Thermal Analysis as an Important Research Tool for Colleges and Universities

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THERMAL ANALYSIS AS AN IMPORTANT RESEARCH TOOL FOR COLLEGES AND UNIVERSITIES

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and the College of Graduate Studies by

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Dr. Tobili Sam-Yellowe

Date: December 7, 2011
I would like to thank my advisor Dr. Alan Riga for his never ending support and encouragement throughout my research. His knowledge, insight and guidance helped make this thesis possible. I would like to thank my fellow graduate students Lakshmi Kaza and Shravan Singh for their help and support of my research, along with the whole Riga research team, who provided help when I needed it most.

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Lastly I wish to thank my mother Joan Fruscella, who passed away in 2008. If it wasn’t for her guidance and encouragement to pursue a graduate education, this thesis would have never been written.
THERMAL ANALYSIS AS AN EDUCATIONAL TOOL FOR COLLEGES AND UNIVERSITIES

JEFFREY ALLEN FRUSCELLA

ABSTRACT

Three experiments were performed to demonstrate that thermal analysis is an important tool for use in colleges and universities for conducting scientific research. The first experiment used thermogravimetry, differential scanning calorimetry and thermal mechanical analysis to compare polymer resins from two ResinKit®s, one from 1994 and the other from 2010. Analysis was done to determine if resins from the 1994 kit were viable standards. The experiments showed significant thermal differences between select resins and it was concluded that resins from the 1994 ResinKit® are no longer acceptable as standards.

The second experiment used thermogravimetry and differential scanning calorimetry to determine the concentration of bound and un-bound water in commercial and generic samples of milk of magnesia. Those thermal methods were compared to traditional methods and it was determined that thermogravimetry was best suited for determining bound water and that differential scanning calorimetry revealed thermal differences that none of the other thermal techniques could detect.

In the third experiment, four chemically similar aldohexose monosaccharides were evaluated using thermogravimetry to determine if the thermal analytical technique was sensitive enough to differentiate between the four monosaccharides. It was determined that thermogravimetry could detect differences between two groups of monosaccharides, but not between each monosaccharide individually.
The result of these experiments clearly shows that thermal analysis is a valuable tool for scientific research and needs to be included more as part of the curriculum for chemistry students and not delegated as a “niche” study of only limited value.
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CHAPTER I

INTRODUCTION

Thermal analysis is an analytical technique that is rarely taught in colleges and universities on the undergraduate level and is only taught on the graduate level if the graduate student is fortunate enough to find a research advisor trained in the field. Most college instructors consider thermal analysis a “niche” science not worthy of in depth study. Even the authors of chemistry text books treat thermal analysis as “niche” and delegate any chapters on the subject to the back of the book. One popular analytical text book titled Principles of Instrumental Analysis, by Holler et. al [1] has 34 chapters with a chapter on thermal analysis delegated to chapter 31, near the end of the book. Any college student knows that chapters near the end of any text book are rarely if ever covered during a semester. Those chapters are relegated to the abyss of un-tapped knowledge, which with proper instruction could provide an additional marketable skill to make the student more employable in the job market.

Some instructors are trying to turn this trend around. More instructors in colleges and universities are giving thermal analysis a second look and realizing that there is potential
for thermal analysis to enhance their knowledge and achieve their research goals. Work has been done to further educate instructors in the field on thermal analysis and papers have been published on the subject, notably a paper entitled, *Career Development and Project Planning for Emerging Thermal Analysis Scientists*, by M. Ellen Matthews and Alan T. Riga [2]. The paper outlines the market need for thermal analysis experts and discusses methods for teaching thermal analysis, including a research learning contract, which is a document that a student studying thermal analysis prepares, outlining their project goals and learning objectives.

The purpose of this research is to demonstrate that thermal analysis is an important analytical tool, which should be included more in college and university curriculums and taken more seriously by instructors. The following chapters highlight three research projects that were done using thermal analytical techniques. Each project resulted in gaining new scientific knowledge and scientific papers have been written, which have been submitted to the Journal of Thermal Analysis and Calorimetry (JTAC) for publication. The research is shown in its entirety with each individual abstract and introduction included to provide sufficient background for the reader to understand the purpose of the research being done.

As noted, the research is broken up into chapters. Chapter II discusses the use of thermal analysis to evaluate and compare polymer resins. Very little has been published on this topic and the research highlights three thermal analytical techniques: thermogravimetric analysis or thermogravimetry (TG), differential scanning calorimetry (DSC), and thermal mechanical analysis (TMA). Chapter III discusses the determination of bound and unbound water and how thermal analysis is used to determine the concentrations of each
in a commercial and generic sample of milk of magnesia. Finally, in Chapter IV the limits of thermogravimetry are explored in the evaluation of aldohexose sugars. Experiments were performed to determine if thermogravimetry had enough sensitivity to detect the molecular and stereo-chemical differences between four chemically similar sugars. Both first and second derivative analysis was used to analyze the monosaccharides.
CHAPTER II

DETERMINING THE VIABILITY OF STANDARD POLYMER RESINS BY COMPARATIVE THERMAL ANALYSIS

ABSTRACT

Samples of polymers from a commercial set of readily available reference polymers were characterized using TG, TMA, and DSC techniques. Thermal stability, thermal expansion, along with glass transition states were identified. The comparison of the reference polymers is based on a wide range of temperatures, focusing primarily on two reference polymer kits, published in 1994 and 2010. For most of the polymers evaluated, the thermal properties have remained the same over time, but others have not. This suggests that polymers from older reference kits should be re-evaluated for thermal stability to determine if they are still viable references.

INTRODUCTION

Thermal gravimetric analysis (TG), differential scanning calorimetry (DSC), and thermal mechanical analysis (TMA) are three common thermal analytical techniques used in the
analysis of polymer resins (plastics). TG is used mostly to determine compositional analysis and decomposition profiles of multi-component systems. TG is an important analytical tool in the various branches of chemistry, geology, fuels science, ceramics, and material science [3-6]. Often referred to as “TGA” or “thermogravimetric analysis”, the accepted term is “TG” or “thermogravimetry” and is accepted by organizations such as ASTM and JTAC. While “TG” is the accepted abbreviation, removing the “A” from “TGA” has not been accepted by many scientists in the thermal analysis field, due to the fact that “TG” is similar to the term “Tg”, the symbol for glass transition, which is studied through differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA) [7].

TG is the modern day analytical method of the much older and well established technique of gravimetry. The difference between TG and gravimetry is that in TG the sample mass is continually measured as it is heated. In gravimetry, the mass is only measured after an extended period time of isothermal heating. TG uses much smaller samples sizes than gravimetry, which allows samples to be analyzed in a much shorter time.

