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Improved Data Acquisition Using a Novel Dynamic Mechanical Analysis Sample Preparation Technique: The Numbers Do Not Lie

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Improved Data Acquisition Using a Novel Dynamic Mechanical Analysis Sample Preparation Technique: The Numbers Do Not Lie

by

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Abstract

Dynamic mechanical analysis (DMA) is a technique commonly used to identify the thermomechanical properties of polymeric materials. In the aerospace industry, a typical DMA sample is a glassy epoxy-amine polymer network. On a laboratory scale, these types of materials are cured in a silicon mold and sanded by hand to yield a sample with testable dimensions. This preparation technique is time consuming and causes sample imperfections which negatively affects data acquisition. This thesis aims to absolve the issues with DMA sample preparation by using a custom vacuum housing and a DeWALT^{TM} brand orbital sander. This novel approach has been shown to improve the efficiency and data acquisition of post-cured epoxy-amine DMA samples.

Keywords: dynamic mechanical analysis, sample preparation, data acquisition, efficiency

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I wish to acknowledge the assistance and advice that I have received from my graduate student, Travis Palmer; my fellow undergraduate researchers Julian Richardson, Iain Miller, Brittany Thompson, Joseph Turner, and Samuel Brister; and my advisors Dr. Heather Broadhead and Dr. Jeffrey Wiggins.

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List of Abbreviations

DMA	Dynamic Mechanical Analysis
Tg	Glass Transition Temperature
DSC	Differential Scanning Calorimetry
TGA	Thermogravimetric Analysis
Hz	Hertz
mm	Millimeter
ASTM	American Society for Testing and Materials
TGDDM	Tetraglycidyl Methylenedianiline
3,3-DDS	3,3-diphenyldiaminosulphone
ml	Milliliter
g	grams

CHAPTER ONE: INTRODUCTION

Dynamic mechanical analysis (DMA) is a technique used in materials science and engineering to probe the elastic properties of a material. It functions by measuring a material's response to a constant sinusoidal force. In polymer science and engineering, the observed DMA responses can be described as the relaxation of polymer chains. By applying a sinusoidal force, the dissipation of energy (dampening), and the ability of the material to recover from deformation (elasticity) can be determined.[1] To further probe material properties and characteristics, material responses are observed under the implementation of variable temperature. Polymeric materials are defined by their viscoelastic properties. This means polymers have a tendency to flow (viscosity) and resist deformation (elasticity). Both viscosity and elasticity change with temperature.[1]

Using a sinusoidal force allows the material properties to be measured as the material is taken over a temperature range of interest. This is important because as polymeric materials are heated past their glass transition temperatures (Tg), the elastic modulus is dramatically decreased.[1] Since the elastic and viscous moduli can describe how a material could behave in a real world application, knowing how modulus is related to temperature can be the difference between life and death. On January 28, 1986, a failure in understanding of material behavior caused an incident in which the death of seven individuals was broadcasted across the United States. That incident was the Challenger Disaster. An O-ring that could not form a seal at low temperatures allowed hot gases and flames to leak out of the Challenger's boosters.[2] These flames burned a hole in the external fuel tank and the part of the rocket that joined the boosters to the shuttle. The O-ring failed because it was below freezing on the day of launch. At that temperature, the O-ring was

below its Tg and behaved more like a glassy solid than an elastic rubber. This change in material behavior caused the O-ring to form an improper seal and caused the disaster. The disaster could have been avoided by understanding the behavior of the O-ring when subjected to a range of temperatures, which is offered by dynamic mechanical analysis.

Figure 1 Typical silicon DMA mold used to cure epoxy-amine samples.

