



Stabilization of Flame Retardant High Temperature Resin Systems

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ABSTRACT

When brominated flame-retardants such as brominated polystyrene are used in high temperature resins they are often subject to degradation. Through the use of metal phosphate complexes this degradation can be limited. Positive results include a lighter color FR compound and lower level of decomposition products. This produces less corrosion and subsequent machine wear. There is also minimal loss in FR properties as the compound is processed. DSC and TGA data demonstrate the stabilization results. Initial pyrolysis GC/MS evaluations of thermal degradation are also presented.

I. Introduction

Nylon 6,6 is a semi-crystalline, off-white engineering thermoplastic known for its heat resistance, rigidity, dimensional stability and abrasion resistance. It is often used in combination with glass fiber, which gives it a marked increase in stiffness. The processing of glass filled Nylon 6,6 does present some challenges. High temperatures are generally needed for extrusion and molding, and this can cause embrittlement and color change unless stabilized or protected (1).

Glass filled Nylon 6,6 is used in a number of electrical and electronic applications. Many of these applications must meet some flame retardancy standard, typically a UL 94 test rating. Flammability requirements for Nylon 6,6 are achieved through the use of additives. One popular approach is the use of a brominated or chlorinated organic in combination with one or several inorganic synergists (2). Typically, the inorganic synergist is antimony oxide. However, one of the major problems associated with flame-retarded nylon is thermal instability under normal processing (molding) conditions (3). Thermal decomposition can lead to heavy mold deposits, plugging of the mold vent and corrosion of the mold. Often, typical heat stabilizers are insufficient to overcome processing challenges.

Kemgard 981 and **981N** are structured zinc oxide/zinc phosphate materials produced by a patented surface treatment. In this work we demonstrate that **Kemgard** products are effective cosynergists with antimony oxide in Nylon 6,6 and function by promoting the formation of a thermally stable char. A key benefit of **Kemgard** in FR Nylon 6,6 is improved thermal stability, demonstrated by both DSC and TGA. Preliminary pyrolysis GC/MS experiments indicate that **Kemgard** can affect degradation products of flame-retarded Nylon 6,6. Differences in polymer decomposition could be the result of differences in char forming processes. This influence on char formation can explain results showing lower levels of brominated flame retardant are needed for UL 94 V-0 in systems containing **Kemgard 981** or **Kemgard 981N**.

II. Experimental

Nylon test specimens were prepared at Smithers Scientific Services using the raw materials shown in Table 1.

Table 1

Material	Product Name	Supplier
Glass Filled Nylon 6,6	Zytel 70G33	DuPont
Antimony Oxide	Fireshield L	Oxy Chem
Brominated Polystyrene	Pyrochek 68PB Saytex HP-7010P	Albemarle
ZnO/Zn Phosphate	Kemgard 981 Kemgard 981N	Sherwin-Williams Chemicals

Compounds were extruded using a Haake twin screw extruder operating at 80 rpm a temperature profile as follows:

$$\begin{array}{ll} \text{Zone 1} = 249^{\circ} \text{ C} & \text{Zone 2} = 271^{\circ} \text{ C} \\ \text{Zone 3} = 274^{\circ} \text{ C} & \text{Zone 4} = 280^{\circ} \text{ C} \\ & \text{Die} = 283^{\circ} \text{ C} \end{array}$$

The materials were ground using a Cumberland grinder and then injection molded using a Cincinnati Milacron “Vista Sentry” model VST-33 with 33 tons clamping force and a 50 gram shot.

Flammability was assessed according to the UL 94 test method. In this test, the prescribed flame is applied for 10 seconds and the time that the sample burns before self-extinguishing is recorded. The flame is then reapplied for another 10 seconds and the time to self-extinguishing is again recorded. A third time is recorded for afterglow and these times are used to establish a “V” rating. In this work, all synergist combinations produced samples with a rating of V-0.

Color measurements of nylon compounds were measured by reflectance using a MacBeth Color Eye. Reported values are the average of three measurements taken directly on UL-94 test specimens.

Differential scanning calorimetry measurements were performed using a TA Instruments 2920 DSC. Materials were heated at a rate of 10° C/min under an air purge of 50 cc/min. The data was analyzed using TA Universal Analysis Software.

Thermogravimetric measurements were performed using a Mettler Toledo Star System. All of the TGA experiments were conducted in air. The initial temperature ramp speed was 20° C/min up to 340° C. Isothermal weight loss was then measured at 340° C for 30 minutes.