Differential scanning calorimetry (DSC) is used to measure the difference in which the rate of heat flows between a sample and a reference (empty pan) as both are heated, cooled, or held isothermal at the same time. Differences in heat flow can occur through exothermic transitions, which result in the release of heat through crystallization, curing or decomposition. Differences can also occur through endothermic transitions, which absorb heat though melting, glass transition or evaporation. In this experiment DSC is
used to determine the glass transition state of the resin polymers. The glass transition state is defined as the temperature at which material physically changes from a glassy-solid to a rubbery-flexible state [8].

Thermal mechanical analysis (TMA) is used to measure the changes in the dimension of a substance as a function of temperature [9]. When a material expands in response to heating, the coefficient of thermal expansion can be measured at the temperature at which the expansion occurs. Thermal contraction or negative thermal expansion is the opposite of thermal expansion and is measured when the sample is penetrated by the weight placed on it. One example of thermal expansion and contraction is the mercury or alcohol used in thermometers, which expand and contract with change of temperature. Another example is the shrink fitting of mechanical components, such as plastic or metal by heating one component to make it expand, then placing it over another component and allowing the first component to cool. While cooling, the component will shrink and form a tight physical bond with the second component. For example, a bushing can be fitted over a shaft by making its inner diameter slightly smaller than the diameter of the shaft, then heating it until it fits over the shaft, and allowing it to cool after it has been pushed over the shaft, achieving a 'shrink fit'.

The Society of Plastic Engineers distributes a reference polymer kit called the ResinKit®. Manufactured by the Plastics Group of America, it is used both in industry for identifying plastics and for educational research. The ResinKit® has over 50 polymer samples which
come in the form of “chips” that are molded so that small pieces of the chip can be easily clipped off and used for analysis.

In an earlier study performed by Riga, et. al [10] in 1997, polymers from two ResinKits® were evaluated to determine if resins from the 1979 kit could still be used as a reference. In that study, the kits compared were from 1979 and 1994. The results concluded that the resins tested from the 1979 kit were virtually identical to the ones in the 1994 kit. The current study evaluated resins from the 1994 ResinKit® used in the previous study compared to resins from a 2010 ResinKit®. Those resins are polystyrene chips numbers 1-3. Also included in this study were resins not tested in the 1997 study. Additional analysis was done with selected polymers form kits dating from 1979 and 1997, as analysis from the 1994 and 2010 kits yielded the need for additional reference polymers for analysis.

It is important to have reliable standards when performing compositional analysis especially if using a standard test method [11]. To determine if the resins from the 1994 kit were still acceptable standards, analysis was done using DSC, TG, and TMA to determine if any of the selected polymers have either changed composition or degraded over the time period between the manufacture dates of ResinKits®.
EXPERIMENTAL

10 polymer resins were chosen for comparative study. The polymers tested are in table I.

**Table I** Polymers selected from 1994 and 2010 ResinKit®

<table>
<thead>
<tr>
<th>Resin</th>
<th>Chemical Family</th>
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<tr>
<td>Cellulose Acetate</td>
<td>Ester</td>
</tr>
<tr>
<td>Ionomer</td>
<td>Olefin</td>
</tr>
<tr>
<td>Polystyrene General Purpose</td>
<td>Olefin</td>
</tr>
<tr>
<td>Polystyrene Medium Impact</td>
<td>Olefin</td>
</tr>
<tr>
<td>Polystyrene High Impact</td>
<td>Olefin</td>
</tr>
<tr>
<td>Polyester Elastomer</td>
<td>Elastomer</td>
</tr>
<tr>
<td>Polyphenylene Sulfide</td>
<td>Thermoplastic</td>
</tr>
<tr>
<td>Synthetic Elastomer</td>
<td>Elastomer</td>
</tr>
<tr>
<td>Thermoplastic Polyester (PETG)</td>
<td>Ester</td>
</tr>
<tr>
<td>Urethane Elastomer</td>
<td>Elastomer</td>
</tr>
</tbody>
</table>

Both sets of polymers were characterized using (DSC) and (TG). The DSC used was a Mettler model DSC 30. The TG used was a TA Instruments model TGA Q500. The TG experimental conditions were: 10-20mg sample, ramp 10°C per minute to 600°C in nitrogen, then switch to air and continue to ramp at 10°C per minute until 1000°C. Each sample was run in triplicate. DSC experimental conditions were: 15-20mg sample,
heating rate at 10°C per minute. Each sample was run singularly. DSC experimental heating and cooling temperatures were selected based on results from TG analysis. In most cases, the maximum heating temperature was 50°C less than the degradation temperature acquired from TG. For TMA, each sample had a weight placed on it that applied 0.1N of constant force to it, while in the sample pan. Table II shows the experimental test conditions for DSC.

**Table II** Experimental test conditions for DSC.

<table>
<thead>
<tr>
<th>Resin</th>
<th>DSC Max Temp</th>
<th>DSC Min Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose Acetate</td>
<td>30°C</td>
<td>-150°C</td>
</tr>
<tr>
<td>Ionomer</td>
<td>30°C</td>
<td>-150°C</td>
</tr>
<tr>
<td>Polystyrene General Purpose</td>
<td>200°C</td>
<td>-20°C</td>
</tr>
<tr>
<td>Polystyrene Medium Impact</td>
<td>200°C</td>
<td>-20°C</td>
</tr>
<tr>
<td>Polystyrene High Impact</td>
<td>175°C</td>
<td>-20°C</td>
</tr>
<tr>
<td>Polyester Elastomer</td>
<td>200°C</td>
<td>-20°C</td>
</tr>
<tr>
<td>Polyphenylene Sulfide</td>
<td>275°C</td>
<td>-20°C</td>
</tr>
<tr>
<td>Synthetic Elastomer</td>
<td>30°C</td>
<td>-150°C</td>
</tr>
<tr>
<td>Thermoplastic Polyester (PETG)</td>
<td>100°C</td>
<td>-20°C</td>
</tr>
<tr>
<td>Urethane Elastomer</td>
<td>30°C</td>
<td>-150°C</td>
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RESULTS AND DISCUSSION

*Thermogravimetric Analysis*

TG data were analyzed using *Universal Analysis 2000* software, by TA Instruments, version 4.4A. The data were plotted and analyzed using the first derivative of the % weight loss versus temperature in °C.