Currently, the simplest and most affordable method of preparing DMA samples on a laboratory scale involves pouring the sample material into a silicon mold specific to the DMA sample dimensions. A typical mold can make 10 samples that are 60 mm long and 5 mm wide as seen in **Figure 1**. Unfortunately, many aerospace materials involve using a class of polymer called a thermoset. Thermosets are classified into three categories during their fabrication: A-stage, B-stage, and C-stage. A-stage is where most of the processing of the thermoset can be performed because the polymers have yet to build substantial molecular weight and cross-linking. As molecular weight

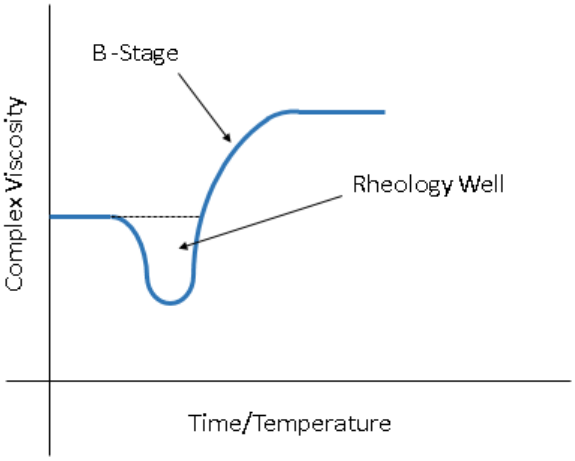

Figure 2 A rheology well depicted on a complex viscosity vs. time/temperature graph.

and cross-linking increase, so does viscosity and insolubility. However, referring to the rheology well in **Figure 2**, we see that we need to heat epoxy-amine networks so they have pourable viscosities, but not heat it so much that they enter B-stage. B-stage is where the polymer chains are cross-linked to the point of insolubility. B-staged material does not flow very well and is difficult to pour. It is usually desirable to have the DMA sample in the mold before this point. C-stage occurs when the material can no longer crosslink and can qualitatively be described as a glassy solid. At this stage we have the finished thermoset, where all reactive sites in the polymer network should be reacted. This is also the type of material tested using DMA. Preparation of an epoxy-amine polymer network sample for DMA testing usually involves pouring the epoxy-amine precursors into a DMA mold, then the mold is placed in an oven. The oven is set to go through a cure prescription that is normally determined by an industrial standard. Once the samples are fully cured they must be sanded to testable dimensions.

Figure 3 (Left) 3 Unsanded DMA bars that have been taken out of the DMA mold. (Right) 3 sets of DMA molds that have fully cured samples.

In **Figure 3**, we can see fully cured DMA samples as they typically come out of their molds. It is not uncommon to have to sand over 1 mm from the surface of a DMA sample before it can be tested. This task can take over 30 minutes for a novice, and around 10 minutes for an experienced sander to prepare a testable sample by hand. To make matters worse, finger impressions are left in the sample at the points where the researcher held down the DMA bar. We postulate that the finger impressions have an adverse effect on data analysis. In order to improve sample preparation efficiency and dimensional control, a new method of sanding DMA bars is proposed in this thesis.

As part of a three-man team, I helped develop a power sanding methodology that helps improve the efficiency and precision of sanding DMA bars. Our method involves manufacturing an aluminum housing that uses vacuum to keep the DMA samples in place as a DeWALT™ 5 in. variable speed random orbit or a sheet palm grip sander is used to power sand the bars to the desired dimensions.

Figure 4 DeWALT™ 5-inch diameter random orbit sander (left) and ¼ sheet palm sander (right).[3,4]

The aluminum housing, as seen in **Figure 5**, has the capability to sand 4 samples at one time. Our primary goal was to sand 5 DMA samples to a thickness between 1-1.35 mm and

