

# EXPERIMENTAL APPLICATIONS OF DIFFERENTIAL SCANNING CALORIMETRY TO TEST AND CHARACTERIZE POLYMERS AT THE UNIVERSITY OF WASHINGTON BOTHELL

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*ABSTRACT: Differential Scanning Calorimetry (DSC) is used for analyzing the thermal properties of polymeric materials used in many engineering applications. The data produced by DSC generates a heat flow curve that reflects the amount of energy required to heat a sample per degree Celsius over time, and heat capacities can be calculated. In addition to comparing enthalpies ( $\Delta h$ ) for different materials, DSC is also a powerful tool to determine other important material characteristics such as melting temperatures ( $T_m$ ), thermal glass transition temperatures ( $T_g$ ), degree of crystallinity, and environmental oxidation. Also, the use of DSC coupled with other analytical techniques, such as Fourier Transform Infrared Spectroscopy (FTIR), Gas Chromatography (GC), and Nuclear Magnetic Resonance (NMR) spectroscopy, gives insight to changes in material molecular composition. This paper describes several projects at the University of Washington Bothell where DSC was effectively utilized to evaluate actual industrial and sports applications of various polymers with the goal of understanding their respective thermal properties. The hands-on experience facilitates making connections with material science concepts learned in-class, and emphasizes the importance of material selection that engineers are involved with throughout their careers. Projects discussed involve degradation mechanisms in hydrocarbon-based binders used in sport track surfaces, analysis of premature cracking and failure of polyurethane molded covers used in electrical transformer housings, determination of an unknown polymer used in high temperature fluid filtration systems, and comparisons of poly vinyl-acetate adhesives used in composite materials.*

## Introduction

Differential Scanning Calorimetry (DSC) is a useful tool in analyzing chemical and thermal properties of polymeric materials against a reference sample. A polymer is defined as a compound of high molecular weight in which the structure is composed of small repeating chains (Callister, 2014). Generally, these chains consist of hydrocarbons with additional side groups of other atoms known as impurities. An example of an impurity is an oxygen or chlorine atom bonded to a small chain of hydrocarbons. Between chemical structure and various impurities, different physical properties of polymers exist. Such properties include strength,

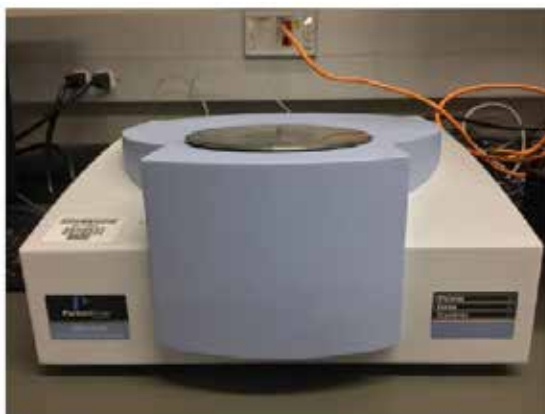
hardness, and thermal behavior. Polymers are classified into two categories when the thermal behaviors of polymers are considered: thermoplastics and thermosets. Thermoplastics exhibit linear chains of hydrocarbons that soften under heating whereas thermosets show cross-linked chains that maintain rigidity under heating (Callister, 2014). Understanding polymeric structure helps identify and characterize a sample by its structure, which is related to its crystallinity, a state in which periodic and repeating atomic arrangement is achieved by molecular chain alignment. However, to characterize a polymer's properties, appropriate analytical techniques are required, such as the use of a DSC. A DSC machine (Figure 1) works by measur-

ing the amount of heat flow through a sample directly in conjunction with a feedback loop to maintain a set temperature. The power required to maintain a specific temperature is recorded against a reference sample in the DSC (Perkin Elmer, 2013). The measurements taken by the DSC machine create a thermal profile of a given sample by recording either energy absorbed or released versus change in temperature or time, respectively. In the generated curve from the DSC endothermic peaks often result such as the one shown at 30 °C for the n-octadecane sample in the DSC scan shown in Figure 2. These endothermic peaks are produced because the sample at that heating point requires more energy input from the DSC to retain the same temperature between the sample and reference sample (Perkin Elmer, 2013). From this profile created at the end of each experimental run, the following properties can be attained:

- heat capacity
- enthalpy ( $\Delta h$  - the internal energy of the material)
- melting temperatures ( $T_m$  - the temperature at which a solid phase transitions to the liquid phase)
- thermal glass transition temperatures ( $T_g$  the temperature at which a non-crystalline polymer transforms from a super cooled liquid into a rigid glass)
- percent crystallinity

From these tests, various polymer characteristics can be determined such as oxidative degradation over time (Callister, 2014). Another advantage of the DSC is the short time required for analyses with average experimental run times ranging between 10 and 60 minutes depending on test specifications. The information provided by DSC helps to understand how different materials may change over time or give insight into process history. Additionally, polymers can be identified, characterized, and compared with one another. When coupled with other analytical techniques such as Fourier Transform Infrared Spectroscopy (FTIR), Gas Chromatography (GC) and Nuclear Magnetic Resonance (NMR)

spectroscopy, greater insight into changes in materials molecular composition can be inferred.