Eight out of the ten polymers displayed the same thermal decomposition curves, concluding that they were in fact the same material. See the appendix for TG analysis of resins not shown here. Two polymers showed significant differences in comparative thermograms. The polymers which showed significant differences were thermoplastic polyester (PETG) and synthetic elastomer.

To illustrate the similarities of most of the selected polymers from the two kits, figure 1 shows a TG of polystyrene general purpose from the 1994 kit. Figure 2 shows the TG of polystyrene general purpose from the 2010 kit.
**Figure 1** Polystyrene general purpose (1994 ResinKit®)

![Graph showing weight loss as a function of temperature for Polystyrene general purpose (1994 ResinKit®).](image)

**Figure 2** Polystyrene general purpose (2010 ResinKit®)

![Graph showing weight loss as a function of temperature for Polystyrene general purpose (2010 ResinKit®).](image)
As seen by TG analysis, the two polymers are virtually identical. This is in contrast to the TG of Thermoplastic polyester (PETG). Analysis showed a 468°C derivative peak temperature, which exists in the 2010 polymer, but doesn’t exist in the 1994 polymer. TG analysis of both polymers is shown in figures 3 and 4.

**Figure 3** TG of PETG (1994 ResinKit®)
The TG of synthetic elastomer shows a derivative peak temperature that exists in the 1994 ResinKit®, which only slightly appears in the TG of the 2010 ResinKit®. TG analysis of synthetic elastomer is shown in figures 5 and 6.
**Figure 5** TG of synthetic elastomer (1994 ResinKit®)

**Figure 6** TG of synthetic elastomer (2010 ResinKit®)
Differential Scanning Calorimetry Analysis

The DSC scans were analyzed using Mettler STARE software, version 8.00. This was used to determine the glass transition state (\(T_g\)) of each polymer. Table III shows the glass transition temperatures determined from the DSC.

**Table III DSC \(T_g\) results for ResinKit® Polymers**

<table>
<thead>
<tr>
<th>Resin</th>
<th>(T_g) (1994 Kit)</th>
<th>(T_g) (2010 Kit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose Acetate</td>
<td>71.6°C</td>
<td>72.4°C</td>
</tr>
<tr>
<td>Ionomer</td>
<td>-44.3°C</td>
<td>-46.2°C</td>
</tr>
<tr>
<td>Polystyrene General Purpose</td>
<td>97.2°C</td>
<td>90.2°C</td>
</tr>
<tr>
<td>Polystyrene Medium Impact</td>
<td>101.5°C</td>
<td>96.4°C</td>
</tr>
<tr>
<td>Polystyrene High Impact</td>
<td>108.1°C</td>
<td>103.0°C</td>
</tr>
<tr>
<td>Polyester Elastomer</td>
<td>-44.7°C</td>
<td>-44.9°C</td>
</tr>
<tr>
<td>Polyphenylene Sulfide</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Synthetic Elastomer</td>
<td>-77.7°C</td>
<td>-81.7°C</td>
</tr>
<tr>
<td>Thermoplastic Polyester (PETG)</td>
<td>81.7°C</td>
<td>137.6°C</td>
</tr>
<tr>
<td>Urethane Elastomer</td>
<td>-44.5°C</td>
<td>-44.6°C</td>
</tr>
</tbody>
</table>

The glass transition state of polyphenylene sulfide could not be determined by DSC. This was most likely caused by crystallization of the polymer right up until the melt point. The TG of polyphenylene sulfide from both the 1994 and 2010 kits were very similar with a derivative peak temperature only a few degrees celsius apart.
PETG had significant glass transition ($T_g$) differences between the two resin kits. These results show a correlation with the differences seen in the TG analysis of the 1994 and 2010 resins. Synthetic elastomer only had a 4°C difference in glass transition temperature between the two resins. This did not correlate with the thermograms, but a visual observation of the 1994 resin (figure 7) and the 2010 resin (figure 8) revealed that the 1994 resin had degraded over time. The polymer chip had fused with its plastic sheath used to house the polymer samples and could not be physically removed from its slot. There was also discoloration of the 1994 synthetic elastomer, giving it a yellowish appearance.

![Figure 7 Synthentic elastomer from the 1994 ResinKit®](image)
Since it was discovered that resin samples of PETG and synthetic elastomer showed significant thermal differences between the two kits additional analysis was done with resins from two different ResinKits®, one published in 1979 and the other in 1997. The PETG resin chip from the 1979 kit was no longer available, but the synthetic elastomer chip was still usable. These resins were analyzed using DSC, TG and TMA. PETG and synthetic elastomer resins form the 1994 and 2010 kits were also analyzed by TMA.

The results showed that the resins form 1979 and 1997 show similar thermal properties to the resins analyzed from the 2010 kit. TG results are shown in figures 9-11.
Figure 9 TG of PETG (1997 ResinKit®)

Figure 10 TG of synthetic elastomer (1979 ResinKit®)
Glass transition points were measured by DSC and are shown in table IV. The glass transition temperatures of the 1979 and 1997 resins are close to that of the 2010 resins. The 1994 resins reveal significantly different temperatures, especially with PETG. TMA showed a correlation with the analysis done through TG and DSC. Both PETG and synthetic elastomer resins analyzed from the 1994 ResinKit® showed significant thermal differences from the same chips analyzed from the other kits. TMA results are shown in figures 12-18.
Table IV PETG and synthetic elastomer $T_g$

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (1979 Kit)</th>
<th>$T_g$ (1994 Kit)</th>
<th>$T_g$ (1997 Kit)</th>
<th>$T_g$ (2003 Kit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETG</td>
<td>NA</td>
<td>81.7°C</td>
<td>141.7°C</td>
<td>137.6°C</td>
</tr>
<tr>
<td>Synthetic Elastomer</td>
<td>-81.6°C</td>
<td>-77.7°C</td>
<td>-80.5°C</td>
<td>-81.7°C</td>
</tr>
</tbody>
</table>

Figure 12 TMA of PETG (1994 ResinKit®)
Figure 13 TMA of PETG (1997 ResinKit®)

Figure 14 TMA of PETG (2010 ResinKit®)
**Figure 15** TMA of synthetic elastomer (1979 ResinKit®)

![Graph showing TMA of synthetic elastomer (1979 ResinKit®)](image)

**Figure 16** TMA of synthetic elastomer (1994 ResinKit®)

![Graph showing TMA of synthetic elastomer (1994 ResinKit®)](image)
Figure 17 TMA of synthetic elastomer (1997 ResinKit®)

Figure 18 TMA of synthetic elastomer (2010 ResinKit®)
TMA of synthetic elastomer also showed that the resin begins to lose flexibility with age. The 1994 synthetic elastomer resin shows less thermal expansion than the 1979 resin, suggesting that the 1994 resin was subjected to conditions that would artificially age the resin. Table V shows the dimensional change in terms of percent compared to synthetic elastomer from the 2010 ResinKit®.