Pyrolysis GC/MS experiments were conducted using an Agilent 6890 Series GC System with a capillary column and an Agilent 5973 Mass Selective Detector. Pyrolyses were performed at both 400° C and 600° C in a Frontier Lab pyrolysis chamber.

III. Kemgard Mateials

Sherwin-Williams Chemicals’ **Kemgard** line of FR synergists/smoke suppressants are structured materials produced by a patented process in which molybdates/phosphates are precipitated on to the surface of a mineral core. **Kemgard 981** and **Kemgard 981N** are both based on zinc oxide/zinc phosphate chemistry and are distinguished by different processing conditions, chemical composition and physical properties. While the exact chemical composition of these products is proprietary, the differences in physical properties are shown in Table 2.

Table 2

Typical Properties	KG 981	KG 981N
% Zn	69.4	73.5
% Moisture	0.2	0.1
Oil Absorption g/100 g	13.1	10

IV. Results

A. Processing and Color Measurement

Seven glass-filled nylon 6,6 samples were prepared on a twin screw extruder and then injection molded into UL-94 test bars. Samples 1-4 contained the brominated polystyrene flame retardant Pyrochek 68PB. Samples 5-7 contained a similar brominated flame retardant, Saytex 7010HP. Three different synergist packages were examined: antimony oxide, a combination of antimony oxide and **KG 981**, and a combination of antimony oxide and **KG 981N**. Compositions of the seven compounds are shown in Table 3. All of the samples containing FR synergist were rated V-0 in the UL 94 test.

Table 3

	1	2	3	4	5	6	7
Zytel Nylon	76.5	69.5	69.5	69.5	69.5	69.5	69.5
Pyrochek 68PB	23.5	23.5	23.5	23.5			
Saytex 7010					23.5	23.5	23.5
Antimony Oxide		7	5	5	7	5	5
KG 981			2			2	
KG 981-N				2			2

Color Values

L*	63.65	67.07	69.86	74.29	78.32	79.99	80.45
a*	3.03	1.86	1.87	1.72	0.94	1.24	0.97
b*	20.93	15.28	15.12	14.53	14.19	14.16	13.97

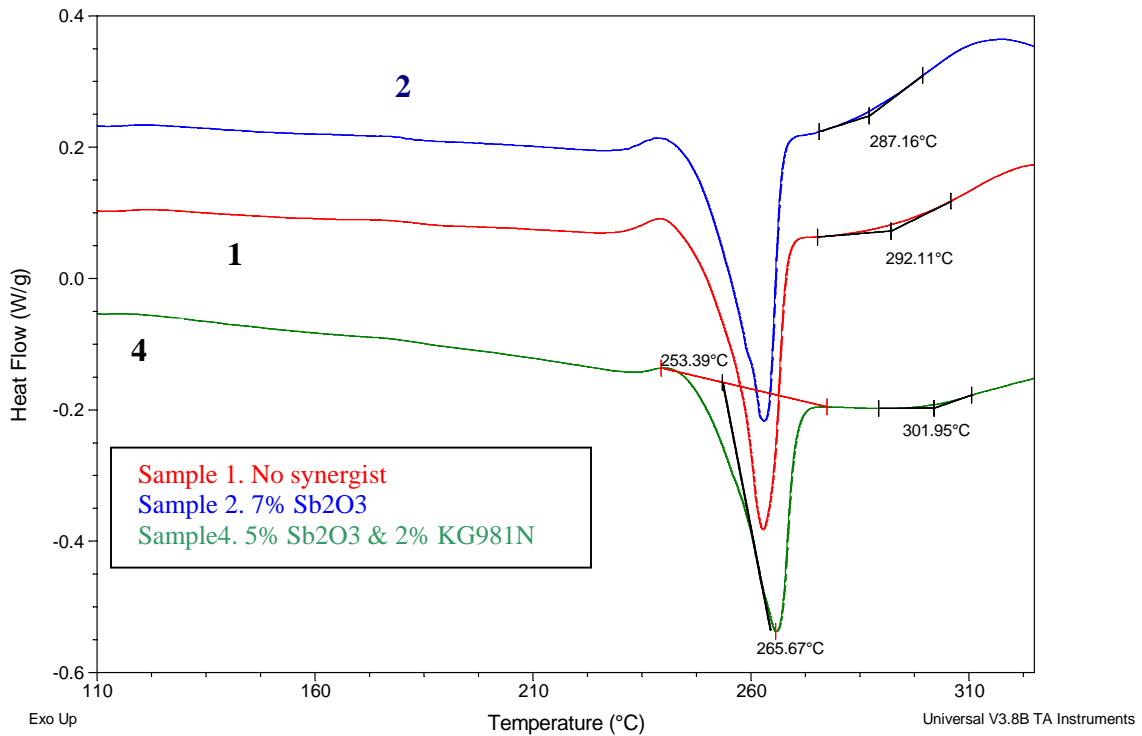
In the samples containing Pyrochek 68PB it was apparent that test specimens containing antimony oxide were lighter in color than the control. This can be seen in the measured L* values of samples 1 and 2. The increase in L* value is an expected result because of the refractive index of antimony oxide (2.3) and its resulting tint strength. A further improvement in whiteness was observed in samples in which 2% of the antimony oxide was replaced with **KG 981** or **KG 981N**. The increase in L* value in sample 4 is quite significant and unexpected given the fact that both zinc oxide and zinc phosphate are

