TMG News

The Madison Group
2615 Research Park Drive Madison, WI 53711 USA
608-231-1907 info@madisongroup.com madisongroup.com

January 2021

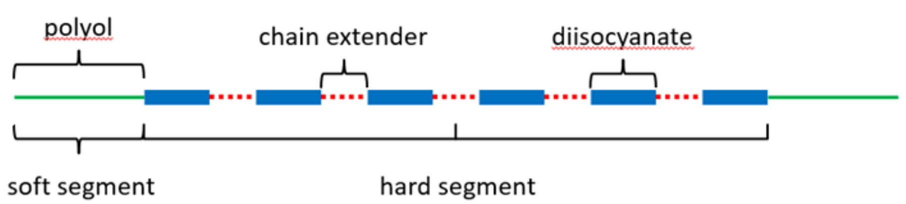
# Polyurethanes: Where Rubber Meets the Road
# Part 3 – When Things Go Wrong

*Bruce Davis, Ph.D.*

Polyurethane materials may be one of the most versatile polymers in existence. This three-part series highlights this incredible material through an understanding of its structure and diverse properties.

In the first two parts of this series, we examined the underlying chemistry and some of the interesting material properties of polyurethanes. Now we turn our attention to how things can go wrong when using this versatile material. Invariably, whenever problems occur with TPUs or cast polyurethane elastomers the root cause can often be traced back to a misunderstanding or oversight of some aspect of the basic chemistry or the manner in which the molecules are assembled.

Recall that all polyurethane (both thermoplastics and elastomers) molecules are comprised of hard segments (diisocyantes) joined together by soft block segments (polyols). For a cross-linked polyurethane elastomer, these molecules are chemically linked during the processing stage when the isocyanate rich pre-polymer (A-side) is mixed with an appropriate amount of polyol/amine based curative (B-side). In this type of two-part cast system, the components may also be pre-heated before being mechanically mixed and cast into a preform/mold. Ultimately, it is the stochiometric ratio of the A-side to B-side that must be carefully controlled to ensure the mechanical properties of the finished part. For example, the fatigue life of some cast polyurethane materials can be affected by a factor of 10,000 with only a 10% change in the ratio of these two mixed components.




**Polyurethane molecule construction**

Another factor that affects the end properties of a polyurethane cast system is the post-cure maturation stage. Because perfect mixing of the two components is impossible on a production scale, there will always exist some unreacted species within a cast polyurethane system. Most resin producers provide detailed post-cure recommendations to subject the finished part to an elevated temperature for a specified period of time. While some molders may consider this an inconvenient “option” that unnecessarily prolongs cycle time and increases costs, it does far more than simply relieve residual stresses in the finished part. In fact, the post-cure stage provides the molecules with a certain amount of mobility that both permits further reactions to occur as well as to achieve a more refined (lower energy) microstructure. The resulting effects on the mechanical properties lead to increases in tear strength, tensile strength, creep resistance and heat deflection temperature, among others. This “maturation” of properties will also occur in the absence of heat, albeit at a slower rate.

