

The Pyrolytic Characterization of a Surfactant/ Polymer/Ceramic Composite System Using Combined Thermogravimetric Analysis- Mass Spectrometry

K. M. NELSON, J-A. E. MANSON, and J. C. SEFERIS,* *Polymeric Composites Laboratory, Department of Chemical Engineering, University of Washington, Seattle, Washington 98195*, and R. B. PRIME, *IBM General Products Division, 5600 Cottle Road, San Jose, California 95193*

Synopsis

An experimental technique of combined thermogravimetric analysis (TGA) -mass spectrometry (MS) was used to study the pyrolysis process during binder removal from a ceramic/binder system. The effect of a fluorocarbon surfactant on the pyrolysis process was also investigated and it was discovered that the surfactant had no significant effect on pyrolysis. A simple paraffin binder system was implemented so as to enhance the effects of the surfactant. The identification of the fragments created during pyrolysis is also discussed.

INTRODUCTION

The use of polymers to bind unconsolidated ceramic precursor particles is being considered for processing complex ceramic shapes.^{1,2} After obtaining the desired shape at relatively low temperatures, the polymeric binder is pyrolyzed in a controlled manner, producing a void free, nonsintered ceramic part.^{3,4} The choice of a polymer depends primarily on its pyrolytic and rheological properties and how these properties interact with the ceramic constituent. In some instances, although the polymer is burned off, its residue (char) may become part of the final ceramic part. Even though these ideas are currently in the development stage, the technology of using thermoplastic polymers for processing ceramic powders by traditional means is being investigated by several industrial and academic laboratories.^{2,4,5} In polymer/ceramic composites it has been found advantageous to incorporate a surfactant that modifies the rheological behavior of the system, allowing high particle dispersion with minimum agglomeration along with high particle loading.

A basic and fundamental requirement is to understand the pyrolysis step of the polymeric matrix that essentially must be burned off in a controlled fashion during the sintering of an already preformed polymer/ceramic composite.¹ However, polymer pyrolysis is a complex physiochemical process where depolymerization and/or macromolecular scission takes place and the different mo-

* To whom correspondence should be addressed.

lecular entities must diffuse through the bulk composite structure. As a first step in the study of the controlled pyrolysis in polymeric composites, we have utilized a simultaneous thermogravimetric analysis-atmospheric pressure chemical ionization/tandem triple quadrupole mass spectrometer (TGA-APCI/MS/MS) developed by Prime and Shushan.⁶

A paraffin wax (average MW 352) was chosen as a model polymer matrix that was used with Al_2O_3 particles either in neat form or coated with a particular fluorocarbon surfactant. This has proven to be an excellent model system to study rheological and compositional characteristics and establish the fundamental principles of Al_2O_3 particles as applied to the different manufacturing processes of high performance composites.

The combined method of thermogravimetric analysis and mass spectrometry allows simultaneous assimilation of the molecular species information with the conditions imposed on the polymer during pyrolysis.^{7,8} Accordingly, the method can provide powerful information for interrelation of processing structure and properties for polymers used as matrices that undergo pyrolysis as an integral part of the manufacturing process.

EXPERIMENTAL

A control sample, containing no surfactant (designated as Al_2O_3 /Paraffin), was analyzed in parallel with a sample containing surfactant (designated as Al_2O_3 /Paraffin/FC). A relatively small amount of surfactant is needed to significantly affect the rheology of the system. The composition of the system was determined analytically using TGA (Figs. 1 and 2), as reported in Table I.

A uniquely configured Perkin-Elmer TGS-2 thermogravimetric analyzer was coupled with a SCIEX TAGA 6000 triple quadrupole mass spectrometer.⁶ By fitting the Perkin-Elmer TGA with a special glass coupler, the evolved gases