lower in refractive index than antimony oxide. Therefore the improvement is not a result of tint strength, but is more likely an indication of improved thermal stability.

There are color differences between the two brominated polystyrene flame-retardants. This is seen in comparing the color of Samples 2 and 5. However, even in the lighter colored Saytex containing systems, the replacement of 2% antimony oxide with **Kemgard** did produce an improvement in whiteness. Again, the lightest color was achieved in the sample containing 2% **KG 981N**.

B. Differential Scanning Calorimetry

It is known that discoloration often indicates the onset of thermal decomposition. Differential Scanning Calorimetry has proven to be an effective tool to study oxidative thermal decomposition in Nylon 6,6 (4). To examine the influence of FR synergist on thermal stability, three samples (Samples 1, 2 and 4) were studied by differential scanning calorimetry. DSC curves for three molded glass-filled nylon 6,6 specimens are shown in Figure 1 below.



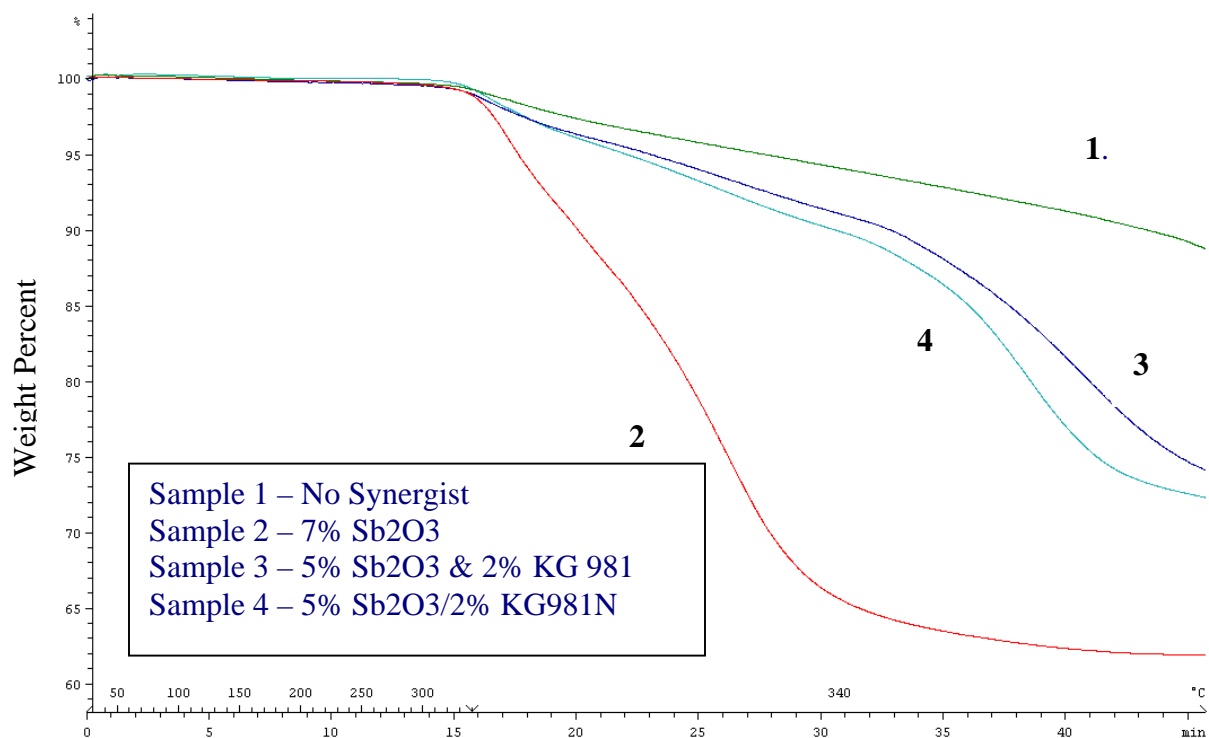
All of the samples exhibited a large endothermic peak at 263° – 265° C, corresponding to melting. However there is differentiation between the samples in terms of the onset of oxidative thermal decomposition. The presence of antimony oxide appears to diminish