**Table V** TMA expansion and contraction results for synthetic elastomer

<table>
<thead>
<tr>
<th>Synthetic Elastomer</th>
<th>Expansion (µm)</th>
<th>Contraction (µm)*</th>
<th>Average (µm)</th>
<th>% Dimensional Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>1979</td>
<td>20.81</td>
<td>347.20</td>
<td>184.01</td>
<td>-45.13%</td>
</tr>
<tr>
<td>1994</td>
<td>-61.91</td>
<td>167.60</td>
<td>52.85</td>
<td>-84.24%</td>
</tr>
<tr>
<td>1997</td>
<td>72.73</td>
<td>541.40</td>
<td>307.07</td>
<td>-8.44%</td>
</tr>
<tr>
<td>2010</td>
<td>91.61</td>
<td>579.10</td>
<td>335.36</td>
<td>0.00%</td>
</tr>
</tbody>
</table>

*Absolute values

The results provide enough evidence to conclude that the PETG and synthetic elastomer resins from the 1994 ResinKit® have been compromised and are no longer viable standards. This may be due to possible mishandling of the 1994 ResinKit®, since the results from the resins analyzed from the 1979 and 1997 kits follow so closely to the newer 2010 reference kit. It’s possible that the 1994 kit may have been exposed to heat for long periods of time, which would cause thermal degradation of resins in the kit. This would occur if the kit was placed near a portable heater or placed in the trunk of a hot automobile. The resin kit could have also been exposed to UV radiation, which may have photo degraded the resins. This could happen if the kit was open and exposed to a UV
light source or exposed to direct sunlight for long periods of time. The fact that the polystyrene resins analyzed from the 1994 kit showed no thermal differences form the same resins analyzed in the 2010 kit, concludes that some resins are more thermally stable than others and care needs to be taken to properly store and maintain the ResinKit®.

CONCLUSIONS

The differences in the thermal decomposition curves between the resins were consistent with each repeated trial. Most of the resins analyzed showed little to no difference in their TG, DSC, and TMA results. Two resins which showed significant differences in their decomposition had significant differences in glass transition temperature and thermal expansion. A visual inspection of synthetic elastomer from the 1994 ResinKit® and the inability to physically remove the polymer chip from its plastic holder suggest that the polymer has chemically degraded. This concludes that some polymers from the 1994 ResinKit® can no longer be used as a reference. The results of this experiment show that if proper care is taken of the ResinKit®, it can prove to be a viable reference for many years, but improper care can lead to a ResinKit® where some polymers are viable and others that are not.
CHAPTER III

THERMAL ANALYSIS OF WATER AND MAGNESIUM HYDROXIDE CONTENT IN COMMERCIAL PHARMACEUTICAL SUSPENSIONS OF MILK OF MAGNESIA

ABSTRACT

A standard protocol was developed to determine the water content by thermal analysis of milk of magnesia (MOM). Differential scanning calorimetry (DSC) and Thermogravimetry (TG) were used in a novel manner for examining the physical characteristics of the commercial pharmaceutical suspensions. Moisture analyzer and oven-dry methods validates the proposed protocol.

MOM consists primarily of water and magnesium hydroxide \((\text{Mg(OH)}_2)\). Experimental design of the thermal analysis parameters were considered including sample size, flowing atmosphere, sample pan and heating rate for both DSC and TG. The results established the optimum conditions for minimizing heat and mass transfer effect. Sample sizes used were: 5-15 mg for DSC and 30-50 mg for TG. DSC analysis used crimped crucibles with a pinhole, which allowed maximum resolution and gave well defined mass (water) loss. TG analysis used a heating rate of \(10^\circ\text{C min}^{-1}\) in an atmosphere of nitrogen.
The heat of crystallization, heat of fusion and heat of vaporization of unbound water are 334, 334 and 2257 Jg\(^{-1}\), respectively. The DSC average water content of MOM was 80% for name brand and 89.5% for generic brand, based on the relative crystallization, melting and vaporization heats (Jg\(^{-1}\)) of distilled water. The TG showed a two step process, loosing water at 80-135°C for unbound water and bound water (MgO\(\cdot\)H\(_2\)O) at 376-404°C, yielding a total average water loss of 91.9% for name brand and 90.7% for generic brand by mass. The difference between the high temperature TG and the lower temperature DSC can be attributed for the decomposition of magnesium hydroxide or MgO\(\cdot\)H\(_2\)O. Therefore in performing this new approach to water analysis, heating to a high temperature decomposed the magnesium hydroxide residue. It was determined that the TG method was the most accurate for determining bond and unbound water.

INTRODUCTION

In general, water can be organized by phases of matter: liquid, solid and gas. The liquid phase is the most common among all the water phases on the surface of the earth and this phase is noted as “water”. The solid phase of water is a physically hard structure, which is commonly known as ice. The gas phase of water is recognized as water vapor or the “vapor phase” of water. The physical chemistry of water is denoted as one molecule of water where two hydrogen atoms are covalently bonded to a single oxygen atom [12]. Liquid water has no taste or odor and at normal atmospheric temperature and pressure water is colorless, however it can have a very light blue hue. Ice is colorless, water vapor or steam cannot be seen as a gas [13]. At standard conditions, 25°C and pressure of 1atm water is a liquid. The water molecule has a net positive charge on the hydrogen atoms and a net negative charge on the oxygen atom. The net result is that each water molecule
has a dipole moment. Water is a polar liquid that can form a hydronium ion (H$_3$O$^+$) and is interactive with hydroxide ion (OH$^-$).

\[ 2 \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{OH}^- (aq) \]

The heat of vaporization, ($\Delta H_v$) is the energy to change a given quantity of water into its gas phase at standard temperature and pressure. Heat of vaporization for water is 2257 Jg$^{-1}$. The heat of fusion ($\Delta H_f$) is the result of the change in the phase of water from solid to liquid which occurs at the melting temperature ($T_m$). Heat of fusion for water is 334 Jg$^{-1}$. The heat of crystallization ($\Delta H_c$) is the result of the change in the phase of water from liquid to a solid which occurs at the crystallization temperature ($T_c$) [14].