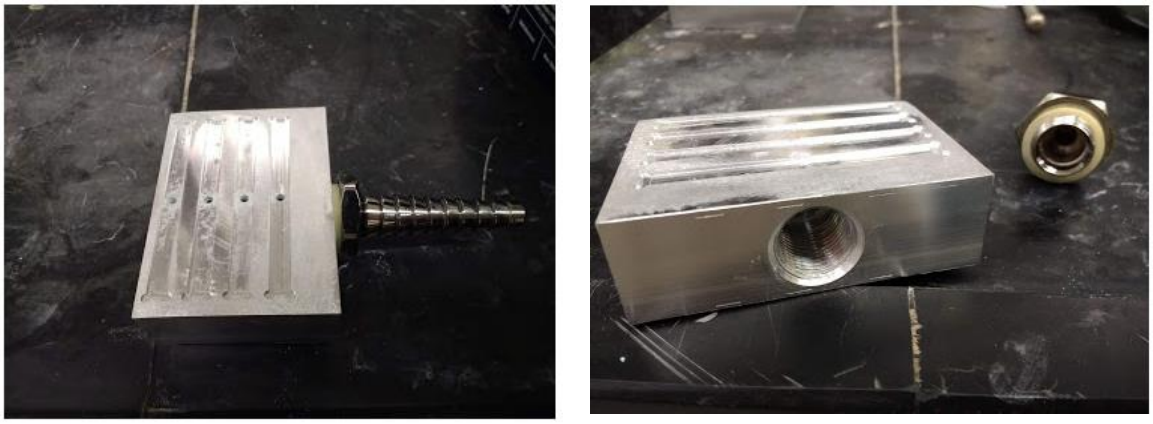

Figure 5 2nd prototype housing used for testing, designed by Julian Richardson. The right image shows the housing with the vacuum nozzle attached. The left image shows the housing threads with the nozzle to the side.

thereby improve the output of a typical undergraduate researcher. Our secondary goal was to efficiently sand the bars so that the thickness of the DMA sample was uniform across the bar's surface. Therefore, the purpose of the research reported in this thesis is to conclude if this novel DMA sample preparation method is more efficient and precise than the traditional hand-sanding technique.

CHAPTER TWO: LITERATURE REVIEW

One of the motivations for this project was to establish a method to standardize preparation of DMA samples. A problem arises when trying to compare DMA results ~~in~~ from the scientific literature because it is not well reported how DMA samples are prepared or the preparation techniques are not consistent. In Palmese and McCullough's work on *Effect of Epoxy-Amine Stoichiometry on Cured Resin Material Properties*, it is mentioned that a diamond saw was initially used to machine cured matrix systems to make a DMA sample with 3 X 10 X 50 mm dimensions.[2] However, the matrix was too glassy to machine, so the researchers had to carefully sand the specimens. The specifics on how these samples

were sanded, and to what dimensions are not mentioned. In *DMA testing of epoxy resins: The importance of dimensions* by McAninch et al. (2015), it is mentioned that a Sanford surface grinder is used to machine epoxy-amine DMA samples to 60 x 12.7 x 3.2 mm dimensions.[3] From experience, this technique can be too abrasive on brittle samples and can cause samples to fracture before reaching the desired dimensions. Surface grinders can also cost up to $12,000, which is not a resource all research labs possess. In an article written by Hu et al. (2015), the authors mentioned that the epoxy-amine matrix was cast in a rubber DMA mold, but make no mention of how the cured DMA samples were prepped for testing.[4] Mentioning how the samples were cast, but not prepared, is a common trend found in most literature about epoxy-amine DMA sample analysis. This may negatively impact the validity of publications because we hypothesize that sample preparation has an effect on the performance of the material.

CHAPTER THREE: EXPERIMENTAL

An epoxy network synthesized using tetraglycidyl methylenedianiline (TGDDM) and 3,3-diphenyldiaminosulphone (3,3-DDS) was used to make the samples. TGDDM and 3,3-DDS were chosen because they are common aerospace materials and readily available in an aerospace composites lab. To synthesize the network, an oil bath was preheated to 115°C. Next, 31.49 g of TGDDM and 18.51 g of 3,3-DDS were weighed out into a 250 ml sidearm flask. The mixture was placed into the preheated oil bath and degassed with stirring until the mixture stopped bubbling (approx. 1 hour). Once the mixture was fully degassed, it was carefully poured into three silicone DMA molds. The silicone DMA molds were made using liquid polysiloxanes and a platinum catalyst, so no mold release was required. The molds were then placed into an oven preheated to 120°C. The following heating