oxidative thermal stability when compared to sample with no synergist. Antimony oxide lowers the onset temperature for exothermic thermal decomposition by 5° C (292° C to 287° C). In addition the exotherm peak is shifted to lower temperature (312° C. vs. > 325° C). In contrast, the sample with 5% antimony oxide and 2% **KG 981N** has greater thermal stability than the control. The onset temperature for thermal decomposition is increased by 10° C to 302° C. The peak for the exothermic decomposition occurs above 325° C. This data suggests that the zinc oxide/zinc phosphate chemistry of **KG 981** and **KG 981N** improves the thermal stability of nylon 6,6 containing brominated polystyrene. This data is also consistent with the improvement in color observed with the use of **Kemgard** .

C. Thermogravimetric Analyses

Thermal stability of all of all the samples in Table 3 was examined by TGA. In these studies the temperature was ramped to 340° C and then held at 340° C for 30 minutes. TGA plots for samples 1-4 are shown in the figure below.

Figure 2



In all of the samples, weight loss begins to occur at around 330° C. This is 30° – 40° C higher than the onset of thermal decomposition as determined by DSC. Generally DSC will provide a more accurate onset temperature because thermal events can be detected that do not necessarily result in weight loss and there is better thermal contact in the DSC. Also, In TGA, initial weight loss is very small and this can influence the accuracy of onset temperature determination.

Examining the isothermal plots of samples 1 and 2, it is apparent that the addition of antimony oxide significantly increases the rate of polymer decomposition, although the onset temperature may be unchanged. The destabilization effect of antimony oxide is well known and often limits the processing temperature of FR Nylon 6,6.

TGA plots of samples 3 and 4 (containing **KG 981** and **KG 981N**, respectively) clearly demonstrate that both materials improve thermal stability at 340° C when compared with the pure antimony oxide system. For the first 15 minutes at 340° C, the TGA plots for samples 3 and 4 are indistinguishable. However, beyond 15 minutes, sample 3 (**KG 981**) appears to slow thermal decomposition more than sample 4 (**KG 981N**). This possibly could indicate the formation of a slightly more thermally stable char. A more robust char could translate into improved flame retardancy.

Similar TGA plots for samples 5-7 are shown in the Figure 3. Again it appears that the addition of either **KG 981** or **KG 981N** greatly improves the isothermal stability of Nylon 6,6 containing Saytex 7010.

