

Polyurethanes: Where Rubber Meets the Road– Part 1 –Back to Basics *Whitepaper Series* *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.

If you were to ask ten engineers to name something manufactured from a polyurethane material, you may very well receive ten different responses. To one it may be the hard, protective coating they use as a wood finish. To another it may denote the rigid foam insulation for weatherproofing or the soft foam underlayment for carpeting. Polyurethane materials can be used to manufacture running shoes, upholstery, cushioning, suspension bushings in heavy equipment, in-line skate wheels, flexible tubes/film/sheets, soft-touch over-molded features, adhesives, binders, coatings as well as automotive spoilers, bumpers and internal features.



Some typical applications for polyurethane materials.

Polyurethanes can be prepared as cross-linked thermosets that are cured through two component systems, thermoplastic elastomers that can be melt processed (and re-processed) or even foamed structures that can be soft and flexible or rigid materials. Though the properties can vary dramatically, some general benefits of polyurethanes can include:

- Excellent resistance to oils, greases and many solvents
- High elasticity/flexibility over a wide range of temperatures
- Abrasion and wear resistant
- Tear resistant and good compression set
- Good weather and UV resistance
- Ease of coloring
- Good tactile properties
- Wide range of processing methods
- Good bonding/adhesive properties
- Excellent impact and rebound properties

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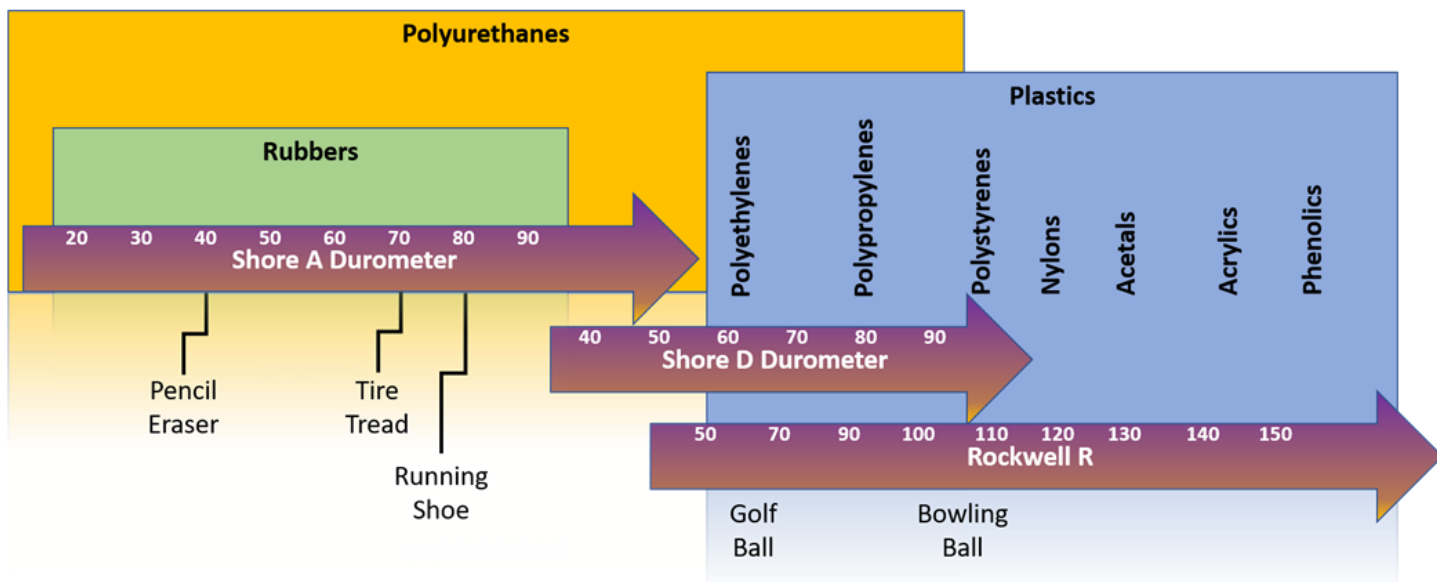
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Polyurethanes: Where Rubber Meets the Road-Part 1 (cont.)

Whitepaper Series

Bruce Davis, Ph.D.

Given the tremendous range of applications and diverse properties of polyurethanes, it is often convenient to categorize them according to their hardness. Though it is tempting to correlate some mechanical properties with hardness, to do so would be misleading and incomplete. (A more thorough review of properties and behavior will be discussed in Part 2 of this series.) The tremendous range of hardness available in commercial polyurethanes spans from soft rubbers to hard thermoplastics. How can a single synthetic material find so many different applications and take so many forms? The simple answer to this diverse range of properties and behavior can be traced back to its roots – chemistry.



