Rapid Analysis of Liquid Polyester Resins using Trimethylsulfonium Hydroxide (TMSH) and Gas Chromatography (GC)

Frederick Jaeger and Dave Grandy
Reichhold Inc., RTP, NC USA

Abstract

Past efforts to achieve quantitative analysis of liquid polyester resins have relied on either a multi-step ASTM FAME-type method coupled to a GC based separation and analysis or by using Nuclear Magnetic Resonance (NMR) spectroscopy. The multi-step ASTM FAME method is based on first performing a caustic digestion and then an esterification on the sample. This methodology while effective, is time consuming, labor intensive, needs a large amount of glassware and suffers from a low sample throughput. The NMR methodology has the significant drawback of being cost prohibitive for most laboratories in addition to having severe limitations when analyzing multiple glycols and halogenated species among others.

Presented here is a single step, in situ, GC based methodology that can prepare a liquid polyester resin sample for qualitative and/or quantitative analysis in 30 minutes. This single step methodology has the advantages of simplicity, speed, small sample size, minimal labor and glassware requirements and an extremely high sample throughput. This paper will demonstrate this improved methodology with the analysis of several classes of liquid polyester resins, with samples containing a variety of glycols and acids.

Introduction

The ability to quickly, accurately and cost effectively analyze liquid polyester resins is vital to companies in the resin business for a variety of reasons. First and foremost is the ability to evaluate resin quality. A company must be able to evaluate the contents of a resin in prow the customer was in specification and made according to formula.

A good analytical methodology can be called upon to do several different things by an analyst. First, the method can be called upon to perform a qualitative analysis. A qualitative analysis can quickly tell the analyst if all of the right components are there, if something is missing or if a contamination is present. Second, an analyst may require a semi-quantitative analysis. This type of analysis allows an analyst to compare a control sample, be it a lab cook or known good plant batch to a suspect or problematic sample. Third, a methodology may need to perform an absolute quantitative analysis on some or all components present in a sample. This type of analysis is useful when no reference sample is available for semi-quantitative analysis or if a contamination needs to be characterized.

Initial attempts to analyze polyester resins have relied first on multi-step ASTM based methodologies that were coupled to a GC. Problems with these methodologies include the amount of time it takes to perform, the number of hours involved, the large amount of glassware that needs to be cleaned, prepared and used, along with the low sample throughput. (1-5)

Other well characterized methods have included the use of NMR spectroscopy. NMR methods are very effective in garnering the molar ratios of acids and glycols in liquid polyester resins with minimal sample preparation and quick turn around time under ideal conditions. Unfortunately, because of the extreme costs involved in their procurement, operation and maintenance, these instruments are cost-prohibitive for most companies. NMR spectroscopy has the further drawback of not easily being able to identify and quantify components that contain multiple glycols and halogenated species among others.

We describe here a much simplified sample preparation solution for rapid qualitative, semi-quantitative or quantitative analysis of polyester resins. This methodology can be performed in a single step and is based on an in situ saponification using TMSH as the reagent. This methodology has the advantages of simplicity, speed, small sample size, minimal glassware requirements and an extremely high sample throughput when compared to the existing ASTM based methodologies (1-5).

Experimental

Materials. Acetonitrile (ACN), stabilized tetrahydrofuran (THF), and benzene (EMD Chemicals). TMSH was purchased in a 0.2M solution in methanol (TCI America) and pentadecane (Sigma-Aldrich, Inc.). All reagents were HPLC grade or equivalent. 1.0mL Gastight syringe (SGE). 10mL and 100mL Class A volumetric flasks (VWR Scientific). 100mL graduated cylinder (VWR Scientific).
Solution Preparation. In a 500 mL glass bottle place 300mL of Acetonitrile (ACN), 100mL Stabilized Tetrahydrofuran (THF) and 100mL Benzene to make the extraction solution (ES). In a 100mL volumetric flask place 10mL of the TMSH solution and bring to volume with the ES solution to make the reaction solution (RS). Weigh 100mg of pentadecane into a 10mL volumetric flask and bring to volume with ES to make the internal standard solution (ISTD).

Standard Preparation. In a 10mL volumetric flask weigh 100mg of the standard of interest then bring to volume with RS. Place volumetric flask onto a 60°C hot plate for 30 minutes. This will produce a 10mg/mL standard. In another 10mL volumetric flask place 1.0mL of each 10mg/mL standard of interest. This will make a 1.0mg/mL stock solution (SS) that all further dilutions will be made from. An example curve point preparation using the SS and a 10mL volumetric flask: using the equation $C_1 \times V_1 = C_2 \times V_2$ a 10mg/mL curve point is desired. $1.0\text{mg/mL} \times X\text{µL} = 10\text{µg/mL} \times 10\text{mL}$ where $X=100\text{µL}$. Place the calculated amount of SS into a volumetric flask along with 10µL of ISTD and bring to volume with ES. Repeat calculation for each curve point desired.