prescription was used to cure the epoxy-amine network: start at 120°C, raise the temperature by 1°C/min. to 180°C, hold the temperature for 3 hours at 180°C, ramp the temperature by 1°C/min. to 225°C, then hold the temperature at 225°C for 3 hours. This heating prescription was chosen because it is commonly used to cure matrices in the aerospace industry. Once the samples were cured, 5 samples were sanded by hand and 5 samples were machine-sanded.

Hand-sanded samples were prepared using 1913 Siawat 500 grit sandpaper. The samples were rubbed face-down on the sandpaper and held perpendicular to the rubbing direction. Machine-sanding was performed by plugging the random orbit and palm sander into a Variac variable voltage transformer set to 60% power output. A cotton ball was placed in the inside of the vacuum nozzle attachment to prevent matrix particulates from entering the vacuum pump. The housing was loaded with 4 samples, the vacuum pump was turned on, and two machine-sanding experiments were performed: first, by holding the sanders still for 3 minutes; second, by moving the sander in circular motions for 3 minutes. Sanding was performed on a ventilated benchtop and undergraduate researchers with a range of experience sanding DMA bars participated in the sanding process. The time it took for the undergraduate researchers to hand-sand the samples to 1.35 mm, and the time it took for the undergraduate researchers to machine-sand the samples below 1.50 mm was recorded. The samples' thicknesses were determined by measuring 3 points along the DMA bar using calipers. These points were designated as L for the left side of the sample, M for the middle, and R for the right side.

Once the samples were sanded to the desired dimensions, they were analyzed using DMA to see if there were any trends in improved data acquisition. The instrument used

was a TA Instruments Q800 series dynamic mechanical analyzer. The samples were tested using the tensile testing grips under 0.05 % strain. The analysis procedure used was a temperature ramp from room temperature to 300°C at 5°C/min. The frequency of oscillation was set to 1 Hz and the Poisson's ratio was set to 0.44. The procedure was chosen because it is an American Society for Testing and Materials (ASTM) standard procedure for finding Tg, specifically ASTM D7028. The data was analyzed using the software Universal Analysis provided by TA Instruments and Microsoft Excel. To analyze the data, the storage moduli vs. temperature of 5 hand-sanded samples were plotted on one plot and the same was done for 5 machine-sanded samples on a different plot. The storage moduli results were then exported to Microsoft Excel. The percent difference between the sample that appeared to have the most average results from the hand-sanded preparation plot and the remaining 4 hand-sanded samples was determined. The same was repeated for the machine-sanded samples.

CHAPTER FOUR: RESULTS AND DISCUSSION

A core part of this thesis was to develop a faster, more precise method of sanding DMA bars. The current method involves rubbing samples on sandpaper in order to get desired sample dimensions. The time it takes to get a usable sample varies with the experience of the individual sanding, and sample thickness is never the same throughout the DMA bar because of inherent finger impressions. The following table shows how 3 undergraduates with various experience sanding DMA bars performed in sanding DMA samples to a desired average thickness of 1.35 mm.

Table 1 Undergraduate DMA sample preparation performance.

Experience	Beginning Thickness (mm)			Ending Thickness (mm)			**Avg. (mm/min.)**	**Time (min)**
	Left	Middle	Right	Left	Middle	Right		
Novice	2.29	2.44	2.45	1.35	1.34	1.33	**0.0303**	**34.77**
Intermediate	2.38	2.54	2.66	1.28	1.34	1.33	**0.0285**	**42.50**
Expert	2.71	2.17	1.99	1.32	1.32	1.33	**0.0998**	**9.68**

The data shows a full DMA bar (2 samples) can take between 30-45 minutes for a newer undergraduate researcher to prepare and around 10 minutes for an experienced researcher to prepare. Preliminary testing was performed using the palm grip sander and the orbital sander. The orbital sander vastly outperformed the palm grip sander, so only its performance will be discussed further in this thesis. After 9 minutes of sanding using the orbital sander, the following results were found:

Table 2 Results from sanding 4 samples at once using the prototype housing and holding the orbital sander stationary over the samples. This table shows results for bars 1 and 2.