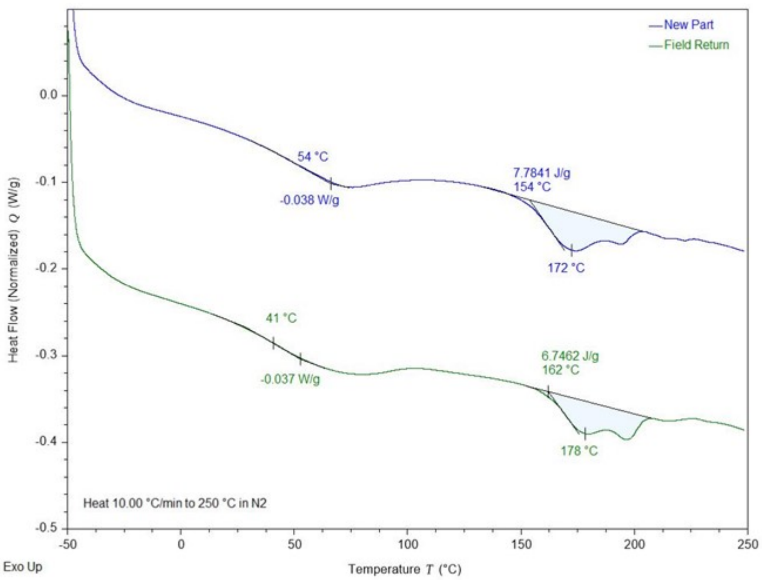
**Inside This Issue:**



# Polyurethanes: Where Rubber Meets the Road *(cont.)*
# Part 3 – When Things Go Wrong *Bruce Davis, Ph.D.*

This "cold aging" of polyurethane materials is common in both cast systems as well as with TPU materials. The "rearrangement" that occurs through further cross-linking or crystallization can result in changes in hardness, stiffness or even the glass transition temperature of the material. If these changes take place while the part is in service, they can certainly result in customer complaints or even catastrophic failures. For example, consider the differential scanning calorimetry (DSC) results for a TPU component. The manufacturer began fielding customer complaints regarding the "feel" of new production TPU components. It was found that "old" unused parts that the customer had kept in inventory for several months behaved differently than newly manufactured components. Though nothing had been changed in the material specification or injection molding process, there was a definite material difference between parts from the two eras. DSC testing found that the stored parts had undergone a form of cold aging, which resulted in a decrease of the glass transition temperature ($T_g$) of 13° C and a corresponding increase in melt temperature ($T_m$) of 6° C. The physical rearrangement of the TPU molecules that had occurred during storage had actually improved the perceived properties of the part and by implementing a controlled "annealing" step after injection molding, these effects could be realized in new production parts as well.




**Differential Scanning Calorimetry of a TPU Component**

Another overlooked aspect of polyurethane materials is the base chemistry of the building blocks used in its construction. For instance, consider the polyurethane shoe tread material that exhibited severe wear while in use. Since wear appears to be the primary mechanism for failure, the base hardness of the polyurethane material may come into question as the cause of failure. Indeed, an examination of the tread shows a soft, spongy material that is easily removed and torn from the substrate. Yet, the state of the failed shoe tread is quite different from its as-manufactured state. A microscopic examination of the wear structure at the polyurethane tread reveals evidence of material flaking, cracking, pitting and deterioration. These effects are visual indicators of material degradation in the polyurethane. To understand the mechanism responsible for this degradation one only needs to review the base chemistry used in the material.

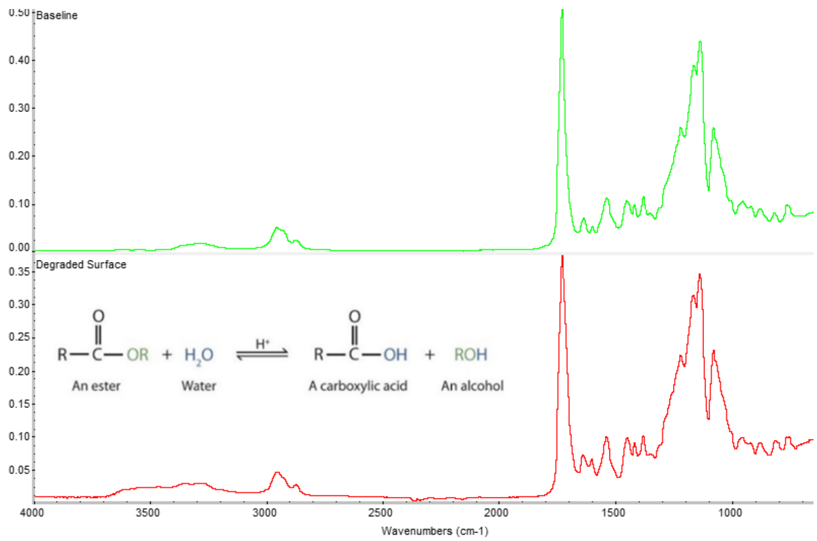
**Polyurethane Shoe Tread Failure**

Analytical testing of the shoe material via Fourier Transform Infrared Spectroscopy

