conjunction with functional group information obtained by GC/FT/IR. The primary degradation reactions proposed to support the products identified, involved homolytic cleavage at either the C-O or C-C bonds with disproportionation (Equations 3 and 4), hydrogen abstraction (Equations 6, 7, and 8), or other reactions involving oxidation with O_2 (Equations 9 and 10). Nitrogen pyrolysis favored disproportionation and intramolecular reactions, enhancing the product distribution of the homologous series of compounds identified. Pyrolysis in oxygen favored oxidation over inter- and intra-molecular reactions reducing the amount of detectable degradation products.

Table 3. Homologous Series of Pyrolysis Products.

Series Label	Series Formula
A	CH_3-O-(CH_2-CH_2-O-)$_n$-CH_2-CH_2-OH
B	CH_3-CH_2-O-(-CH_2-CH_2-O-)$_n$-CH_2-CH=O
C	CH_3-CH_2-(-O-CH_2-CH_2-)$_n$-O-CH_3
D	CH_3-CH_2-O-(-CH_2-CH_2-O-)$_n$-CH_2-CH_2-OH
E	CH_3-CH_2-O-(-CH_2-CH_2-O-)$_n$-CH_2-CH_3

$$\sim\sim CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O\sim\sim \longrightarrow \underset{\mathbf{I}}{\sim\sim CH_2{-}CH_2\cdot} + \underset{\mathbf{II}}{\sim\sim CH_2{-}CH_2{-}O\cdot} \tag{3}$$

$$\sim\sim CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O\sim\sim \longrightarrow 2\underset{\mathbf{III}}{\sim\sim CH_2{-}O{-}CH_2\cdot} \tag{4}$$

$$\underset{\mathbf{I}}{\sim\sim CH_2{-}CH_2\cdot} + \underset{\mathbf{II}}{\sim\sim CH_2{-}CH_2{-}O\cdot} \longrightarrow \begin{array}{c} \sim\sim CH{=}CH_2 \quad + \quad HO{-}CH_2\sim\sim \\ \text{or} \\ \sim\sim CH{=}O \quad\quad H_3C{-}CH_2\sim\sim \end{array} \tag{5}$$

where $\sim\sim$ represents the continuation of the polymer chain. Also **I, II,** or **III** can abstract hydrogen from an available source:

$$\underset{\mathbf{I}}{\sim\sim CH_2{-}CH_2\cdot} + RH \longrightarrow \underset{\text{(Groups C, D, and E)}}{\sim\sim CH_2{-}CH_3} + R\cdot \tag{6}$$

$$\underset{\mathbf{II}}{\sim\sim CH_2{-}CH_2{-}O\cdot} + RH \longrightarrow \underset{\text{(Groups A and D)}}{\sim\sim CH_2{-}CH_2{-}OH} + R\cdot \tag{7}$$

$$2\underset{\mathbf{III}}{\sim\sim CH_2{-}O{-}CH_2\cdot} + RH \longrightarrow \underset{\text{(Groups A and C)}}{\sim\sim CH_2{-}O{-}CH_3} + R\cdot \tag{8}$$

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

$$\underset{\mathbf{IV}}{\sim\!\sim CH_2{-}CH_2{-}O{-}\dot{C}H{-}CH_2{-}O{-}CH_2{-}CH_2{-}O\sim\!\sim}$$

I, II, III, and **IV** are also subject to oxidation reactions with O_2, if present.

$$\underset{\mathbf{I}}{\sim\!\sim CH_2{-}CH_2\cdot} + [O_2] \longrightarrow \sim\!\sim CH_2{-}CH_2{-}OH + 2H\cdot + \mathbf{II} + H\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2\sim\!\sim \qquad (9)$$

$$\underset{\mathbf{II}}{\sim\!\sim CH_2{-}CH_2{-}O\cdot} + [O_2] \longrightarrow H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + \mathbf{I} \qquad (10)$$

$$\underset{\mathbf{III}}{\sim\!\sim CH_2{-}O{-}CH_2\cdot} + [O_2] \longrightarrow 2H\cdot + CO_2 + \mathbf{II} \qquad (11)$$

$$\underset{\mathbf{IV}}{\sim\!\sim CH_2{-}CH_2{-}O{-}\dot{C}H{-}CH_2{-}O\sim\!\sim} + [O_2] \longrightarrow \sim\!\sim CH_2{-}CH_2{-}O{-}\overset{\overset{\displaystyle O{-}O\cdot}{|}}{C}H{-}CH_2{-}O* \qquad (12)$$

$$\sim\!\sim CH_2{-}CH_2{-}O{-}\overset{\overset{\displaystyle O{-}O\cdot}{|}}{C}H{-}CH_2{-}O* \longrightarrow \sim\!\sim CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O\cdot + HO{-}CH_2\sim\!\sim \qquad (13)$$

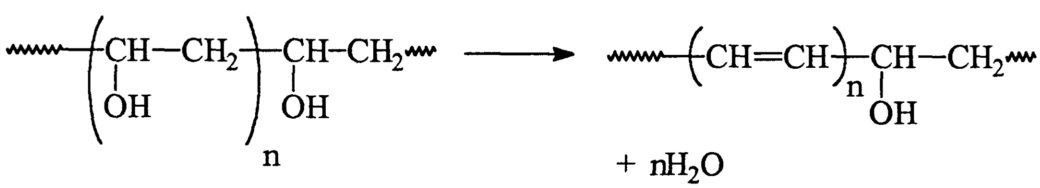
Because analysis of the pyrolysis products from polyethylene glycol is done by GC/MS, a key to understanding and interpreting the products is a knowledge of the mass spectral fragmentation patterns of this polymer. Chemical analysis of polyethylene glycol and polypropylene glycol has been done by tandem mass spectrometry [10]. It was found that desorption ionization produced stable sodium attachment ions ($M+Na^+$) for daughter analysis. Tandem mass spectrometry (MS/MS) of these ions is done by collisionally fragmenting the ion and mass analysis (daughter ion fragmentation). Understanding the fragmentation pathways of polyethylene glycol can help to identify compounds seen by GC/MS.

Further work in this area by Lattimer [11] with fast atom bombardment (FAB)-MS/MS was done with proton and deuteron attachment ions to linear (hydroxyl- and methyl-terminated) and cyclic (crown ether) ethylene glycol (PEG) oligimers. Experiments showed that linear PEG and cyclic crown ethers produce almost the same fragmentation patterns. This can be explained by a charge site initiated cleavage of the cyclic ring into an intermediate that is the same as for the linear PEG. The fragmentation patterns for the cyclic ether and the linear ether are very similar.

Polyvinyl Alcohol

Tsuchiya and Sumi [12] studied the thermal decomposition products of polyvinyl alcohol. Their experiments consisted of pyrolysis of the polymer in vacuum at 240°C for 4 hrs. The pyrolyzate products were collected in a liquid N_2 trap. The remaining residue in the furnace was then further pyrolyzed at 450°C for 4 hrs. Pyrolysis products from the remaining residue were also collected in the liquid N_2 trap. Analysis of the pyrolysis products was done by GC using a comparison of the retention times of known compounds against the unknown peaks.

The major products of degradation from the initial reaction (240°C pyrolysis) were; water, aldehydes, and ketones. The products were explained by dehydration (Equation 14) of the polymer backbone and then subsequent cleavage of the C-C bonds forming aldehydes and methyl groups (Equation 15). Cleavage at the remaining alcohol carbon produced a ketone and an aldehyde (Equation 16). Because aldehydes are formed in two different types of carbon cleavages and ketones only in one, it is expected that aldehydes will be more abundant.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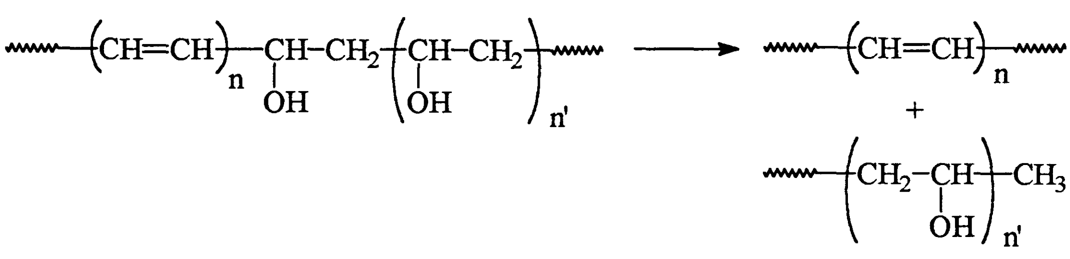
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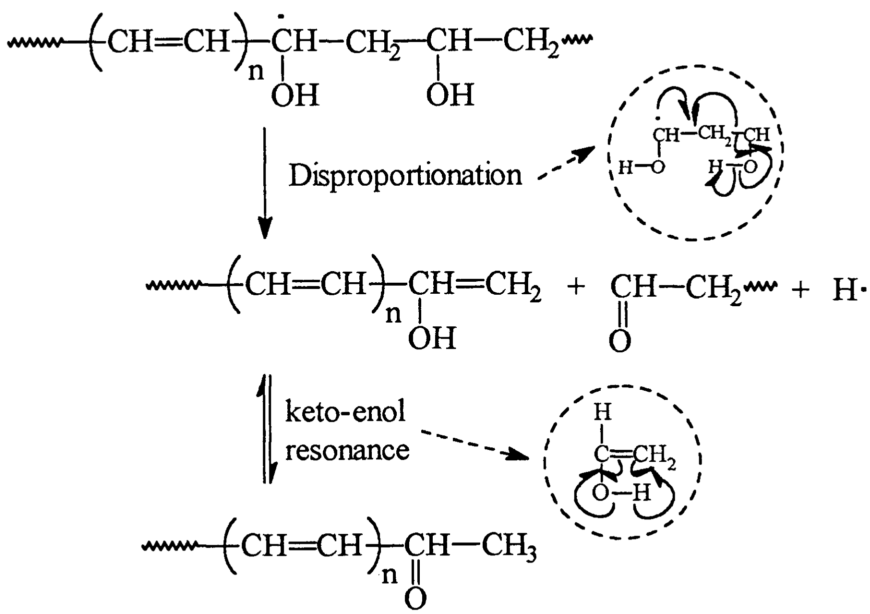


(16)

Analysis of the pyrolysis products from the initial pyrolysis residue showed that the main degradation products were alkanes, alkenes, and aromatic or unsaturated hydrocarbons [12]. The degradation products for the polyene residues are very similar to that of polyvinyl chloride (PVC), and polyvinyl acetate (PVAc). This is a strong indication that the degradation mechanism for the residue from each of the polymers is very similar.

Lattimer and Kroenke [13] investigated the pyrolyzates from polyvinyl chloride by GC-MS. One step in the degradation of PVC is the dehydrochlorination of the polymer. The loss of HCl produces a conjugated polyene that can then undergo further pyrolysis reactions. Polyvinyl alcohol degrades in a similar manner to that observed for PVC. There is a dehydration of the polymer producing an unsaturated polyene residue. The polyene can then undergo further degradation reactions. The polyenes produced by loss of HCl from PVC, or H_2O from PVA are similar and any subsequent degradation of either would produce similar products. Information obtained about the degradation of the polyene residue from PVC would be useful in understanding PVA degradation mechanisms.

Results from the degradation of PVC residue, or the polyene, indicate that there are three types of reactions that can occur. The first is intramolecular formation of benzene and naphthalene through cyclization reactions of the polyene chain. The second reaction is a mixed inter- intra-molecular formation of styrene by hydrogen transfer between chains or intra-molecularly. The third reaction is intermolecular formation of toluene by hydrogen transfer between PVC chains.

The formation of benzene occurs when three conjugated bonds from the PVC polyene cyclize to form cyclohexadiene. Cleavage of cyclohexadiene from the polyene chain leads to the formation of benzene from the cyclohexadiene. Cleavage of the polyene leaving a methyl radical and abstraction of hydrogen produces toluene.

Baugh [9] also investigated the pyrolysis of polyvinyl alcohol in air and nitrogen using the same experimental protocol as defined for the polyethylene glycol. Thermogravimetric analysis in air and nitrogen were similar indicating that the reaction was not sensitive to oxygen. Identification of pyrolysis products was done by GC/MS using electron ionization (EI). Water and acetic acid were the main pyrolysis products and the residue from the reaction had an empirical formula of C_6H_6 as determined by C, H, and N analysis. This is a strong indication of a highly crosslinked and unsaturated compound.

Zhang *et. al.* [14] applied solid state ^{13}C NMR techniques to understand the thermal degradation interactions of polymer blends consisting of polyvinyl alcohol (PVA)/polymethracrylic acid (PMAA) and polyvinyl alcohol/polyacrylic acid (PAA). The neat polymers were also analyzed by solid state ^{13}C NMR for thermally treated samples. The cross polarization-magic angle spinning sample (cp-mass) spectra for pure PVA is of direct interest to this research. As the PVA polymer is heated to different temperatures, the ^{13}C spectra record the change in functional groups for the polymer (Figure 3). Three types of carbon environments were detected (as indicated by an asterisk); a) *CH-OH, b) CH-$^{*}CH_2$-CH, and c) *CH=*CH. Their conclusions based on the ^{13}C cp-mass spectra was that the thermal degradation products of the blends and complexes produced products similar to the pure polymers heated in the same fashion.

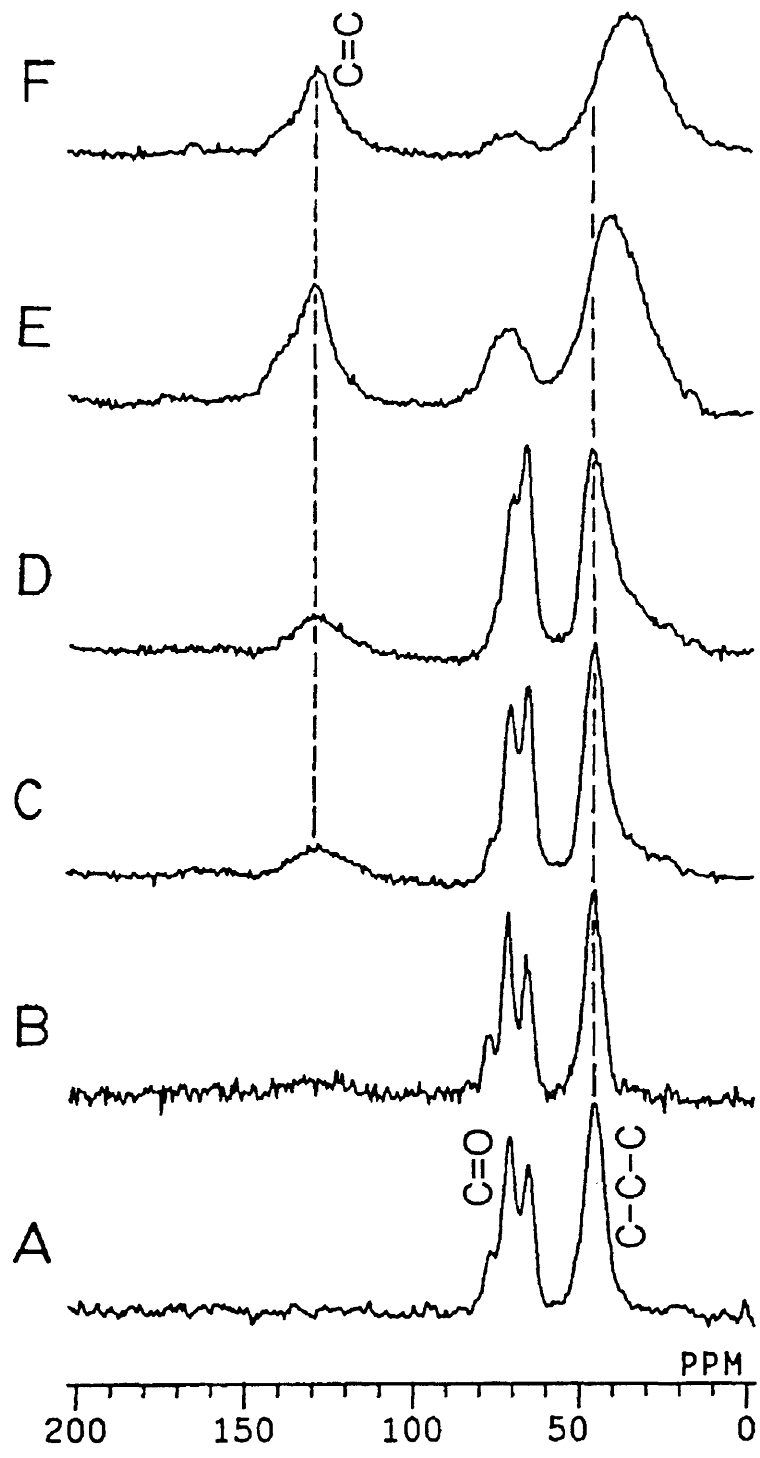


Figure 3. ^{13}C cp-mass NMR Spectra of PVA (A) No heating, (B) 180°C for 1 hr, (C) 215°C for 1 hr, (D) 250°C for 0.5 hr, (E) 250°C for 1 hr, (F) 310°C for 10 min.

EXPERIMENTAL

Description of Samples

The polymer binders investigated in this study were polyethylene glycol PEG 20M (20,000 Daltons), PEG 8M (8,000 Daltons), PVA (10,000 Daltons), Methoxy PEG (5,000 Daltons), and Polyox WSRN80, an 80,000 Dalton polyethylene oxide. The PEG 20M is a double epoxide cross linked polymer made up of two or three PEG 8M units. The 20,000 molecular weight is based on the average of the 16,000 and 24,000 molecular weight macromolecules. Methoxy polyethylene glycol is essentially polyethylene glycol capped with a methyl group, while polyox is a high molecular weight non-crosslinked polyethylene oxide. The polyvinyl alcohol used in this study was manufactured by the hydrolysis of polyvinyl acetate. The manufacturer specifies 99% hydrolysis.

The standard alumina (AD-96-A6) used in this study was produced by mixing aluminum oxide with several different additives to aid in processing the powder. These additives are kaolin, talc, sodium lignosulfonate (marasperse), oleic acid (emsorb), Triton X-100, callozine green, and methylene blue.

Oleic acid is useful as an aid in dry mill processing of the aluminum oxide powder. Kaolin and talc are added because they are additional sources of oxides as they degrade. Other components such as sodium lignosulfonate and Triton X-100 are deflocculants used to facilitate the mixing process. They do this by helping to avoid clumping of the powders as they are wetted and mixed together. Callozine green and methylene blue are added as a color code to identify the type of dry press powder being produced.

Sample Preparation

Binder coated alumina samples were prepared for this investigation at the Coors ceramic plant (Golden, CO). Alumina powder was ball milled, with deflocculant and dyes already added, to ensure uniform mixing and particle size. After the mixture had been milled for a sufficient time, it was drained from the ball mill and placed into a 40 gallon container and stirred to keep the particles in suspension. The slip, or mixture, was then divided into 4 batches for addition of the polymer binders. The first batch was spray dried directly without addition of binder. In the second batch, 2% (20% on solids), polyvinyl alcohol (2% PVA-alumina) was combined with the slip and the resulting mixture was spray dried and screened to -42 mesh. To the third batch, 6% (15% on solids) polyethylene glycol (6% PEG-alumina) was added, and the batch spray dried and screened. The fourth batch had 0.5% (5% on solids) polyvinyl alcohol and 6% (15% on solids) polyethylene glycol (6% PEG- 0.5% PVA-alumina) added 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 were stored in a desiccator to minimize water adsorption before analysis. Powder samples from each batch were analyzed by thermogravimetric/differential thermal analysis (TG/DTA) to determine total loss of binder and other additives to the alumina. The results of these analyses are shown in Table 4. Methoxy PEG and polyox were analyzed by heating the polymer directly.

Table 4. Total Loss on Ignition Weight Loss for Alumina Binder Systems.

System	% Binder
Polyethylene Glycol	7.9 %
Polyvinyl Alcohol	4.3 %
Polyethylene Glycol & Polyvinyl Alcohol	7.9 %

Several samples were subjected to partial thermal degradation to varying weight loss percentages before analysis. These percentages were calculated by taking the ratio of weight loss from the partial thermal degradation and total weight loss determined by TG/DTA for the sample in question. This procedure is referred to in this work as thermal pre-treatment. Table 5 lists sample names used for this investigation and a brief description of the sample analyzed.

Table 5. List of Samples Analyzed in This Work.