	Bar 1			**Bar 2**		
	Thickness (mm)			Thickness (mm)		
Time (min)	Left	Middle	Right	Left	Middle	Right
0	2.38	2	1.94			
3	2.08	1.9	1.75	2.07	2.06	1.66
6	1.72	1.67	1.43	1.67	1.67	1.65
9	1.59	1.6	1.38	1.4	1.55	1.56
Avg. (mm/min)	0.087778	0.044444	0.062222	0.111667	0.085	0.016667
Total Avg. (mm/min.)		**0.064815**			**0.071111**	

Table 3 Results from sanding 4 samples at once using the prototype housing and holding the orbital sander stationary over the samples. This table shows results for bars 3 and 4.

	Bar 3			**Bar 4**		
	Thickness (mm)			Thickness (mm)		
Time (min)	Left	Middle	Right	Left	Middle	Right
0				2.68	2.2	2.26
3	1.87	1.88	1.8	1.84	1.91	1.63
6	1.47	1.57	1.66	1.44	1.43	1.46
9	1.02	1.28	1.44	0.75	0.88	1.07
Avg. (mm/min)	0.141667	0.1	0.06	0.214444	0.146667	0.132222
Total Avg. (mm/min.)		**0.100556**			**0.164444**	

The data indicates that using the orbital sander to prepare four DMA samples at once sands about as much as, if not more than, an expert level sander per bar. After 9 minutes of sanding we see that the orbital sander sands an average of 0.065, 0.071, 0.10, and 0.16 millimeters per minute from bars 1-4 respectively. For a comparison, the expert level sander was able to sand about 0.10 millimeters off a sample per minute. While the ability to control dimensions using the machining method is not as controlled as preparing the samples by hand, the results do show there is a degree of dimensional control specifically looking at the samples after 6 minutes of sanding. The ability to control dimensions can be expressed using the standard deviation equation in Microsoft Excel. The standard deviation of the expert's hand-sanded sample dimensions is 0.0058. The standard deviations for the machined-sanded samples after 6 minutes of sanding are 0.16, 0.012, 0.090, and 0.015 for bars 1-4 respectively. However, dimensional control was hypothesized to improve trends with data acquisition. The following storage modulus results for 5 hand-sanded samples and 5 machine-sanded samples suggests otherwise.

