TMG News

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

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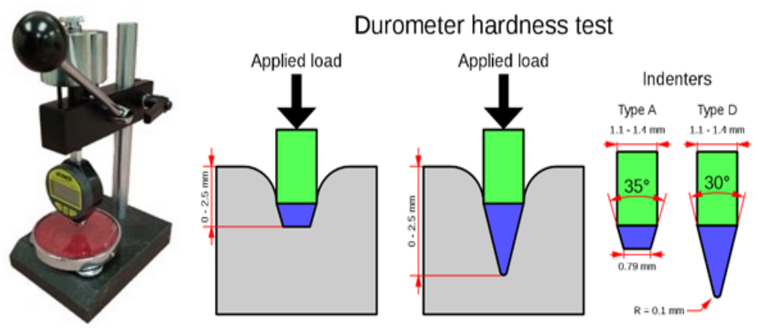
Polyurethanes: Where Rubber Meets the Road
Part 2 – It's Not All That Hard

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.

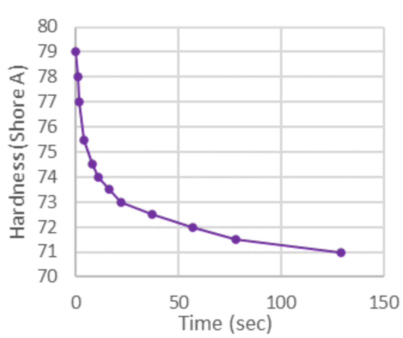
Whenever polyurethane materials are discussed they tend to be categorized in terms of their hardness. Like most other elastomers, that hardness is typically expressed in terms of the Shore A scale for softer materials and Shore D for harder grades. While useful in describing the relative "feel" of the finished product, hardness is only the tip of the iceberg in terms of the underlying properties and complex behavior of a polyurethane.

Unfortunately, some end-users still attempt to correlate the hardness of a polyurethane to other properties such as flexural modulus, tensile strength, or tear resistance. While hardness and modulus may both reflect how the product feels to the touch, the two properties measure very different material behaviors. Therefore, an attempt to infer a polyurethane's strength from its hardness would be misleading and incomplete.



A typical durometer and indenters for hardness testing

For plastics and rubbers, the standard test method for Durometer Hardness is governed by ASTM D2240. This hardness test measures the penetration of a precision indenter into the material under the conditions of force and time. The specimen is first placed on a hard and flat surface and the indenter is pressed perpendicularly into the sample. A calibrated digital or dial gage displays the hardness value that is read within one second of firm contact with the specimen.



Hardness test data for a TPU

The specifics of ASTM D2240 also permit different time durations to be used (based on customer specifications) for the hardness test. For this reason, many polyurethane material suppliers will specify a hardness value at 10-15 seconds for their materials. However, this brings up an interesting point in that a polyurethane hardness is not a fixed material property but will vary over time. For example, the measured hardness for the thermoplastic polyurethane (TPU) material shown to the left appears to "*soften*" depending on how long the hardness test indenter has been applied. The instantaneous initial hardness reading is 79 Shore A, but after only 2 minutes the hardness has apparently

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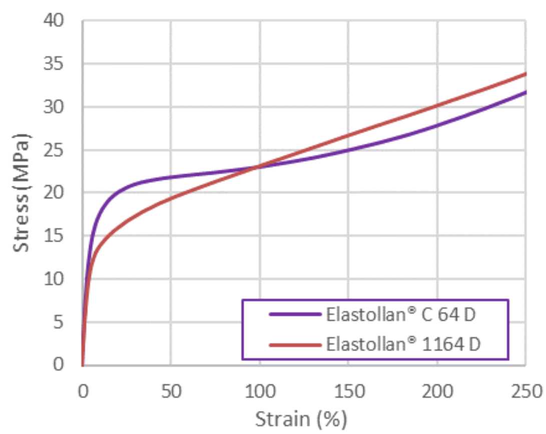
dropped by 10% to 71 Shore A. Clearly, hardness is not a fixed property of the material but a time-dependent single-point data reference that depends on the underlying chemistry as well as the viscoelastic nature of the polyurethane molecule itself.