The following is a summary from W.J. Sichina’s paper “Characterization of Water of Hydration of Pharmaceuticals Using the DSC”, in which a test was developed to characterize the properties associated with the waters in a pharmaceutical material. The method includes an automated sample pan puncturing accessory for the study of free and bound waters in pharmaceuticals. Sichina’s DSC protocol includes a thermal procedure: sample mass approximately 4 mg, sample pan 30 µl aluminum pan with a hole, and purge gas nitrogen, heat from room temperature at 10°C min$^{-1}$ [15].

milk of magnesia is a suspension of magnesium hydroxide Mg(OH)$_2$ in water. It was widely used as an antacid to neutralize stomach acid, but is now used primarily as a laxative. Low solubility of Mg(OH)$_2$ in water makes it a weak base and a strong electrolyte. The United States Pharmacopeia states that single strength milk of magnesia should contain not less than 90.0 % and not more than 100.0% of the labeled amount of 80 mg of Mg(OH)$_2$ mL$^{-1}$. It is commercially produced by the precipitation of magnesium
hydroxide paste from seawater. The paste can have varying degrees of viscosity, which determines whether a suspending agent is required or not. Water, whose melting, crystallization temperature and enthalpy are not significantly different from those of normal (pure) water, is called free water or unbound water. Those water species exhibiting large differences in transition enthalpies and temperatures, or those for which no phase transition can be observed calorimetrically are referred to as bound water.

The purpose of these experiments is to find the best analytical method to determine bound and unbound water. Oven-dry and moisture analyzer methods are traditional methods, which are used in this experiment as controls. They are used to determine the total water lost from the test samples. Since both traditional methods can only determine the total amount of water lost, these methods cannot be used to determine bound or unbound water, but can be used to check the accuracy of the TG and DSC methods [16-20].

TG rapidly measures changes in mass as a sample is heated and is eventually vaporized. This can be used to create a water loss profile that can show the different temperature ranges in which water and other components of a sample vaporize. DSC analyzes the phase changes in matter and can also be used to determine a water loss profile. Both methods can be used to determine the amounts of bound and unbound water and can be used to determine the total amount of water lost in a sample. The total water determined by DSC and TG will be compared to the traditional controls to determine if the novel methods can be accurately used to determine bound, unbound and total water in a sample of milk of magnesia.
EXPERIMENTAL

The laxatives used in the study were a name brand milk of magnesia and a generic milk of magnesia. Each product was tested for water content using two conventional methods: 110°C oven, and moisture analyzer and two novel methods: Differential scanning calorimetry and thermogravimetry.

110°C Oven Method

This method used small aluminum pans, a vacuum oven set to 110°C, and a desiccator. First, the aluminum pans were analytically weighed and recorded to 3 decimal places. Next, two samples of each product were analytically weighed from 1.5-2.0 grams on separate pre-weighed pans to 3 decimal places and recorded. Then the pans were then placed into the vacuum oven. The oven used was a Fisher Scientific Isotemp® vacuum oven model 282A (figure 19). Pans and samples were left in the oven for 3 hours at 15 kPa vacuum. After 3 hours, the pans were removed from the oven and immediately placed into a desiccator under vacuum for 1 hour. After one hour, the pans were removed from the desiccators and were analytically weighed, which was recorded to 3 decimal places.
Moisture Analyzer Method

Samples of each product were analyzed for moisture content using the LabWave 9000 Moisture Analyzer (figure 20). The moisture analyzer uses an analytical balance inside of a microwave oven (figure 21), which dries the sample, while recording a change in mass. At the end of the test the percent moisture of the sample is automatically calculated. First, two absorbent pads are placed on the analytical balance inside the moisture analyzer and the balance is tared. Next, 1.0-1.5 grams of sample is placed in between the absorbent pads. Then the moisture analyzer is activated, using 80% power. The sequence is completed when the moisture analyzer no longer records a change in mass. The instrument then displays the percent moisture, percent solids, and the amount of time it took to complete the analysis.
Thermogravimetry Method (TG)

A TA Instruments Hi-Res Thermogravimetric Analyzer model 2950 (figure 22) was used to measure bound and unbound water in milk of magnesia samples. The samples were prepared by placing one drop of material on to a pre-tared platinum TG pan. The pan was placed onto the auto-loading mechanism of the TG analyzer and an automated loading sequence was initiated. The sample is placed into a furnace which heats the sample, while measuring the mass of the sample every 0.5 seconds. The TG experimental conditions were: Ramp 10°C per minute to 500°C in nitrogen. 30-50mg of sample was used in each run.
Differential Scanning Calorimetry Method (DSC)

The Mettler Toledo DSC 823e 20 instrument (figure 23) was used to measure the heat flow properties of the milk of magnesia samples, which involve exothermic or endothermic processes as a function of time and temperature. Samples ranging from 5mg to 15mg were placed in solid fat index (SFI) aluminum pans, covered with a lid and were sealed. The samples were cooled from 25 to -50°C and then heated to 120°C at 5°C min⁻¹ heating rate with nitrogen gas purge of 50 mL/min⁻¹. The DSC scan provided data on the following thermal properties: Heat of fusion (ΔH_f), melting temperature (T_m), peak melt temperature (T_{mp}), heat of crystallization (ΔH_c), crystallization temperature (T_c), peak crystallization temperature (T_{cp}), heat of vaporization(ΔH_v), vaporization temperature(T_v) and peak vaporization temperature (T_{vp}).
RESULTS AND DISCUSSION

Water analysis results from the 110°C pan method are shown in Table VI.

**Table VI** % water results from pan method

<table>
<thead>
<tr>
<th>Source drug suspension</th>
<th>Sample</th>
<th>Water</th>
<th>Average</th>
<th>SDEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milk of magnesia (name brand)</td>
<td>1</td>
<td>91.8%</td>
<td>91.8%</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>91.7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milk of magnesia (generic brand)</td>
<td>1</td>
<td>90.6%</td>
<td>90.6%</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>90.7%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The results were obtained by subtracting the mass of the pan and sample after testing, from the initial mass of the pan and sample before testing. The difference was the amount of solids left in the pan. From there, the mass of the material left in the pan was subtracted from the initial mass of the sample. The results show that the amount of water in the commercial brand of milk of magnesia was 91.8% and the generic brand of milk of magnesia was 90.6%. The moisture analyzer results were virtually identical to the results obtained from the 110° C pan method as seen in Table VII.