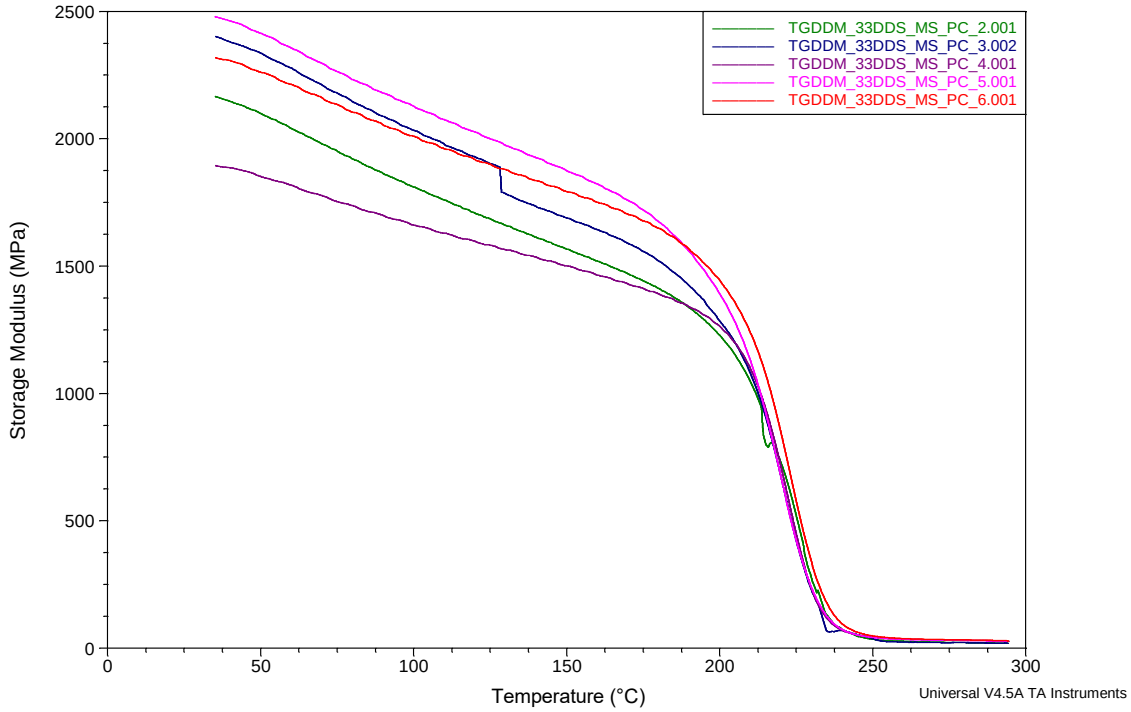

Figure 7 Overlapping storage modulus results for 5 machine-sanded DMA bars.

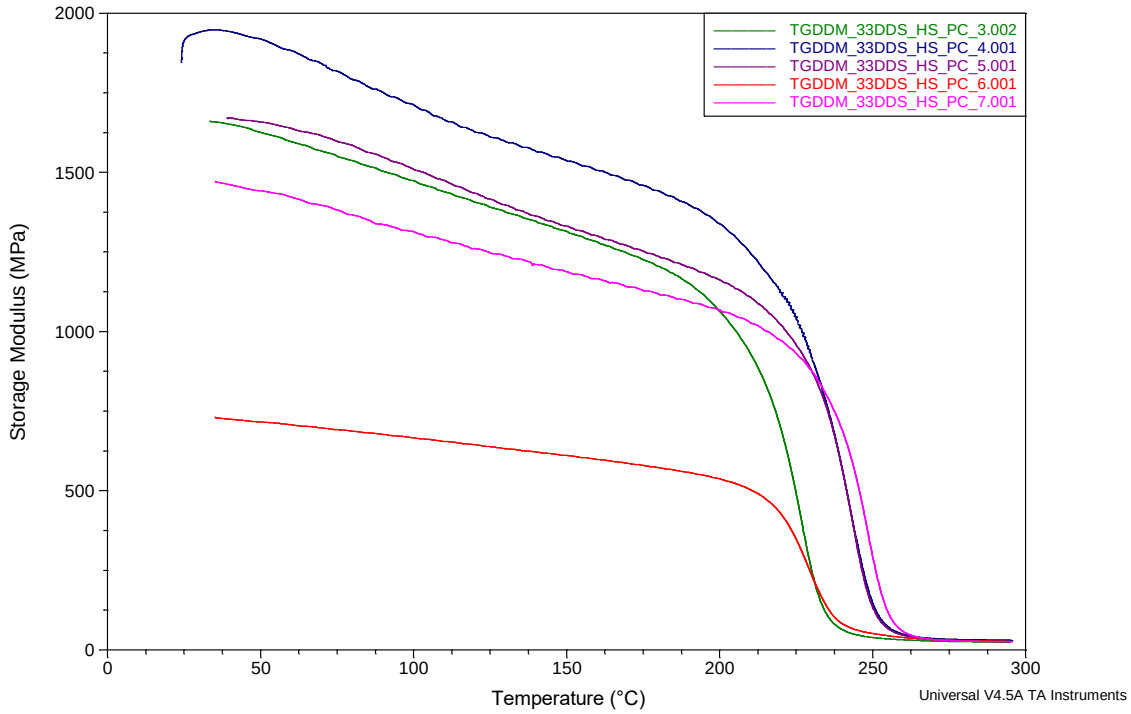

Figure 6 Overlapping storage modulus results for 5 hand-sanded DMA bars.