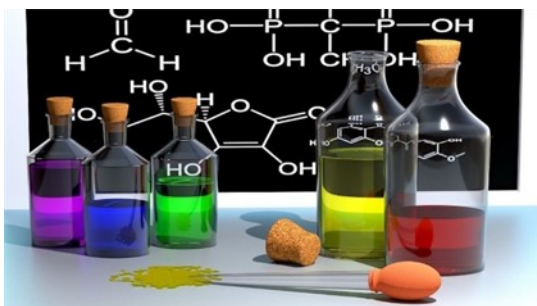
Hardness scales for various materials and products.

Often considered a “necessary evil” to a polymer engineer, chemistry forms the basis for all polymer structures – and ultimately defines many of their properties. Yet, one does not need an intimate understanding of the stoichiometric calculations of reactants, additives and byproducts necessary to synthesize a polyurethane. Instead, a basic understanding of the underlying chemistry will suffice to appreciate the broad spectrum of behaviors found in polyurethanes.



Otto Bayer demonstrates polyurethane in 1952 (Public Domain).

Polyurethane was originally patented under the work of Otto Bayer and his coworkers at IG Farben in Leverkusen, Germany in 1937 while they reportedly were trying to copy a Nylon 6,6 structure. The single-claim patent discloses the method to produce polyurethane by reacting a polyol (-OH group) with a diisocyanate (-NCO group). The specific choice of these base chemistries (along with a suitable chain extender and additives), their relative ratios and the way they are assembled, are what ultimately will control the final properties and behavior of the polyurethane material.



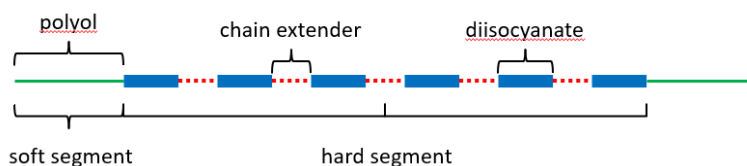
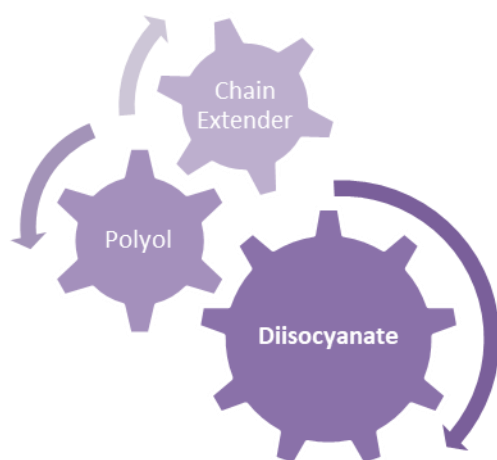
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Polyurethanes: Where Rubber Meets the Road – Part 1 – (cont.)

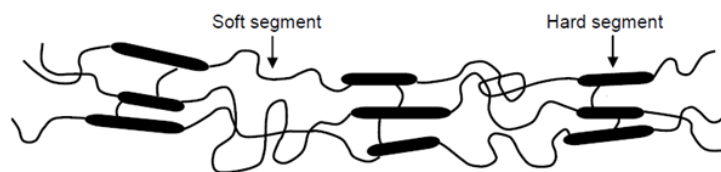
Whitepaper Series

Bruce Davis, Ph.D.

A polyurethane molecule can be considered as a block copolymer that is constructed from three basic constituents: a polyol, a chain extender and a diisocyanate. The specific chemistry of these constituents as well as the way in which the resulting soft and hard block segments are arranged, provide toughness as well as flexibility for the elastomer. The hard segments within the polyurethane molecules can order with one another to form crystalline regions. For thermoset polyurethanes the same ordering may also occur but additional functionality within the curative will produce cross-linked chemical reactions between the individual molecules. For both thermoplastic and thermoset varieties, it is this carefully planned ordering that offers polyurethanes the tremendous range of mechanical properties and behavior.



For thermoplastic polyurethane (TPU) ordering between hard segments form crystalline regions that melt. For thermoset polyurethanes, additional chemical bonds between molecules are formed by a suitable amount of curative (>2 functionality) to promote a controlled degree of cross linking.



Polyurethane molecule construction.