**Table VII** Conventional methods for water content in milk of magnesia

<table>
<thead>
<tr>
<th>Total Water (Oven)*</th>
<th>Total Water (Analyzer)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milk of magnesia (name brand)</td>
<td>91.8%</td>
</tr>
<tr>
<td>Milk of magnesia (generic brand)</td>
<td>90.6%</td>
</tr>
</tbody>
</table>

*Average values

TG data were analyzed using *Universal Analysis 2000* software by TA Instruments, version 4.4A. The data were plotted and analyzed using the first derivative of the percent (%) mass loss versus temperature in °C. From there, each peak was identified and the percent material loss was calculated. Also identified were the initial and end points at which mass loss began and ended. All remaining material in the sample was calculated as percent residue. The results are shown in figures 24 and 25.
**Figure 24** TG analysis for name brand MOM

**Figure 25** TG analysis for generic brand MOM
In comparison to the conventional methods, TG analysis showed both bound and unbound water. Water vaporization results are shown in Table VIII. The unbound water vaporized between 80°C and 119°C in the name brand MOM. The unbound water in generic brand MOM vaporized between 91° and 135°C. The bound water in the name brand MOM vaporized between 376° and 398°C and between 374° and 404°C in the generic brand MOM.

**Table VIII** % of unbound water and bound water for test samples by TG

<table>
<thead>
<tr>
<th></th>
<th>Unbound Water</th>
<th>Bound Water</th>
<th>Total Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milk of magnesia (name brand)</td>
<td>88.0%</td>
<td>2.2%</td>
<td>90.2%</td>
</tr>
<tr>
<td>Milk of magnesia (generic brand)</td>
<td>88.3%</td>
<td>2.4%</td>
<td>90.7%</td>
</tr>
</tbody>
</table>

DSC results are summarized in the Figures 26, 27 and 28 as well as Tables IX and X. The free water concentrations were determined based on the cool and heat DSC curves. The heat of crystallization ($\Delta H_c$) (from the cooling curve) and the heat of fusion ($\Delta H_f$) (heating curve after crystallization) were calculated for pure water and the commercial and generic suspensions of milk of magnesia. Assuming a two component suspension of water and magnesium hydroxide ($\text{Mg(OH)}_2$ suspended in the water), various samplings of the commercial suspensions were evaluated by the DSC curves. The average, standard deviation and percent relative error were calculated from the $\Delta H_c$ and $\Delta H_f$ measured and are reported in Table IX. The standard deviation was ±17 to ±22 and the % relative error was 5.3 to 7.6% for the heat measurements. The heat of vaporization was recorded during
the DSC run but due to baseline variations and sampling techniques were not used for the calculation of the water content.

**Figure 26** DSC analysis for distilled water
Figure 27 DSC analysis for name brand MOM

Figure 28 DSC analysis of generic brand MOM
**Table IX** Average, standard deviation and % relative error of $\Delta H_c$ and $\Delta H_f$

<table>
<thead>
<tr>
<th>Drug (liquid)</th>
<th>Average $\Delta H_c$/Jg$^{-1}$</th>
<th>Standard deviation/±</th>
<th>% Relative error</th>
<th>Average $\Delta H_f$/Jg$^{-1}$</th>
<th>Standard deviation/±</th>
<th>% Relative error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>338</td>
<td>19</td>
<td>5.5</td>
<td>373</td>
<td>20</td>
<td>5.3</td>
</tr>
<tr>
<td>Name brand MOM</td>
<td>276</td>
<td>17</td>
<td>6.1</td>
<td>291</td>
<td>18</td>
<td>6.2</td>
</tr>
<tr>
<td>Generic MOM</td>
<td>312</td>
<td>18</td>
<td>5.4</td>
<td>326</td>
<td>22</td>
<td>7.6</td>
</tr>
</tbody>
</table>

*All values $H_c$ and $H_f$ are based on three samplings*

**Table X** Relative $\Delta H_c$, $\Delta H_f$ and average of $\Delta H_c$ and $\Delta H_f$

<table>
<thead>
<tr>
<th>Drug (liquid)</th>
<th>$T_c$°C</th>
<th>$T_{cp}$°C</th>
<th>$\Delta H_c$/Jg$^{-1}$</th>
<th>Relative $\Delta H_c$%</th>
<th>$T_m$°C</th>
<th>$T_{mp}$°C</th>
<th>$\Delta H_f$/Jg$^{-1}$</th>
<th>Relative $\Delta H_f$%</th>
<th>Average $\Delta H_c$ and $\Delta H_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>-18</td>
<td>-14</td>
<td>338</td>
<td>100</td>
<td>0</td>
<td>3.0</td>
<td>373</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Name brand MOM</td>
<td>-17</td>
<td>-13</td>
<td>276</td>
<td>82</td>
<td>-1.2</td>
<td>2.0</td>
<td>291</td>
<td>78</td>
<td>80</td>
</tr>
<tr>
<td>Generic MOM</td>
<td>-17</td>
<td>-12</td>
<td>312</td>
<td>92</td>
<td>-1.3</td>
<td>2.0</td>
<td>326</td>
<td>87</td>
<td>89.5</td>
</tr>
</tbody>
</table>

The final summary of the DSC analysis includes: the temperature profile of the free or unbound water, its water content relative to the $\Delta H_f$ and $\Delta H_c$ and the average result of the water by both analytical techniques. The milk of magnesia, name brand and generic brand was 80.0% and 89.5%, respectively, by DSC. Therefore, there appears to be a 10% variation between the two MOM samples. An overview of the water content by four analytical techniques is reported in Table XI.
Table XI Percent of water content from all the techniques and viscosity for test samples

<table>
<thead>
<tr>
<th>Source Suspension</th>
<th>Oven 110°C</th>
<th>Moisture Analyzer</th>
<th>TG</th>
<th>DSC</th>
<th>Viscosity* mPa·s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name brand MOM</td>
<td>91.8%</td>
<td>91.9%</td>
<td>90.2%</td>
<td>80.0%</td>
<td>1585</td>
</tr>
<tr>
<td>Generic brand MOM</td>
<td>90.6%</td>
<td>90.8%</td>
<td>90.7%</td>
<td>89.0%</td>
<td>2980</td>
</tr>
</tbody>
</table>

*Brookfield DV II+ viscometer (#3 RVT spindle at 20rpm)

The differences between the name brand and generic were the same for the oven, moisture analyzer and TG methods. There was a repeatable difference based on the DSC analysis of 10% more water in the generic sample. Further, there was a sizable viscosity difference of 88% between the name brand and generic. The generic had more water and a higher viscosity according to DSC. The latter may be due to the additional additives denoted by 20 mg calcium and 2 mg sodium in the generic product. There is also a difference between naturally mined sodium hydroxide and synthetic sodium hydroxide, which is made from magnesium chloride. It’s possible that differences in the preparation of magnesium hydroxide may play a role in the thermal differences shown in the DSC. The results show that the DSC was able to determine that the name brand milk of magnesia and the generic brand are chemically different from each other. Table XII shows the thermal differences between the two products using distilled water for comparison.
Table XII DSC thermal properties of name brand and generic compared to distilled water

Water activity is a measure of the energy status of the water in a system [21-23]. It is defined as the vapor pressure of a liquid divided by that of pure water at the same temperature, yielding a value of one or 100%. The interpretation of the differences noted in the DSC analysis may also be due to the differences between the water activities of the two samples.