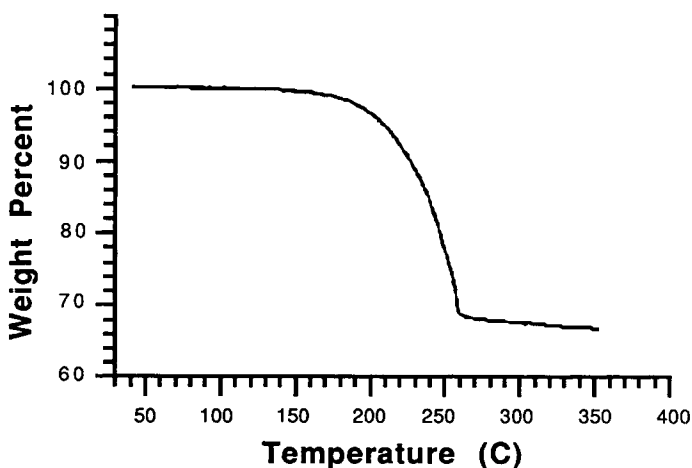


Fig. 1. The weight loss during combined MS-TGA experiment in air, sample *without surfactant* (Heating rate $10^\circ\text{C}/\text{min}$).

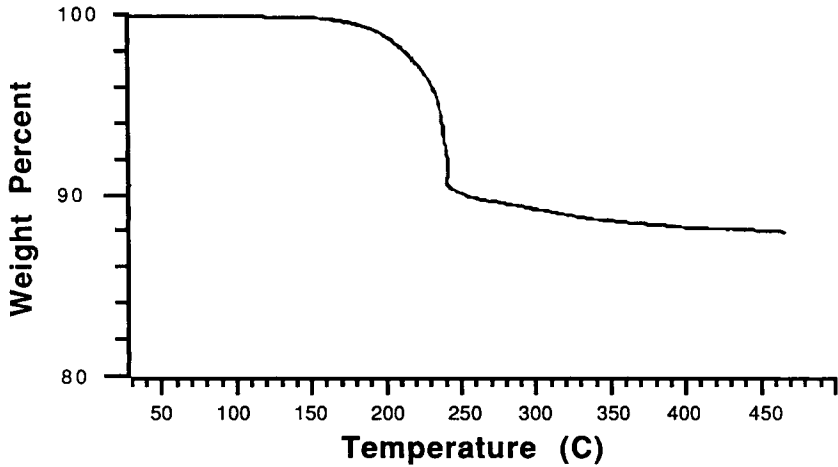


Fig. 2. The weight loss during combined MS-TGA experiment in air, sample with surfactant (Heating rate 10°C/min).

of the TGA are passed directly from the TGA into the mass spectrometer where the full benefits of both instruments are realized. A minicomputer monitors the instruments and records the mass spectra and weight loss with respect to temperature and time.

A method of atmospheric pressure chemical ionization (APCI)⁹ was chosen over the more common method of electron impact (EI) ionization which is generally unsuitable in the atmospheres resulting from thermo-oxidative processes. APCI converts trace compounds to their pseudo-molecular ions at atmospheric pressure by a charge transfer reaction. Since this ionization process causes little or no fragmentation of ions, the mass spectra give a true representation of the size distribution of the evolved gases.

In the positive ion mode, a common chemical ionization agent are hydrated protons¹⁰ $H^+ \cdot (H_2O)_n$. The ionization mechanism, which forms predominantly MH^+ protonated molecular ions, is thus

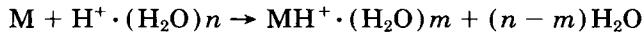


TABLE I
Thermogravimetric Analysis of Model System

	Weight (%)
System Al_2O_3 /Paraffin	
Al_2O_3	62
Paraffin	38
System Al_2O_3 /Paraffin/FC (Fluorocarbon Surfactant)	
Al_2O_3	88
Paraffin/FC	12

Only volatile products formed during degradation and with proton affinities greater than that of water were ionized and subsequently detected. Saturated hydrocarbons have proton affinities less than water and were not detectable. Furthermore, fluorine-containing species are not easily protonated and thus were not detected. In these studies only nonfluorinated degradation products of the surfactant, which are formed in significant abundance, were detected. One method of detecting compounds which are electron-affinitate, such as fluorocarbons, is with O_2^- reagent in negative ion mode of APCI.

Sample size ranged from 2–10 mg. Samples were heated from ambient temperature at $10^\circ\text{C}/\text{min}$. until the run was terminated at $350\text{--}450^\circ\text{C}$. Data recording is controlled by a minicomputer and stored on a hard disk. Scans are recorded with respect to time and temperature so that mass spectra may be viewed at any particular point in time (or temperature), or intensity of a single ion may be plotted with respect to time (or temperature).