Sample	Description
Oleic Acid	(*cis*) 9,10-octadecanoic acid
Marasperse	Sodium Lignosulfonate
Triton X-100	Polyethoxylated 4-(1,1,3,3-tetramethylbutyl)-phenol
PVA0	AD-96-A6 2% Polyvinyl Alcohol-Alumina
PEG0	AD-96-A6 6% Polyethylene Glycol-Alumina
PEG70	AD-96-A6 6% Polyethylene Glycol-Alumina Thermally Pre-Treated to 70% Weight Loss
PEG80	AD-96-A6 6% Polyethylene Glycol-Alumina Thermally Pre-Treated to 80% Weight Loss
STD0	AD-96-A6 0.5% Polyvinyl Alcohol-6% Polyethylene Glycol-Alumina
MPEG	Neat Methoxy Polyethylene Glycol (5000 AMU)
Polyox	Neat Polyox WSR-N-80 80M (80,000 AMU)

Solid State ^{13}C NMR Analysis

The ability to routinely examine carbon atoms in the solid state directly by nuclear magnetic resonance is fairly recent [15, 16, 17]. The ^{13}C atom shows the same spin (½) as does hydrogen, but is only 1.1% abundant as ^{12}C. With the advent of computers and the ability to time average and transform data into the frequency domain by fast fourier transform (FFT) algorithms, ^{13}C analysis became a standard method of analysis of samples with weak NMR signals.

Another important development was the ability to noise decouple the NMR spectra. Noise decoupling removes carbon and hydrogen couplings and the resultant peaks in the spectrum are of non-equivalent carbon atoms, unless they happen to coincide. Solid samples are analyzed by magic angle spinning sample (mass) NMR. This technique is done by spinning the solid sample at kilohertz frequencies at an angle of 54.7° to the poles of the magnet (H_o). This angle is derived from the solution of the partial equation ($3\cos^2\theta$ - 1) where θ is the angle between H_o and the sample axis. At this angle, the proton-carbon dipole interaction is removed. Pressed samples, thermally pre-treated in approximately 20% weight loss intervals, ground into a fine powder, were subjected to cross polarization magic angle spinning sample (cp-mass) ^{13}C NMR analysis.

Thermogravimetric Analysis

Analysis of materials by thermogravimetric/differential thermal analysis (TG/DTA) can provide information about temperatures associated with degradation and weight loss. Other information regarding exothermal and endothermal events, as a function of temperature, can provide clues to the type of reactions that are occurring within the sample. A representative powder sample from each batch was analyzed by TG/DTA for weight loss and thermal events. All samples were analyzed with a Seiko SSC/5200 TG/DTA 320 thermal analysis system.

The neat polymers, methoxy PEG and polyox were analyzed by a method which became available late into the study called auto step-wise TG [18]. The principle behind this method is that by drastically reducing the rate of temperature increase when a decomposition occurs, there will be significantly greater resolution of the thermal event. The auto step-wise method is performed by heating the sample at a constant rate until a mass loss event occurs which is greater than a pre-determined threshold, such as 175 μg/min. The instrument remains in the isothermal hold until the mass change falls to a rate which is less than the exit threshold rate which may be 20 μg/min. The instrument then resumes the original heating rate until the next mass loss occurs. This process is repeated for all mass changes which occur during the experiment. The auto step-wise method is useful for obtaining detailed resolution of thermal events which are close to the same temperature.

Pyrolysis

The decomposition products from the pressed binder-alumina samples were generated using a tube furnace. A diagram of the furnace is shown in Figure 4.

The temperature used for pyrolysis was determined by TG/DTA. A pyrolysis temperature of 500°C was chosen because it was above the temperatures of maximum degradation for both polyethylene glycol and polyvinyl alcohol. For the neat polymers polyox and methoxy polyethylene glycol, a pyrolysis temperature of 450°C was chosen. Air was used as the carrier gas.

Pressed bars weighing approximately 10 g (0.79 g binder) were pyrolyzed by placing them into the heated portion of the furnace. The pyrolysis products were transferred from the furnace through a heated transfer line maintained at 200°C and trapped in impingers filled with methanol cooled in an ice water bath. Polymer powders (methoxy PEG and PEG80M) were analyzed by placing them in the warm end of the quartz tube and allowing the polymer to melt and degas. After melting and degassing the samples were moved to the heated area of the tube and pyrolyzed.

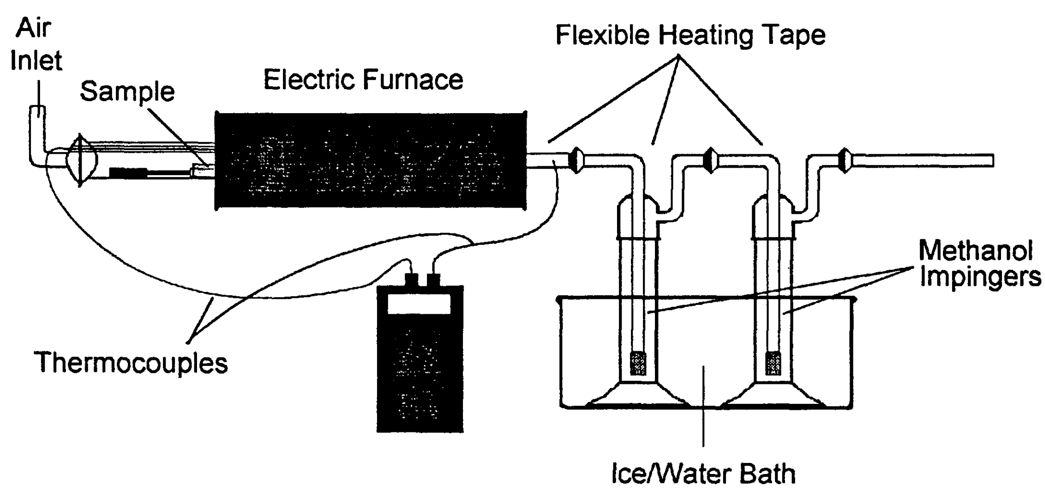


Figure 4. Tube Furnace and Impinger Setup for Pyrolysis.

After cooling, methanol was used to rinse the transfer line. These rinses were combined with the impinger methanol and the collected products were evaporated to concentrate the samples. The last few ml (approximately 5 ml) of the methanol solution was then placed in a vial with a teflon lined cap. The methanol was further evaporated by gently blowing argon into the mouth of the vial until there was approximately 0.5 ml remaining which was stored in the freezer. After collection, the concentrated 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® shown in Figure 5. The trap was cooled in a dry ice-methanol bath. The volatile products from pyrolysis were trapped by pulling the hot gases through the U-tube at 1 L/min per minute for 10 minutes. This was accomplished by using a small vacuum pump with a flow restrictor limiting the flow to 1 L/min.

The U-tube was connected to the transfer line and the vacuum pump with Cajon fittings. This was done for ease of removal from the trapping unit and installation on the desorbing unit shown in Figure 6.

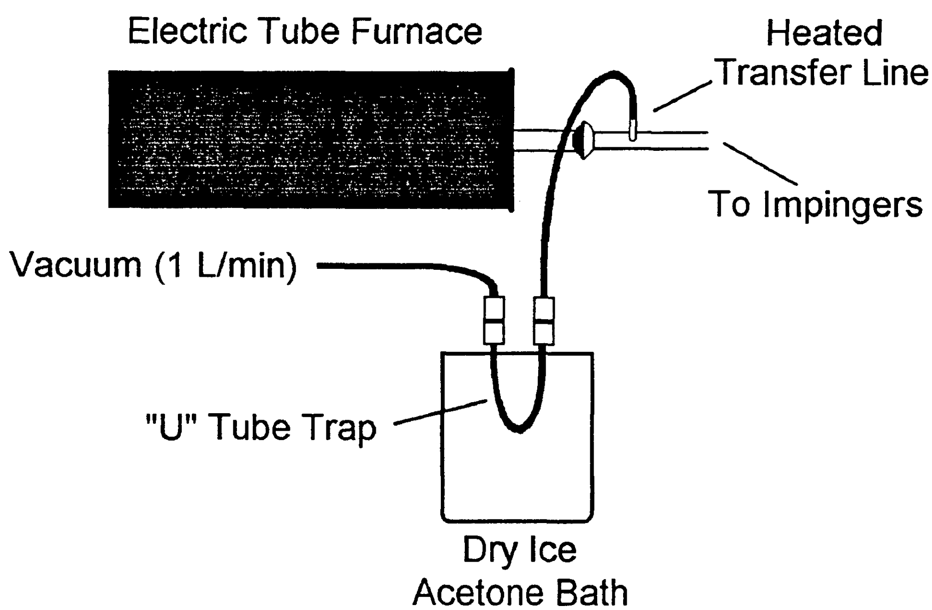


Figure 5. Pyrolysis Tube Furnace Setup for Cryotrapping of Volatile Products.

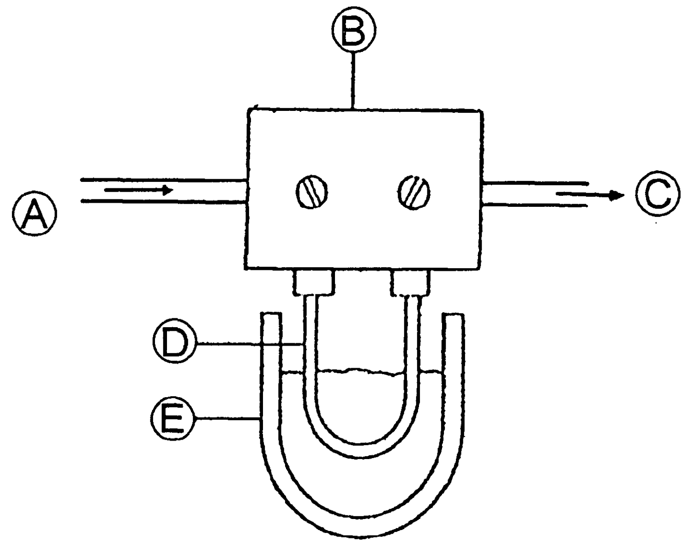


Figure 6. Thermal Desorption Unit. (A) Carrier Gas (B) Interface (C) U-tube Trap (D) Coolant or Heat Source for Adsorption or Desorption (E) Effluent to GC.

Product Analysis

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

C_1 to C_6 volatile product analysis:

Injector- 250°C; Column- 1% SP2100 on Carbopak C; Flow- 40 ml per min; 30°C 2 min; 10°C per min to 230°C; 20 min hold.

C_6 and greater volatile product analysis

Injector- 250°C; Split- 10:1, 1:30 delay; Column- DB5, 0.32 mm id x 30m, 0.25 µm film thickness; Flow 40 cm/sec; Initial temp- 35°C, 2 min; 6°C/min to 280°C, 5 min hold.

Mass spectrometer conditions were:

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/sec; Run time 48 min.

RESULTS AND DISCUSSION

Polyethylene Glycol

Thermal Analysis:

Thermogravimetric/differential thermal analysis (TG/DTA) provides information concerning heat loss or gain, and weight loss information in relation to the temperature of a thermal event. This information is useful to help determine what type of reactions are occurring in the sample analyzed. Analysis of oleic acid, Triton X-100, and sodium lignosulfonate was done by TG/DTA.

The thermal degradation of oleic acid in air at a rate of 20°C/min, shown in Figure 7 indicates that oleic acid begins to lose weight at 274°C with approximately 79% weight loss by 313°C. This weight loss is associated with an endotherm indicating the oleic acid is evaporating. At 313°C, a weight loss of 14% with a corresponding exotherm was seen. There is a further weight loss of 7% beginning at 350°C and ending at 650°C.

The TG/DTA, in air with a 20°C/min heating rate, of Triton X-100 represented in Figure 8 begins to degrade at 349°C with maximum degradation at 392°C and complete weight loss by 475°C. There was no apparent char formation and smooth continuous weight loss throughout the experiment.

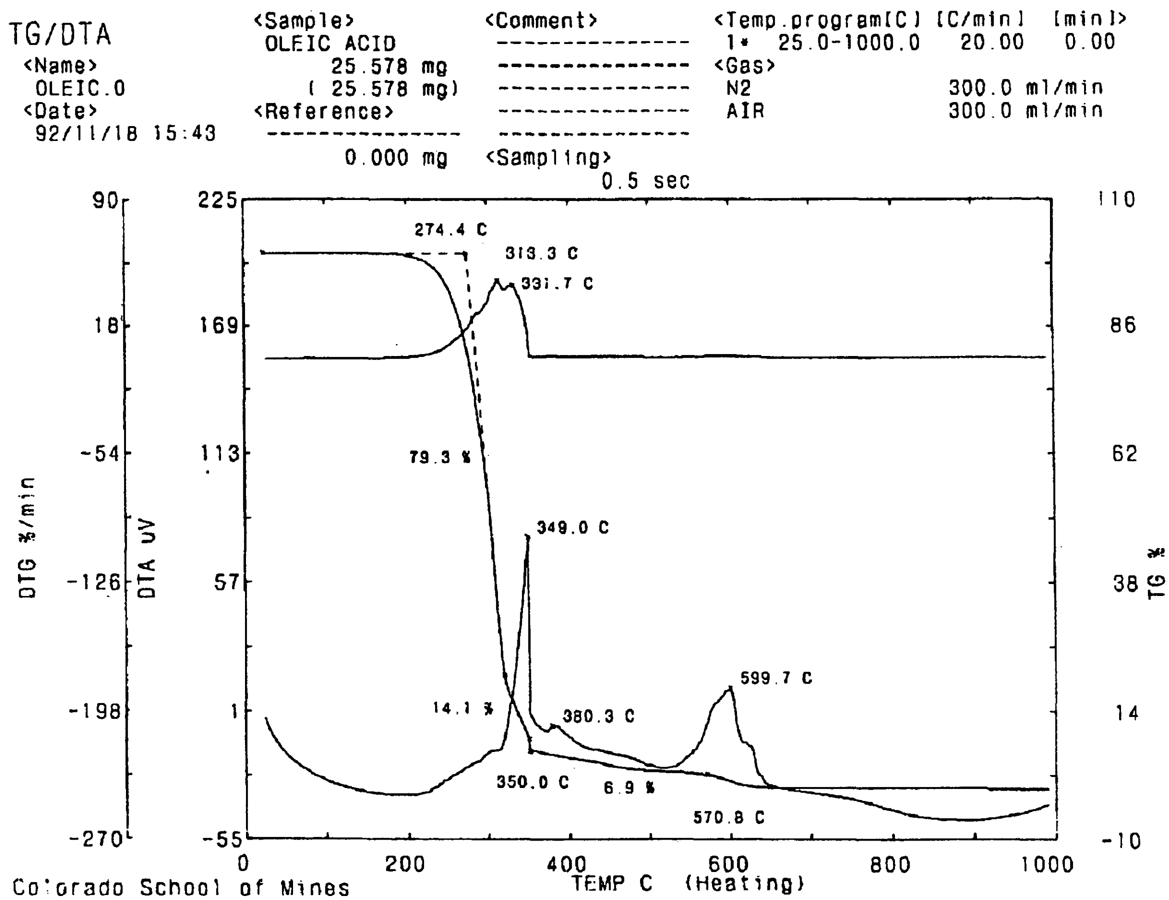


Figure 7. TG/DTA of Oleic Acid in Air With a 20°C Heating Rate.

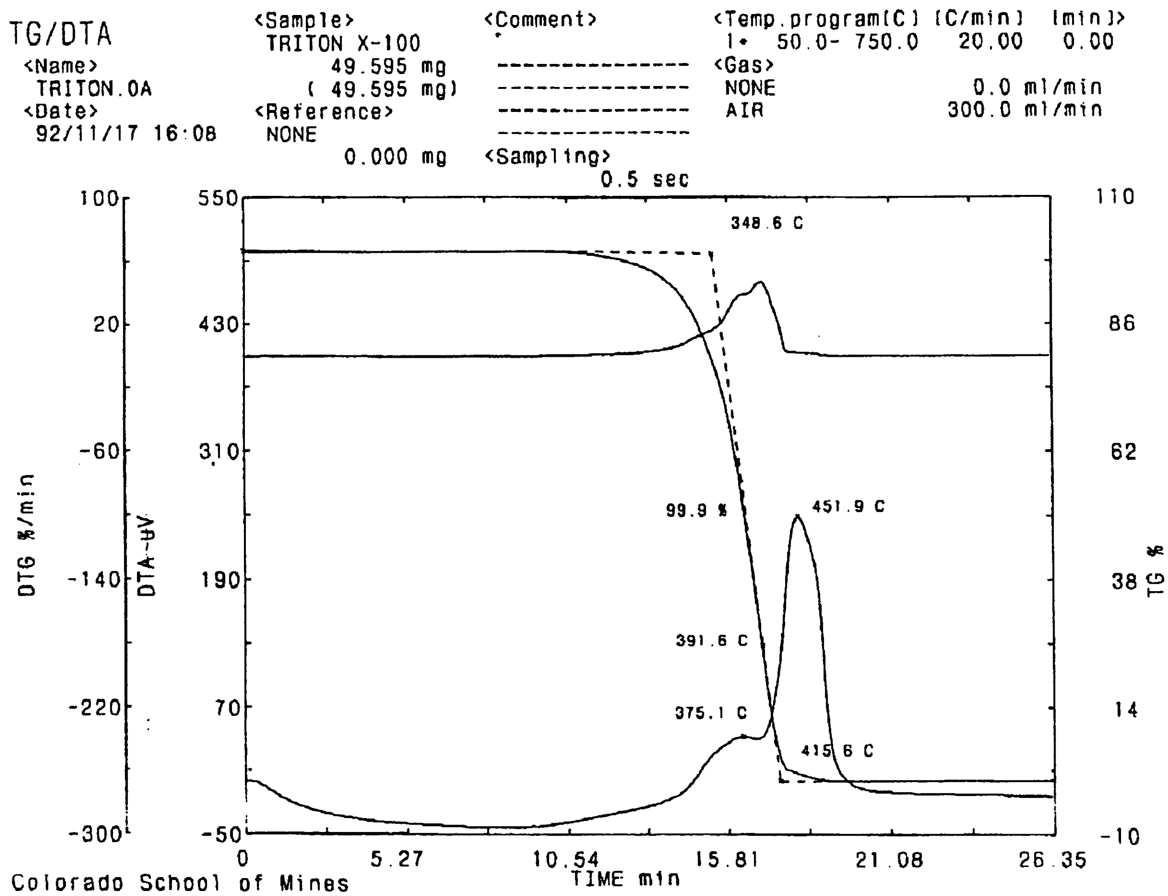


Figure 8. TG/DTA of Triton X-100 in Air With a 20°C Heating Rate.

The sodium lignosulfonate examined by TG/DTA in air with a heating rate of 20°C/min shown in Figure 9 had a 6% weight loss of water by 150 °C. A further weight loss, which began at 240°C and ended at 340°C, of 18% with a related exotherm was also observed. There was then a continuing weight loss of 8% from 340°C to 390°C with an associated exotherm. A gradual weight loss of 8% from 400°C to 800°C was also observed with an exotherm at 610°C. The exotherm at 610°C is believed to be associated with loss of the carbon char. Past 800°C there was a sharp increase in the rate of degradation with a 46% weight loss and two associated exotherms at 843°C and 951°C. This is believed to be due to loss of the inorganic fraction and subsequent crystallization of the sodium salt.

Examination of the thermogravimetric data seems to indicate that the final component to undergo complete thermal degradation in the ceramic piece is the sodium lignosulfonate. All other additives cleanly degraded with little char formation.

Thermogravimetric/differential thermal analysis of polyethylene glycol, added as 6% polymer to standard alumina, with a heating rate of 20°C/min in air is represented by Figure 10. There is a small endotherm at 90°C possibly associated with the melting point of the polymer. There was also a rapid weight loss beginning at 238°C which may be associated with the initiation of the thermal degradation of the polyethylene glycol. The temperature of maximum degradation was at 253°C. There was also a large exotherm associated with this weight loss.