	Elastollan C64D (Ester based)	Elastollan 1164D (Ether based)
Hardness (ISO 7619)	61 Shore D	61 Shore D
Tensile Modulus (ISO 527)	390 MPa	250 MPa
Stress at 300% Elongation (ISO 527)	35 MPa	45 MPa
Stress at break (ISO 527)	45 MPa	50 MPa
Tear Strength (ISO 34-1)	200 kN/m	190 kN/m
Glass Transition (ISO 11357)	-14 C	-6 C

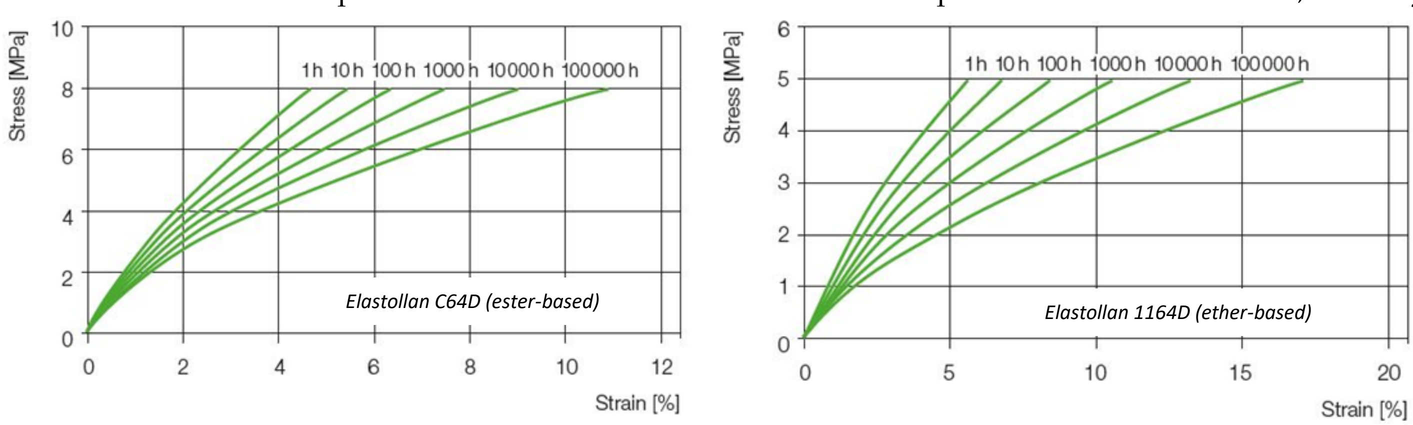
Comparison of properties for an ester- and ether-based TPU [1]

For example, consider the two thermoplastic polyurethane (TPU) Elastollan grades from BASF in the table to the right. Both materials are listed at identical hardness values of 61 Shore D (15 seconds), yet their mechanical properties are distinctly different. The ester-based TPU exhibits a substantially higher tensile modulus than the ether-based grade. Since it is the flexible soft block segment of the molecule that contains the (ester/ether) polyol chemistry, it should come as no surprise that the "bulkier" ester-based linkage would exhibit a stiffer (with lower elongation) initial response for tensile testing. Yet, an interesting effect can be seen when comparing the full stress-strain curves for the two Elastollan materials in the figure to the left. While the ester-based material exhibits a stiffer initial response than the ether-based grade, at approximately 100% strain those responses reverse. Therefore, a prudent designer will look beyond hardness to other key properties when considering a polyurethane during the material selection process for a new product. For instance, an ether-based TPU would be preferable for a hot and humid environment where hydrolysis resistance would be needed. Conversely, an ester-based TPU will generally provide superior wear resistance and better resistance to oils, fuels and solvents. Though hardness can be useful for initial screening purposes, one must ultimately consider the effects of time, temperature, loads and environment of the intended application.