Sample Preparation. In a 10mL volumetric flask weigh 100mg of the liquid polyester resin of interest. Add 10µL of the ISTD to the same volumetric flask and bring to volume with RS. Place volumetric flask onto a 60°C hot plate for 30 minutes. This will produce a 10mg/mL sample.

Instrumentation. All GC samples were analyzed using a 6890 Plus Gas Chromatograph coupled to an Agilent 5973N quadrupole Mass Spectrometer (Agilent, Palo Alto, CA), upgraded with an inert ion source and enhanced electronics package. Chromatographic separations were achieved with a BPX-50 Phenyl polysilphenylene-siloxane GC capillary column 30 m × 0.25 mm × 0.25 μm (SGE, Australia). The helium carrier gas was set to 1.1 mL per min. One microliter of sample was injected into the instrument in splitless mode. The injection port was set at 280°C with an initial oven temperature of 50°C. A 20°C per minute ramp was applied until the oven temperature reached 320°C where it was held for 5 min. The mass spectrometer was set in scan mode from 30 amu to 550 amu. Data were gathered using Agilent’s Chemstation software.

All NMR samples were analyzed using a Bruker Avance III 400MHz NMR. Samples were dissolved in deuterated chloroform and a deuterated water exchange was performed if necessary. Samples were analyzed using both 1D and 2D $^1$H and $^{13}$C techniques where necessary. Data were gathered using Bruker’s Topspin 2.1 software package.

Results and Discussion

Analysis on a liquid polyester resin using a GC based analysis is impossible without some sort of chemical digestion to break down the polymer chain to its monomeric components. This is mainly caused by the fact that large molecules are not volatile or thermally stable enough to be put into the GC system, get through the analytical column and then get to the detector. The methodology presented here uses an in situ saponification and subsequent methylation in order to accomplish this break down. A saponification is the hydrolysis of an ester under basic conditions to form an alcohol and the salt of a carboxylic acid. (6) The acids then undergo methylation by having our saponification reagent (TMSH) in the presence of an excess of methanol. This method results in our getting the polyester’s glycols in original form and getting the acids in the form of a methyl ester derivative. Please note that maleic anhydride will be seen mostly as fumaric acid dimethyl ester along with a small amount of maleic acid dimethyl ester because of isomerization. Partially etherified by-products of the glycols are also produced if there is too much excess TMSH; this phenomenon is demonstrated in Figure 1 where the same resin is analyzed using increasing amounts of TMSH. This phenomenon can affect the quantitative outcome of the analysis unless these by-products are taken into account in an additional standard curve. Most, if not all of these byproducts have commercially available standards. Table 1 shows a breakdown of a resin analysis and what some of these partially etherified by-products are that need to be accounted for when performing a formula comparison. The calculated amounts of each partially etherified by-product are added back to the total of their corresponding glycol on a per mole basis.

Figure 2 shows the chromatogram of a resin that has undergone the in situ saponification and methylation process. Present in the chromatogram are all of the glycols and partially etherified glycols along with the acids of interest. Other peaks found in the chromatogram are other monomers and additives not of interest for this analysis (i.e. styrene, etc.). This chromatogram generated by the GC instrument can now be used either for qualitative analysis, semi-quantitative analysis or if coupled to a standard curve can now be used for quantitative analysis.

Solving a resin performance issue or customer complaint through a qualitative analysis is troubleshooting in its most basic form. Figure 3 shows a chromatogram of a problematic resin batch produced in the lab. The analyst was told that the resin was a PG-Maleic-Ortho based resin that was off-specification. After saponification and a GC based analysis a dicyclopentadiene alcohol (DCPD-OH) peak was found that was determined to be the cause of the issues.

Figure 4 shows an overlay of two chromatograms of two separate batches of the same resin product. It is
easily seen that one chromatogram shows a significant
difference in the levels of adipic acid along with ortho-
thalic acid. One of the resins is considered a control and
therefore using raw area counts a semi-quantitative
determination of differences can be obtained. In this case
adipic acid and orthophthalic acid was found to be 15%
and 14% less respectively when compared to the control.

It was shown that the molar ratio data generated
with the new methodology closely matched the formula
and NMR data and was a marked improvement over the
old style ASTM based methodology. Table 2 shows a
table comparing the techniques of interest to the formula
of the supplied resin. It can be seen that the new metho-
dology gives comparable results to the NMR data gener-
ated but at a fraction of the cost. The new methodology
also was able to improve on the accuracy of the old
ASTM-based methodology while minimizing the time
required to perform. The new methodology also was
able to limit the glassware used to one volumetric flask
per sample.

The average reproducibility of the GC/MS instru-
ment using all glycols and acids in the example resin was
3.0% with 8 replicates. The RSD of the methodology
was found to be 3.4% also with 8 replicates. The limit of
detection (LOD) for some of the most common glycols
was found to be as low as 100ppm and acids were found
to be 1ppm or better. The coefficient of determination
($R^2$) for standard curves using the most common glycols
and acids was found to be consistently 0.995 or better.
Data not shown.