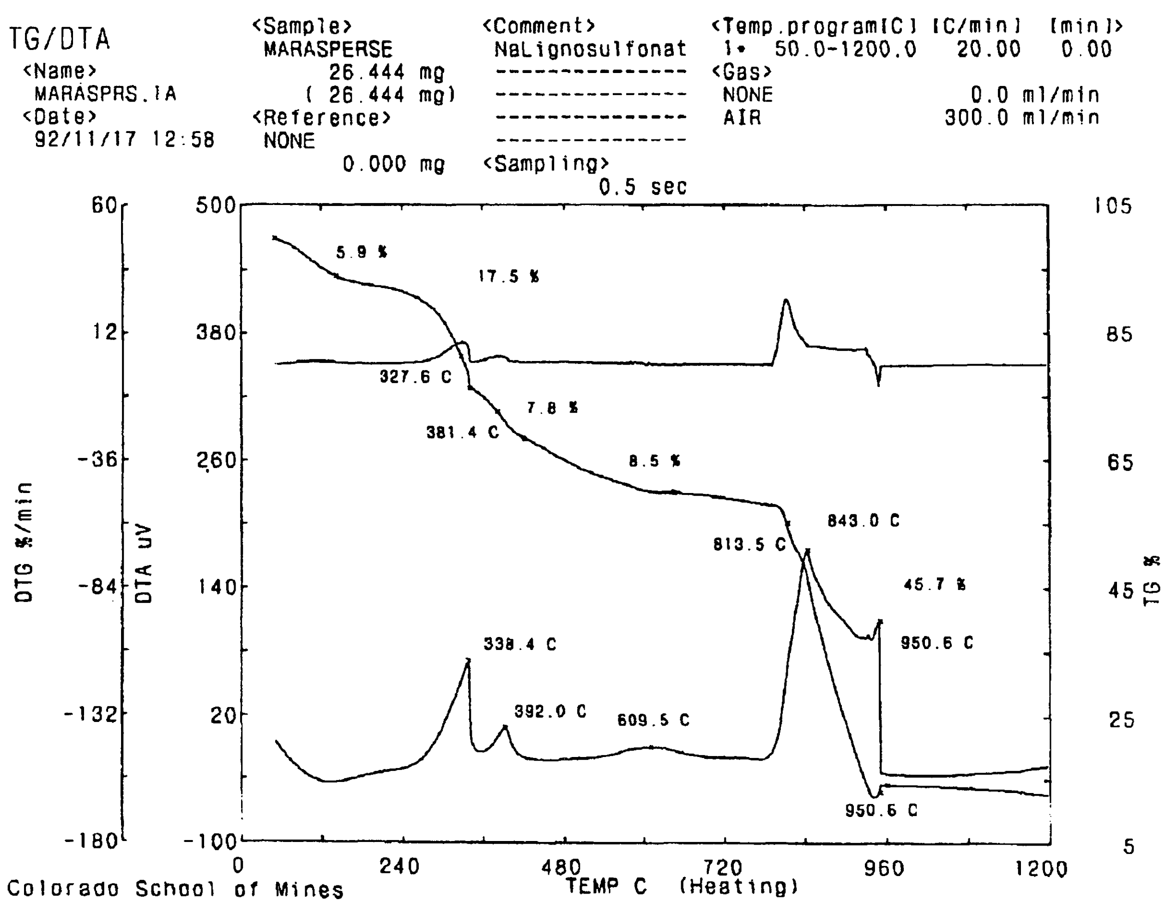


Figure 9. TG/DTA of Sodium Lignosulfonate in Air With a 20°C Heating Rate.

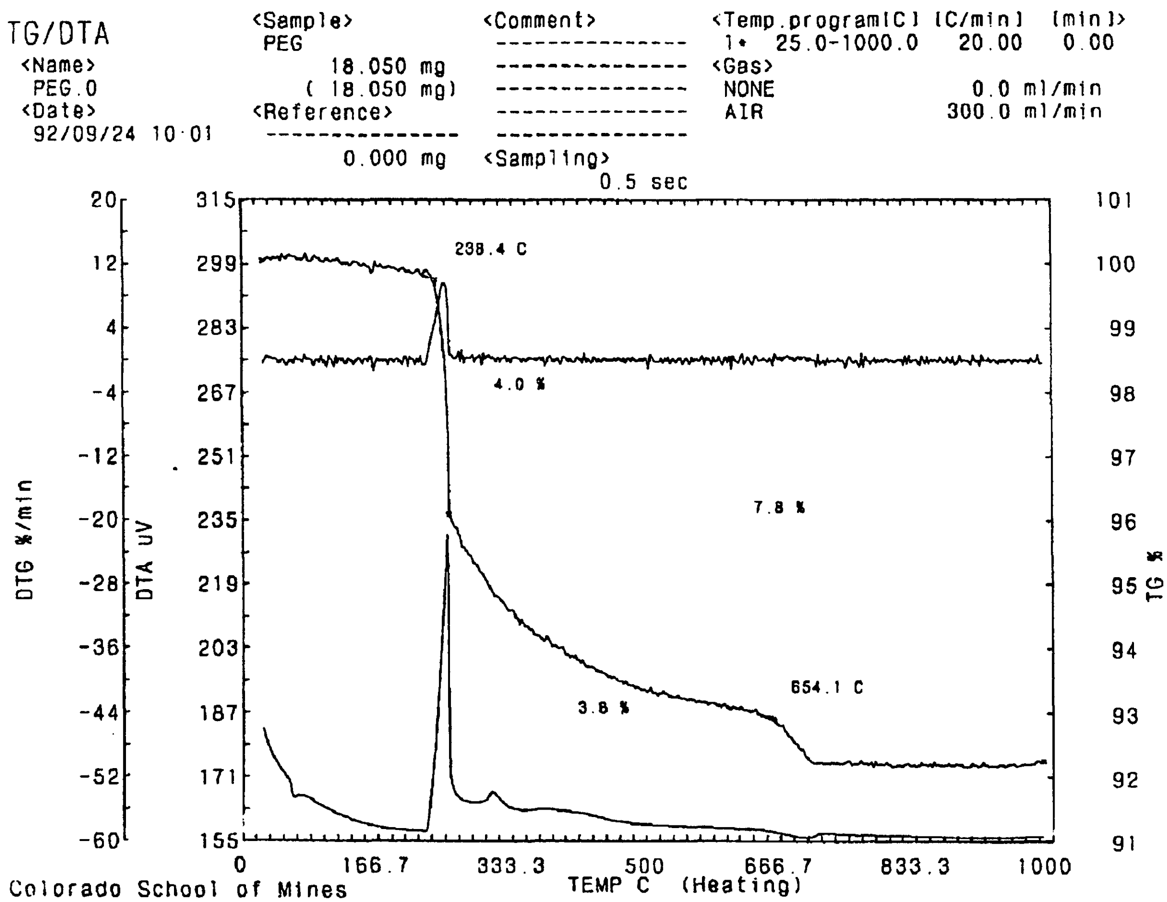


Figure 10. TG/DTA of 6% PEG-Alumina in Air With a 20°C Heating Rate.

At the completion of the initial 4% weight loss and accompanying thermal event, there was a gradual weight loss from 267°C to 654°C where the rate of degradation increased. The weight loss over the 267°C to 700°C temperature range was 3.8%. A small endotherm associated with this weight loss was also observed. This weight loss could be associated with the degradation the deflocculants in the alumina. The total weight loss for this sample was 7.9%

Further investigation of a sample of PEG-alumina thermally pre-treated to have an 80% weight loss, was analyzed by TG/DTA in air with a 20°C/min heating rate. The representation of the TG/DTA shown in Figure 11 indicates that there was an initial weight loss and endotherm corresponding to the loss of water and instrumental startup. The weight loss from 250°C to 750°C may be associated with the thermal degradation of standard alumina additives. To demonstrate that there is no influence due to the PEG in the system for the degradation products stable above 500°C the deflocculant-alumina system without PEG was analyzed by TG/DTA and is represented in Figure 12. The thermal profiles from 80% weight loss PEG-alumina and deflocculant-alumina are very similar. This seems to provide evidence that by 80% weight loss, there is very little PEG remaining in the sample.

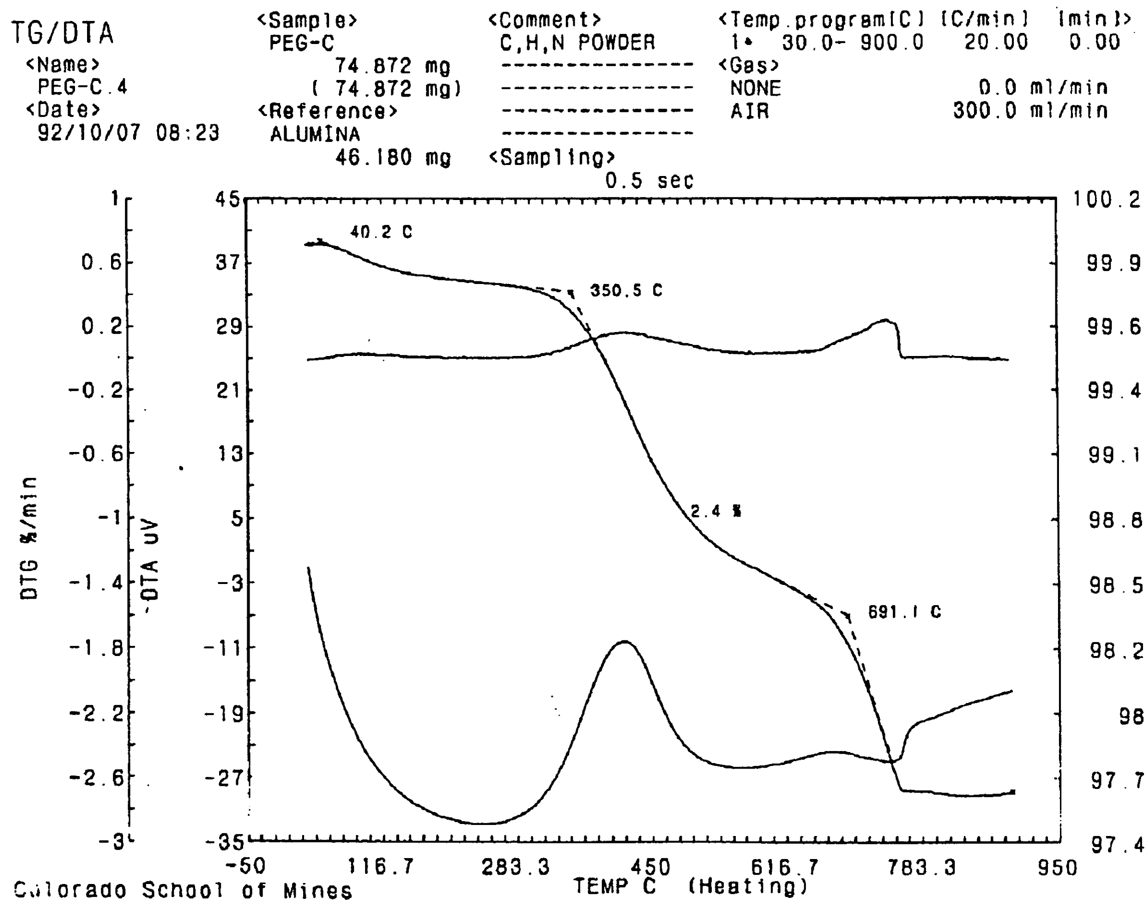


Figure 11. TG/DTA of 6% PEG-Alumina Thermally Pre-Treated to 80% Weight Loss in Air With a 20°C Heating Rate

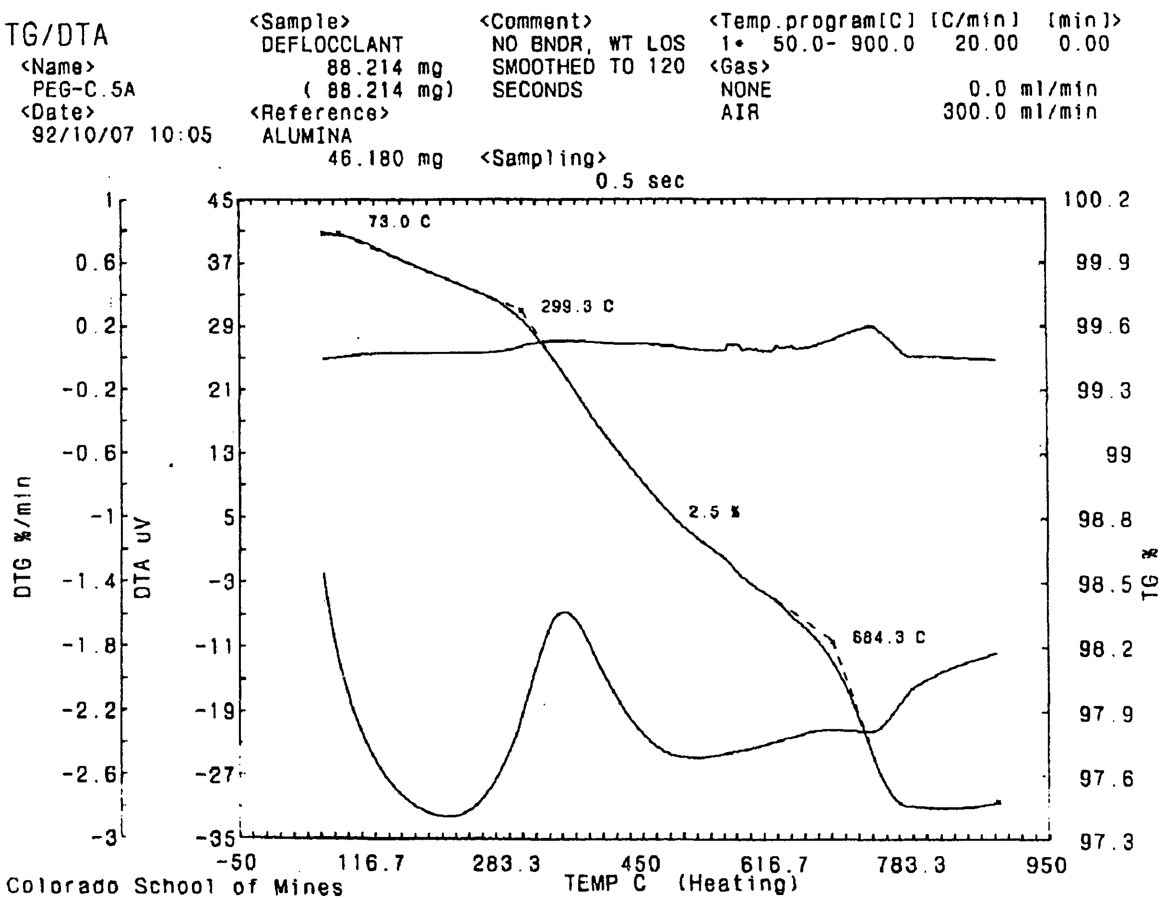


Figure 12. TG/DTA of Deflocculant-Alumina in Air With a 20°C Heating Rate.

Volatile Product Analysis

Cryotrapping and GC/MS of the volatile products in the range of C_1 to C_6 carbons was done on 6% PEG-alumina samples pyrolyzed at 450°C in air. The total ion chromatogram (TIC) for PEG-alumina is shown in Figure 13. Analysis of the volatile products from the thermally pre-treated 60% weight loss is represented by the TIC in Figure 14 and the thermally pre-treated 80% weight loss TIC is seen in Figure 15.

The products identified from the PEG-alumina GC/MS analysis are listed in Table 6. They represent the low molecular weight degradation products that are to be expected from the pyrolysis of polyethylene glycol. The methylene chloride identified is not a degradation product but a laboratory contaminant.

Analysis of the PEG-alumina sample thermally pre-treated to 60% weight loss with identification of the degradation products is shown in Table 7. The intensity of the peaks in the TIC at this level of thermal pre-treatment is less than that observed for the PEG-alumina sample. However, the product distribution remains consistent with that seen for the PEG-alumina analysis.

At 80% thermal pre-treatment weight loss, there is a reduction in the number and intensity of peaks present in the TIC. This is consistent with other information which shows that by approximately 70% weight loss there is very little original polymer left in the ceramic piece. Degradation of the Triton X-100 surfactant, which is polyethylene glycol based, may also be a source of degradation products. The products identified are shown in Table 8 and represent polyethylene glycol degradation products.

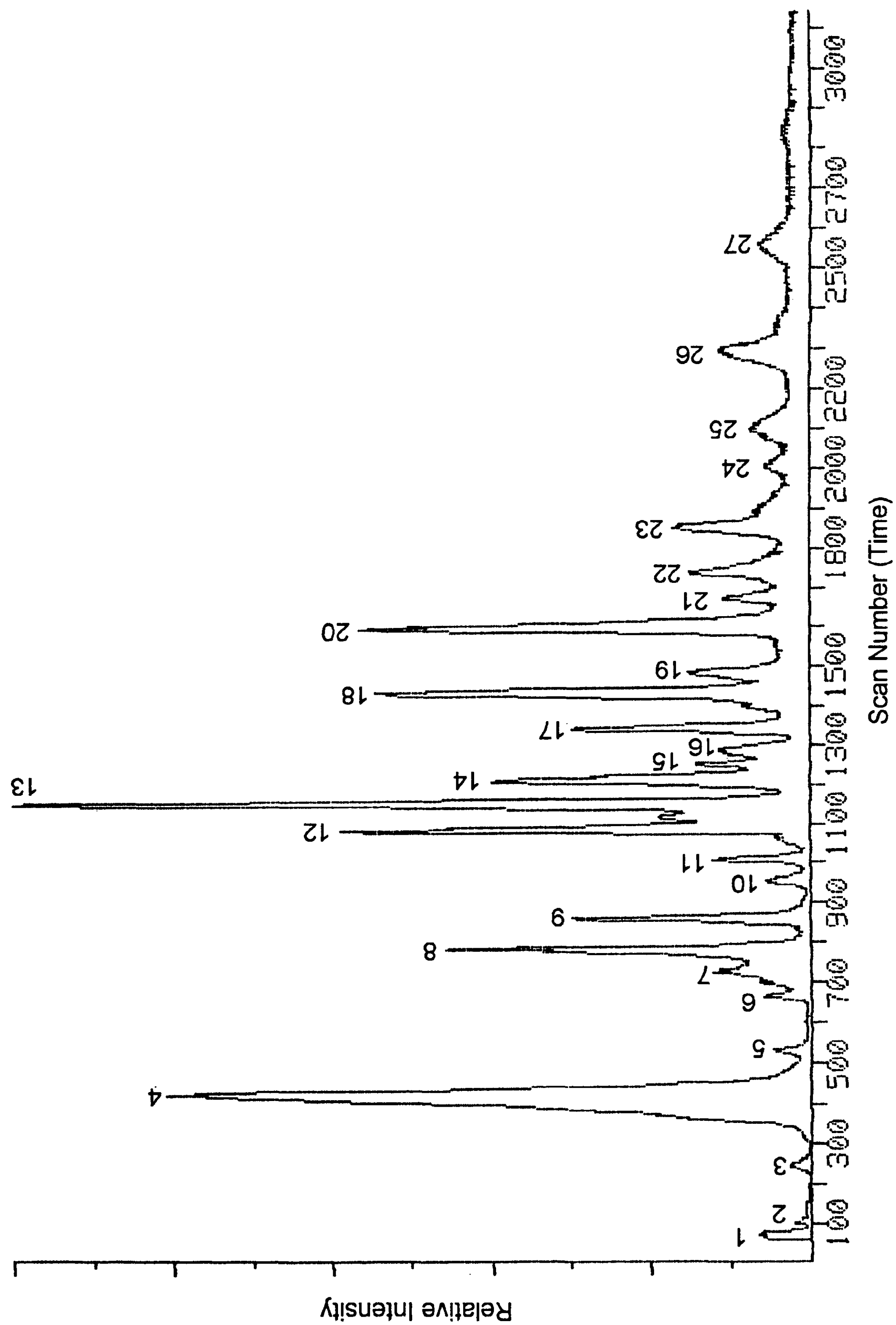


Figure 13. 6% PEG-Alumina Cryotrapped GC/MS Chromatogram.

Table 6. 6% PEG-Alumina Cryotrapped Products.

Peak	Compound Name	Formula
1	Air	
2	Carbon dioxide	CO_2
3	Methylene chloride	CH_3Cl
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)-	$C_6H_{14}O_3$

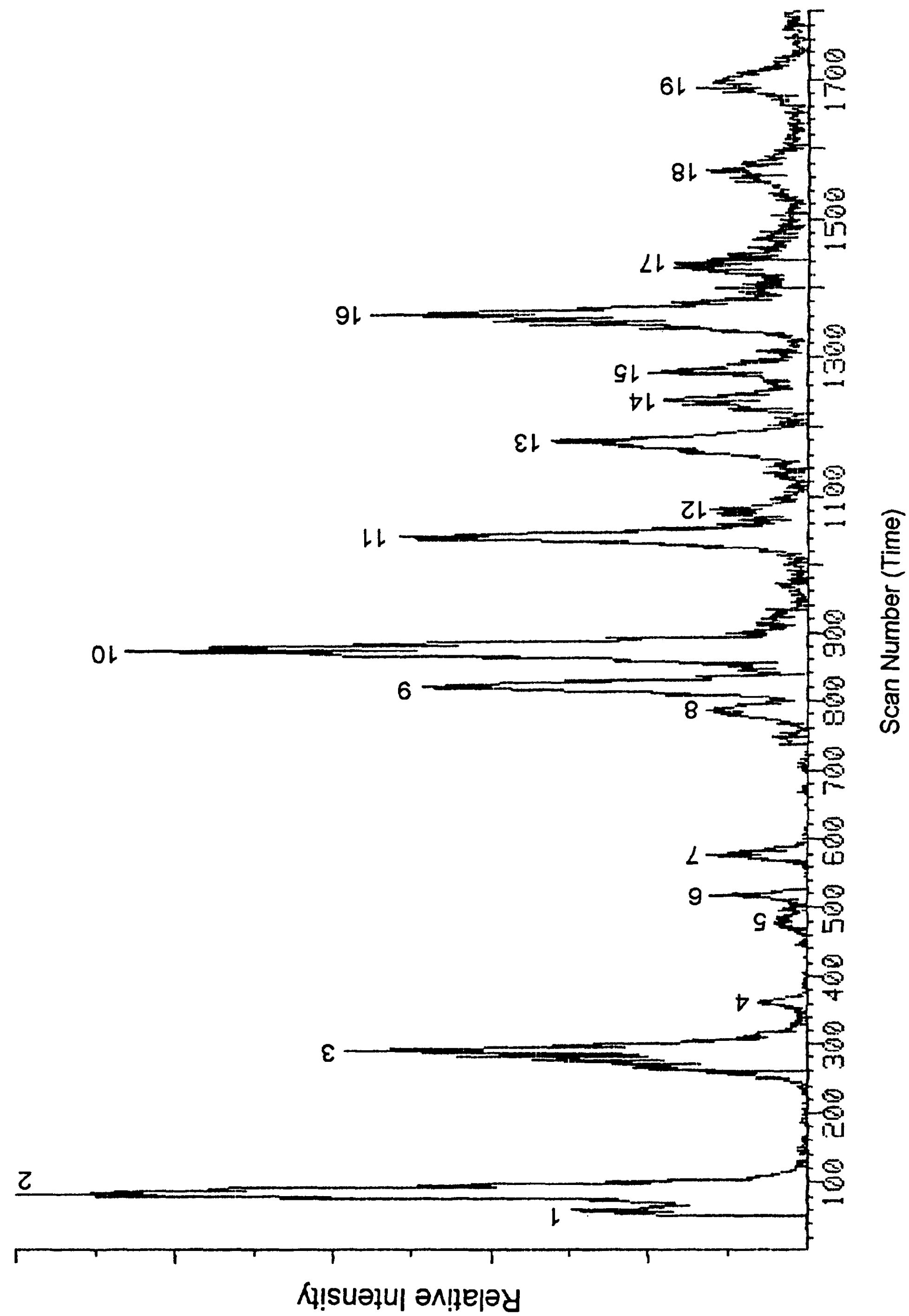


Figure 14. 6% PEG-Alumina Thermally Pre-Treated to 60% Weight Loss Cryotrapped GC/MS Chromatogram.