RESULTS AND DISCUSSION

Pyrolysis is a complex chemical and physical process¹¹ where the molecular species decompose and subsequently diffuse through the bulk phase. The pyrolysis products, at any given time, are a manifestation of the decomposition, oxidation and diffusion processes. The surfactant, paraffin, and Al_2O_3 constitute the model system on which this study is centered. The surfactant is a common fluorocarbon used in consumer products and shall be referred to as FC in this report.

Significant weight loss begins at about 150°C (Figs. 1 and 2) and by 250°C roughly 90% of the ultimate weight loss has occurred. The final 10% occurs gradually between temperatures of 250 and 450°C . In particular, in the sample with FC, the bulk of the weight loss is completed at a lower temperature (240°C), possibly because there was less paraffin to be pyrolyzed.

Mass spectra of the two mixtures are shown in Figures 3, 4, and 5. Figure 3 is the spectrum at 240°C of $Al_2O_3/FC/Paraffin$ showing the distribution of the ions emanating from the sample during the maximum rate of weight loss. This is the inflection point of the TGA curve at 240°C . A similar scan is shown in Figure 4 of the same sample at 400°C after 95% weight loss has occurred, showing a broader distribution of products shifted towards higher molecular weights; note increased abundance of $m/z = 45$ and 59, both oxygen containing species. Finally, Figure 5 shows the spectrum of the sample without the surfactant, taken at 250°C corresponding to the temperature of maximum rate of weight loss. Both spectra of the $Al_2O_3/Paraffin$ (Fig. 5) and $Al_2O_3/Paraffin/FC$ (Fig. 3) show the same general distribution of decomposition products at 250°C .

Figures 6 and 7 show several of the ketone and/or aldehyde species evolving with respect to temperature. The ketones and/or aldehydes, as with most other ions, begin evolving at about 230°C and continued up to around 330°C . Figure 6 contains the MS trace vs. time for the $Al_2O_3/FC/Paraffin$ system, while Figure 7 contains the trace of the $Al_2O_3/Paraffin$ system.

Three major chemical families are tentatively identified from the mass spectra. These can be positively identified by further experimentation using sec-

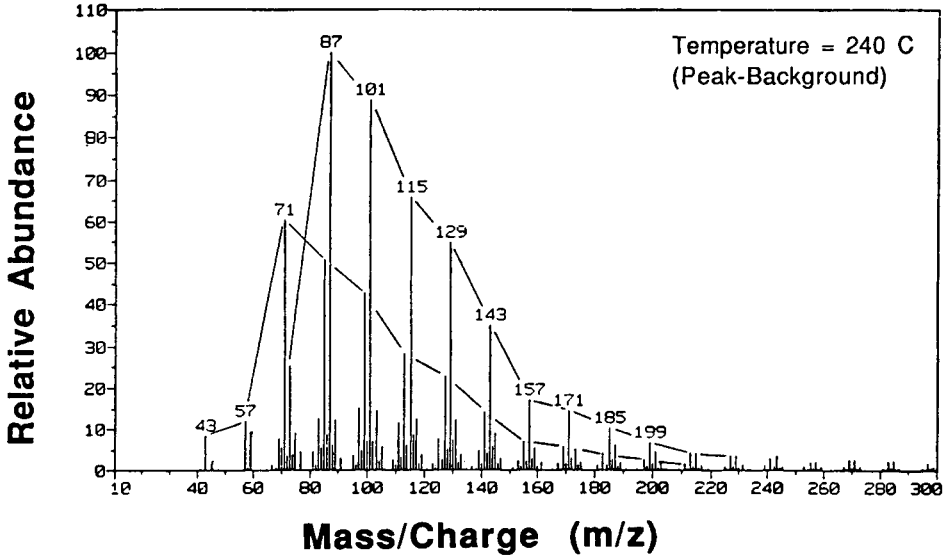


Fig. 3. Mass spectrum of ceramic/surfactant/paraffin system showing the distribution of emanating ions from the TGA at a temperature of 240°C, corresponding to the temperature of maximum rate of weight loss.

ondary MS/MS whereby the ions are fragmented again and analyzed.⁶ The spectra show a periodicity of 14 mass/charge (one CH₂ unit) with respect to each family member. These families are summarized in Table II.