Conclusion

We have presented here a single step, in situ, GC
based methodology that can prepare a liquid polyest-
er resin sample for analysis in as little as 30 minutes. This
methodology is a marked improvement over past ASTM
and GC based methodologies and also an improvement
over NMR based techniques. This single step methodol-
yogy has the advantages of simplicity, speed, small sam-
ple size, minimal labor and glassware requirements and
an extremely high sample through-put.

This methodology was found to be reproducible,
with an RSD of 3.4% along with being sensitive enough
to detect many common acids and glycols in the low
ppm range. Furthermore, it was demonstrated that this
methodology can be used for qualitative, semi-
quantitative and quantitative analysis.

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Authors:

Frederick Jaeger is a Senior Analytical Chemist
with Reichhold, Inc. He has 10 years of analytical chem-
istry experience specializing in mass spectrometry.
Fred has worked for Reichhold for 5 years in the Tech-
ology Testing Services Department. He received an M.S.
degree in Chemistry from North Carolina State Uni-
versity.

Dave Grandy is a Technology Manager with
Reichhold, Inc. Dave has been manager of the Tech-
ology Testing Services department at Reichhold, Inc. for
the past 18 years and has been in the resin industry for
the past 23. He received an M.S. degree in Chemistry
from the University of Pittsburgh.

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Figures

Table 1. Shows some of the partially etherified by-products generated by this methodology and how they are accounted for in the formula comparison.

<table>
<thead>
<tr>
<th>Compounds Quantified</th>
<th>Formula**</th>
<th>Resin 1 Liquid**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Glycol</td>
<td>81</td>
<td>88.1</td>
</tr>
<tr>
<td>Ethylene Glycol Half-Ether</td>
<td>*</td>
<td>*3.8</td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td>12.9</td>
<td>15.1</td>
</tr>
<tr>
<td>Propylene Glycol Half-Ether</td>
<td>*</td>
<td>*1.1</td>
</tr>
<tr>
<td>Diethylene Glycol</td>
<td>15.9</td>
<td>19.9</td>
</tr>
<tr>
<td>Diethylene Glycol Half-Ether</td>
<td>*</td>
<td>*1.1</td>
</tr>
<tr>
<td>Fumaric Acid, Dimethyl Ester</td>
<td>*</td>
<td>*24.7</td>
</tr>
<tr>
<td>Maleic Acid, Dimethyl Ester</td>
<td>23.6</td>
<td>25</td>
</tr>
<tr>
<td>Isophthalic Acid, Dimethyl Ester</td>
<td>*</td>
<td>*0.2</td>
</tr>
<tr>
<td>Orthophthalic Acid, Dimethyl Ester</td>
<td>76.4</td>
<td>75</td>
</tr>
</tbody>
</table>

*Compounds not found in formula, but present in sample due to impurities, partial methylation from TMSH reaction or isomerization. Totals for these compounds have been added back to their corresponding glycols on a per Mole basis.

**Total moles of acids are set equal to 100, with amount of glycols adjusted accordingly.
Table 2. Resin 1 technique comparisons to formula.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula*</th>
<th>NMR*</th>
<th>Old Method Resin 1 Liquid*</th>
<th>TMSH Method Resin 1 Liquid*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Glycol</td>
<td>81</td>
<td>61.2</td>
<td>112.4</td>
<td>88.1</td>
</tr>
<tr>
<td>Diethylene Glycol</td>
<td>15.9</td>
<td>27.1</td>
<td>35.1</td>
<td>19.9</td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td>12.9</td>
<td>12.9</td>
<td>16.3</td>
<td>15.1</td>
</tr>
<tr>
<td>Orthophthalic Acid</td>
<td>76.4</td>
<td>77.8</td>
<td>73.9</td>
<td>75</td>
</tr>
<tr>
<td>Maleic Acid</td>
<td>23.6</td>
<td>22.2</td>
<td>26.1</td>
<td>25</td>
</tr>
</tbody>
</table>

*Total moles of acids are set equal to 100, with amount of glycols adjusted accordingly
Figure 1. A resin saponified using increasing levels of the TMSH reagent. A. Shows the partially etherified byproduct of DEG (DEG monomethyl ether) increasing with TMSH concentration. B. Shows the amount of DEG found in the sample decreasing with increasing levels of TMSH.
Figure 2. Chromatogram of an example Polyester Resin

Legend:
1. Propylene Glycol Half-Ether
2. Ethylene Glycol Half-Ether
3. Propylene Glycol
4. Ethylene Glycol
5. Fumaric Acid, Dimethyl Ester
6. Diethylene Glycol Half Ether
7. Maleic Acid, Dimethyl Ester
8. Butanedioic acid, Methoxy-, Dimethyl Ester
9. Diethylene Glycol
10. Isophthalic Acid, Dimethyl Ester
11. Orthophthalic Acid, Dimethyl Ester
Figure 3. Chromatogram demonstrating qualitative analysis leading to the discovery of a contaminant.
Figure 4. Overlay and zoom-in of the chromatograms of two separate batches of the same product to demonstrate semi-quantitative analysis.