Table 7. 6% PEG-Alumina Thermally Pre-Treated to 60% Weight Loss Cryotrapped Products.

Peak	Compound Name	Formula
1	Air	
2	Carbon dioxide	CO_2
3	Ethylene oxide	C_2H_4O
4	1,2 Ethanediol monoformate	$C_3H_6O_3$
5	Ethene methoxy	C_3H_6O
6	1,3-Dioxolane	$C_3H_6O_2$
7	Unknown	
8	2-Methyl, 1,3-dioxolane	$C_4H_8O_2$
9	1,4-Dioxane	$C_4H_8O_2$
10	1,2-Ethanediol, diformate	$C_4H_6O_4$
11	1,2-Ethanediol, monoacetate	$C_4H_8O_3$
12	1.3-Dioxolane, 2-methoxy-	$C_4H_8O_3$
13	Unknown	
14	Unknown	
15	Diethylene glycol	$C_4H_{10}O_3$
16	Ethanol, 2-(2-methoxyethoxy)	$C_5H_{12}O_3$
17	Unknown	
18	Unknown	
19	Ethanol 2-(2-ethoxyethoxy)-	$C_6H_{14}O_3$

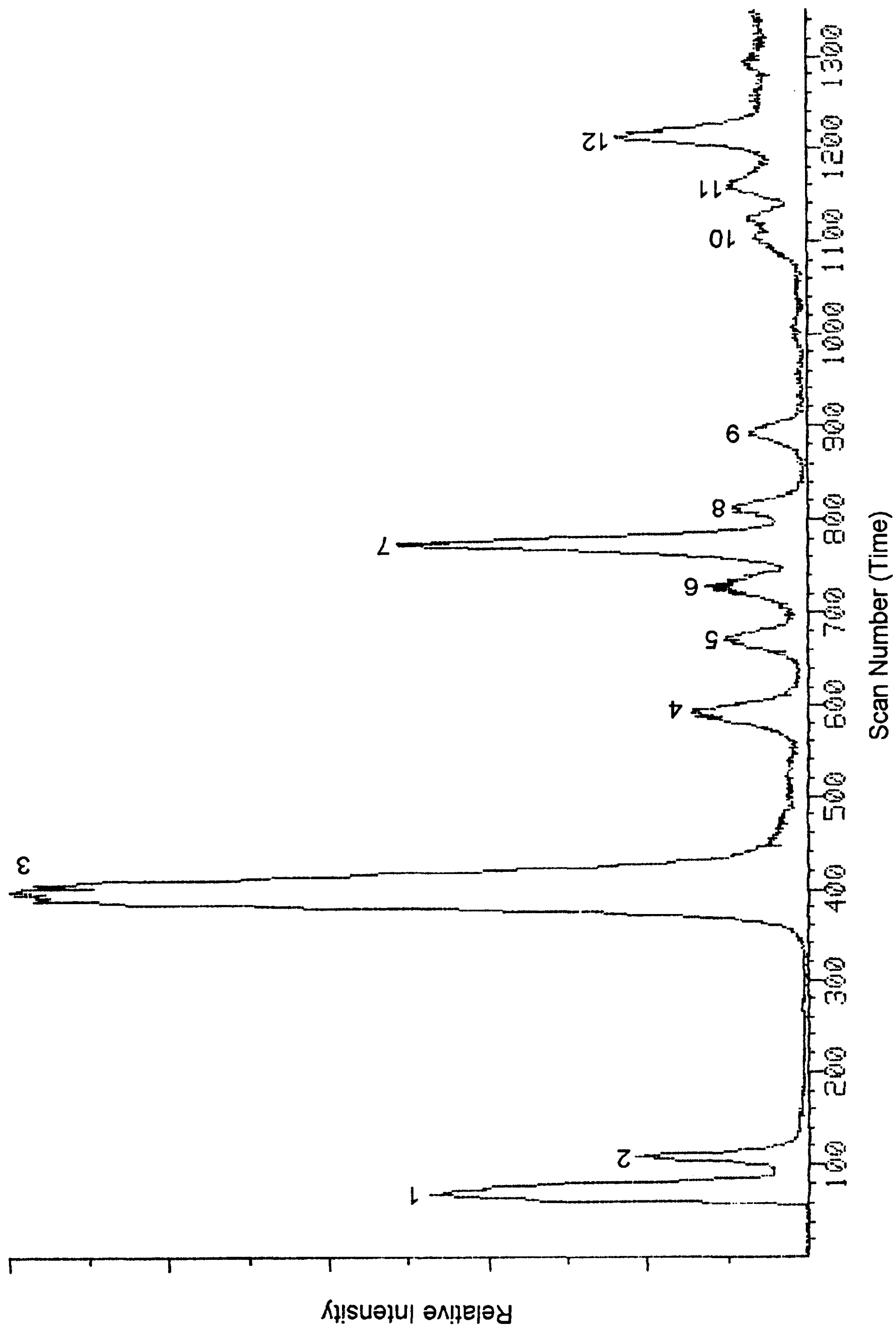


Figure 15. 6% PEG-Alumina Thermally Pre-Treated to 80% Weight Loss Cryotrapped GC/MS Chromatogram.

Table 8. 6% PEG-Alumina Thermally Pre-Treated to 80% Weight Loss Cryotrapped Products.

Peak	Compound Name	Formula
1	Air	
2	Carbon dioxide	CO_2
3	Ethylene oxide	C_2H_4O
4	Acetonitrile	C_2H_4N
5	Ethene methoxy	C_3H_6O
6	Ethane methoxy	C_3H_8O
7	Furan	C_4H_4O
8	Ethene ethoxy	C_4H_8O
9	Unknown	
10	Unknown	
11	2-Methyl, 1,3-dioxolane	$C_4H_8O_2$
12	1,4-Dioxane	$C_4H_8O_2$
13	Unknown	
14	Diethylene glycol	$C_4H_{10}O_3$

The intensity of the peaks in the TIC for the PEG-alumina, 60%, and 80% thermally pre-treated samples show a decrease in intensity for the degradation products as the amount of polymer present at the time of pyrolysis decreases. This provides evidence for a thermal degradation mechanism where the polymer continues to readily degrade into smaller volatile pieces which can escape the alumina binder system.

Analysis of the deflocculant by cryotrapping the volatile products and subsequent GC/MS investigation (Figure 16), shows a distribution of products similar to that observed for PEG-alumina thermally pre-treated to an 80% weight loss. This is in correlation with the TG/DTA thermal profiles which compare PEG-alumina to the 80% thermal pre-treatment weight loss and the deflocculant-alumina system. The identified deflocculant volatile products are in Table 9. It appears that by 80% thermal pre-treatment weight loss, that the sample is mostly the remaining deflocculant system. Specifically the degradation products could be coming from the Triton X-100 which is a polyethoxylated 4-(1,1,3,3-tetramethylbutyl) phenol surfactant.

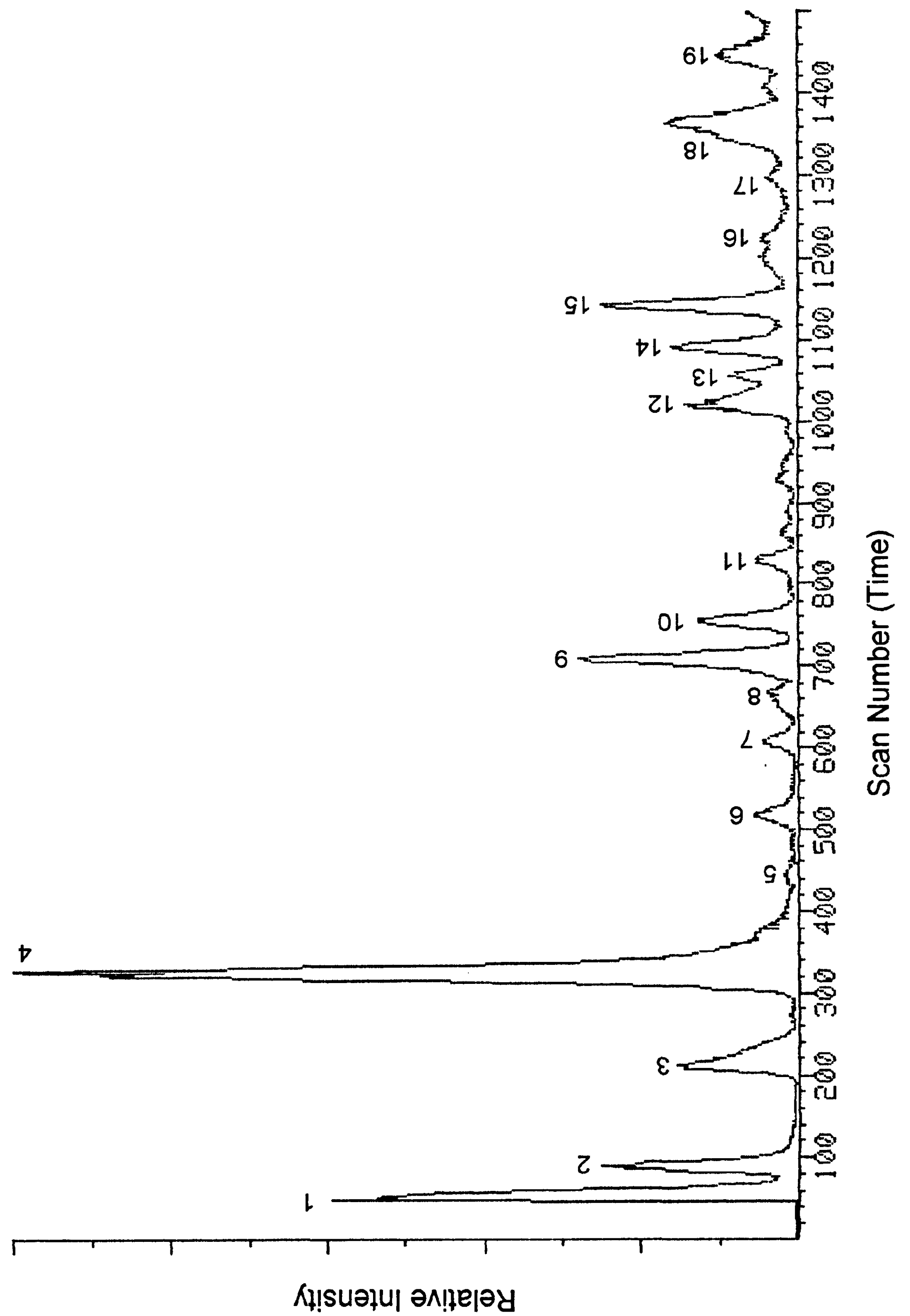


Figure 16. Cryotrapped Deflocculant-Alumina GC/MS Chromatogram.

Table 9. Deflocculant-Alumina Cryotrapped Products.

Peak	Compound Name	Formula
1	Air	
2	Carbon dioxide	CO_2
3	Methyl chloride	CH_3Cl
4	Ethylene oxide	C_2H_4O
5	Urea	CH_4N_2O
6	Methyl isocyanoate	C_2H_3N
7	Unknown	
8	Unknown	
9	Unknown	
10	Furan	C_4H_4O
11	1,3-Dioxolane	$C_3H_6O_2$
12	Unknown	
13	Unknown	
14	2-Methyl, 1,3-dioxolane	$C_4H_8O_2$
15	1,4-Dioxane	$C_4H_8O_2$
16	2-Butenal	C_4H_6O
17	Unknown	
18	Benzene	C_6H_6
19	Unknown	

Semivolatile Product Analysis

Analysis of pressed powder samples pyrolyzed in air indicated that the degradation of 6% PEG-alumina (PEG 20M) is essentially the same as for neat PEG8M. The product distribution of homologous compounds as seen in Figure 17 is very similar to that reported by Baugh [9] which is presented in Figure 18 for his PEG8M results.

The thermal degradation products, observed by Baugh [9], for pyrolysis of pure PEG8M in nitrogen were also found in this study for PEG-alumina pyrolyzed in air. The results of the analysis are shown in Table 10. Pyrolysis GC/MS of 6% PEG-alumina which was thermally pre-treated to a 70% weight loss, is represented by the TIC in Figure 19. The identified products show a product distribution that is the same as for samples without any pre-pyrolysis thermal treatment and are shown in Table 11. The silicon compound, identified as peak 2 in Table 11, is a contaminant possibly from surfactant or the GC column or septum. There were no detectable semivolatile products from the pyrolysis of PEG-alumina samples thermally pre-treated to 80% weight loss. Several attempts were made to isolate the degradation products from this level of thermal pre-treatment without success.

The results of the experiments done in this study indicate that the PEG major products are produced independent of the presence of alumina. It also indicates that the PEG8M and PEG20M degrade in a similar fashion regardless of the atmosphere in which they are subjected.

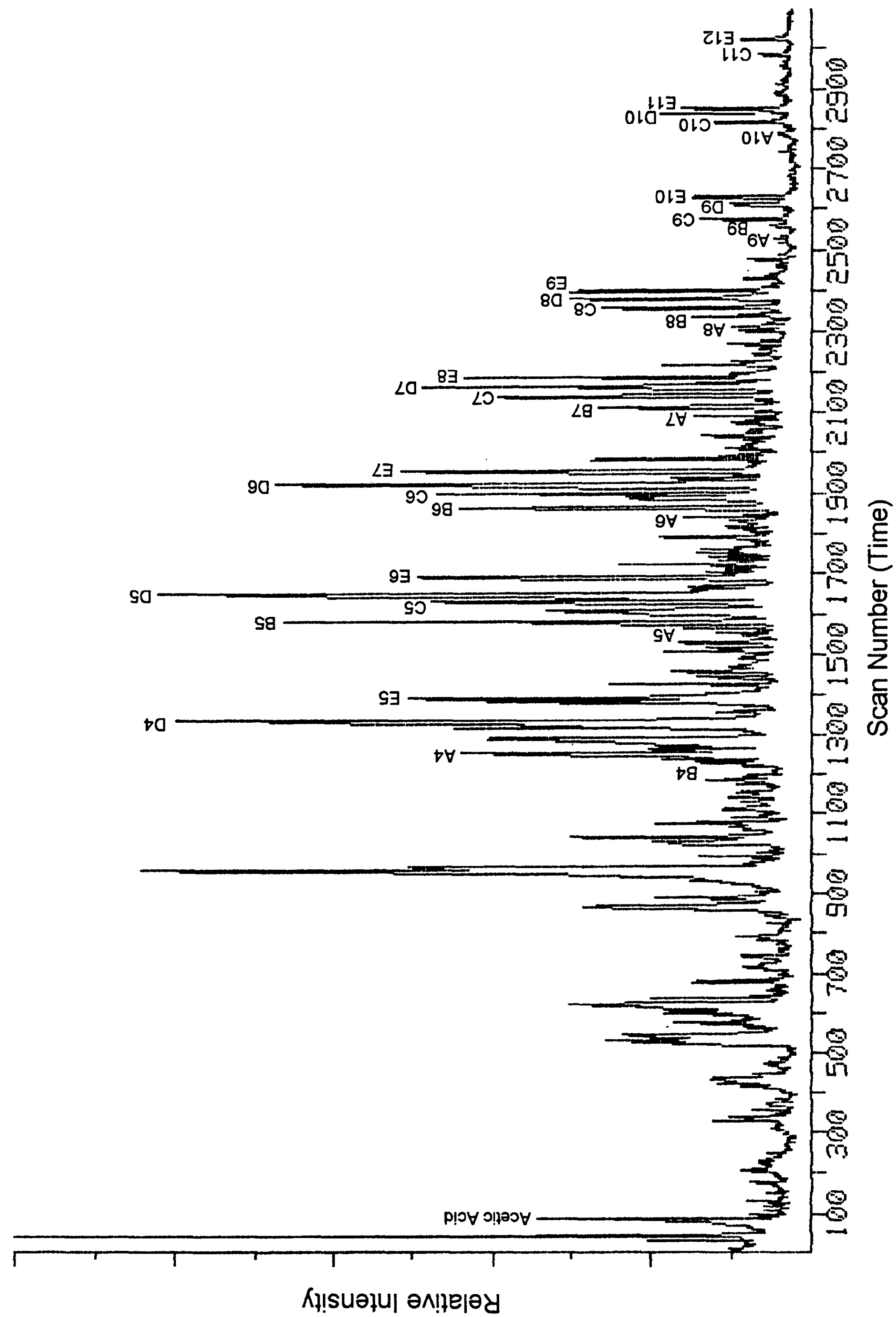


Figure 17. 6% PEG-Alumina (20,000 Dalton) Pyrolyzed at 500°C in Air.

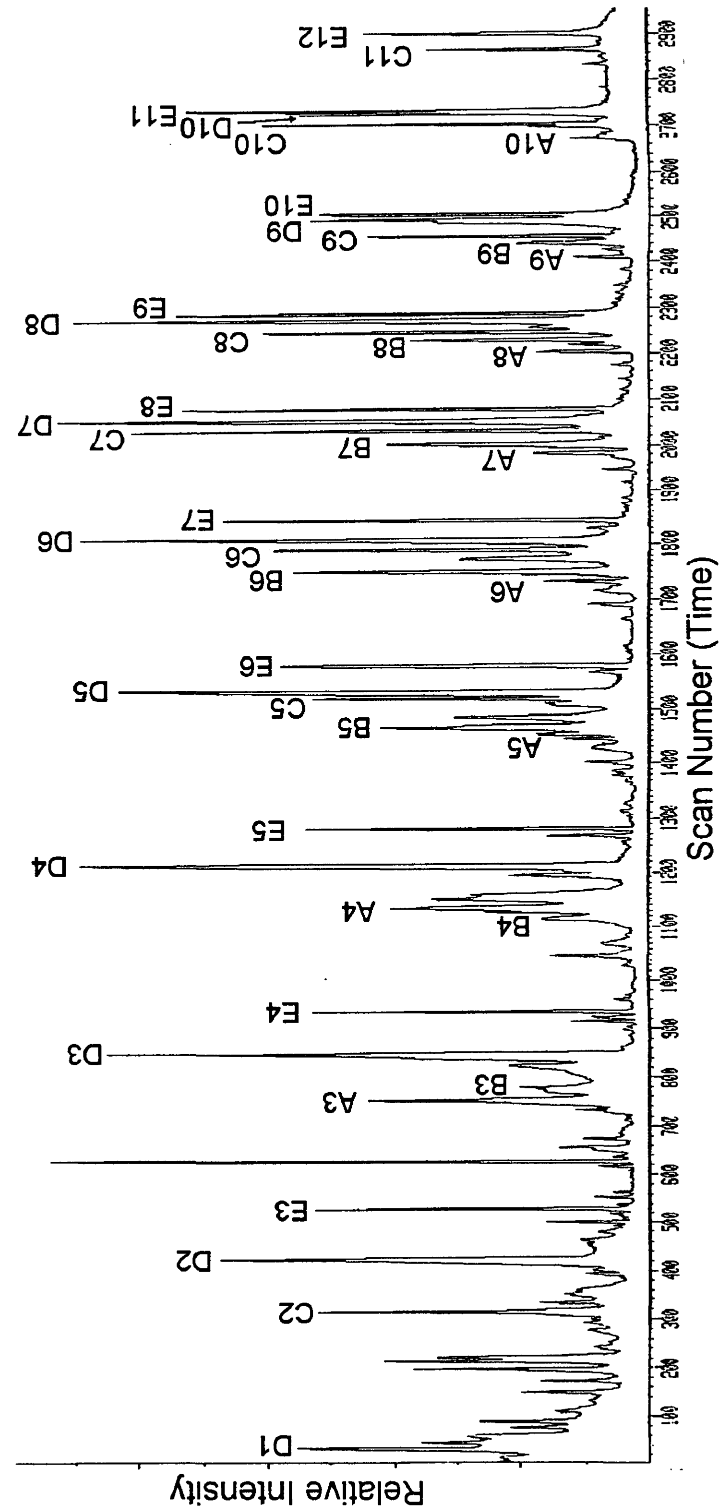


Figure 18. 6% PEG (8,000 Dalton) Neat Polymer Pyrolyzed at 450°C in Nitrogen.