# Polyurethanes: Where Rubber Meets the Road
# Part 3 – When Things Go Wrong *Bruce Davis, Ph.D.*

(FTIR) reveals the polyurethane as an MDI polyester based material. Furthermore, analysis of the spectra shows absorbances that indicate severe hydrolysis within the polyurethane material. This ester-based material has an affinity for water and will readily absorb moisture from the surrounding environment. Over time (and accelerated by elevated temperatures) the water molecules break down ester linkages in the polymer chain to create acids and alcohols. The acid byproducts act as catalysts to accelerate still further, hydrolytic degradation of the polymer chains. The resulting scission at the soft-segment of the polymer chain leads to loss of elasticity, embrittlement, cracking and premature loss of material. Though certain acid-scavaging/anti-hydrolysis additives can be formulated into the material to improve the hydrolytic resistance, they generally provide limited protection by creating barrier layers and/or decreasing the rate of hydrolysis but do not eliminate it entirely. By comparison, a ether-based polyurethane formulation would provide an inherent resistance to hydrolysis effects. However, even an ether-based mated can suffer from hydrolysis in harsh environments such as high-temperature marine applications. Therefore, it is important to properly test any material selected for the end-use environment for the application.




**Fourier Transform Infrared Spectroscopy of a Degraded Polyurethane**

Given the diverse range of end applications for polyurethane materials, careful consideration must be taken during material selection. Some of the many available standardized tests shown here can be used to assess certain aspects of a polyurethane for a specific application. Yet, it is the knowledge of the underlying chemistry of the material that is needed to ensure success when choosing a polyurethane for your next application. The Madison Group is ready to assist you with that endeavor.

| *ASTM Standard* | Test Description |
|---|---|
| *D0149* | Test Method for Dielectric Breakdown Voltage |
| *D0395* | Rubber Compression Set |
| *D0412* | Tensile Methods for Rubber Elastomers |
| *D0413* | Rubber Adhesion to Flexible Substrates |
| *D0429* | Rubber Adhesion to Rigid Substrates |
| *D0470* | Crosslinked Insulations and Cable/Wire Jackets |
| *D1004* | Graves Tear Resistance |
| *D1044* | Taber Abrasion Resistance |
| *D1630* | Rubber Footwear Abrasion Resistance |
| *D2632* | Rubber Resilience by Vertical Rebound |
| *D5963* | Rotary Drum Abrasion |

*The Madison Group has been a recognized global leader providing consulting services, technical expertise and innovative technology to the plastics industry since 1993. What we do is simple, we solve plastic problems and find economic solutions that help drive product development to yield higher quality parts. Whether the problem occurs during manufacturing or during the lifetime of a product, our knowledge and technical expertise can provide you with solutions. From consulting and technical expertise to engineering and design solutions, The Madison Group can help!*

To read Parts 1 and 2 of the original article—**Where Rubber Meets the Road:**
Click here to read Part 1.

Click here to read Part 2.

# Announcements

## TMG—Industry News


**The Madison Group is excited to offer our training for all Autodesk Moldflow products, both Insight and Advisor.**

The need for optimizing our plastic part designs, processes and mold designs prior to first shots, is more critical than ever. Autodesk Moldflow has multiple products to help assist and optimize your project at any stage. Whether you are a part designer that is interested in better understanding your externally provided Moldflow reports, a user that is looking to take full advantage of the tools you already have, or explore what additional tools are available to take you to the next level, we have a training package that can help you accomplish just that.

The Madison Group has a training plan option for any circumstance and budget.

**Choose any of the following options:**

- **On-site Training**
- **Remote Instructor-Led Training**
- **Private Training**

**Benefits of Investing in Moldflow Training**

- Keep up to date on the newest solvers and simulation tools for all the Autodesk Moldflow Products designed to save you time.
- Improve your results interpretation skills and help optimize your design.
- Increase your internal knowledge quickly and economically to improve communication and create a culture of innovation.
- Explore additional simulation capabilities to improve overall customer satisfaction.