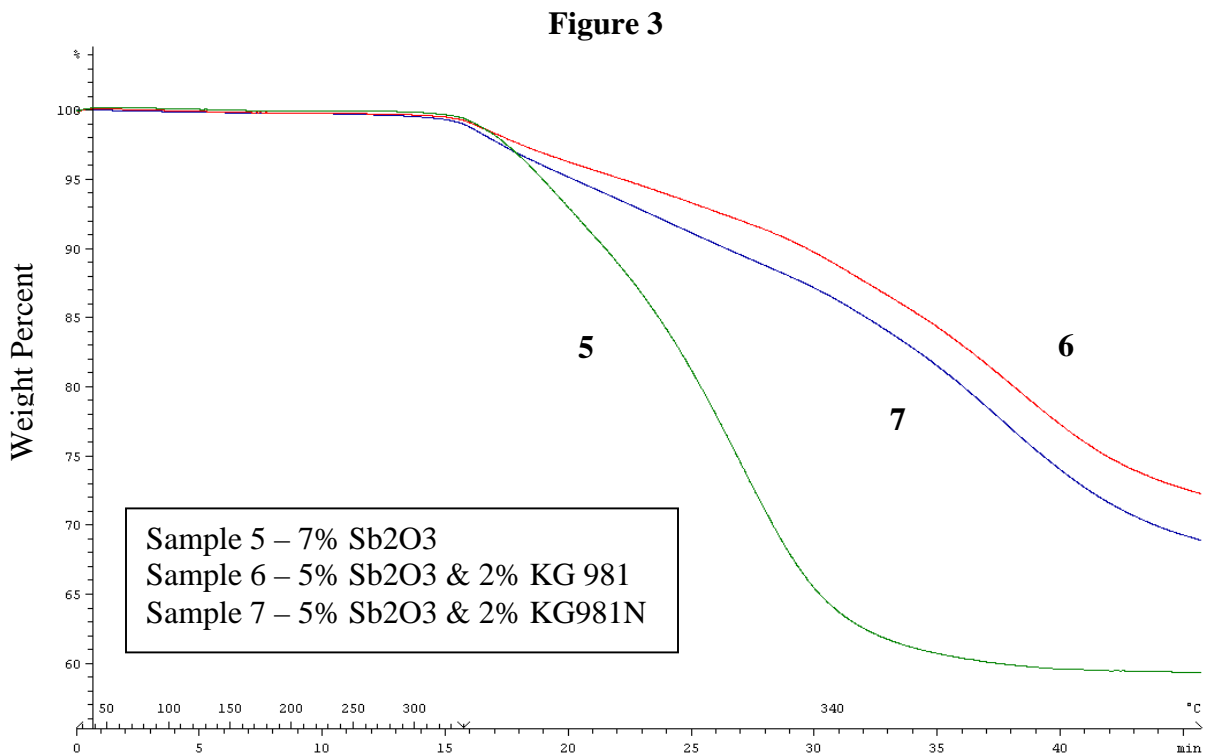
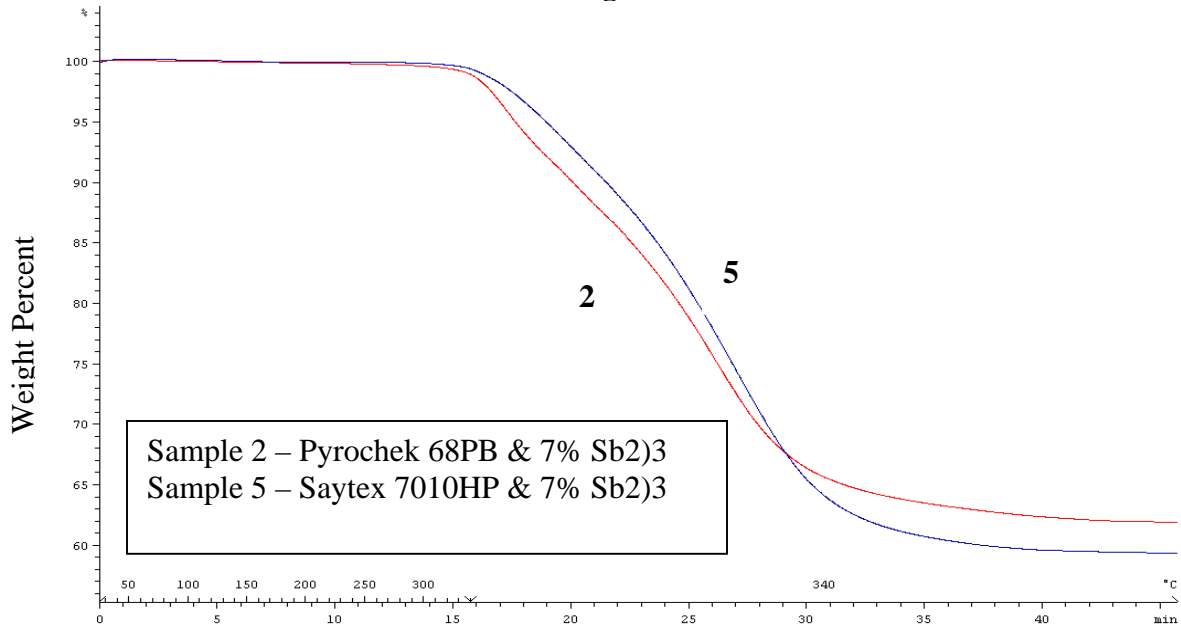