As we can see in **Figure 6**, analyzing samples of similar compositions and similar testing procedures yields dramatically different analytical results. This is believed to be a result of

finger impressions negatively influencing material properties during sample preparation. When comparing the two plots in **Figure 6** and **Figure 7**, qualitatively the machine-sanded samples have more overlapped data, which is indicative of greater precision. After plotting the data, it was then exported to Microsoft Excel so that the percent difference between sample 3 of the hand-sanded samples, and sample 2 of the machine-sanded samples could be quantified when comparing plots of similar preparation techniques. The results showed that the average percent difference between hand-sanded sample numbers 3 and 4 was 161%; 3 and 5 was 53%; 3 and 6 was 44%; and, finally, 3 and 7 was 79%. In comparison, the average percent difference between the machine-sanded sample numbers 2 and 3 was 9.7%; 2 and 4 was 13%; 2 and 5 was 20%; and, finally, 2 and 6 was 22%. Clearly, the machine-sanded samples had an overall lower percent difference than the hand-sanded samples. This would indicate that preparing DMA samples using the developed prototype would lead to more precise data.

CHAPTER FIVE: DESIGN CRITIQUE AND CONCLUSION

In conclusion, the current prototype is remarkably more efficient at preparing samples for DMA when compared to the traditional methods of hand-sanding. The proposed novel preparation technique has also shown to have some control over sample dimensions and the potential to improve data acquisition. However, it is undetermined whether this method is useful for DMA samples that are not glassy solids or samples that are more brittle than a TGDDM/3,3-DDS matrix. The design of the proposed prototype can be further improved by automating the machine-sanding process. Some concepts that have been drafted include implementing two vacuum holes per bar to increase suction. This would allow the use of higher rotation per minute with the sander; thus, reducing required

sanding time. In addition, the sander could be mounted above the housing, and sample housing lifted to the sander via a lab jack. This would remove any human error in sample preparation and improve dimensional control.

REFERENCES

1. Menard, Kevin P.; *Dynamic Mechanical Analysis A Practical Introduction*, 2nd ed.; CRC Press, 2008
2. Palmese, G.; McCullough, R.; Effect of epoxy-amine stoichiometry on cured resin material properties; *App. Polymer*, ***1992,*** 46, 1863-1873
3. McAninch, I.; Palmese, G.; Lenhart, J.; La Scala; DMA testing of epoxy resins: The importance of dimensions; *Poly Eng & Sci*; **2015**, 12, 2761-2774
4. Hu, F.; Yadav, S.; La Scala, J.; Sadler, J.; Palmese, G.; Preparation and Characterization of Fully Furan-Based Renewable Thermosetting Epoxy-Amine Systems; *Macr. Chem. & Phy.*; **2015**, 13, 1441-1446
5. Think Reliability: Root Cause Analysis – Challenger Explosion https://www.thinkreliability.com/case_studies/root-cause-analysis-challenger-explosion/ (accessed Feb. 28, 2019)
6. DeWALT™; 5 in. Random Orbit Sander/Variable Speed/ H&L Pad https://www.dewalt.com/products/power-tools/sanders/5-in-random-orbit-sander--variable-speed--hl-pad/dwe6423k (accessed Mar. 13, 2019)
7. DeWALT™; ¼ Sheet Palm Grip Sander Kit https://www.dewalt.com/products/power-tools/sanders/14-sheet-palm-grip-sander-kit/dwe6411k (accessed Mar. 13, 2019)