**Benefits of Remote Instructor-Led Training Sessions:**

- Allow any of your employees to gain the training without being out of the office.
- Eliminate travel costs so you can have more employees trained.
- Choose interactive, live, instructor-led classes for one-on-one assistance with solver set-up and results interpretation.
- Installation of software not needed prior to training opportunities.

**Find a listing of all of our Upcoming Training Sessions here.**

# Material Characterization

## *Tier 1—(Part 1 of 3)* *Richie Anfinsen*

Whether you are a designer, manufacturer, or end user of polymeric products, the question is often asked what is or should my polymeric component be made from. These thoughts can be founded from an honest curiosity about what material is in a product, necessity during a part design cycle, or in the worst- case scenario, a product failure. While these three reasons for asking the question have the same goal in mind, they are completely different in the level of detail required and the techniques used to achieve the end goals. This leads to different tiers of material characterization that are dependent upon the specificity required. In my experience, there are three different tiers of characterization that our customers require to move their project forward. In this series of articles, we will be analyzing the intricacies of each tier of characterization and the expected results from each.

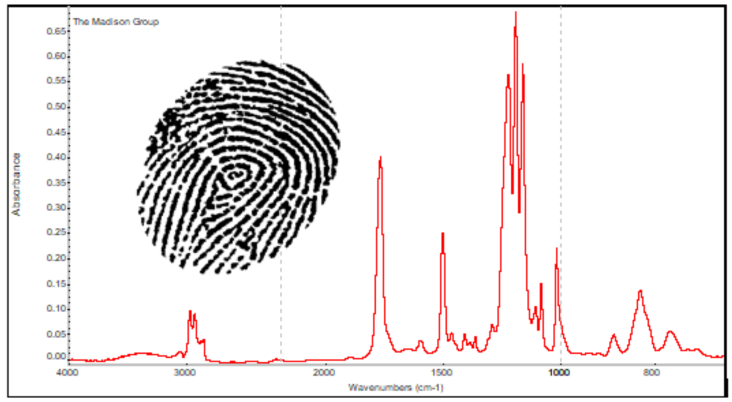



Figure 1 – FTIR analysis is like a chemical fingerprint that can be used for identification of polymeric materials.

**Tier 1**

The first tier of characterization is for the person who is looking to identify the basic polymer family that is utilized in a product. In this situation, we are trying to detect if the part is made from polyethylene, polypropylene, polyamide, or any other multitude of materials. Customers that are asking for this level of resolution are typically doing so to investigate contamination of a part or get the ball rolling on a project with the intention of a more involved analysis or research and development, further down the road.

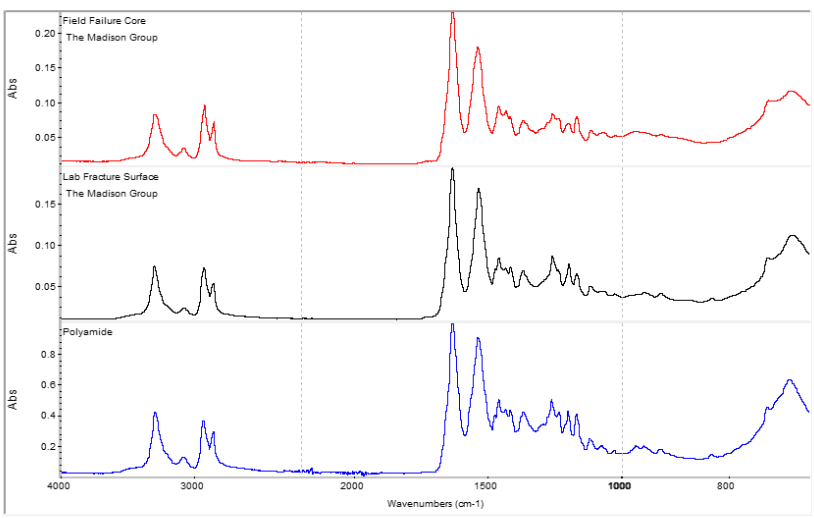



Figure 2 – FTIR analysis shows the material family of samples, such as this polyamide resin shown above. It does not provide the specific type of polyamide. This would require additional testing to determine.