Additionally, many of the mechanical and physical properties exhibited in a polyurethane material are directly affected by the specific chemical choices for the polyol, diisocyanate and chain extenders. Though beyond the scope of this introductory white paper, each of these constituents can be broadly categorized in terms of their chemical classes, bonds and ring structures. Though other hybrids and options are available, the polyols used for most commercial polyurethanes can be described as either polyether- or polyester-based. Similarly, the diisocyanate's used during the synthesis of polyurethane materials can be generally classified by their ring structures as aliphatic or aromatic. Finally, the chain extenders, low molecular weight (short chain) diols or amines align themselves to connect with the stiff hard segments. For thermoset polyurethanes, higher functionality (>2) polyols and amines act as crosslinkers between the molecules.

Therefore, it is the combination of the base chemistry of the "ingredient" components used for the polyurethane, as well as the order/manner in which they are assembled onto the molecule that control the material's properties. Ultimately, it is the complex interaction between the soft and hard segments in a polyurethane system that provides the desirable physical properties such as elasticity, tensile strength, tear resistance, and elongation. However, the details of how these properties are developed and used are left to the next installment of this whitepaper series on Polyurethanes: Where Rubber Meets the Road.

Polyurethanes: Where Rubber Meets the Road – Part 1 –Back to Basics

Whitepaper Series

Bruce Davis, Ph.D.

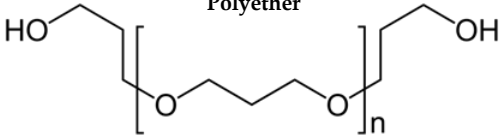
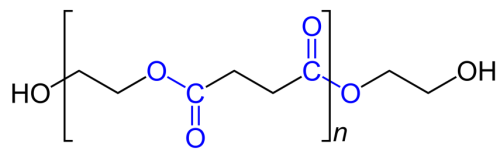
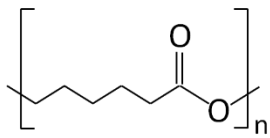
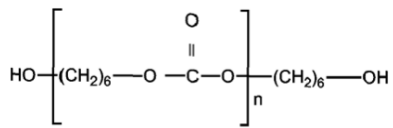
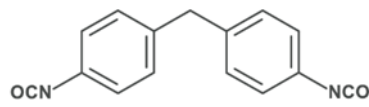
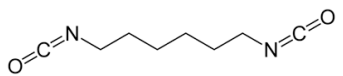

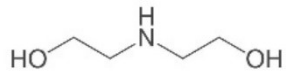
	<u>Sample Molecule Type/Structure</u>	<u>Properties/Benefits Provided</u>
Polyols	Polyether 	<ul style="list-style-type: none"> Resilient and impact resistance Improved low-temp performance Hydrolytic stability (resistant in H₂O) Low heat build up
	Polyester 	<ul style="list-style-type: none"> Cut and tear resistance Sliding abrasion resistance Oil and solvent resistance Heat aging resistance Higher tensile strength Poor hydrolysis resistance (degrade in H₂O)
	Polycaprolactone 	<ul style="list-style-type: none"> More expensive Enhanced abrasion resistance Oil, fuel & solvent resistance Cut, chip, and tear strength Improved hydrolysis resistance
	Polycarbonate 	<ul style="list-style-type: none"> Superior hydrolysis resistance Excellent high-temp properties More difficult processing
Diisocyanates	Aromatic  MDI (Methylene Diphenyl Diisocyanate)	<ul style="list-style-type: none"> Good flexibility, strength and toughness Used for elastomers, sealants, adhesives and coatings Good chemical resistance
	Aliphatic  HDI (Hexamethylene Diisocyanate)	<ul style="list-style-type: none"> UV & light stable (non-yellowing) Excellent optical clarity Excellent adhesion and bonding
Chain Extenders	Diols  BDO (1,4-Butanediol)	<ul style="list-style-type: none"> Wide use and compatibility Good balance of hardness and temperature flexibility
	Amines  DEA (Diethanolamine)	<ul style="list-style-type: none"> Increased modulus/strength Decreased elongation