TPU stress-strain curves at 23°C [1]

The time-dependent "*softening*" effect shown previously in the hardness test also reveals something about the underlying viscoelastic properties of the polyurethane molecule. Though most engineers tend to have a solid understanding of elastic properties, in reality all polymers are viscoelastic materials. Therefore, a TPU will exhibit both an elastic response as well as a viscous "flow" that will depend on the stress duration, intensity



Isochronous stress-strain data at 23° C for (left) an ester-based TPU and (right) an ether-based TPU [2]

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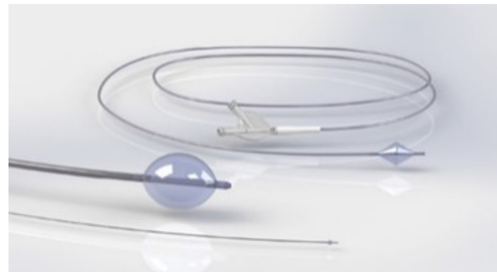
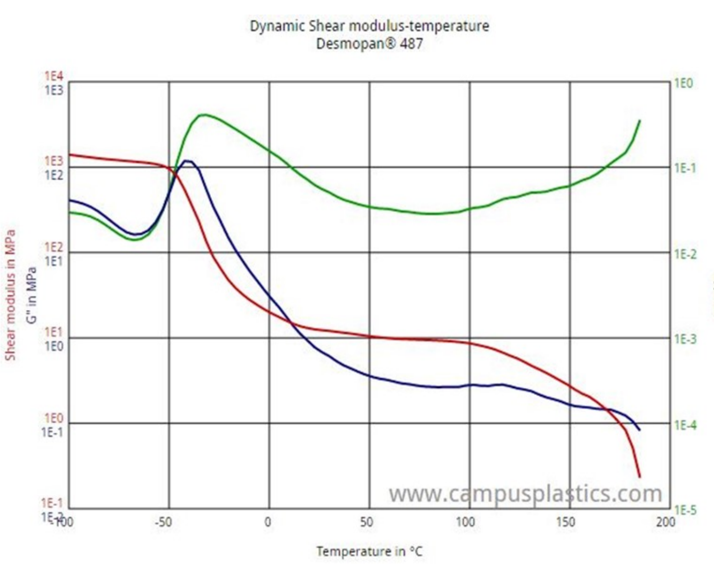
and ambient temperature. This behavior under a long-term static stress can be characterized by means of creep tests, such as ISO 899. Here, test specimens are subjected to a static tensile stress and the strain responses are measured over time. When this test is conducted at different loads, the creep data can be used to construct an isochronous stress-strain diagram for the material.



TPU thin-walled balloon application.

These calculated isochronous curves represent an "apparent" stress vs. strain response for the material as if tested for a specific amount of time. While isochronous stress-strain curves are sometimes spurned by academics, they can prove to be incredibly useful for design engineers during early product development. For example, consider the thin-walled balloon tubing application shown to the right. In the inflated condition, the balloon geometry is designed to carry a sustained hoop stress of 4 MPa. While well below the tensile strength of either of the two 61 Shore D Elastollan TPU grades, the balloon design also requires a strain limit of less than 5%. Viewing the iscochronous data above, it is clear that the ester-based Elastollan C64D would satisify this strain limit well past 100,000 hours of service. In comparison, the ether-based Elastollan 1164D reaches the 5% strain after only 10 hours of continuous stress. Clearly, more than hardness matters when it comes to designing with a TPU material.