The first tier of material characterization requires, as would be expected, less testing to achieve. However, with the large diversity of polymeric and elastomeric materials in existence, the techniques required still vary. Let us look at some of the most common techniques that are required to achieve the first tier of characterization.

Most material analyses start with a technique called Fourier transform infrared spectroscopy (FTIR). This technique provides an analyst with a graph that contains peaks and valleys that are created by the vibration of the chemical bonds in the material. This graph is akin to a human fingerprint and provides a graphical representation of the bonds within a material that can be used for identification, Figure 1. With this technique, we can differentiate the base polymer and identify the most basic characteristics of the material. It is important to note that while this test can provide families of material (polyethylene, polyoxymethylene, etc.) there are many nuances within these groups of resins that are not fully resolved with just one test. For example, if the base polymer is a polyamide, FTIR alone cannot tell us if it is a polyamide 6, (6,6), (6/12), etc., Figure 2. Since these sub-

# Material Characterization
## *Tier 1—(Part 1 of 3)* *Richie Anfinsen*

groups within a material family can be so diverse, the first level of characterization typically will utilize another technique to further identify the material.

The second test method to obtain a tier 1 characterization is typically differential scanning calorimetry (DSC). This analysis technique subjects the material to heat at a known rate and measures the change in heat flow for identification. The results provide information on the glass transition temperature and the melting temperature, which helps an analyst determine material characteristics such as if it is a blend, homopolymer/copolymer, or the specific subset within a polymer family, Figure 3. A good example of the necessity of this technique is polyamide materials, which have many designations such as polyamide (6), (6,6), (12) and several others, Figure 4. These designations identify the chemical structure, which plays a larger role in the physical and thermal properties. Additionally, identifying this sub-group is important to distinguish your material from the copious possibilities within the polyamide family.

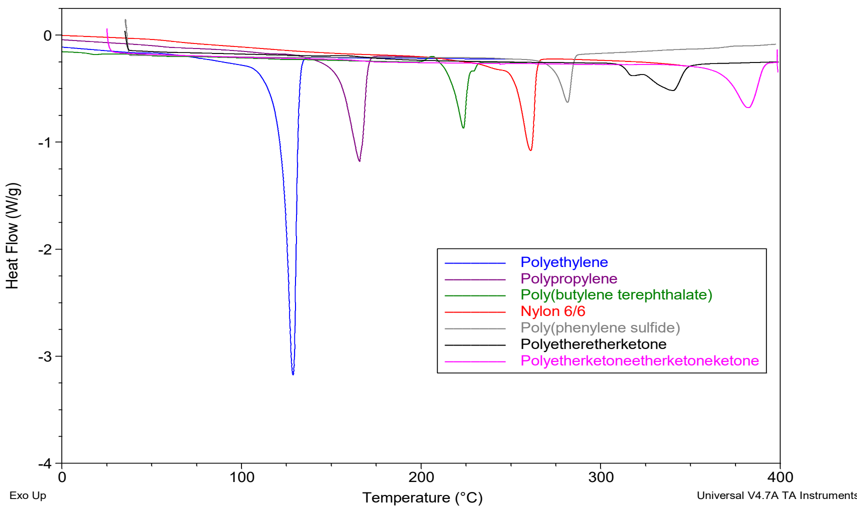



Figure 3 – DSC analysis showing the differences in melting temperature of various semi-crystalline materials.

The information provided from a tier 1 analysis is extremely useful to understand the type of material used. This will give some basic information on expected thermal behavior and general ideas of performance based on the polymer morphology. Further, this level of characterization will aid to pinpoint the source of contamination. However, this basic information will not allow the end user to design a component for performance or understand how the material will process during manufacturing. To get more information that will help to compare to data sheet values for performance we need to move to a tier 2 analysis. This stage will look further into the material composition, molecular weight, and some of the major additives within the material. This will allow for a more detailed review of datasheets and expected properties of the material in your design.