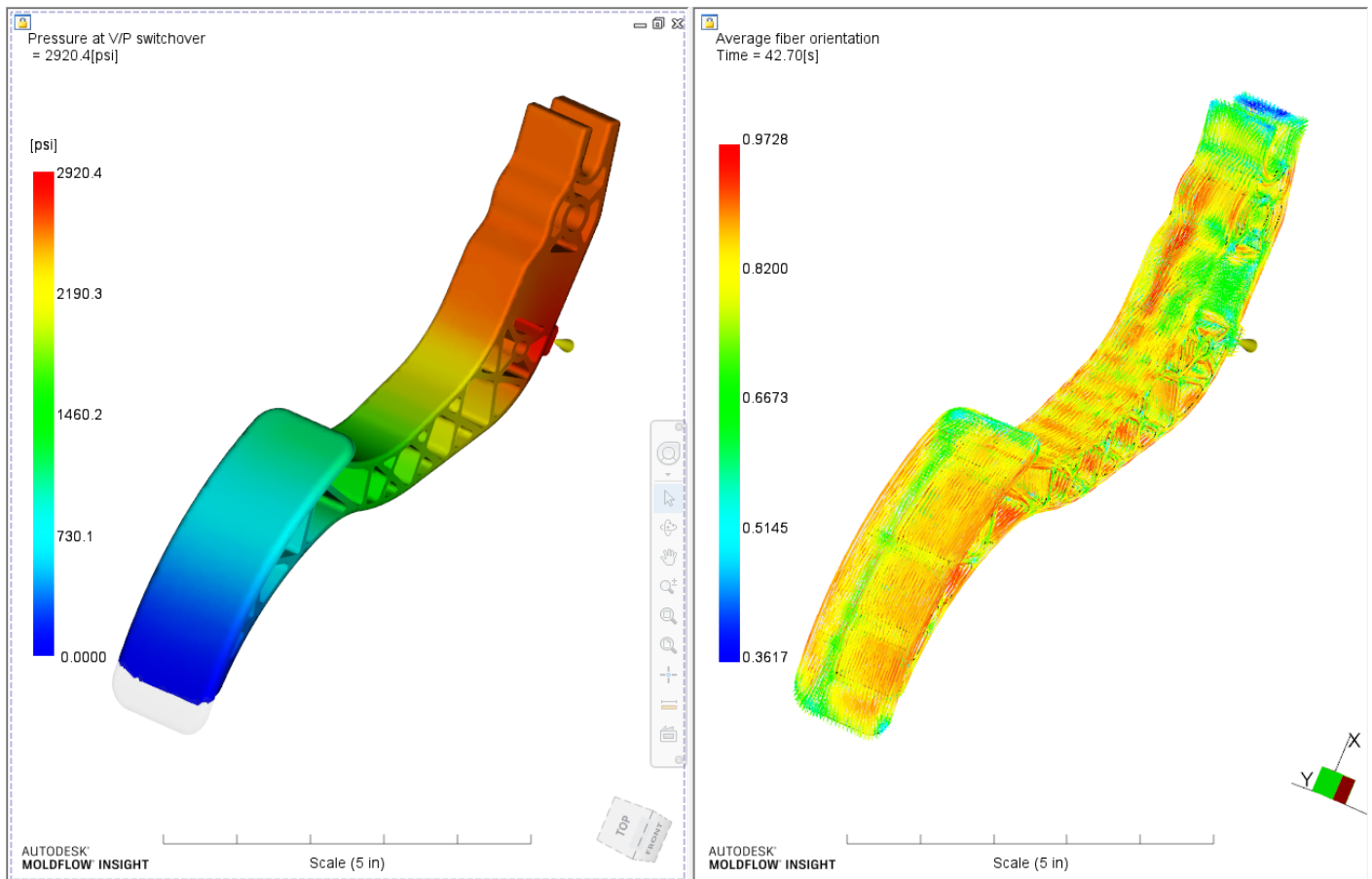
Table showing some typical polyurethane constituent chemistries and their effects on properties.

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and Structural FEA's
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Information regarding more Moldflow information can also be found at:
<https://www.madisongroup.com/moldflow-analysis.html>



#TMGPLASTICEDU

In May and June, The Madison Group was able to educate 265 attendees from over 50 organizations on six different, plastics related topics.

We are excited to continue to extend our complimentary education program, **#TMGPLASTICEDU**.

We will be offering both public and private learning opportunities on these topics in **August** and **September**:

Introduction to Thermoplastic Materials
Basic Rubber Technology
Elastomeric Materials: Thermoset versus Thermoplastic
Fatigue Failure of Plastics
Hands-On Troubleshooting Approach for Injection Molding
Synergies of Plastic Materials and Part Design

More information regarding these public events, including their abstracts, schedules, and registration links, can be found at

www.madisongroup.com/events.html



If you have a team of 5 or more people eager to develop their understanding of plastics please contact **Melissa Kurtz** at [**melissa.kurtz@madisongroup.com**](mailto:melissa.kurtz@madisongroup.com) to discuss a private learning opportunity.