Table 10. 6% PEG-Alumina Pyrolysis Products.

LABEL GIVEN	COMPOUND FORMULA	MOLECULAR WEIGHT
A4	CH_3-O(CH_2-CH_2-O)$_3$-CH_2-CH_2-OH	208
A5	CH_3-O(CH_2-CH_2-O)$_4$-CH_2-CH_2-OH	252
A6	CH_3-O(CH_2-CH_2-O)$_5$-CH_2-CH_2-OH	296
A7	CH_3-O(CH_2-CH_2-O)$_6$-CH_2-CH_2-OH	340
A8	CH_3-O(CH_2-CH_2-O)$_7$-CH_2-CH_2-OH	384
A9	CH_3-O(CH_2-CH_2-O)$_8$-CH_2-CH_2-OH	428
A10	CH_3-O(CH_2-CH_2-O)$_9$-CH_2-CH_2-OH	472
B4	O=CH-CH_2(O-CH_2-CH_2)$_3$-O-CH_2-CH_3	220
B5	O=CH-CH_2(O-CH_2-CH_2)$_4$-O-CH_2-CH_3	264
B6	O=CH-CH_2(O-CH_2-CH_2)$_5$-O-CH_2-CH_3	308
B7	O=CH-CH_2(O-CH_2-CH_2)$_6$-O-CH_2-CH_3	352
B8	O=CH-CH_2(O-CH_2-CH_2)$_7$-O-CH_2-CH_3	396
B9	O=CH-CH_2(O-CH_2-CH_2)$_8$-O-CH_2-CH_3	440
C5	CH_3-O(CH_2-CH_2-O)$_4$-CH_2-CH_3	236
C6	CH_3-O(CH_2-CH_2-O)$_5$-CH_2-CH_3	280
C7	CH_3-O(CH_2-CH_2-O)$_6$-CH_2-CH_3	324
C8	CH_3-O(CH_2-CH_2-O)$_7$-CH_2-CH_3	368
C9	CH_3-O(CH_2-CH_2-O)$_8$-CH_2-CH_3	412
C10	CH_3-O(CH_2-CH_2-O)$_9$-CH_2-CH_3	456
C11	CH_3-O(CH_2-CH_2-O)$_{10}$-CH_2-CH_3	500
D4	CH_3-CH_2-O(CH_2-CH_2-O)$_3$-CH_2-CH_2-OH	222
D5	CH_3-CH_2-O(CH_2-CH_2-O)$_4$-CH_2-CH_2-OH	266
D6	CH_3-CH_2-O(CH_2-CH_2-O)$_5$-CH_2-CH_2-OH	310
D7	CH_3-CH_2-O(CH_2-CH_2-O)$_6$-CH_2-CH_2-OH	354
D8	CH_3-CH_2-O(CH_2-CH_2-O)$_7$-CH_2-CH_2-OH	398
D9	CH_3-CH_2-O(CH_2-CH_2-O)$_8$-CH_2-CH_2-OH	442
D10	CH_3-CH_2-O(CH_2-CH_2-O)$_9$-CH_2-CH_2-OH	486
E5	CH_3-CH_2-O(CH_2-CH_2-O)$_4$-CH_2-CH_3	250
E6	CH_3-CH_2-O(CH_2-CH_2-O)$_5$-CH_2-CH_3	294
E7	CH_3-CH_2-O(CH_2-CH_2-O)$_6$-CH_2-CH_3	338
E8	CH_3-CH_2-O(CH_2-CH_2-O)$_7$-CH_2-CH_3	382
E9	CH_3-CH_2-O(CH_2-CH_2-O)$_8$-CH_2-CH_3	426
E10	CH_3-CH_2-O(CH_2-CH_2-O)$_9$-CH_2-CH_3	470
E11	CH_3-CH_2-O(CH_2-CH_2-O)$_{10}$-CH_2-CH_3	514
E12	CH_3-CH_2-O(CH_2-CH_2-O)$_{11}$-CH_2-CH_3	558

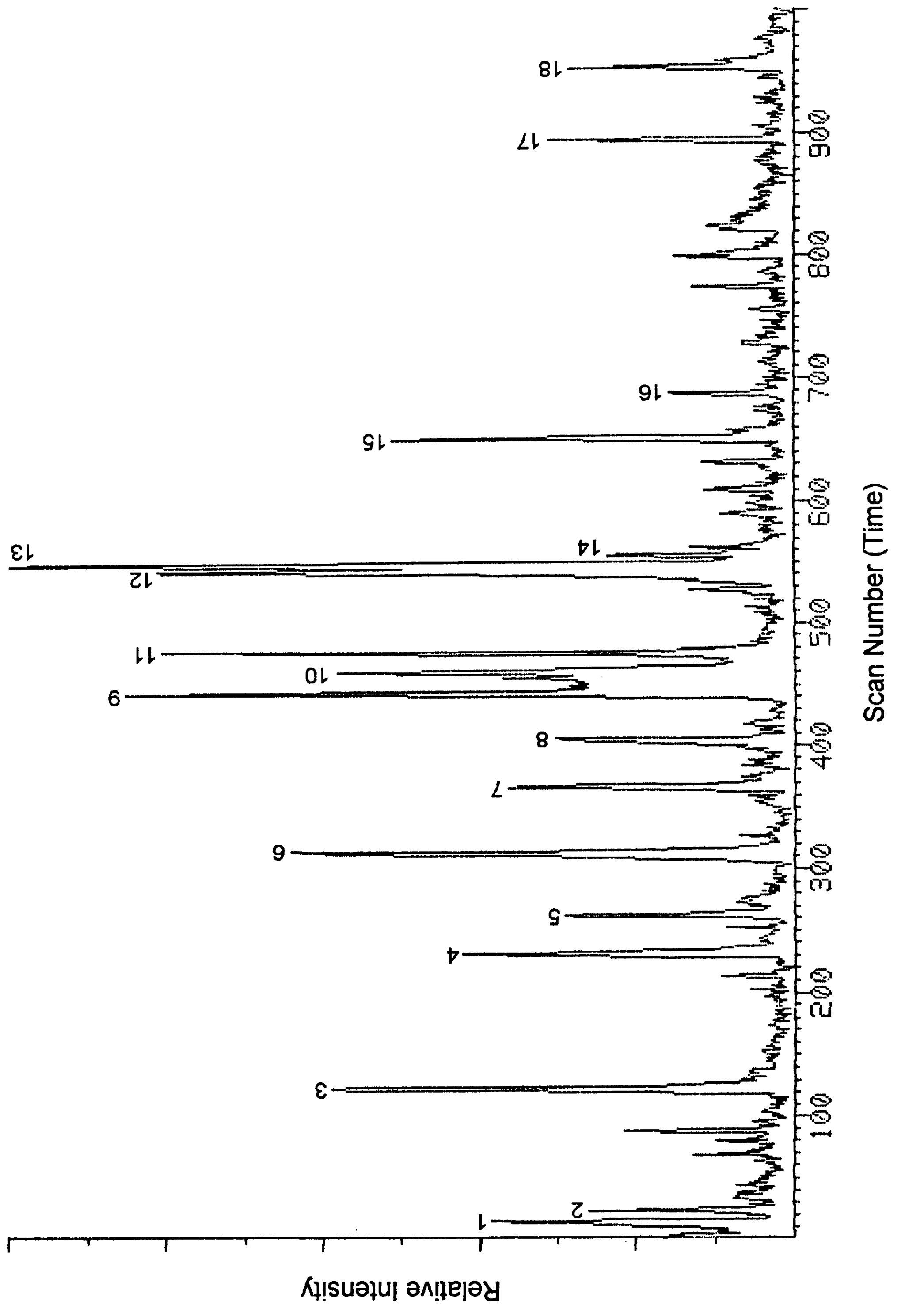


Figure 19. 6% PEG-Alumina Thermally Pre-Treated to 70% Weight Loss Pyrolyzed at 450°C in Air GC/MS Chromatogram.

Table 11. 6% PEG-Alumina Thermally Pre-Treated to 70% Weight Loss Pyrolysis Products.

Peak	Compound Name	Formula
1	Acetic Acid	$C_2H_4O_2$
2	Silane, dimethoxydimethyl	$C_4H_{12}O_2Si$
3	Acetaldehyde, hydroxy	$C_2H_4O_2$
4	2-Propanone, 1-hydroxy-	$C_3H_6O_2$
5	1,3-Dioxolane	$C_3H_6O_2$
6	Unknown	
7	Ethanol, 2-(2-methoxyethoxy)-	$C_5H_{12}O_3$
8	Unknown	
9	Phenol	C_6H_6O
10	Acetic acid, methoxy	$C_4H_8O_3$
11	Ethanol, 2-(2-ethoxyethoxy)-	$C_6H_{14}O_3$
12	Unknown	
13	Unknown	
14	2-Methyl-phenol	C_7H_8O
15	Unknown	
16	2,2'-Bi-1,3-dioxolane	$C_6H_{10}O_3$
17	Ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]	$C_8H_{18}O_4$
18	Unknown	

Solid State ^{13}C NMR Analysis:

The cp-mass spectrum of 6% PEG-alumina with no thermal pretreatment (0%) shown in Figure 20 has a strong peak at approximately 50 ppm corresponding to the C-O carbon in the polymer backbone. Also present in this spectrum are the peaks due to the deflocculant in the dry press powder at 25 ppm and 125 ppm. The deflocculant-alumina system is represented in Figure 21 to demonstrate the peaks which are directly attributable to deflocculant-alumina.

Thermal pre-treatment to 20% weight loss and subsequent examination of the residue by ^{13}C cp-mass analysis is represented in Figure 20. The 50 ppm peak due to the C-O carbon is still present; however, there are two new peaks that are present at 125 ppm and 175 ppm. These peaks are assigned to the alkene and carbonyl carbons respectively. In the sample thermally pre-treated to 40% weight loss, the spectrum shows that the alkene carbons continue to increase while the carbonyl carbon remains constant, and the C-O carbon decreases. For the sample thermally pre-treated to 55% weight loss, there is significant decrease of C-O carbons and carbonyl carbons, while alkene carbon concentration has increased. This trend continues as thermal pre-treatment weight loss continues to 80%, where the peak in the alkene region begins to decrease in intensity. Although not shown, the sample which was thermally pre-treated to 100% weight loss, had no detectable carbon signal.

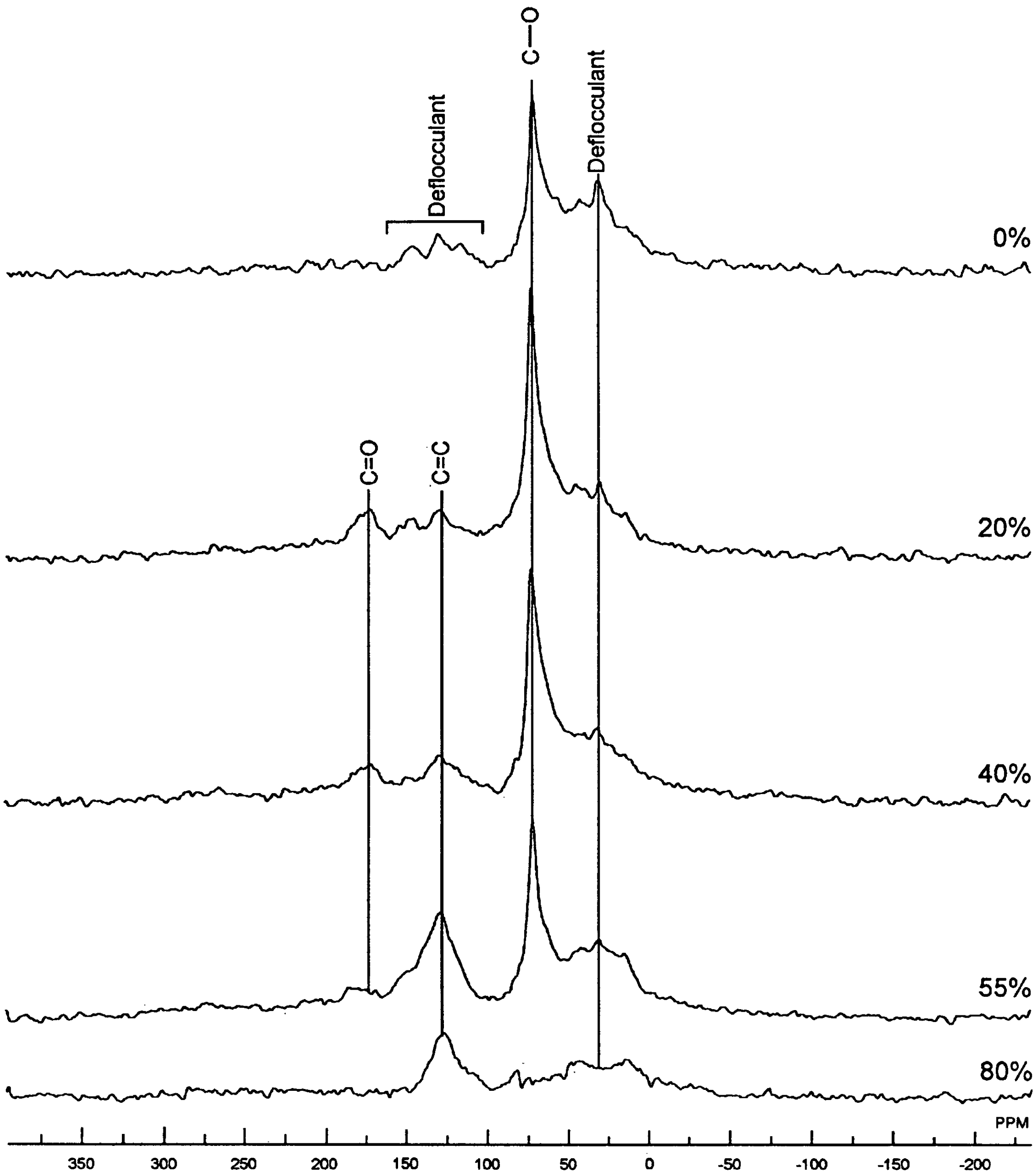


Figure 20. Solid State ^{13}C cp-mass NMR Spectrum for 6% PEG-Alumina Thermally Pre-Treated With Varying Weight Losses.

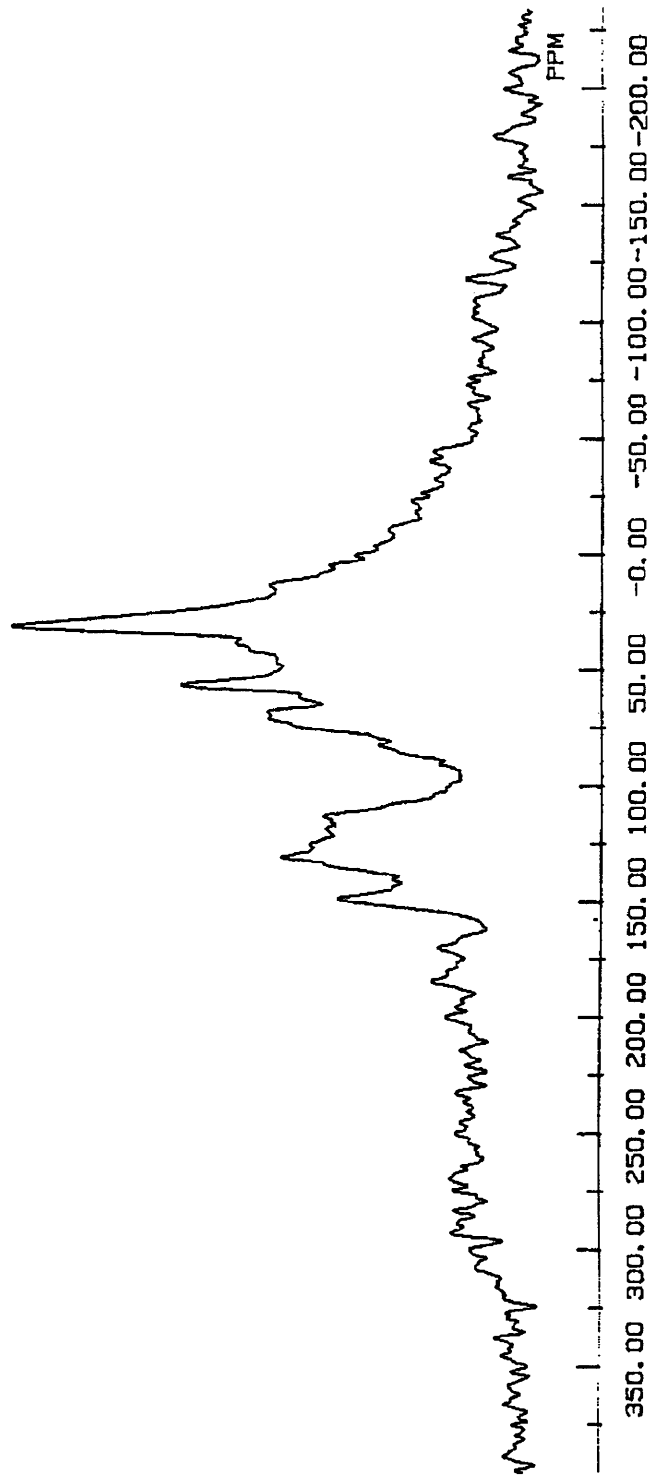


Figure 21. Solid State ^{13}C cp-mass NMR for the Deflocculant-Alumina System.

Polvinyl Alcohol

Thermal Analysis:

Thermogravimetric/differential thermal analysis of 2% PVA-alumina in air at 20°C/min heating rate is represented in Figure 22. The TG/DTA analysis showed that the thermal degradation of the polymer began at approximately 260°C with the maximum degradation at 290°C. Associated with this weight loss was an exotherm indicating an oxidation of the polymer.

As with the PEG-alumina thermal degradation profile, there is an initial weight loss associated with the polymer oxidation at 260°C. The initial weight loss is followed by a more gradual weight loss to 290°C with a corresponding exotherm. The initial weight loss for the PVA-alumina is not as rapid as that seen for PEG-alumina and is likely due to the dehydration process which the PVA undergoes as it is heated. The slower loss of weight beginning at 300°C may be associated with the oxidation of the polyene residue formed after dehydration of the PVA backbone. There is also a weight loss and endotherm at 650°C which is related to the degradation of the pre-binder additives in the alumina powder which are the same as in PEG.

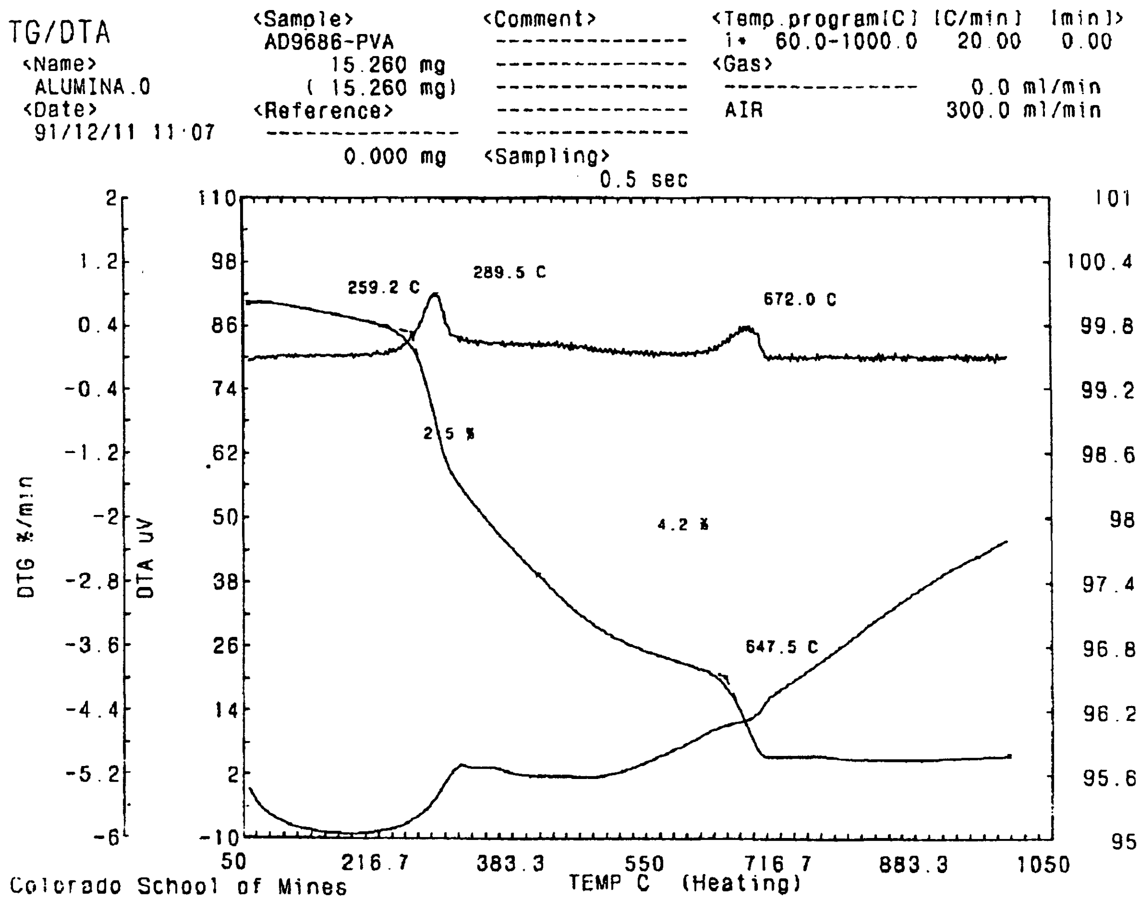


Figure 22. TG/DTA of 2% PVA-Alumina in Air With a 20°C Heating Rate.