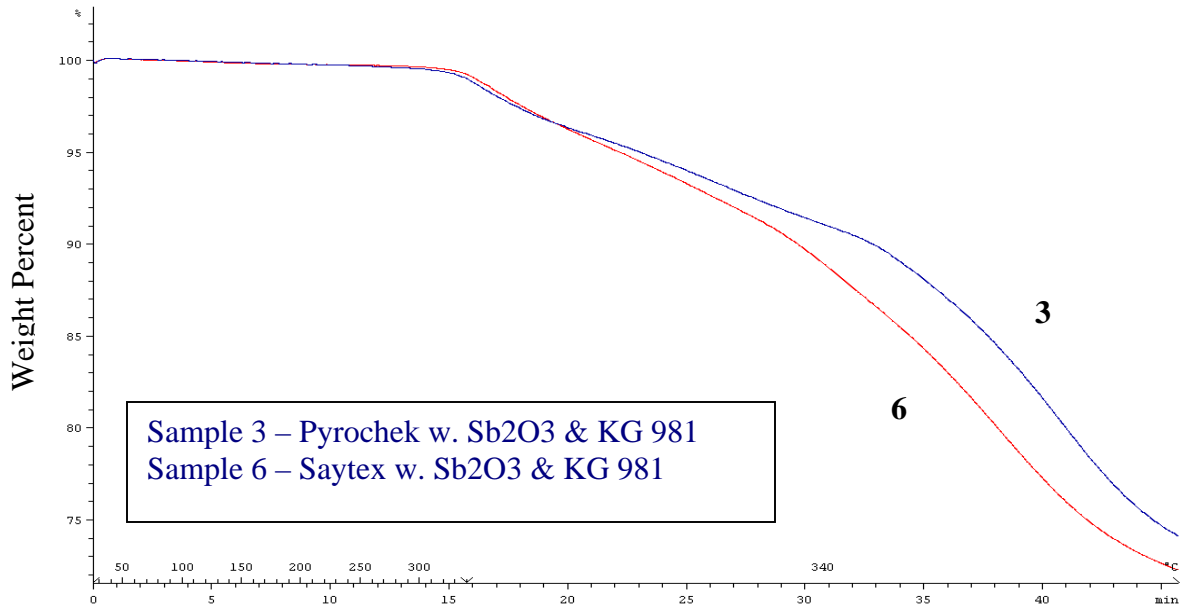
Figure 4 compares the TGA plots for the two samples that use only antimony oxide as the synergist. Sample 2 uses Pyrochek 68PB and sample 5 contains Saytex 7010. Here it appears that the Saytex system is slightly more thermally stable. This result is consistent with the observed differences in color.

Figure 4



In presence of **Kemgard 981**, the influence of the brominated polystyrene type on thermal degradation is changed. In Figure 5 the Isothermal TGA curves for Sample 3 (Pyrochek) and Sample 6 (Saytex) are compared. At less than 10 minutes, the TGA plots of samples containing either Pyrochek or Saytex flame-retardants are indistinguishable. However, beyond 10 minutes, the Pyrochek containing sample actually shows a slower weight loss. This result suggests that an interaction between the organic FR and Kemgard may affect char formation, and this difference can be detected by isothermal TGA at longer times.