To more completely assess the viscoelastic properties of a polyurethane material, a Dynamic Mechanical Analysis (DMA) can be performed. This highly instrumented technique applies a sinusoidal stress to a small sample and measures the strain response. By varying the frequency of the stress or the temperature of the sample, the complex modulus can be determined as well as key transition temperatures for the material. For example, the figure to the left shows the material response to a torsion load over a range of temperatures for an ester-based Desmopan 487 TPU from Covestro. The red curve is a measure of the shear elastic modulus for the sample. The blue curve signifies the loss modulus (damping response) while the green curve (tan δ) is a measure of the ratio of the damping characteristics to the elastic response. The peak in tan δ for this TPU grade occurs at around -35 °C and signifies the glass transition temperature for the material. Below this temperature, the TPU exhibits a rigid/brittle elastic behavior. However, above this temperature the damping effects increase and the TPU exhibits a rubbery plateau. This rubber-elastic behavior continues with increasing temperature until the shear modulus rapidly decreases above approximately 150 °C when melting of the hard segments ensues. Therefore, DMA is extremely useful in understanding how a specific polyurethane material will behave over the range of temperatures that it may experience in service. Furthermore, DMA can also be used to measure the elastic-damping response as a function of frequency or even extended to provide lifetime predictions for long-term loading conditions.



Dynamic Mechanical Analysis (DMA) for an ester-based TPU.

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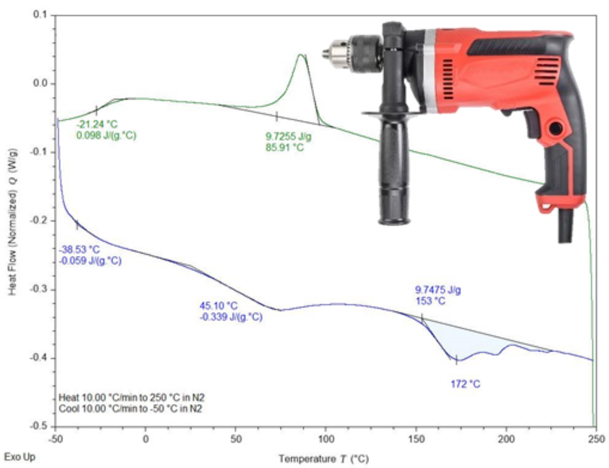
In Part 1 of this series we also saw that it is both the underlying chemistry and the *manner* that the molecules are assembled that will ultimately control the end properties for the material. For example, consider the two ester-based polyurethane materials that exhibit nearly identical hardnesses of 87 Shore A. These materials were both prepared from an ester-based MDI but the first column shows a cast elastomer (chemical bonds between molecules) while the second shows a melt-processable TPU (physical bonds between molecules). While some of the properties are quite similar for the two polyurethanes, the bold values show a marked advantage to the cast system for tensile strength and rebound and to the TPU for tear and abrasion resistance. In this case, the physical bonds between molecules of the TPU are able to resist distortion and breakage in tear and abrasion. Likewise, the presence of the strong chemical cross-link bonds for the cast urethane provides strength and extends the operating temperatures that can be experienced while in service.

Test (ASTM #)	Units	Cast	TPU
Durometer (D2240)	Shore A	88	87
100% Modulus (D412)	psi	1200	1300
Tensile (D412)	psi	**6800**	2800
Elongation (D412)	%	300	250
Split Tear (D470)	pli	120	**150**
Rebound (D2632)	%	**37**	29
DIN Abrasion (D5963)	mg loss	56	**47**

Properties for two ester-based polyurethanes. [3]



Thermal behavior for an overmolded TPU material

To wrap up this overview of polyurethane properties, let's further consider temperature effects on the structure and ultimately the mechanical behavior of the polymer. In this case, a TPU material was chosen for an overmolding application on an electric hand drill. The soft and resilient nature of the TPU was well-suited to provide enhanced comfort and durability for the drill over the expected service temperatures of -20 to 50°C. However, it was found that the TPU experienced dimensional changes and "hardening" during accelerated testing of the drill at elevated temperatures. Differential Scanning Calorimetry (DSC) testing of the TPU resin showed an expected melting temperature (T_m) of 172°C. However, the testing also showed that this particular thermoplastic polyurethane experiences a glass transition temperature (T_g) in the hard block segments at 45°C as well as the potential for recrystallization at temperatures approaching 50°C. The observed dimension changes and "hardening" of the overmolding was an artifact of the TPU molecules re-aligning while in service to cause physical changes in the properties. This effect is why some TPU grades may actually benefit from an "annealing" step following the molding process. However, that discussion is best left to the final installment of this whitepaper series on Polyurethanes: Where Rubber Meets the Road when we'll examine when things go wrong and failures occur.