__Volatile Product Analysis__

The volatile degradation products of PVA-alumina pyrolyzed in air at 450°C were cryotrapped and analyzed by GC/MS and are represented by the chromatogram shown in Figure 23. Table 12 summarizes the identified products which are consistent with those reported in the literature [9, 12-13]. The thermal degradation products identified which include aldehydes and ketones can be formed by the postulated degradation pathways shown in Equations (14-16) [9]. Benzene, a product of the cyclized hexadiene from the polyene residue is also present [13].

Degradation of PVA with alumina appears to be independent of the alumina as indicated by the identified volatile pyrolysis products. This is important in that the degradation pathways for PVA can be determined on the neat polymer. The methylene chloride is a laboratory contaminant.

$$\sim\!\left(\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}\right)_n\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}\!\sim \;\longrightarrow\; \sim\!\left(\mathrm{CH}{=}\mathrm{CH}\right)_n\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}\!\sim + \; n\mathrm{H_2O} \qquad (14)$$

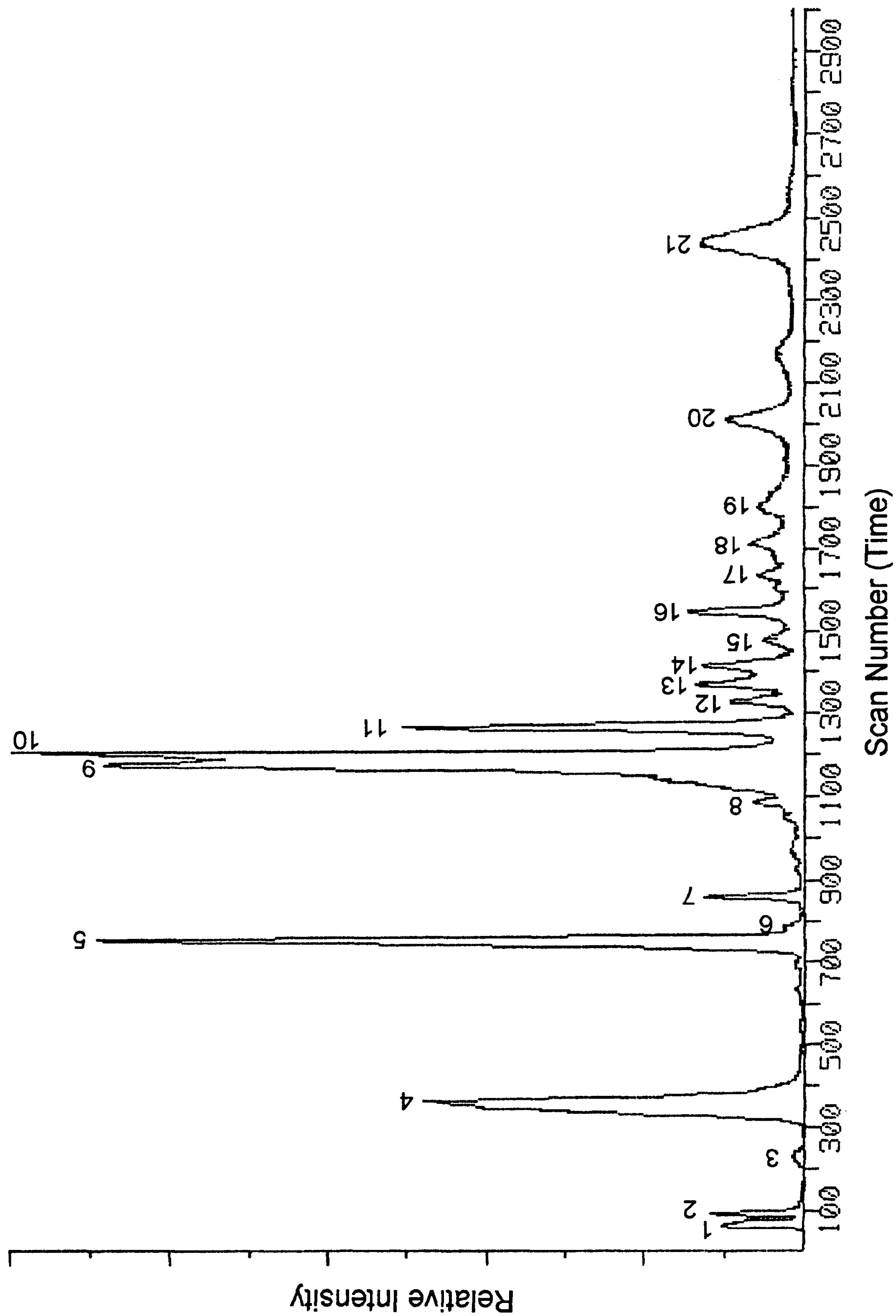
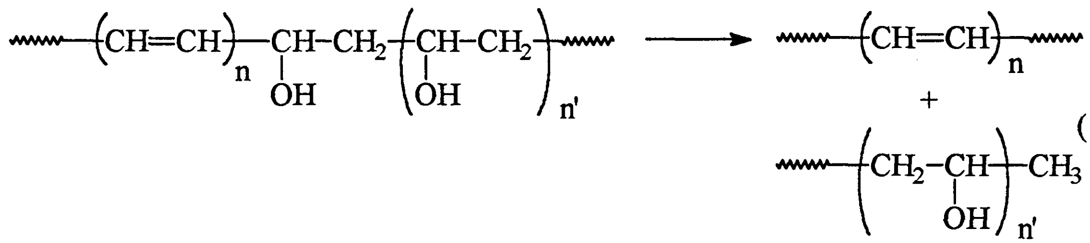


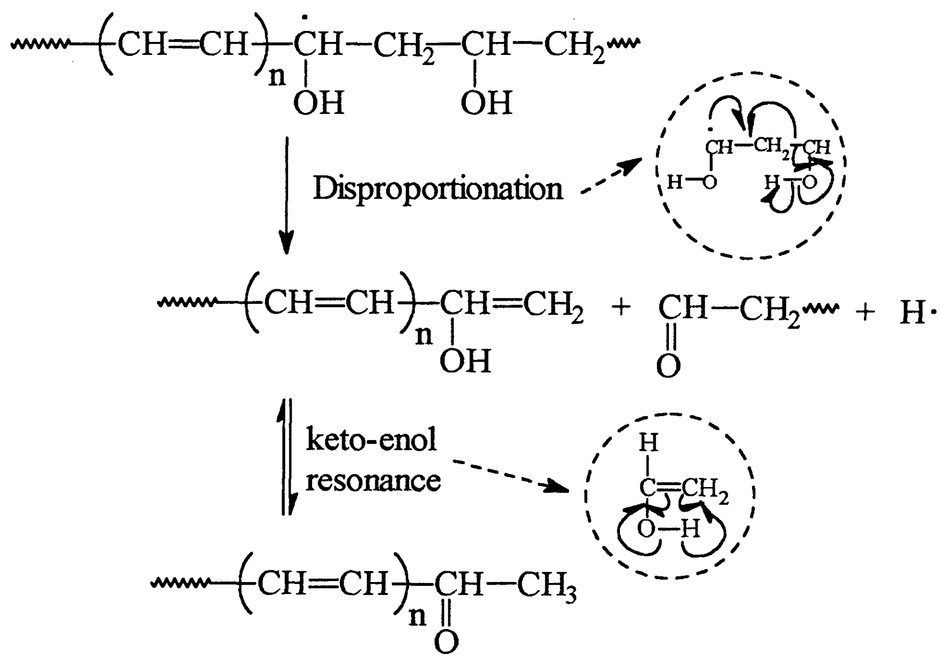
Figure 23. 2% PVA-Alumina Cryotrapped Pyrolysis Products GC/MS Chromatogram.

Table 12. 2% PVA-Alumina Cryotrapped Volatile Products.

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



(15)



(16)

Semivolatile Product Analysis

Analysis of PVA-standard alumina pyrolyzed at 450°C in air and analyzed by GC/MS is represented by the TIC in Figure 24. The number of peaks observed for pyrolysis of PVA-alumina is much less than those observed for PEG-alumina pyrolysis. The products have more characteristic mass spectral fragmentation patterns than those from PEG. Table 13 summarizes the products identified for the pyrolysis of PVA-alumina.

Products which are expected to be observed from the thermal degradation of PVA-alumina such as aldehydes and ketones are present in the identified products. However, benzene a major polyene degradation product which was present in minor amounts in the volatile analysis is not present for this analysis. Benzene was also not reported by Baugh [9] as a degradation product in his investigation of the neat polymer PVA.

All products that were observed in this study for the PVA-alumina sample were also reported by Baugh [9] for pure PVA. The near identical products from the two studies indicate that the degradation process for PVA-alumina is very similar to that observed for neat PVA.

Solid State ^{13}C NMR Analysis:

The solid state ^{13}C cp-mass NMR spectrum of PVA-alumina is represented in Figure 25 and indicated by 0%. The peaks due to the carbons in the backbone of the polymer are present at 45 ppm and 70 ppm. The peak at 45 ppm is from the CH_2 carbon and the peak at 70 ppm is due to the CH-OH carbon. The other peaks at 120, 130, 150, and 175 ppm could be due to polyvinyl acetate and deflocculant. The sample thermally pre-treated to 20% weight loss, indicates there is a large increase in the amount of alkene type carbon (130 ppm) present in the system. The alkene carbon results from the reported dehydrolysis of the PVA polymer chain to produce a polyene. For the sample thermally pre-treated to 40% weight loss, there is very little PVA backbone carbon remaining. The dominant peak at 130 ppm is due to the polyene or alkene buildup in the ceramic powder. The sample thermally pre-treated to 60% weight loss, showed a carbon residue at 130 ppm which is alkene in nature. With thermal pre-treatment of 80% weight loss, there is a continued reduction in the amount of the alkene carbon remaining in the system. As the polymer continues to degrade the residue that remains, which is alkene in nature, eventually degrades completely.

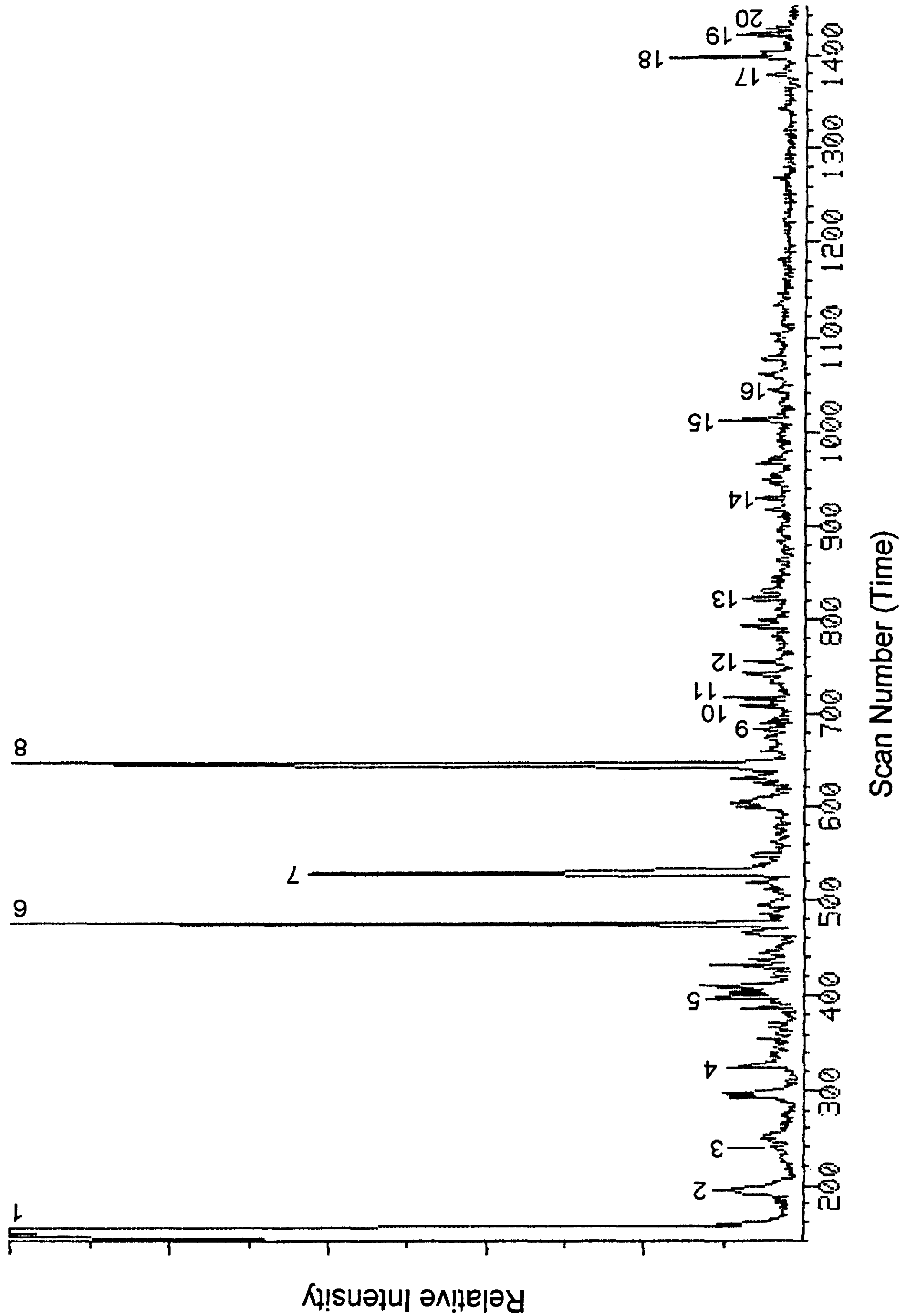


Figure 24. 2% PVA-Alumina Pyrolyzed at 450°C in Air GC/MS Chromatogram.

Table 13. 2% PVA-Alumina Pyrolysis Products.

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)	
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	

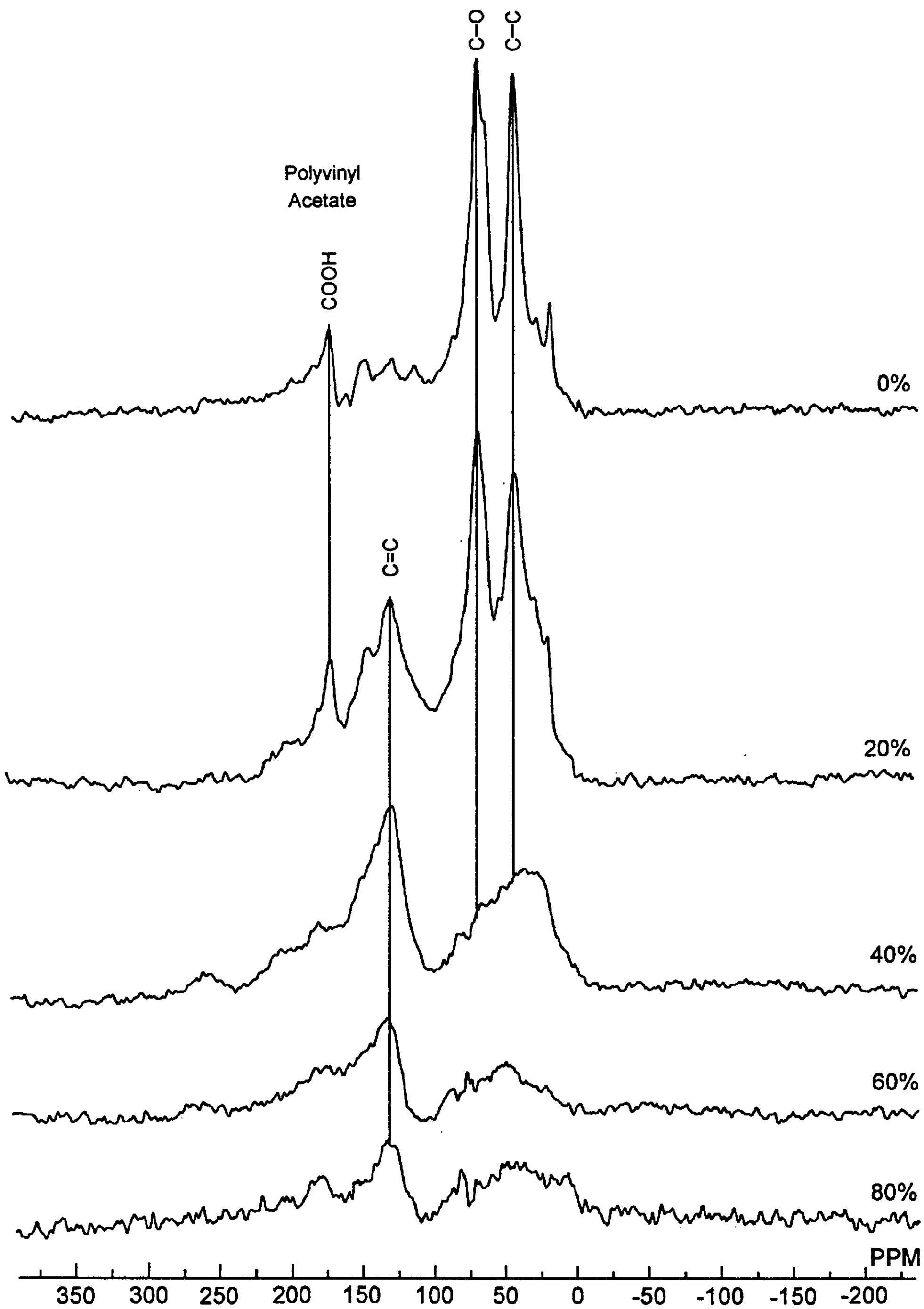


Figure 25. Solid State ^{13}C cp-mass NMR of 2% PVA-Alumina Thermally Pre-Treated With Varying Weight Losses.

Polyvinyl Alcohol and Polyethylene Glycol

Thermal Analysis:

Thermogravimetric analysis of 6% PEG- 0.5% PVA-alumina binder system in air with a 20°C/min heating rate illustrated in Figure 26, shows that initial thermal degradation began at 242°C. Maximum degradation of the sample was at 255°C with the majority of the binder lost by 268°C. Associated with this weight loss is a large exotherm providing evidence for the oxidation of the polymer. Starting at 260°C and going to 650°C there is a change in the rate of degradation from a fast initial rate to a gradual weight loss. Beginning at 650°C the rate of degradation increases again and the overall weight loss for the system is 7.9%. At 650°C the weight loss has an endotherm associated with it.

The thermogravimetric curve for the degradation of the standard PEG-PVA-alumina binder system is very similar to that observed for PEG-alumina alone. This is due to the ratio of PEG to PVA in this system. The slower gradual weight loss, observed in Figure 26 can be correlated to that observed for PEG-alumina thermally pre-treated to 80% weight loss represented in Figure 11. The similarity of the TG/DTA profiles for PEG-alumina, PVA-alumina, and PEG-PVA-alumina indicate that the final compounds remaining in the sample after the polymers have degraded are from the additives to the alumina powder. Specifically, the kaolin, talc and sodium lignosulfonate are the final species in the system to degrade.