Navigating the Plastic Material Selection Process: Temperature Considerations

Paul J. Gramann, Ph.D.

We all learned at a very early age that plastics cannot survive in temperatures as high as metals. Plastics will melt or soften at a relatively low temperature. **Figure 1** shows an assembly that was exposed to conditions greater than the plastic's melt temperature. However, it is not just the high-end temperature that defines the range we need to consider when selecting a material for an application. When choosing a plastic for an application we likely need to understand how it will perform at very low temperatures as well. This article will review temperature considerations when choosing a plastic material for your application.

The mechanical behavior of all plastics will change *significantly*, within the temperature range we live in or expect plastic materials to survive. Here, "significantly" means in most situations the change in properties will be enough that they need to be considered. The huge number of different plastic materials provides the engineer/designer with many options to choose from. **Figure 2** provides an illustration of the relative high temperature range of some common plastic materials. The material selection process should not end with this diagram. When navigating through the plastic material selection process it is important to understand more than just the high-end use temperature. Knowing how the material will behave over the expected temperature range the part will be used, can be critically important.

Testing for Mechanical Properties

The two primary testing methods for measuring and understanding the change in mechanical properties with temperature are dynamic mechanical

analysis (DMA) and tensile testing. Each test provides necessary information for making an informed and appropriate material selection. Though this article is too brief to provide a full explanation of each test, the following highlights are given:

DMA

- Provides the storage (elastic) and loss modulus of the plastic over a large temperature range.
- The primary method used to determine the glass transition temperature of a plastic.
- Using time-temperature superposition (TTS) can be used to provide insight into the lifetime (creep) of the plastic part.

Tensile Testing

- Provides the yield point, strength and elongation at break at discrete temperatures.
- Most utilized mechanical testing technique by industry.



Figure 1 – Plastic assembly that was exposed to a high temperature.

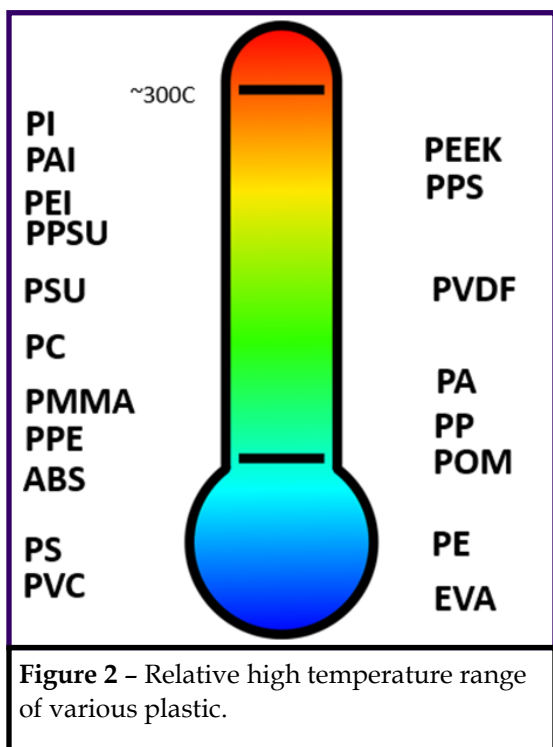


Figure 2 – Relative high temperature range of various plastic.

Navigating the Plastic Material Selection Process: (cont.)

Paul J. Gramann

Figure 3 shows DMA results and **Figure 4** tensile testing results, for polyamide 66 Zytel 70G33Hs1L (33% glass) over a large temperature range for both dry-as-molded (DAM) and conditioned [1]. These Figures illustrate how significantly the properties will change over a temperature range that this material may experience. One of the keys to successfully choosing a plastic material for an application is understanding what the changes in properties will be, and their effect on part performance. For instance, one can observe that the modulus and strength of this material have decreased significantly from room temperature. This information can be used for “back of the envelope” calculations or in a finite element analysis (FEA).