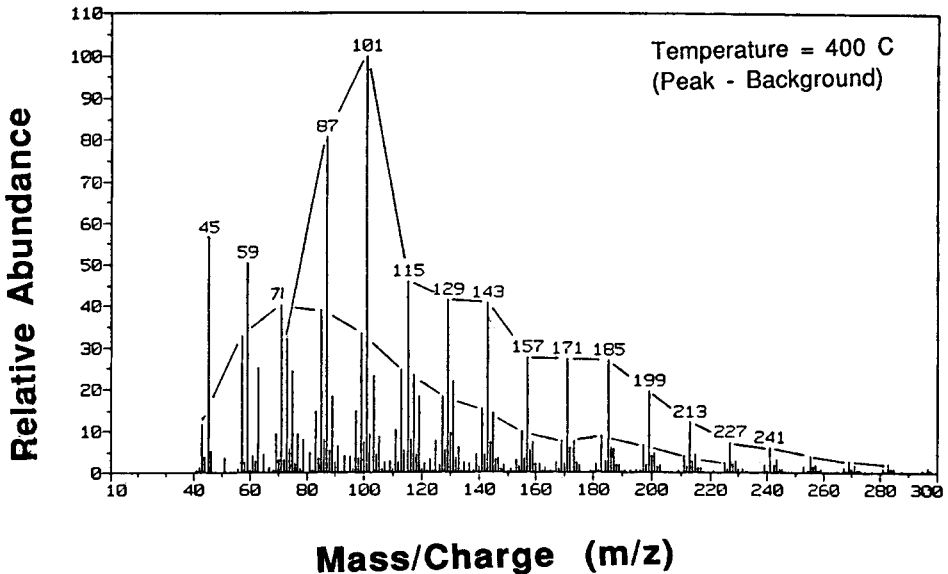


Fig. 4. Mass spectrum of ceramic/surfactant/paraffin sample at 400°C showing ions shifted to higher molecular weights.

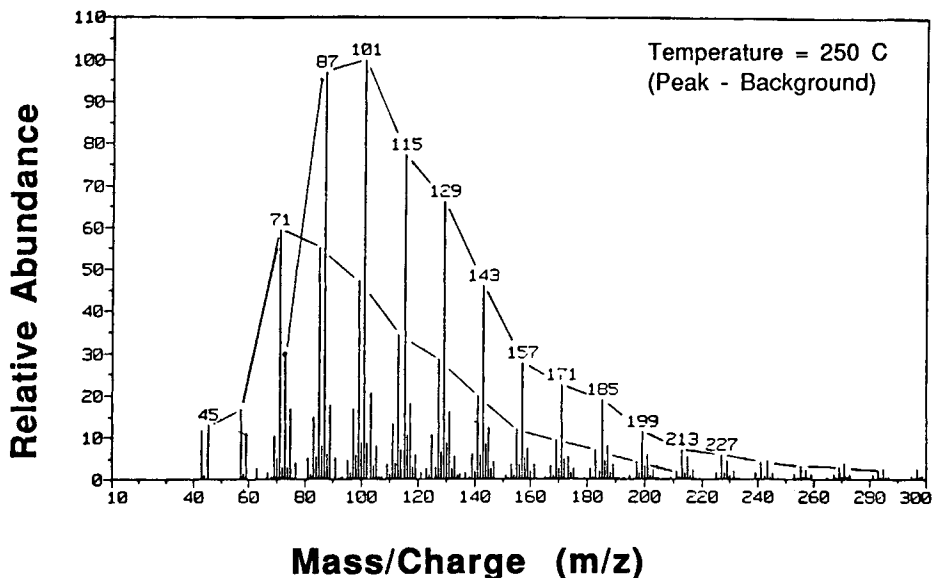


Fig. 5. Mass spectrum of sample without surfactant taken at 250°C, corresponding to the temperature of maximum weight loss.