CONCLUSIONS

The control methods could not effectively determine bound and unbound water in the test samples, but were effective in determining total water concentration. TG was determined to be the best method to determine both bound and unbound water. DSC was not effective in determining bound, unbound, or total water concentration, but showed that the commercial and generic brands were chemically different from each other.
CHAPTER IV

IDENTIFICATION OF ALDOHEXOSE MONOSACCHARIDES USING SECOND DERIVATIVE TG ANALYSIS

ABSTRACT

Four aldohexose monosaccharides, D-galactose, D-glucose, D-mannose and D-sorbose, were examined by thermogravimetry (TG). Thermal derivative peak temperatures were identified using both first and second derivative analysis. Second derivative analysis was used to determine if the thermogravimetry could be used as an identification tool to better differentiate between the monosaccharides.

INTRODUCTION

It is widely known that thermogravimetry, while an important technique for identifying thermal decomposition, is not very reliable as an identification tool if the difference between two chemicals is subtle. It lacks the higher resolution that is found in techniques such as NMR or IR-Spectroscopy. While thermogravimetry has a lower resolution than the
The before mentioned techniques, it may be possible to use it as an identification tool if the data is analyzed in greater depth.

In a typical TG run, the temperature can be set to increase incrementally at 10°C per minute from room temperature to 1000°C, with a weight measurement taken every 0.5 seconds. This generates on average of over 11,000 weight measurements to plot and analyze. If the upper temperature limit is raised or lowered from 1000°C, the total number of weight measurements will increase or decrease accordingly.

Once the TG sample has been decomposed and the data collected, first a graph of the raw data is drawn. Depending of the chemical component’s composition, the graph of the raw data will show a sloping line, or a series of slopes if it’s a multi-component chemical compound. Then, the first derivative of that data is calculated and graphed. The first derivative is displayed as a series of peaks depending on the composition of the chemical being tested. From there, all the thermal derivative peak temperatures are identified and measured, using the peaks generated from the first derivative as a guide. This method has a level of resolution that can be used for identification if two chemical compounds are significantly different from one another, such as polystyrene and polyphenylene sulfide. These are both polymer resins which can be easily differentiated through TG (figure 29).

To analyze TG data further the second derivative is taken of the data. The second derivative is used in order to identify inflection points. An inflection point is defined as the maximum of the first derivative or the point where there is a significant change from the zero point on a graph [1]. In this experiment, four chemically similar aldohexose
monosaccharides were analyzed using TG. The monosaccharides come from two groups that have the same molecular formula but are isomers of each other (have different structural formulas). The first group consists of D-fructose, D-galactose. The second group includes D-mannose, and D-sorbose. After analyzing the first derivative of the data, the second derivative was plotted and the inflection points were identified to determine if a greater differentiation could be used to individually identify the monosaccharides.

**Figure 29** TG of raw data and first derivative of polystyrene (left) and polyphenylenesulfide (right)

**EXPERIMENTAL**

The monosaccharides tested were as follows: D-fructose, D-galactose, D-mannose, and D-sorbose. Chemical structures are shown in figure 30.
The TG used was a TA Instruments model TGA Q500. The TG experimental conditions were: 20mg sample, ramp 10°C per minute to 600°C in nitrogen, then switch to air and continue to ramp at 10°C per minute until 1000°C. The TG pans were carefully cleaned and a butane torch was used to burn off any un-decomposed matter from previous runs. Each TG run was done one at a time, with the sample being weighed and then immediately run to prevent any additional moisture from the air being absorbed into the sample. Each monosaccharide sample was run in duplicate.

RESULTS AND DISCUSSION

TG data were analyzed using *Universal Analysis 2000* software, by TA Instruments, version 4.4A. The data were plotted and analyzed using the first derivative of the % weight loss versus temperature in °C. The analysis is shown in figures 31-34.
Figure 31 D-fructose first derivative

Figure 32 D-galactose first derivative
Figure 33 D-mannose first derivative

Figure 34 D-sorbose first derivative
From the first derivative analysis it appears that D-galactose and D-mannose have a similar thermal decomposition profile and D-fructose has a decomposition profile that matches D-sorbose. D-fructose and D-sorbose can also be differentiated from D-galactose and D-mannose since they have a 50% thermal derivative peak temperature that shifts over 30°C lower than the other two monosaccharides. This is noted in the first major peaks of figures 31-34, that show D-fructose and D-sorbose, with a 50% thermal derivative peak temperature of 260°C versus the same (first major peak) with D-galactose and D-mannose at 290°C.

Further analysis was done with the existing data in which the second derivative was calculated and plotted. Major inflection points were identified in figures 35-38.

![Graph](Image)

**Figure 35** D-fructose second derivative
Figure 36 D-galactose second derivative

Figure 37 D-mannose second derivative
Figure 38 D-sorbose second derivative

Table XIII shows the temperature and the percent of remaining material at two major inflection points analyzed.
Table XIII Second derivative results of aldohexose monosaccharides

<table>
<thead>
<tr>
<th></th>
<th>Point 1 (Temp)</th>
<th>Point 1 (Material)</th>
<th>Point 2 (Temp)</th>
<th>Point 2 (Material)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-fructose (sample 1)</td>
<td>263.42 °C</td>
<td>63.24%</td>
<td>611.48 °C</td>
<td>17.01%</td>
</tr>
<tr>
<td>D-fructose (sample 2)</td>
<td>260.40 °C</td>
<td>61.71%</td>
<td>611.48 °C</td>
<td>15.99%</td>
</tr>
<tr>
<td>D-sorbose (sample 1)</td>
<td>263.42 °C</td>
<td>63.24%</td>
<td>611.48 °C</td>
<td>17.01%</td>
</tr>
<tr>
<td>D-sorbose (sample 2)</td>
<td>261.41 °C</td>
<td>63.85%</td>
<td>612.49 °C</td>
<td>17.24%</td>
</tr>
<tr>
<td>D-galactose (sample 1)</td>
<td>294.70 °C</td>
<td>52.30%</td>
<td>611.48 °C</td>
<td>12.27%</td>
</tr>
<tr>
<td>D-galactose (sample 2)</td>
<td>292.60 °C</td>
<td>51.70%</td>
<td>612.49 °C</td>
<td>13.35%</td>
</tr>
<tr>
<td>D-mannose (sample 1)</td>
<td>290.66 °C</td>
<td>61.46%</td>
<td>612.49 °C</td>
<td>9.17%</td>
</tr>
<tr>
<td>D-mannose (sample 2)</td>
<td>291.43 °C</td>
<td>60.24%</td>
<td>611.56 °C</td>
<td>10.35%</td>
</tr>
</tbody>
</table>