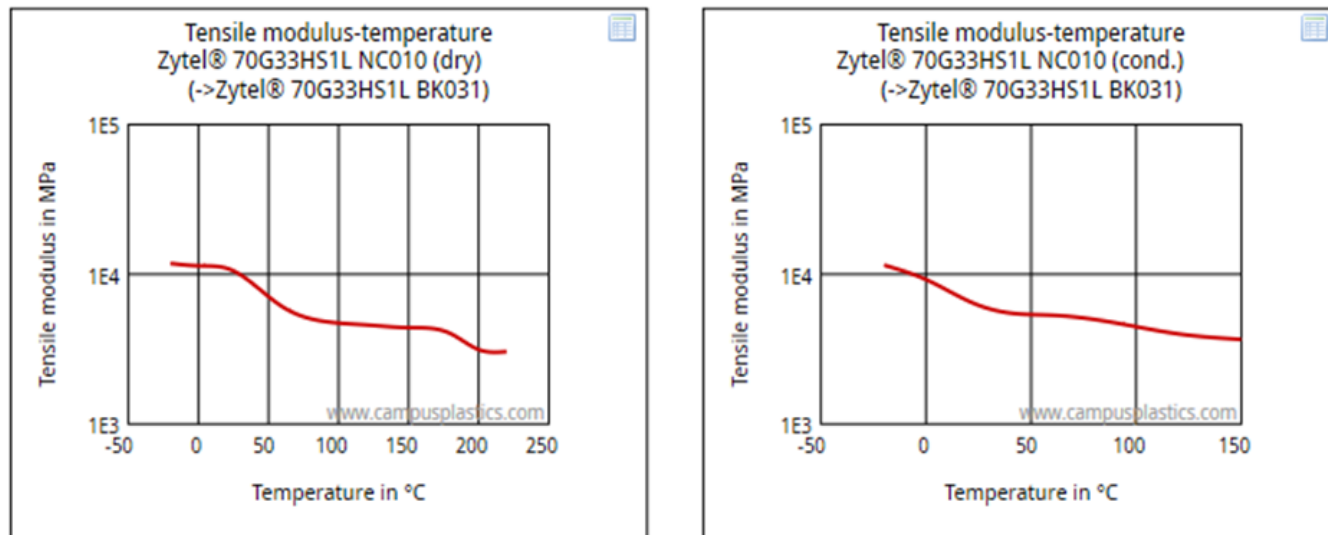


Figure 3 – Modulus of nylon 66 Zytel 70G33HS1L over a large temperature range (dry and conditioned) [1].

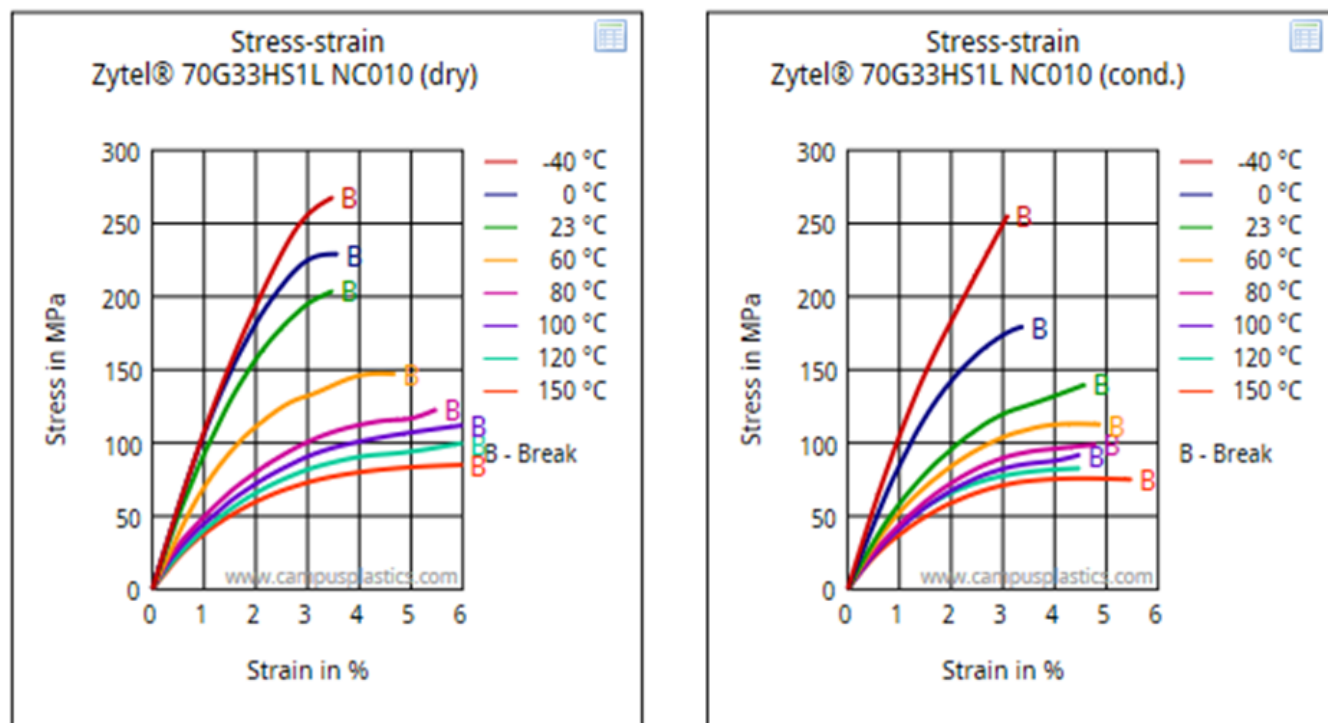


Figure 4 – Tensile test results of polyamide 66 Zytel 70G33HS1L over a large temperature range (dry and conditioned) [1].