A common pyrolysis product is acetaldehyde ($MH^+ = 45$) and is prominent in the 400°C spectrum. Acetone and/or propionaldehyde ($MH^+ = 59$) is also a common ion during pyrolysis at high temperatures.

As these data indicate, the surfactant had no discernable effect on the types of species evolved. We attribute this to the very small amount of surfactant in the sample and to the similarity of positive ion forming decomposition products.

From the relative abundance of the ions within their respected families, both the number average molecular weight and weight average molecular weight of

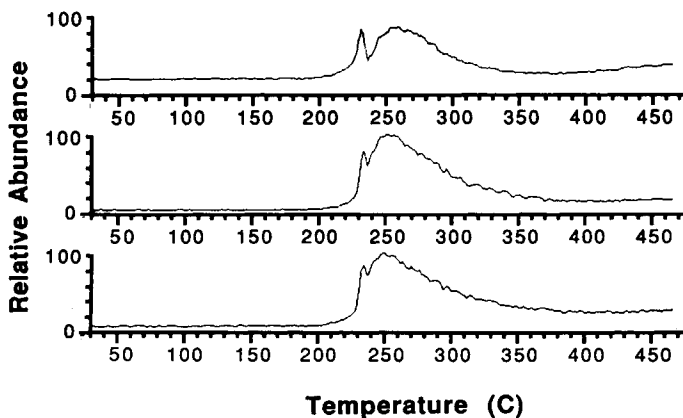


Fig. 6. Ion intensity vs. temperature of species 73, 87, and 101 in sample *with surfactant*.

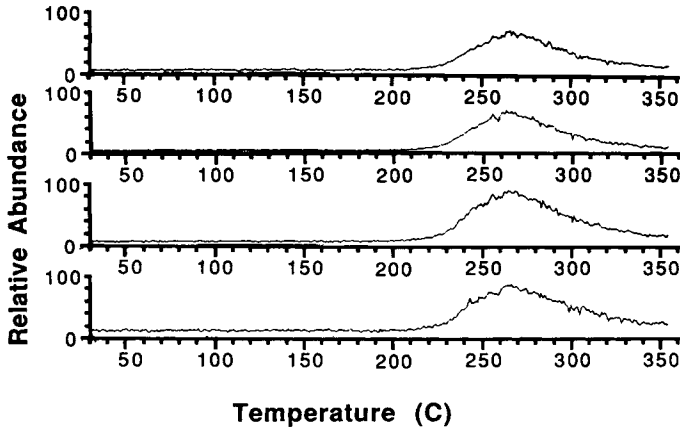


Fig. 7. Ion intensity vs. temperature of species 101, 115, 129, 143 in sample *without surfactant*.

each family can be determined. The polydispersity is the ratio of the weight average and the mass average molecular weights:

$$M_n = \frac{\sum NiMi}{\sum Ni} \tag{1}$$

TABLE II
Functional Groups and Their Structure

Functional group	MH+	Typical chemical structure
Ketones/Aldehydes	73, 87, 101, etc	$\text{CH}_3(\text{CH}_2)_m\text{C}(\text{CH}_2)_n\text{CH}_3$ $\begin{array}{c} \parallel \\ \text{O} \end{array}$
Alkane Fragments	29, 43, 57, 71, 85, etc	$[\text{CH}_3(\text{CH}_2)_n\text{CH}_2^+]^*$
Alkene Fragments	41, (55), 69, 83, 97, etc	$[\text{CH}_3\text{CH}=\text{CH}(\text{CH}_2)_n\text{CH}_2^+]^*$
Acetaldehyde	45	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C} \\ \diagdown \\ \text{H} \end{array}$
Propionaldehyde & Acetone	59	$\begin{array}{c} \text{O} \qquad \text{O} \\ \parallel \qquad \parallel \\ \text{CH}_3\text{CH}_2\text{C} \qquad \text{CH}_3\text{C} \\ \diagdown \qquad \diagdown \\ \text{H} \qquad \text{CH}_3 \end{array}$
Acids	61, 75, 89, 103, etc	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3(\text{CH}_2)_n\text{C} \\ \diagdown \\ \text{H} \end{array}$