[1] Computer Aided Material Preselection by Uniform Standards (CAMPUS), www.campusplastics.com.
[2] Thermoplastic Polyurethane Elastomers: Elastollan – Material Properties, BASF.
[3] Archibald, R.S., Baldassarri, R. and Donghi, A, "An Overview of the Similarities and Differences of Cast and Thermoplastic (TPU) Polyurethane", May 8, 2017, PMA.

Please click here to read Part 1—Where Rubber Meets the Road.

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 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.

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

Nursery Flowerpot Material Composition

Jeffrey A. Jansen

A few weeks ago, we picked up a couple of flowering mums to cheer up our yard for the fall. After planting the flowers, I was going to put the plastic pots they came in into the recycling bin. I noticed that they were marked with a No. 5 Polypropylene recycling triangle. Given the plastic nerd that I am, I thought this would be an interesting material to analyze.

The analysis started with Fourier transform infrared spectroscopy (FTIR), and those results showed that the material was in fact polypropylene, **Figure 1**. However, other bands associated with a significant level of ethylene functionality were also present. Additionally, the spectrum also showed absorbances that indicated the presence of a thermoplastic polyester, such as poly (ethylene terephthalate) (PET) or poly (butylene terephthalate) (PBT).

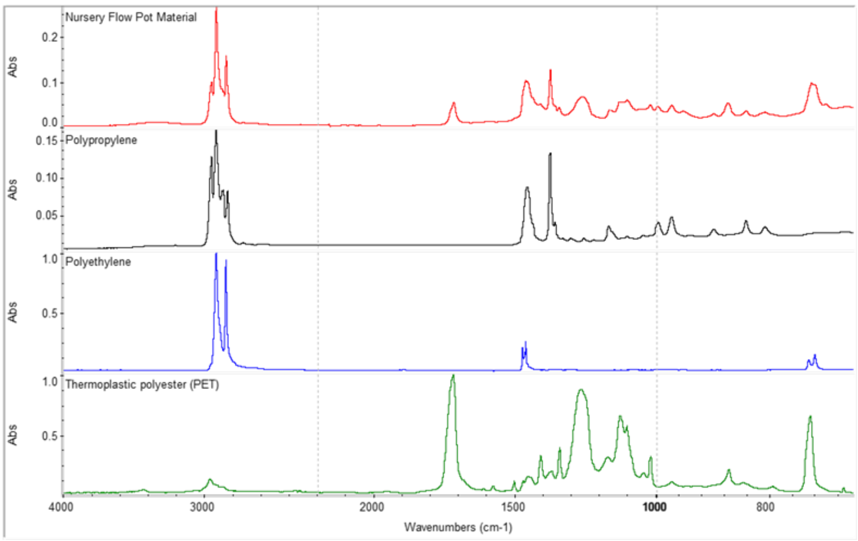


Figure 1: The FTIR spectral results showed absorption bands associated with polypropylene. Bands characteristic of ethylene functionality were also present. Additionally, the results included absorbances indicative of a thermoplastic polyester.

The analysis continued the analysis with differential scanning calorimetry (DSC). The resulting thermogram showed two distinct endothermic transitions associated with the melting of high density polyethylene (HDPE) at 125° C, and polypropylene (PP) at 160 °C, **Figure 2**. The results were consistent with a blend of PP and HDPE, and this was thought to account for the slightly reduced melting temperatures. Based upon the heat of fusion obtained during the second heating run, it was estimated that the HDPE level was approximately 20%. An endotherm associated with poly(ethylene terephthalate) (PET) was also present. The melting point of the PET was somewhat lower than normally expected, likely because it was blended into the HDPE and PP, and potentially due to molecular degradation.