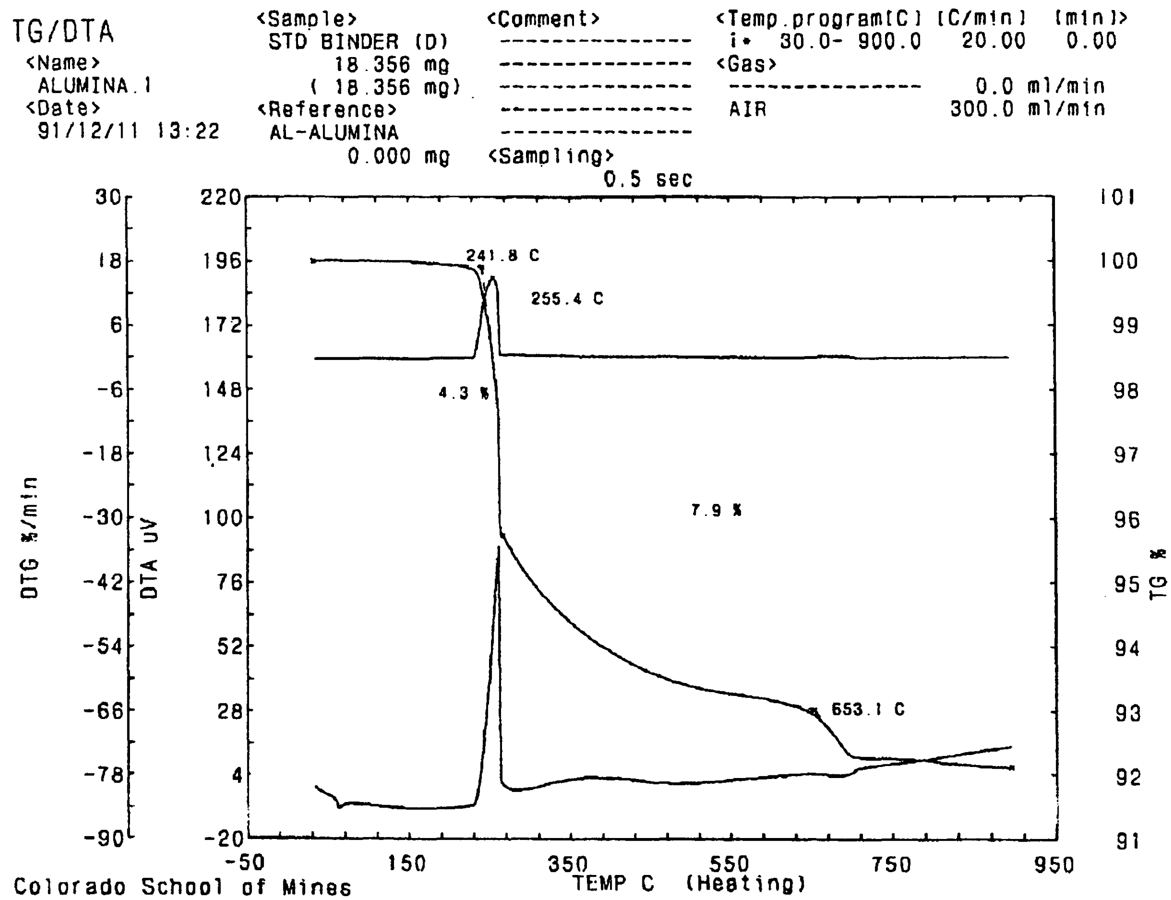


Figure 26. TG/DTA of 6% PEG- 0.5% PVA-Alumina Standard Binder System in Air With a 20°C Heating Rate.

Volatile Product Analysis

The total ion chromatogram (TIC) for the thermal degradation of the 6% PEG-0.5% PVA-alumina standard binder system pyrolyzed at 450°C in air is represented in Figure 27. The volatile products identified from the GC/MS analysis are summarized in Table 14.

The major products observed for the PEG-PVA-alumina binder system are very similar to those seen for the volatile analysis 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-propeneal, 2-pentanone, benzene, and toluene. The products observed indicate that degradation of PEG-PVA-alumina produces a combination of products from the two polymer systems. It appears that the polymers are acting independently of each other as they degrade. By understanding the individual degradation mechanisms for PEG and PVA, the combination of the two would give predictable results.

Semivolatile Product Analysis

The standard binder system pyrolyzed under air at 450°C was studied by GC/MS and the TIC is represented in Figure 28. The PEG-PVA-alumina binder system has a product distribution which is nearly the same as that observed for the PEG-alumina sample. Single ion plotting of the base ions from PVA-alumina produced no co-eluting peaks. This is not surprising considering the ratio of PEG to PVA in this system.

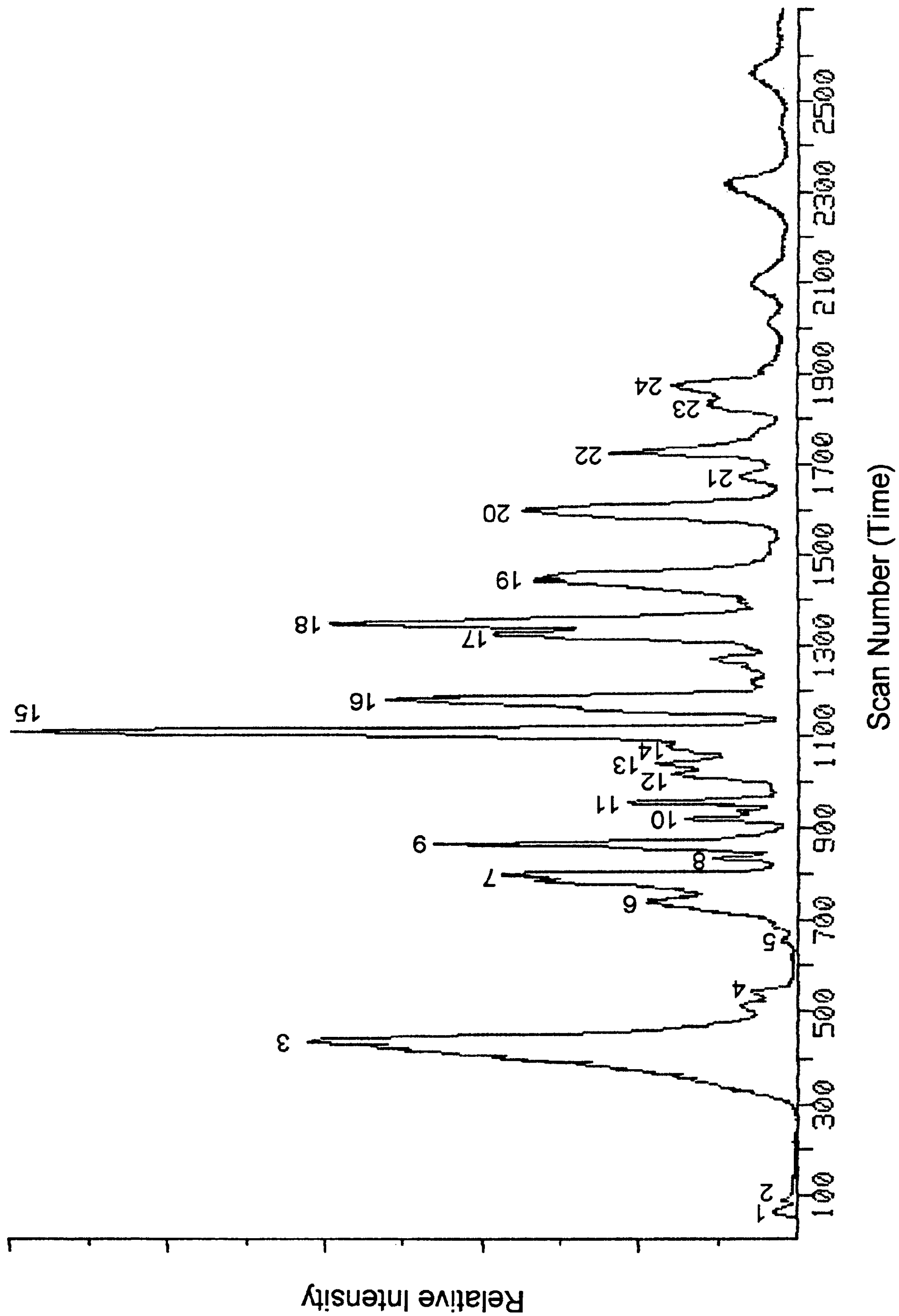


Figure 27. 6% PEG- 0.5% PVA-Alumina Standard Binder System Cryotrapped Pyrolysis Products GC/MS Chromatogram.

Table 14. 6% PEG- 0.5% PVA-Alumina Standard Binder System Cryotrapped Volatile 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-	$C_4H_{10}O_3$

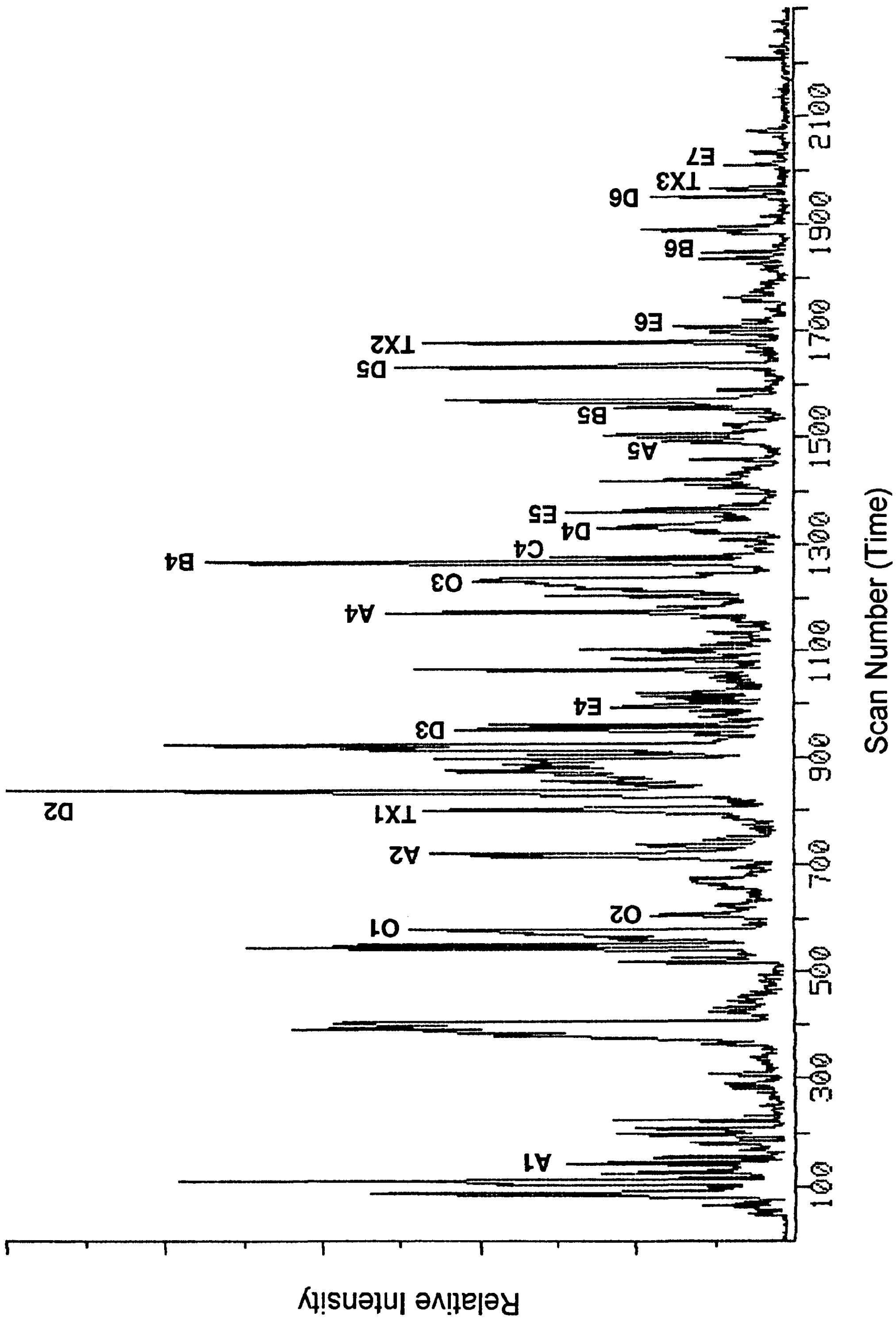


Figure 28. 6% PEG- 0.5% PVA-Alumina Standard Binder System Pyrolysis at 450°C in Air GC/MS Chromatogram.

Table 15. 6% PEG- 0.5% PVA-Alumina Standard Binder System Pyrolysis 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)-	$C_{16}H_{30}O_2$

Solid State ^{13}C NMR Analysis:

A compilation of solid state cp-mass ^{13}C NMR spectra from a series of samples thermally pre-treated in 20% weight loss intervals is represented in Figure 29. The spectrum of the PEG-PVA standard binder is dominated by PEG at 60 ppm, with smaller peaks due to the PVA present at 45 ppm and 65 ppm. Thermally pre-treated with 20% weight loss, there is a reduction in the amount of PVA in the spectrum, but not a significant buildup of the expected alkene carbon at 130 ppm. The dominant form of carbon present at this amount of weight loss is the C-O carbon from PEG. By 40% thermal pre-treatment weight loss, peaks for the alkene at 130 ppm, and carbonyl carbon at 175 ppm, are increasing while the relative amount of C-O carbon from PEG is decreasing. When the thermally pre-treated system is at 60% weight loss, the relative amounts of alkene (130 ppm) and C-O type carbons (60 ppm) appear to be comparable in intensity. When thermal pre-treatment weight loss is 80%, the only detectable type of carbon is alkene in nature and may be due to the deflocculant present in the alumina.

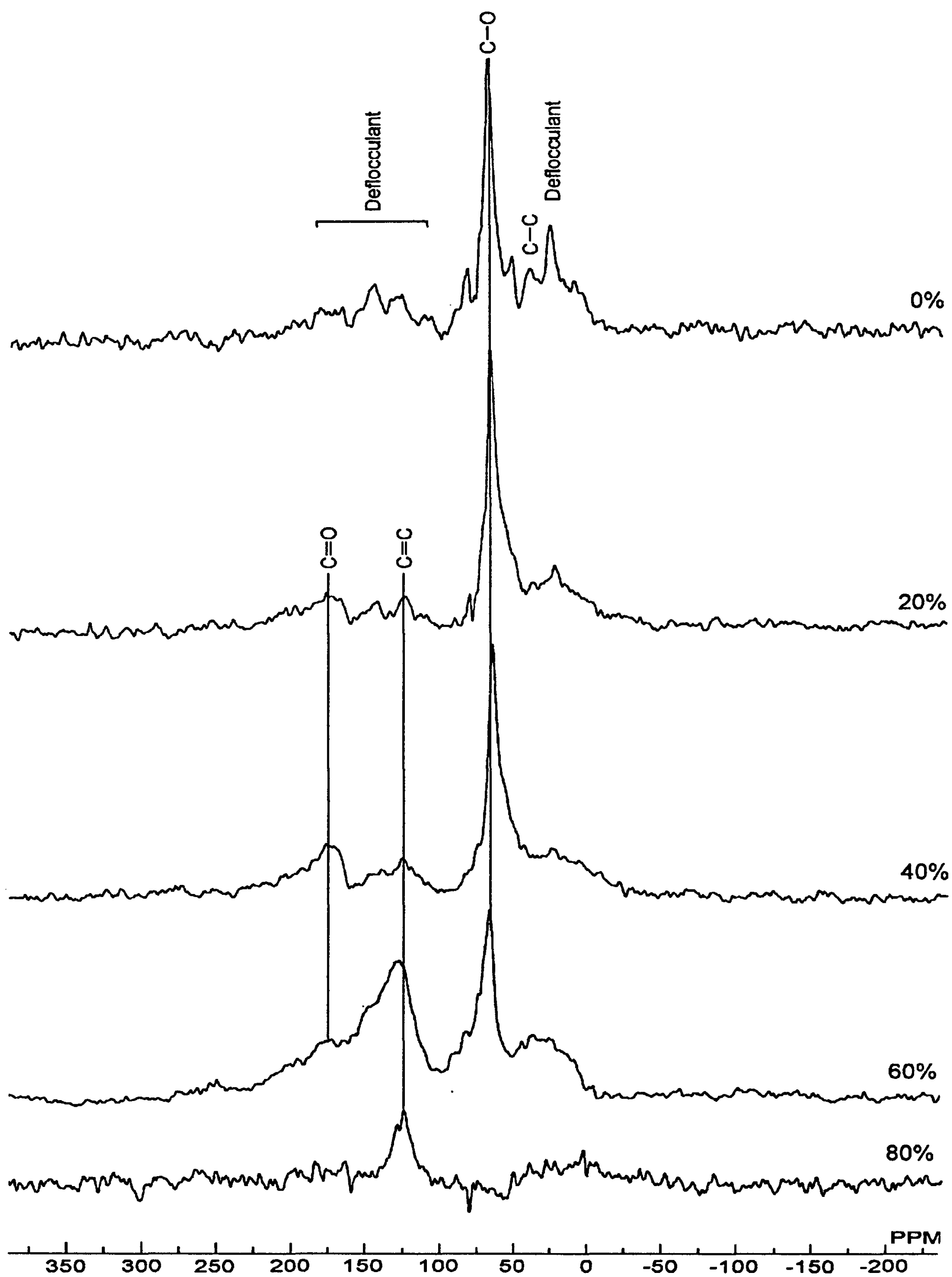


Figure 29. Solid State ^{13}C cp-mass NMR Spectrum for 6% PEG- 0.5% PVA-Alumina Standard Binder System Thermally Pre-Treated With Varying Weight Losses.

Methoxy Polyethylene Glycol

Thermal Analysis:

The pure polymer methoxy-PEG (MPEG) was analyzed using the auto step-wise TG analysis method described in the experimental section [16]. This method of thermal analysis allows for greater resolution of complex thermal events by placing the instrument into an isothermal hold when the rate of weight loss exceeds pre-determined rates of weight loss. The instrument resumes its normal temperature ramp when the rate of weight loss becomes insignificant. The TG/DTA in air with a 20°C/min heating rate representing the thermal degradation of neat MPEG is shown in Figure 30. The endotherm at 67°C is associated with the melting of the polymer. At 240°C, the polymer MPEG begins to degrade. Shortly after this the rate of degradation exceeds the weight loss threshold of 175 μg/min and the instrument changes to an isothermal hold.

The temperature at which this initial degradation took place is at 240°C with a 91% loss of polymer. There is a large exotherm associated with this weight loss. Another significant loss of 5% can be seen at 298°C where there was a small isothermal hold and an exotherm associated with it. After this weight loss there is a gradual loss of 3% until 500°C. This weight loss also has an exotherm associated with it. The polymer MPEG does not appear to form a thermally stable char and totally degrades at a relatively low temperature (< 500°C).

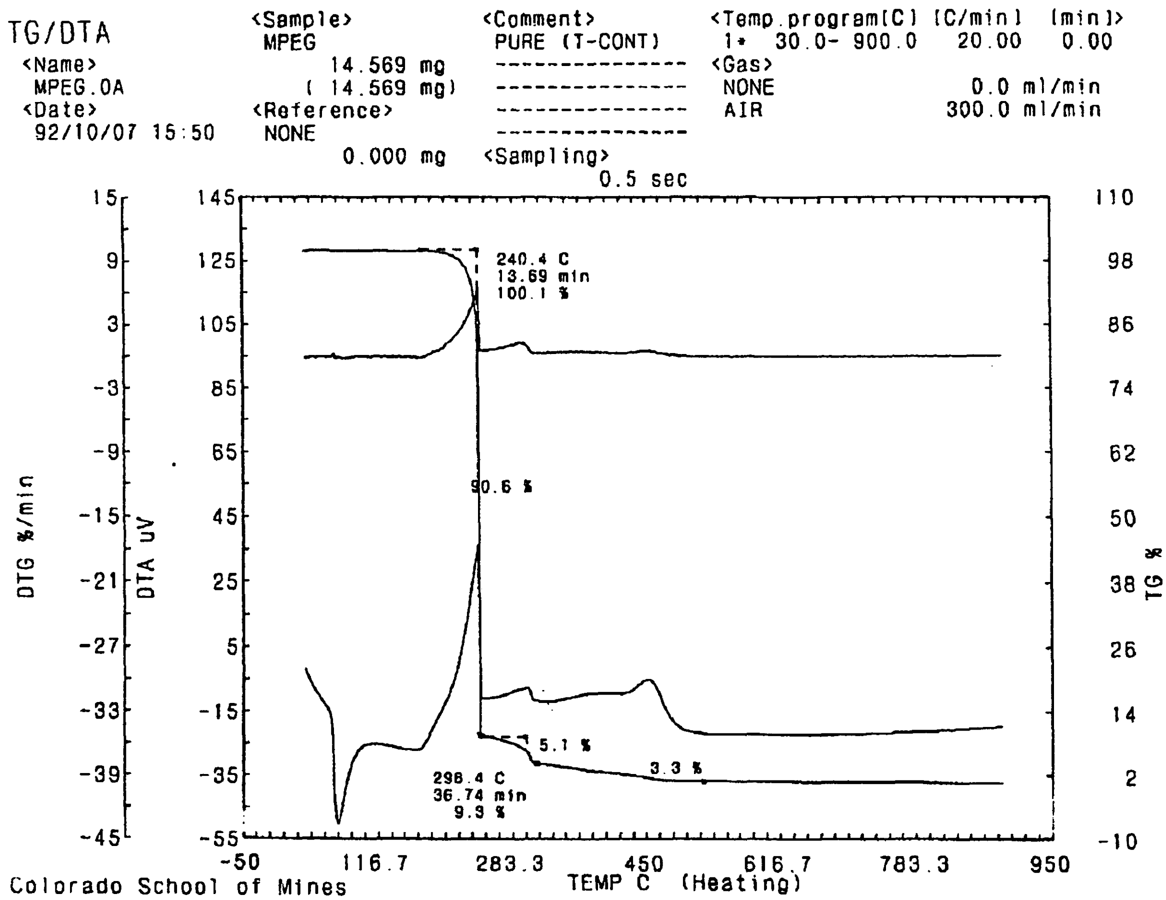


Figure 30. TG/DTA of Neat Methoxy PEG Using Auto Step-Wise Operating Mode in Air With a 20°C Heating Rate.