TABLE III
Molecular Weight of Ketones (Aldehydes) in the Pyrolysis Gas

System	Temp.	Mn	Mw	Pd
Al ₂ O ₃ /Paraffin	220	100	117	1.17
Al ₂ O ₃ /Paraffin	250	122	137	1.13
Al ₂ O ₃ /Paraffin	330	118	140	1.18
Al ₂ O ₃ /Paraffin/FC	210	94	101	1.08
Al ₂ O ₃ /Paraffin/FC	240	115	127	1.10
Al ₂ O ₃ /Paraffin/FC	320	110	129	1.17
Al ₂ O ₃ /Paraffin/FC	400	115	138	1.20

$$Mw = \frac{\sum NiMi^2}{\sum NiMi} \quad (2)$$

$$Pd = \frac{Mw}{Mn} \quad (3)$$

Looking specifically at the ketones and/or aldehydes, and assuming that the relative ease of ionization is not affected by the molecular weight, the results of the above calculations are reported in Table III. The first observation which can be seen is that although both Mn and Mw change slightly with respect to temperature, Mw changes slightly more. This is better reflected in the polydispersity, which leads to an interesting conclusion; as the pyrolysis reaction progresses, the molecular weight distribution of these species broadens as shown by an increasing polydispersity with temperature (Fig. 8). At low temperatures

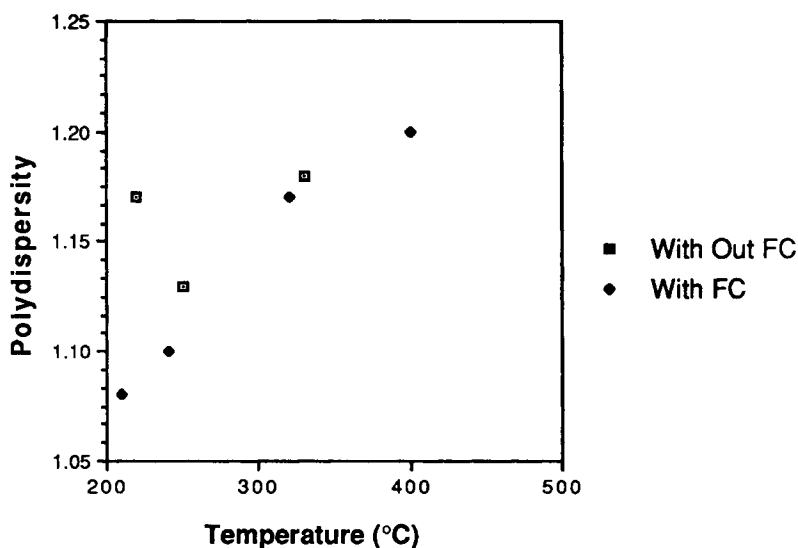


Fig. 8. The polydispersity of ketones (Aldehydes), increasing with temperature, data from Table III.

a sharp distribution is present; at higher temperatures the relative abundance of both high and low molecular weight species increases, broadening the distribution.

CONCLUSIONS

The presence of a surfactant in the ceramic mixture does not have a significant effect on the type or relative abundance of pyrolysis products. This is demonstrated both by comparison of the TGA thermal curves and the mass spectra. The primary difference between the two samples is the amount of solids in the mixture, which is predetermined when the samples were mixed.

Several air pyrolysis products were identified. These include ketones and/or aldehydes, alkanes, alkenes, and acids. Positive identification of these ions could be accomplished by MS/MS, where the ions are fragmented and a mass spectrum taken of the secondary fragments.

The molecular weight distribution of the pyrolysis products broadens at higher temperatures as shown by a larger increase in the weight averaged molecular weight compared to the number averaged molecular weight. This is evident in the increased polydispersion at the higher temperatures. This is counter intuitive as one would expect to see a lower molecular weight distribution in harsher thermal environments, the data show that the relative abundance of both lower MW as well as higher MW species increases. The effect of diffusion of the higher molecular weight species through the bulk alumina is to shift the evolution of these species to higher temperatures. It is proposed that this effect competes with that of the thermal environment, producing both higher molecular weight fragments and lower molecular weight fragments at higher temperatures.

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