The evaluation was concluded with thermogravimetric analysis (TGA). The TGA results showed a multi-step weight loss profile that included an initial transition, centered at 360 °C, corresponding to the PET, **Figure 3**. From these results, the PET content was estimated at 12%. The HDPE and PP

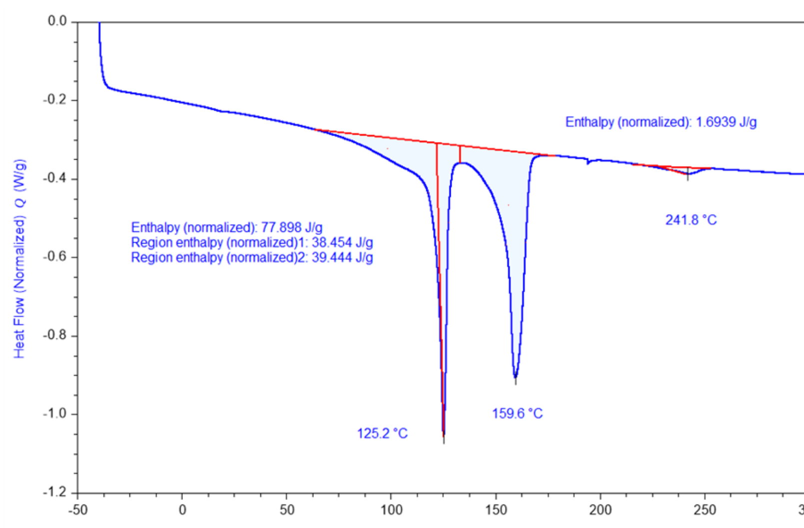


Figure 2: The DSC thermogram showed primary melting transitions associated with polyethylene and polypropylene. A week endotherm corresponding to the presence of PET was also present.

Nursery Flowerpot Material Composition

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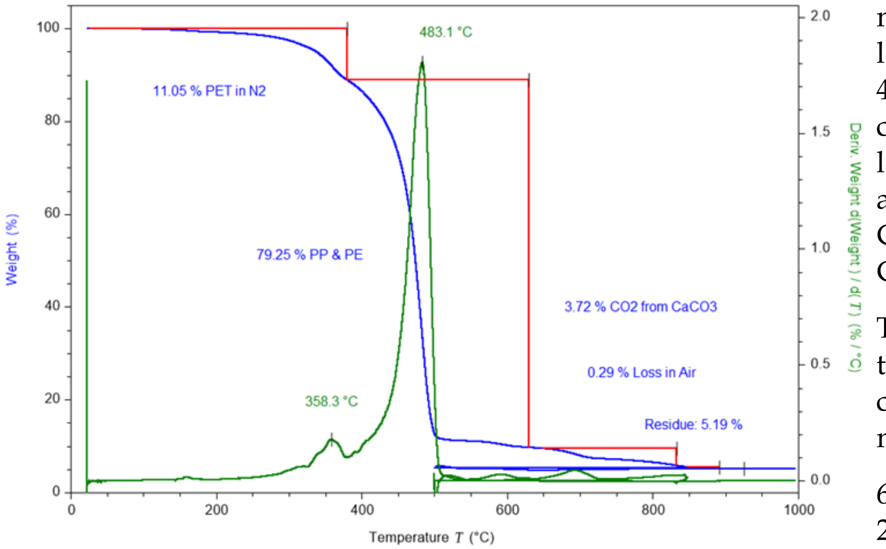


Figure 3: The TGA thermogram provided quantitative results for the PET, HDPE, and PP, and also showed evidence of the presence of calcium carbonate filler.