Navigating the Plastic Material Selection Process: Temperature Considerations

Paul J. Gramann

Glass Transition Temperature

Perhaps the most important thermal property is the glass transition temperature (T_g). The glass transition is a reversible transition in the amorphous regions of the polymer where the molecules can move more freely. In general, the amorphous region transitions from being hard/stiff to being more compliant and rubbery-like. For amorphous polymers, the T_g is the softening point that needs to be exceeded in order to injection-mold or extrude. It is obvious that an amorphous part will not survive if the temperature conditions approach the polymer's T_g . On the other hand, it is quite common for operating conditions to go through the T_g of a semi-crystalline polymer. Because the mechanical properties will change drastically at the T_g , it is critically important that one knows the plastic's T_g and the expected change in properties.

There are several methods that can be used to determine the T_g of a plastic material. Unfortunately, they will all show slightly different results. However, using the same technique will provide consistency and comparative results. The method that this author uses is the relative maximum of the loss modulus when measured using dynamic mechanical analysis (DMA). **Figure 5** shows the storage and loss modulus for a polyether sulfone polymer [2]. The local peak in the loss modulus at 217 °C is the T_g for this material.

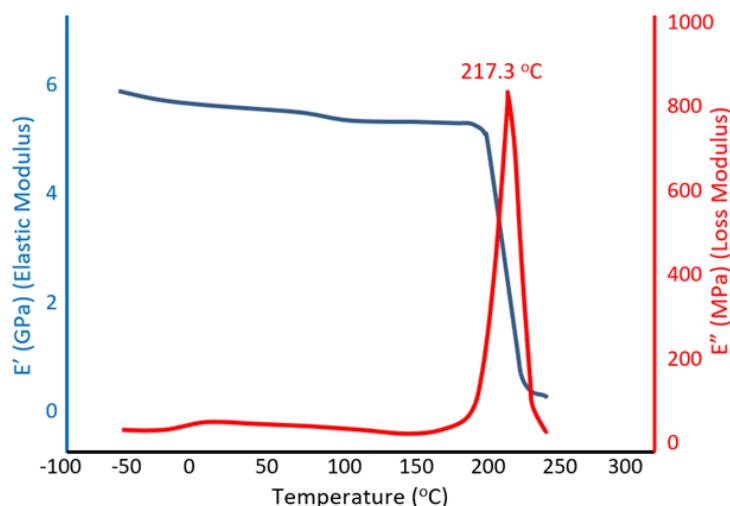


Figure 5 – The storage and loss modulus of polyether sulfone showing the T_g at 217 °C.

Glass transition temperatures of some select resins:

Polymer	~ T_g °C	Notes
Polyethylene	-110	Extremely low T_g , highly crystalline
Polyacetal	-60 - -80	Extremely low T_g , highly crystalline
Polypropylene	0 - -15	Will become brittle around freezing
Polyvinylidene fluoride	-35	Excellent with moisture, oxidation resistance
Polyamide 66	40 - 60 (DAM)	T_g will reduce significantly with moisture
Polycarbonate	150	Will become increasingly brittle ~-20 °C
Polysulfone	195	Good transparency, strength, impact
Polyphenylsulfone	288	Excl. chemical resistance, strength, impact

A Quick Note on Thermal Expansion

It is important to take into consideration the thermal expansion and contraction the plastic part will experience over the temperature range it will live in. Most plastics will expand three to ten times more than metal. Constraining a part

that is expected to go through large temperature swings can result in the generation of significant stresses and/or deformation. These stresses can easily be large enough to cause cracking in the part.

References:

[1] www.campusplastics.com.

[2] Sepe, M., Dynamic Mechanical Analysis, PDL (1998).

Additional information can be found at:

<https://www.madisongroup.com/material-evaluation.html>

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**
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Benefits of Virtual 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.

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.

Find a listing of all of our Upcoming Training Sessions [here](#).

Upcoming Educational Webinars

Webinars provide a cost-effective way to expand your knowledge of plastics.