Figure 5

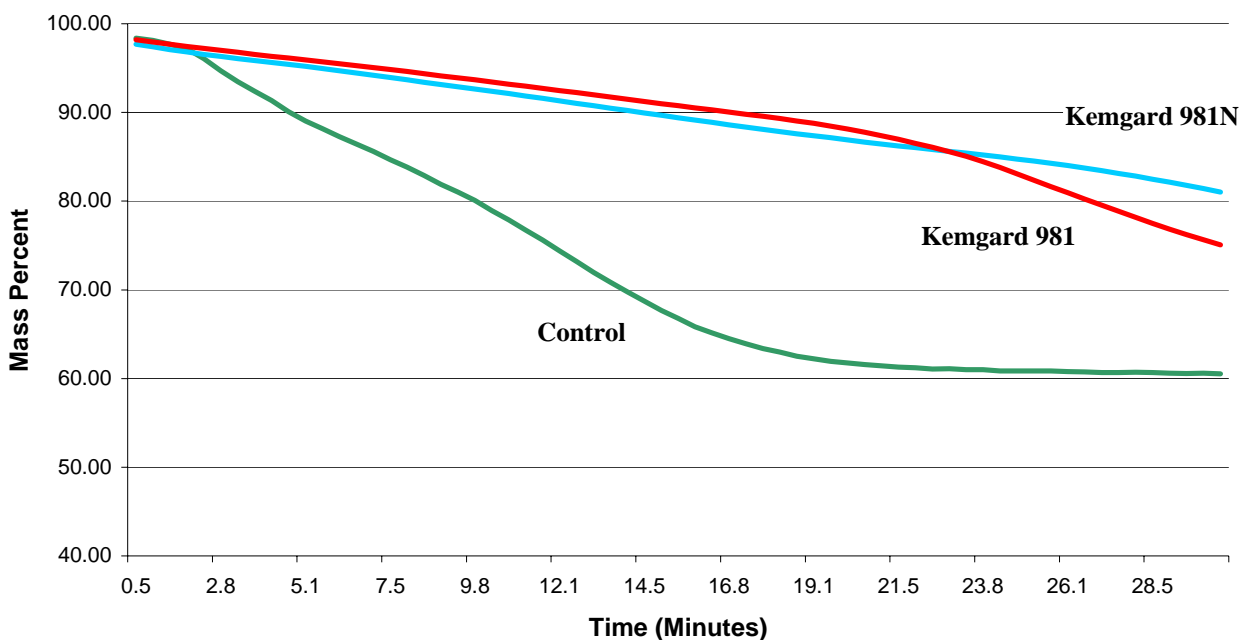


D. Further TGA Studies

Thermogravimetric Analysis was used to determine the influence of Kemgard samples on the thermal stability of commercial systems manufactured at a major Nylon compounder. Although the exact composition of the compounds are proprietary, it is known that the control sample contained a flame retardant system with less than 20% Pyrochek 68PB and an antimony oxide synergist. As in the studies described above, two additional experimental samples were prepared in which 2% of the antimony oxide was replaced with either **Kemgard 981** or **Kemgard 981N**.

Figure 6 shows TGA plots that clearly demonstrate that both **KG 981** and **KG 981N**, improve thermal stability at 340° C. For the first 20 minutes of the study, the **Kemgard** containing samples were indistinguishable. However, at times greater than 20 minutes, it appears that the sample containing KG 981N shows better thermal stability than the sample with KG 981. This result is actually reversed from our previous results. It is interesting that feedback from the compounder also indicates that KG 981N provided the best FR properties. It is possible that improved FR properties are achieved with more thermally stable char.

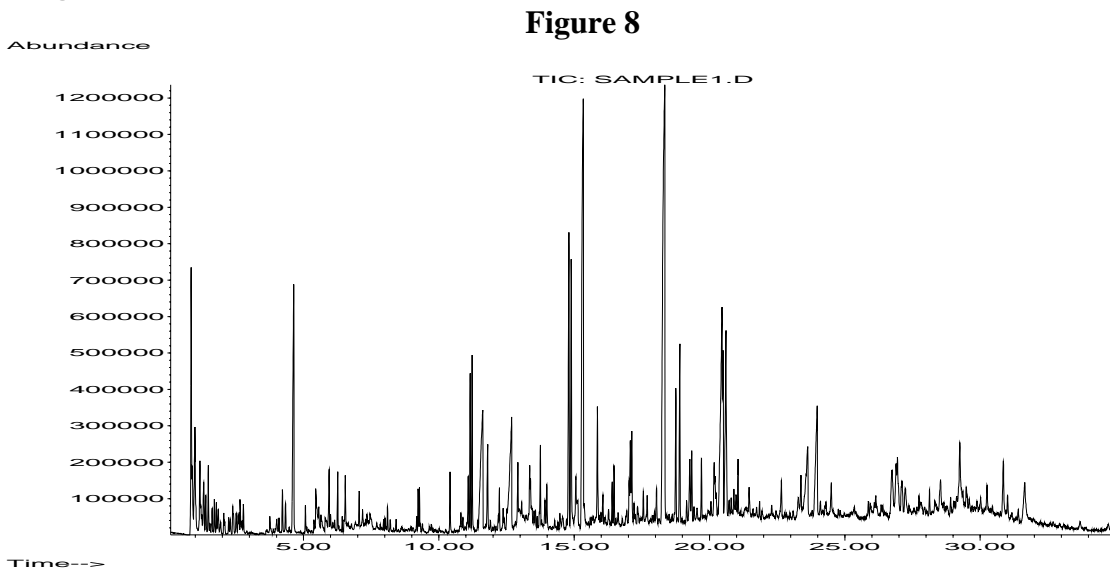
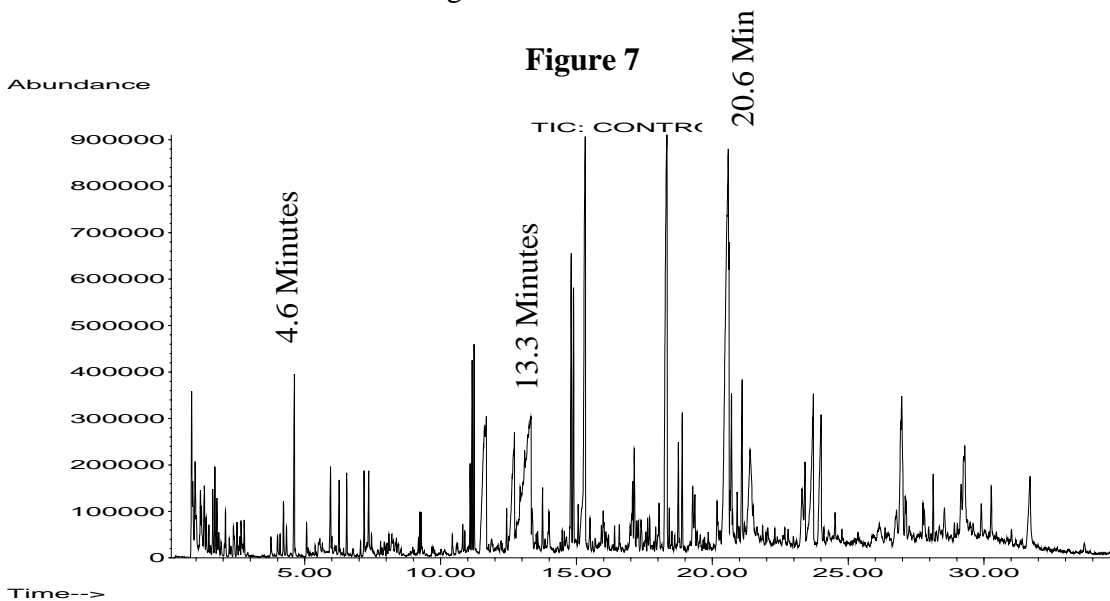
Figure 6