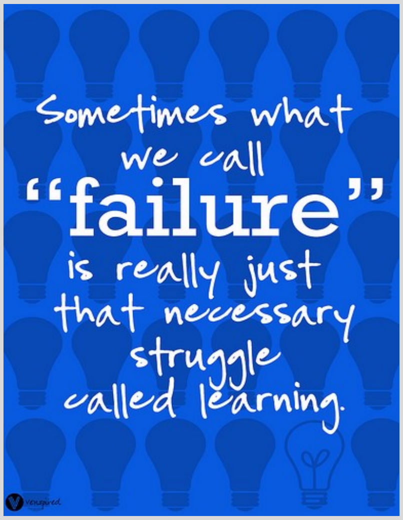
materials underwent a combined weight loss of 79% centered at approximately 483° C. This suggested a nominal PP content of 60%. Additionally, a weight loss of just under 4% was observed, associated with the evolution of CO_2 from $CaCO_3$ (calcium carbonate), indicating a $CaCO_3$ content of 8%.

The combination of FTIR, DSC, and TGA test methods thoroughly characterized the composition of this nursery flowerpot material.

60% PP
20% HDPE
12 % PET
8% $CaCO_3$

Normally, this composition would be highly concerning for a material in an engineering application. However, given that this material has likely been recycled and is being used in the flowerpot application, there is less concern.

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



Upcoming Educational Webinars *(cont.)*

Thursday, November 19, 2020 — *Jeffrey A. Jansen* – Special Chem
Rubber vs. TPE: Which One is Right for Your Application?
9:00 AM (CST)

Elastomeric materials are widely used across a variety of industries. Their performance can vary greatly depending on whether they are thermoset or thermoplastic in nature. Thermoplastic elastomers (TPEs) and thermoset rubbers can look and feel alike and may even behave similarly in the short term at room temperature. However, these two classes of materials offer very different properties as determined by their structure and composition. This webinar will cover the most important topics related to elastomeric materials, and through it the audience will gain a much better understanding of the performance and characteristics of elastomeric materials.

At the conclusion of this webinar, you will understand:

- The structural and compositional differences between thermoset rubber and TPEs.
- How composition and structure determine the performance of elastomeric materials.
- Determine whether an application is best suited for a TPE or a thermoset rubber.

Click here for more information.

Tuesday, December 1, 2020 — *Javier Cruz* — **TMG Webinar**
Introduction to Thermoset Materials
10:00 AM (CST)

Thermoset resins exhibit behavior that are very different when compared to the more common thermoplastic materials. These properties include high temperature and chemical resistance, and a wide realm of possibilities in terms of stiffness and strength. The processing of these materials is key to the realization of their properties, even more so than for thermoplastic materials.

This presentation will provide people not extensively familiar with plastics an understanding of the basics. If words such as polymer, thermoset, cure, and modulus are outside your normal vocabulary, this presentation is for you!

At the conclusion of this presentation, you will understand:

- How thermosets are fundamentally different than thermoplastic resins.
- What the chemistries are behind popular thermosetting resins.
- By what means are thermoset resins processed.
- What role the state of cure plays in shaping the properties of thermosets.

Directly following this event we will host a live Q&A session for up to 30 minutes to cover thermoset related questions.

Click here for more information.

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

Upcoming Educational Webinars

Thursday, December 3, 2020 – *Jeffrey A. Jansen*- SpecialChem
Best Combination of DMA, DSC, FTIR... for Optimal Material Analysis

You often have to **mix multiple tools (DSC, DMA, FTIR, TMA...) to either characterize** your materials or solve complex formulation or processing issues.

However if you are not clear which tool to use, when and how to complement data from these multiple techniques for better analysis, it can cost you lots of time & money.

Join this course and:
1. **Design better material analysis plan** by clarifying the type of information you will get from each characterization method (DMA, DSC, TGA, FTIR...)

2. **Extract more value** (extent of oxidation, HDT, Tg, contamination...) by learning how to **efficiently cross data** from multiple characterization techniques

3. **Wisely optimize performance** of your plastics materials by seeing in practice how to proceed on real-cases (material identification, contamination, failure analysis)

Click here for more information.

Thursday, December 10, 2020 — *Jeffrey A. Jansen* —SPE
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

Click here for more information.

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