The data show that there is no significant decompositional difference between D-fructose and D-sorbose. However, there is a slight difference between D-galactose and D-mannose at the second inflection point. There was a third major inflection point identified during the D-galactose analysis which is noted in figure 36, but it is believed to be water. Even though water was identified in the D-galactose sample, it should have caused the value at the second inflection point to be lower than the one for D-mannose. In fact, the opposite is the case. This analysis was not able to determine distinct decompositional
differences between the all 4 aldohexose monosaccharides, but further experiments including dynamic high resolution TG analysis may have better results.

CONCLUSIONS

Differences in thermal decomposition of the aldohexose monosaccharides could be only identified to a point. However, there was a distinct difference between the two monosaccharides D-fructose and D-sorbose compared to D-galactose and D- mannose. Further analysis including high resolution dynamic thermogravimetry may show better differentiation, but complete differentiation between closely related chemicals is currently beyond the limits of thermogravimetry.
CHAPTER V

FINAL CONCLUSIONS

These experiments demonstrated that thermal analysis is an important tool, not only to educate students on analytical chemical techniques, but to expand knowledge of the physical world. The experiments also demonstrated how diverse thermal analysis is in analyzing materials. The three experiments discussed show how students can use thermal analysis to study the fields of polymer science, medical research and biochemistry. There are many more uses for thermal analysis and a lot of new frontiers have yet to be explored using these techniques. This is why it is important for thermal analysis to be included as part of an analytical chemistry curriculum on the undergraduate level and be used more in depth on the graduate level in colleges and universities and should no longer be treated as a “niche” technique with “limited” uses.
BIBLIOGRAPHY


Cellulose Acetate-Run 1
1994 ResinKit®

Cellulose Acetate-Run 2
1994 ResinKit®
Cellulose Acetate-Run 3
1994 ResinKit®

Cellulose Acetate-Run 1
2010 ResinKit®

Sample: Cellulose Acetate
Size: 11.2890 mg
Method: Ramp TGA
File: E:...\1979 Raw Data\Cellulose Acetate.004
Run Date: 08-Feb-2010 09:08
Instrument: TGA Q500 V20.6 Build 31

Sample: 2003 Cellulose Acetate
Size: 18.9110 mg
Method: Ramp TGA
File: E:...\2003 Cellulose Acetate.003
Run Date: 30-Mar-2010 15:57
Instrument: TGA Q500 V20.6 Build 31

Cellulose Acetate-Run 2
2010 ResinKit®

Cellulose Acetate-Run 3
2010 ResinKit®
Polyphenylene Sulfide-Run 1
1994 ResinKit®

Polyphenylene Sulfide-Run 2
1994 ResinKit®
Polyphenylene Sulfide-Run 3
1994 ResinKit®

Sample: Polyphenylene Sulfide
Size: 10.8530 mg
Method: Ramp

File: E:...Polyphenylene Sulfide new.007
Run Date: 19-Feb-2010 05:19
Instrument: TGA Q500 V20.6 Build 31
Universal V4.4A TA Instruments

- Weight (%/°C)
  - 31.60% (3.430mg) at 485.18°C
  - 24.45% (2.654mg) at 549.85°C
  - Residue: 39.85% (4.325mg) at 635.62°C

- Temperature (°C)
  - 483.23°C
  - 552.70°C
  - 613.44°C
  - 621.17°C
  - 630.56°C

Polyphenylene Sulfide-Run 1
2010 ResinKit®

Sample: 2003 Polyphenylene Sulfide
Size: 20.8390 mg
Method: Ramp

File: E:...2003 Polyphenylene Sulfide.004
Run Date: 31-Mar-2010 21:32
Instrument: TGA Q500 V20.6 Build 31
Universal V4.4A TA Instruments

- Weight (%/°C)
  - 30.28% (6.310mg) at 483.23°C
  - 6.799% (1.417mg) at 562.70°C
  - 19.51% (4.065mg) at 621.17°C

- Temperature (°C)
  - 621.17°C
  - 630.56°C
  - 658.98°C

Residue: 43.42% (9.048mg)
Polystyrene General Purpose-Run 1
1994 ResinKit®

Polystyrene General Purpose-Run 2
1994 ResinKit®
Polystyrene General Purpose-Run 3
1994 ResinKit®

Polystyrene General Purpose-Run 1
2010 ResinKit®
Polystyrene General Purpose-Run 2
2010 ResinKit®

Polystyrene General Purpose-Run 3
2010 ResinKit®
Polystyrene Medium Impact-Run 1
1994 ResinKit®

Polystyrene Medium Impact-Run 2
1994 ResinKit®
Polystyrene Medium Impact-Run 1
2010 ResinKit®

Polystyrene Medium Impact-Run 2
2010 ResinKit®

Universal V4.4A TA Instruments
Synthetic Elastomer-Run 1
1997 ResinKit®

Synthetic Elastomer-Run 2
1997 ResinKit®
Thermoplastic Polyester (PETG)-Run 1
1997 ResinKit®

Sample: PETG 1997-1
Size: 16.4660 mg
Method: 600 N2 800 AIR
Comment: Fruscella

Deriv. Weight Change (%/°C)

Weight (%)

Temperature (°C)

Deriv. Weight (%/°C)

Weight (%)

Temperature (°C)

Thermoplastic Polyester (PETG)-Run 2
1997 ResinKit®

Sample: PETG 1997-2
Size: 16.9220 mg
Method: 600 N2 800 AIR
Comment: Fruscella

Deriv. Weight Change (%/°C)

Weight (%)

Temperature (°C)

Deriv. Weight (%/°C)

Weight (%)

Temperature (°C)
Thermoplastic Polyester (PETG)-Run 1
2010 ResinKit®

Thermoplastic Polyester (PETG)-Run 2
2010 ResinKit®
Urethane Elastomer-Run 3
1994 ResinKit®

Urethane Elastomer-Run 1
2010 ResinKit®