Although some details of this work are proprietary, it does appear that selection of the best **Kemgard** chemistry may be system dependent. TGA is an effective way to assess polymer degradation and the influence of **Kemgard** additives on char formation and the thermal stability of these FR Nylon systems.

E. PYROLYSIS GC/MS

Pyrolysis GC/MS was used to study the influence of **Kemgard** chemistry on the degradation products of flame retarded Nylon 6,6. Two samples, Sample 2 with no Kemgard (Figure 7) and Sample 4, with 2% **Kemgard 981N** (Figure 8) were pyrolyzed. The GC curves are shown in the figures below.



Not surprisingly, many of the major peaks in the two chromatographs are common. For example the peak at 4.6 minutes corresponds to cyclopentanone, a known major

decomposition product of Nylon 6,6. Many other common peaks correspond to decomposition products of brominated polystyrene. For example the major peak at 15.3 minutes corresponds to dibromostyrene. Other common peaks at 11.2, 17.1 and 18.3 minutes are also attributed to brominated material.

Two significant peaks however do appear in the control which are not seen in the **Kemgard** containing sample. One of these is a fairly broad peak, located at 13.3 minutes, attributed to 5-cyanopentanoic acid. The second peak occurs at 20.6 minutes and is likely a bicyclohexenone. While this data alone cannot provide mechanistic information, it can be concluded that the presence of the **Kemgard** zinc oxide/zinc phosphate chemistry can influence the polymer degradation products and this may influence char formation. Additional work is needed in this area.

V. Discussion

Polymer combustion is a complex process that includes thermal degradation, char formation, transport of degradation products, ignition, and fire propagation. When the surface of a material is heated, thermal degradation reactions occur and combustible gaseous products are evolved. Formation of a char layer on the surface of a polymer can interfere with the combustion process by attenuating the release of gaseous products. A stable char can also act as a barrier that can insulate the interior material from further decomposition.

In considering the char process, two key parameters must be considered:

- Onset temperature of char formation
- Char yield and thermal stability of the char layer.

In this work, we have demonstrated that **Kemgard** products **KG 981** and **KG 981N**, both based on zinc oxide/zinc phosphate, can provide flame retardancy in Nylon 6,6. Pyrolysis CG/MS indicates that **Kemgard** materials can influence the decomposition products of Nylon 6,6. Differences in thermal decomposition likely promote the formation of a more thermally stable char layer that can be clearly demonstrated by TGA.

A key performance attribute of **Kemgard** zinc oxide/zinc phosphate chemistry is that it delays the onset of thermal oxidative degradation in FR Nylon 6,6. Improved thermal stability provides multiple benefits in processing and could potentially enable the use of higher mold temperatures and production rates. Improved thermal stability should reduce the amount of decomposition products formed during processing, many of which can lead to excessive corrosion and machine wear.

References

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