Below is a list of the upcoming webinars presented by TMG Engineers:

Thursday, September 10, 2020 – Jeffrey A. Jansen – Society of Plastics Engineers

Fractography in Plastics Failures

10:00 AM (CST)



The goal of a failure analysis is to discern the mechanism and cause of the component failure-essentially to identify how and why the part broke. Fractography plays critical role in this, particularly in identifying the failure mode. Cracking occurs as a result of the exertion of stresses, both external and internal, on a component. Cracking is simply a stress relief mechanism in which the material is attempting to reach a lower energy state. Plastics fail through a disentanglement mechanism in which polymer chains slide past each other. The features on the fracture surface are created based upon a number of parameters:

- Type of material and formulation constituents;
- Type of applied forces (tensile, compression, shear)
- Magnitude of forces
- Frequency of forces (continuous, intermittent, rapidly applied)
- Environmental effects (temperature, presence of chemical)

Much of the information regarding the failure mechanism can be gleaned by interpreting the features found on the fracture surface. The examination and interpretation of the fracture surface is known as fractography. This presentation will explore some common plastics failure mechanisms and the associated telltale features.

Click [here](#) to register.

Thursday, October 29th – Jeffrey A. Jansen – Society of Plastics Engineers

Understanding Wear of Plastics

10:00 AM (CST)



Wear can be defined as damage to a solid surface caused by the removal or displacement of material through mechanical action associated with contact with a mating surface. Plastic components are used in a wide range of demanding applications in which they are subjected to surface damage and wear. These commonly include:

- Gears
- Valves and Pistons
- Tanks and Hoppers
- Bearings
- Fasteners
- Seals
- Conveyor Systems

Wear of plastics is a relatively common failure mechanism, which needs to be understood in order to avoid component malfunction and breakdown. This webinar will address the mechanisms of wear in plastics.

Plastic wear is affected by several factors that may be generally categorized into mechanical, environmental, and thermal aspects. These three groups of factors essentially determine the mechanism of wear of a plastic surface when it comes in contact with another surface.

The topics covered as part of this presentation will include:

- Mechanisms of wear in plastics
- Wear factors
 - Mechanical/ Environmental/Thermal
- Wear resistant plastics

Registration information will be provided at a later date.

Upcoming Educational Webinars (cont.)

Below is a continued list of the upcoming webinars presented by TMG Engineers:

Thursday, November 12, 2020 – Jeffrey A. Jansen – Society of Plastics Engineers

Navigating Plastic Material Selection

10:00 AM (CST)



Material selection is one of the fundamental aspects that will determine the success or failure of a product. With so many choices available today regarding plastic materials, it is imperative that anyone involved in product design or material selection understand resin properties and how they will affect end product performance as well as part design and manufacturability. While plastic material selection is a frequent topic of discussion, it is not as simple as it may first appear. A thorough understanding of the short-term and long-term properties of the potential plastic resins is essential. To help make the best plastic resin choice, is also essential to have a basic knowledge of polymer chemistry.

This webinar will address some of the considerations that need to be made when selecting a plastic resin, and outline the challenges and benefits of selecting an appropriate material. The presentation will introduce a method of systematic selection that will optimize the plastics material selection process.

Registration information available at a later date.

Thursday, December 10, 2020 – Jeffrey A. Jansen – Society of Plastics Engineers

The Consequences of Ductile-to-Brittle Transitions in Plastics

10:00 AM (CST)



Thermoplastic resins are utilized in many applications because of their unique property set, including their ductile response to applied stress. This ductility is associated with the viscoelastic nature of polymers and is attributed to their unique molecular structure. In spite of that inherent ductility, most plastic components fail through one of the many brittle fracture modes. Experience through conducting thousands of plastic component failure analyses has shown that less than 5% were associated with ductile overload. The remainder represent brittle fractures of normally ductile materials. Thus, within evaluations of plastic component failures, the focus of the investigation frequently turns to identifying the nature of the ductile to brittle transition. This relatively brittle response to stress is evident through the examination and characterization of the fracture surface morphology. There are numerous factors, associated with material, processing, design, and service conditions that influence a ductile-to-brittle transition within plastic materials. These include:

- Temperature
- Stress Concentration
- Chemical Contact
- Molecular Weight
- Degradation
- Filler Content
- Contamination
- Poor Fusion
- Strain Rate
- Time Under Load
- Crystallinity
- Plasticizer Content

Registration information available at a later date.

Information regarding upcoming educational opportunities can also be found at:

<http://www.madisongroup.com/events.html>