***Stay tuned for the next installment.***

***Information regarding additional case studies can also be found at:***
**https://www.madisongroup.com/case-studies.html**

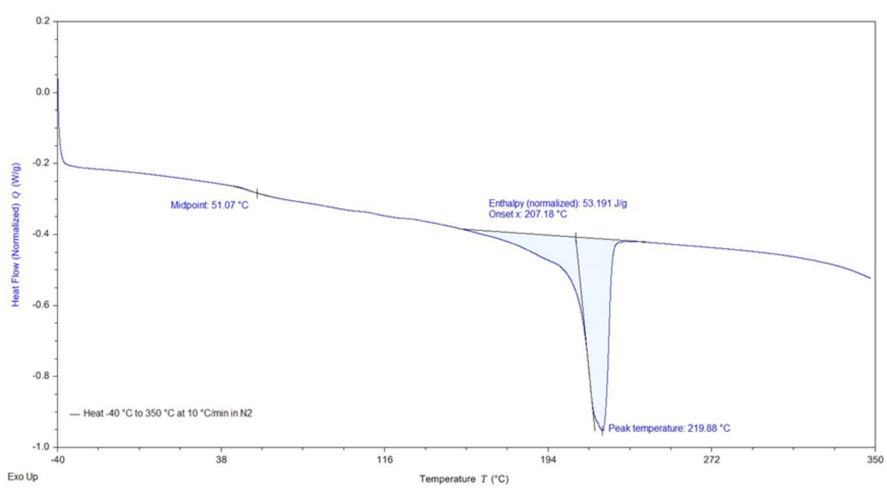



Figure 4 – DSC results from the material in Figure 2, showing a glass transition and melting temperature characteristic of polyamide 6.

# Upcoming Educational Webinars

**Tuesday, February 2, 2021** – *Paul Gramann, Ph.D.*
**"Plastics In:" Series: Water Management Applications**
10:00 AM (CST)

There are countless applications where plastics have changed how an industry functions. Perhaps no other industry has utilized the advantages of plastics more than water management. These industries include municipal water distribution and sewage control, agriculture and landscape irrigation, commercial and residential plumbing, fire protection, and medical, to name a few. Understanding and taking full advantage of the properties plastics have to offer has been a struggle at times for these industries.

This webinar will review the use of plastics in water management applications, from the ideal properties they have to offer this industry to the difficulties that must be avoided to ensure failure does not occur. The plastic selection process to ensure product success will also be reviewed. Case studies will be given showing success stories and failures. This will include background information on why the plastic excelled, to applications where the plastic fell short.

At the conclusion of this presentation, you will understand the following for water management applications:
- Pros and cons of plastics typically used.
- Insight into the successful selection of plastic materials.
- Real world examples demonstrating successes and failures within the industry.

Click here for more information.

**Tuesday, February 16th, 2021**—*Melissa Kurtz and Tom Hansen*
**Design and Material Considerations for Elastomeric Seals**
10:00 AM (CST)

O-rings are generally one of the first considerations when choosing a sealing feature between assembled components. They can be a simple and effective way to prevent air and water ingression or egression. However, following proper design guidelines as well as appropriate material selection are needed to ensure robustness. This presentation will discuss common applications for O-ring seals along with design and materials considerations for the O-ring and mating components.

At the conclusion of this presentation, you will understand:
- The best seal for a variety of applications.
- Important dimensional factors for seal design.
- How material selection can impact seal performance.

Click here for more information.

***Information regarding upcoming educational opportunities can also be found at:***
***http://www.madisongroup.com/events.html***

**If you are interested to have**
**The Madison Group**
**provide training to your team,**
**please feel free**
**to contact us at**
**info@madisongroup.com.**

**Training Topics**
- Failure Analysis
- Plastic Material Selection
- Plastic Part Design
- Moldflow
- Other