Semivolatile Product Analysis

The total ion chromatogram for the pyrolysis products pyrolyzed at 450°C in air from neat methoxy PEG is represented by Figure 31. The number of significant peaks in the chromatogram is less than that observed for the PEG system and could be due to the difference in the molecular weights of the two polymers. Methoxy-PEG has a molecular weight of 5000 Daltons while PEG has a molecular weight of 20,000 Daltons. Methoxy-PEG also lacks any crosslinking of the polymer chain which could favor degradation. The degradation products are very similar to those expected for PEG based on the mechanisms proposed.

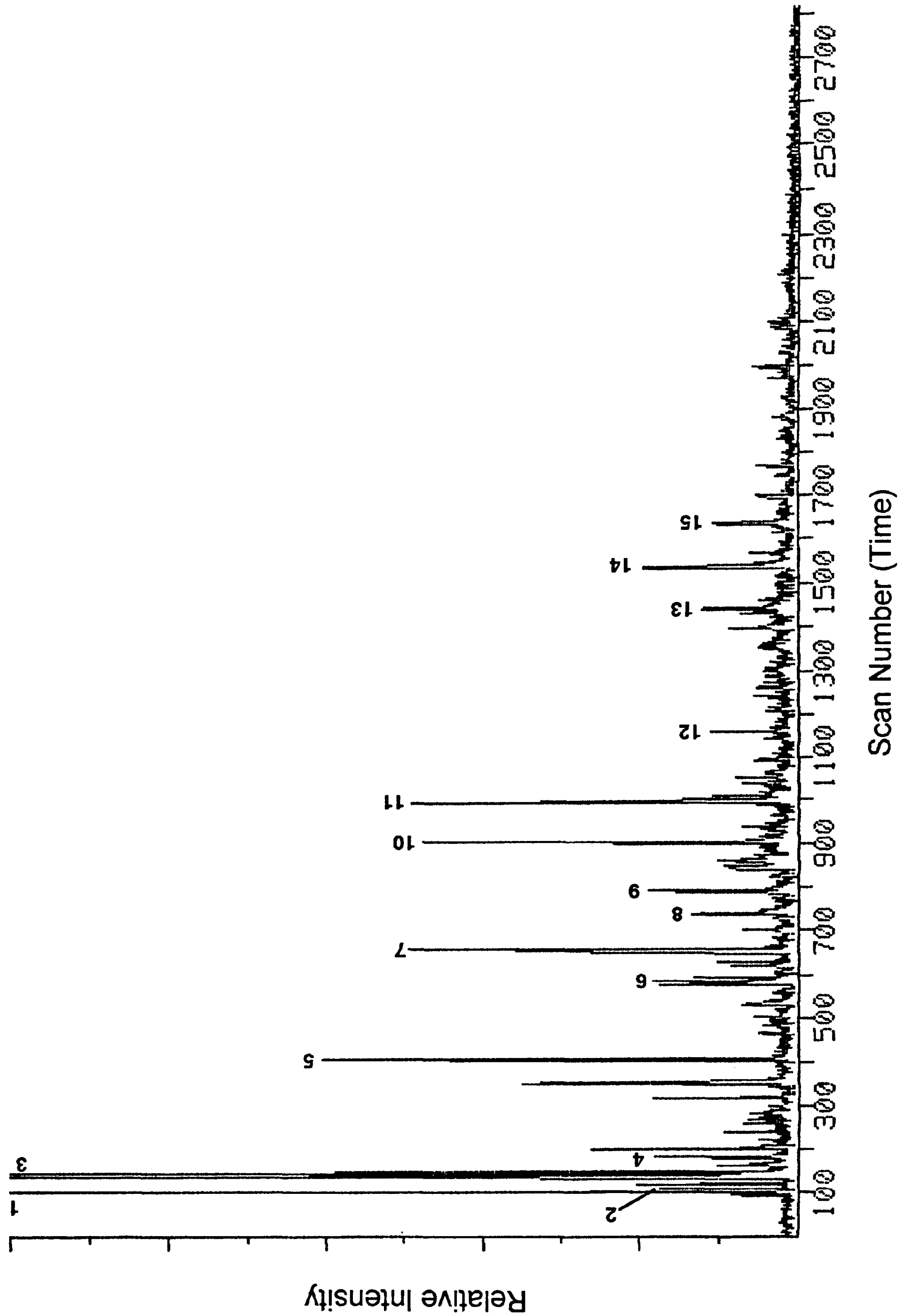


Figure 31. Neat Methoxy PEG Pyrolyzed at 450°C in Air GC/MS Chromatogram.

Table 16. Neat Methoxy PEG Pyrolysis Products.

Peak	Compound Name	Formula
1	Acetaldehyde, hydroxy	$C_2H_4O_2$
2	Methyl acetate	$C_3H_6O_2$
3	Ethane, 1,1-dimethoxy-	$C_4H_{10}O_2$
4	1,3-Dioxolane, 2-methyl-	$C_4H_8O_2$
5	Unknown	
6	Ethane, 1-ethoxy-1-methoxy-	$C_5H_{12}O_2$
7	Unknown	
8	Ethanol, 2-(2-methoxyethoxy)-	$C_5H_{12}O_3$
9	Unknown	
10	Ethanol, 2-(2-ethoxyethoxy)-	$C_6H_{14}O_3$
11	Unknown	
12	Unknown	
13	Ethanol, 2-[2-(2-methoxyethoxy)ethoxy]-	$C_7H_{16}O_4$
14	Ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]-	$C_8H_{18}O_4$
15	Unknown	

Polyox

Thermal Analysis:

Analysis of neat Polyox 80M (polyethylene oxide 80M) in air at a rate of 20°C/min was done using the auto step-wise thermal degradation method previously described. An initial isothermal hold of the instrument corresponding to a significant weight loss, occurred at 240°C. Associated with this weight loss of 86% was a large exothermal event which correlated to the oxidation of the polymer and represented in Figure 32. A loss of 10% occurred at 314°C with a gradual loss of 5% by 500°C. Corresponding exothermal events for the weight losses of 10% and 5% may be related to oxidation of cross linked polymer residues. Polyox 80M degrades cleanly and does not form degradation residues that are stable above 500°C.

Semivolatile Product Analysis

Neat polyethylene oxide (polyox) was pyrolyzed at 450°C in air and analyzed by GC/MS. The total ion chromatogram is represented by Figure 33. There appears to be a decrease in the complexity of peaks that are associated with this sample compared to the PEG-alumina sample and appears to have degraded into distinct series. This may be due to the lack of crosslinking associated with this polymer. The corresponding decrease in the number of peaks associated with the methoxy-PEG polymer may also have been

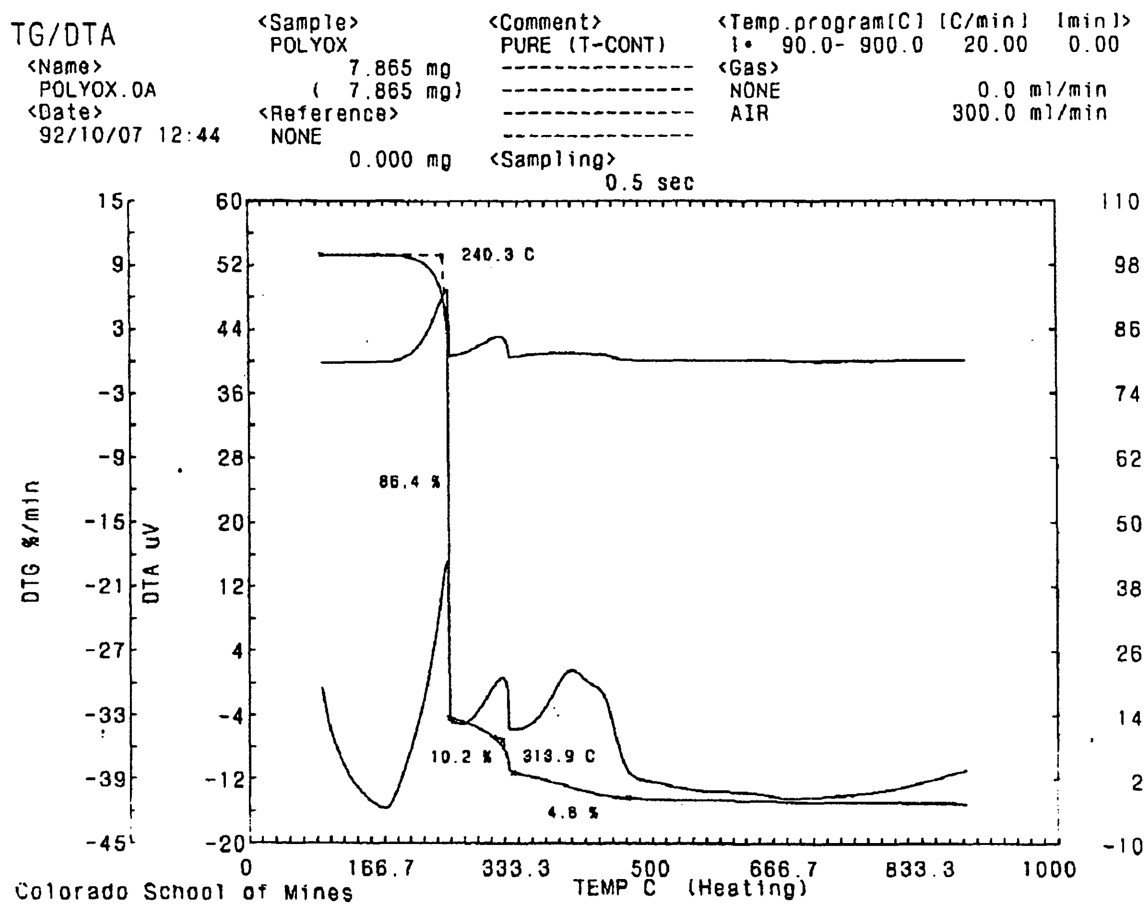


Figure 32. TG/DTA of Neat Polyox WSRN80 Using the Auto Step-Wise Operating Mode in Air With a 20°C Heating Rate.

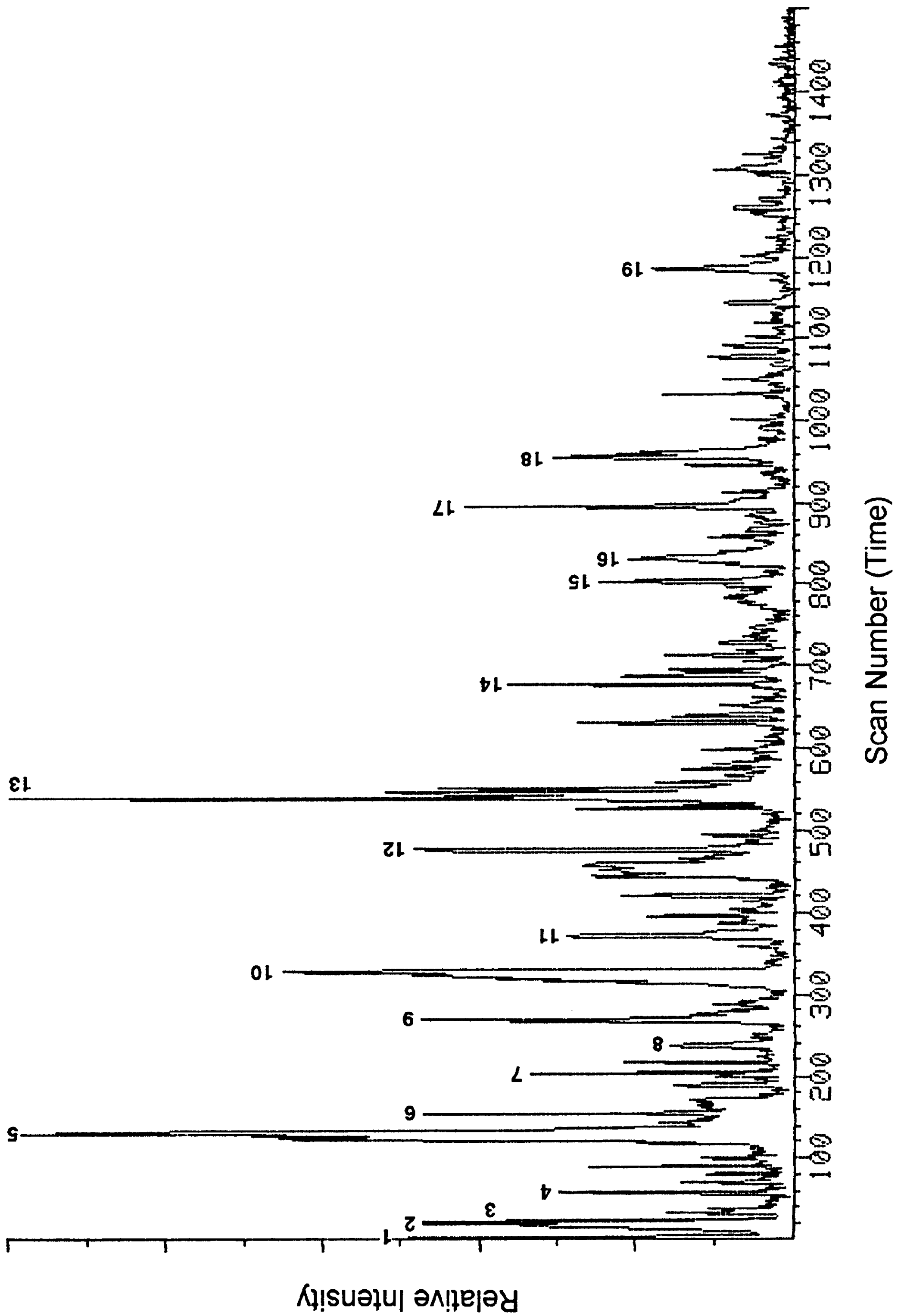


Figure 33. Neat Polyox WSRN80 Pyrolyzed at 450°C in Air GC/MS Chromatogram.

Table 17. Neat Polyox WSRN80 Pyrolysis Products

Peak	Compound Name	Formula
1	Ethane, 1,1-dimethoxy	$C_4H_{10}O_2$
2	Acetic acid	$C_2H_4O_2$
3	1,3-Dioxolane, 2-methyl-	$C_4H_8O_2$
4	Methyl hydroxyacetate	$C_3H_6O_3$
5	Unknown	
6	Silanol, trimethyl-	$C_3H_{10}OSi$
7	Unknown	
8	1,2-Ethanediol, monoacetate	$C_4H_8O_3$
9	Ethane, 1-ethoxy-1-methoxy-	$C_5H_{12}O_2$
10	Unknown	
11	Ethanol, 2-(2-methoxyethoxy)-	$C_5H_{12}O_3$
12	Ethanol, 2-(2-ethoxyethoxy)-	$C_6H_{14}O_3$
13	Ethane, diethoxy	$C_6H_{14}O_2$
14	Unknown	
15	Ethanol, 2-[2-(2-methoxyethoxy)ethoxy]-	$C_7H_{16}O_4$
16	Ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]-	$C_8H_{18}O_4$
17	Ethane, 1,1'-oxybis[2-ethoxy-]	$C_8H_{18}O_3$
18	Unknown	
19	Unknown	

due to the end groups (methyl capped PEG) and the lack of crosslinking as well. However, the identified degradation products observed are similar to those seen for the PEG-alumina system.

CONCLUSIONS

Polyethylene Glycol

Work done on the degradation of neat PEG 8M (8000 Daltons) by Baugh [9] using thermogravimetric and differential thermal analysis indicated that it was sensitive to oxygen present in the system. Most product identification by Baugh was done on samples pyrolyzed in a nitrogen atmosphere. Five series of compounds were identified and correlating degradation mechanisms were proposed [9]. The present study has investigated the degradation of the polymer PEG 20M (20,000 Daltons) with an alumina system currently being used at Coors Ceramics. All samples were pyrolyzed in air. For samples pyrolyzed in nitrogen by Baugh [9], the abundance of the homologous series of degradation compounds is greater than that observed for the same samples pyrolyzed in air. The product distribution remains the same for pyrolysis in the two atmospheres.

To better understand the degradation process as a whole, a series of PEG-alumina pressed powder samples were thermally pre-treated in approximately 20% weight loss intervals and the samples ground up into a fine powder. These powders were then analyzed by solid state ^{13}C cp-mass NMR. The results of these analyses indicated that as the polymer PEG degraded there was an expected decrease in the amount of the backbone (C-O) carbon present. There were also increases in the amount of carbonyl and alkene carbons in the sample. As the thermal pre-treatment weight loss process continued, the carbonyl carbon and C-O carbon degraded to the point where they were no longer detectable by solid state ^{13}C cp-mass NMR. However, late into the degradation process there was a strong alkene carbon peak present. It was determined that an understanding of what was producing this particular peak would be important in understanding the binder burnout process. Several pyrolysis experiments were performed to collect and identify this residue by GC/MS without success.

To further isolate the source of the remaining ^{13}C NMR alkene peak thermogravimetric analysis of the alumina additives was done. Oleic acid, Triton X-100, and sodium lignosulfonate were the additives of interest. It was found that the only additive that is stable at the higher temperatures (>550°C) was sodium lignosulfonate. It is possible that any carbon particles found in the ceramic piece after sintering are due to the sodium lignosulfonate and may be responsible for the remaining ^{13}C cp-mass NMR peak.

Analysis of the volatile and semivolatile products from samples which had been thermally pre-treated before pyrolysis indicate that PEG continues to degrade throughout the burnout process. This was true for samples which had been degraded to less than 70% thermal pre-treatment weight loss. There were no products observed for semivolatile analysis of samples which had greater than 70% thermal pre-treatment weight loss. This is in correlation with the ratio of polymer binder and the amount of additives in the alumina. Volatile analysis of samples with greater than 70% thermal pre-treatment weight loss indicated that the polymer had almost completely degraded and the remaining pyrolysis products were due to additives in the alumina powder.

Degradation of the PEG-alumina system was done on pressed powder samples. Analysis by GC/MS indicated that the PEG in this system pyrolyzed in a similar fashion to the neat PEG 8M in nitrogen. Product identification showed the same five series of compounds seen in the earlier work by Baugh [9].

Polyvinyl Alcohol

Pyrolysis of neat PVA by Baugh [9] in nitrogen showed virtually the same thermal degradation products as the PVA-alumina from the present study. From these results, it is apparent that the alumina has little or no effect on the degradation process of PVA. The degradation mechanisms proposed in the literature [9, 12,13] appear to explain the degradation products of PVA.

Solid state cp-mass ^{13}C NMR analysis of PVA-alumina and subsequent degradation residues indicate that as the polymer degrades there is an increase in the amount of alkene carbon present. This trend continues as the PVA-alumina continues to degrade. The results of the ^{13}C NMR analysis from this study are nearly the same as that seen by Zhang [14] for the neat PVA polymer. Based on the results of these experiments, it implies that the PVA degrades independently of alumina.

Polyethylene Glycol and Polyvinyl Alcohol

Analysis of the degradation products from the standard binder system indicate that there is a mixture of products from PEG and PVA. It appears that the two polymers act independently of each other. The PVA at this low concentration appears to not have any contribution towards forming carbon particles in the system. However, the additives to the alumina still remain in the system after the binders are degraded. Specifically the sodium lignosulfonate is stable at temperatures up to 850°C and may a contribute to formation of char particles.

Analysis of the PEG-PVA-alumina system by solid state ^{13}C NMR indicates that the standard binder degradation is very similar to that seen for the PEG-alumina system. The PVA is identifiable in the NMR spectra by the C-C peak at 45 ppm, but does not appear to change the degradation products from those seen with the PEG-alumina. By 80% thermal pre-treatment weight loss the only remaining peak is an alkene carbon peak.

Methoxy-PEG and Polyox

The pyrolysis GC/MS for both methoxy-PEG and polyox show degradation products that are similar to those seen for the degradation of PEG. The methoxy-PEG (5,000 Daltons) has fewer products than the PEG 20M (20,000 Daltons) but they are consistent with the PEG products. The polyethylene oxide (80,000 Dalton) is a straight chain polymer has a less complex product distribution than the PEG. Both polymers degrade cleanly without a char residue forming. The degradation mechanisms presented in this work for PEG seem to apply to these other polymers.

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