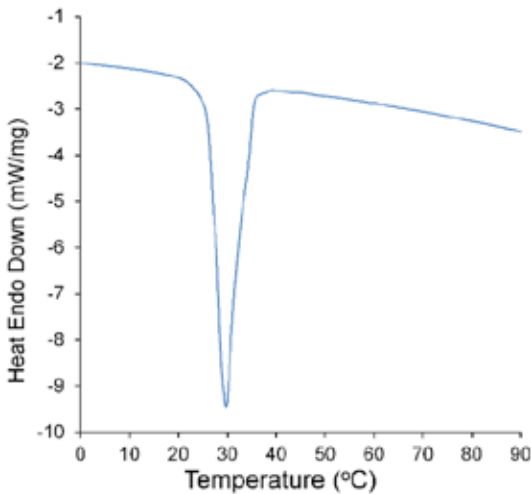


**Figure 1:** A Perkin Elmer Differential Scanning Calorimeter (DSC) 6000 used at University of Washington Bothell (UWB).

The University of Washington Bothell (UWB) Materials Testing and Characterization Lab (MTCL) began in January 2015 testing multiple polymers using our DSC machine. This paper provides four examples of how the DSC is used in the MTCL and involve; 1) phase changes and oxidative degradation in hydrocarbon-based binders used in sport track surfaces, 2) pre-mature cracking of polyurethane molded covers used in electrical transformer housings, 3) the determination of an unknown polymer used in high-temperature fluid filtration systems, and 4) comparisons of poly vinyl-acetates (PVA) used as a resin in a composite material. The techniques used involve creating a thermal profile of energy absorbed versus rise in temperature and then determining each sample's  $\Delta h$ ,  $T_m$ , or  $T_g$ . Conclusions were drawn after determining each material's thermal properties over multiple DSC runs.

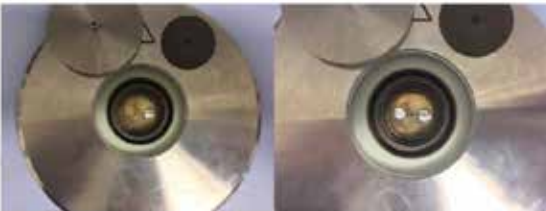
### Materials and Experimental Methods

The DSC machine used was a Perkin Elmer DSC6000 with power compensation under nitrogen flow (20 mL/min) and Intracooler SP that allows cooling down to -70 °C. For all DSC projects, approximately 10±1.0 mg samples are placed into a small aluminum



**Figure 2:** DSC Scan of n-Octadecane wax with an endotherm pointing downwards at 30°C.

sample pan. The sample pan with a press-fitted lid (using a crimping device) is placed into the furnace section of the DSC machine (Figure 3).



**Figure 3:** Placement of the aluminum sample pan into the furnace of Perkin Elmer DSC 6000 against a reference pan.

Test parameters are then entered into the DSC's operating program called Pyris Manager. Typical parameters entered are the samples mass, desired heating and cooling ranges, and the duration of holding at specified temperature(s). The length of each test is dependent on each step added to the program and the temperature difference between heating and cooling. In a typical test, a sample is heated or cooled at 10 degrees Celsius per minute. Additionally, the sample is held at a desired temperature for at least one to two minutes between heating and cooling cycles to ensure a uniform temperature throughout the sample. Upon completion of a run at a desired temperature range, a generated curve of Heat Flow (mW) vs. Temperature (°C) with the endotherms pointing downwards is produced (Figure 2). Furthermore, the data can be normalized by dividing the Heat Flow by its mass

to compare between DSC runs. From this generated graph, the enthalpy ( $\Delta h$ ), thermal glass transition temperature ( $T_g$ ), and melting point ( $T_m$ ) can then be determined in accordance to the American Society of Testing and Materials (ASTM) standards and specifications.

### **Oxidative Degradation in Hydrocarbon-Based Binders Used in Equine Sport Track Surfaces**

DSC use at UW Bothell began with testing hydrocarbon-based binders used in equine sport track surfaces. These surfaces consist of granular composites made from sand, polymer fiber, rubber, and a high-oil paraffin wax binder. An extracted sample of the binder as well as a typical racetrack surface, before and after oxidation, can be seen in Figures 4 and 5. The aim of this ongoing investigation was to analyze the hydrocarbon-based binder to help determine and quantify oxidative degradation of the binder that holds the granular composite material together. It is hypothesized that binder degradation leads to reduced performance of the track surface over time. Over 50 DSC runs of this material have been completed with samples taken over a seven-year period from one thoroughbred horse racetrack. This test was conducted in accordance with ASTM Standard D4419 (ASTM D4419, 2005) and D7414 (ASTM D7414, 2009). After each test method was performed, only the heat flow from the last heating cycle was analyzed. All data was normalized, the enthalpies were calculated, and the transition temperatures were recorded using the intersection of tangents on the slopes of the endothermic peaks pointing downward.

#### **Test Method Applied**

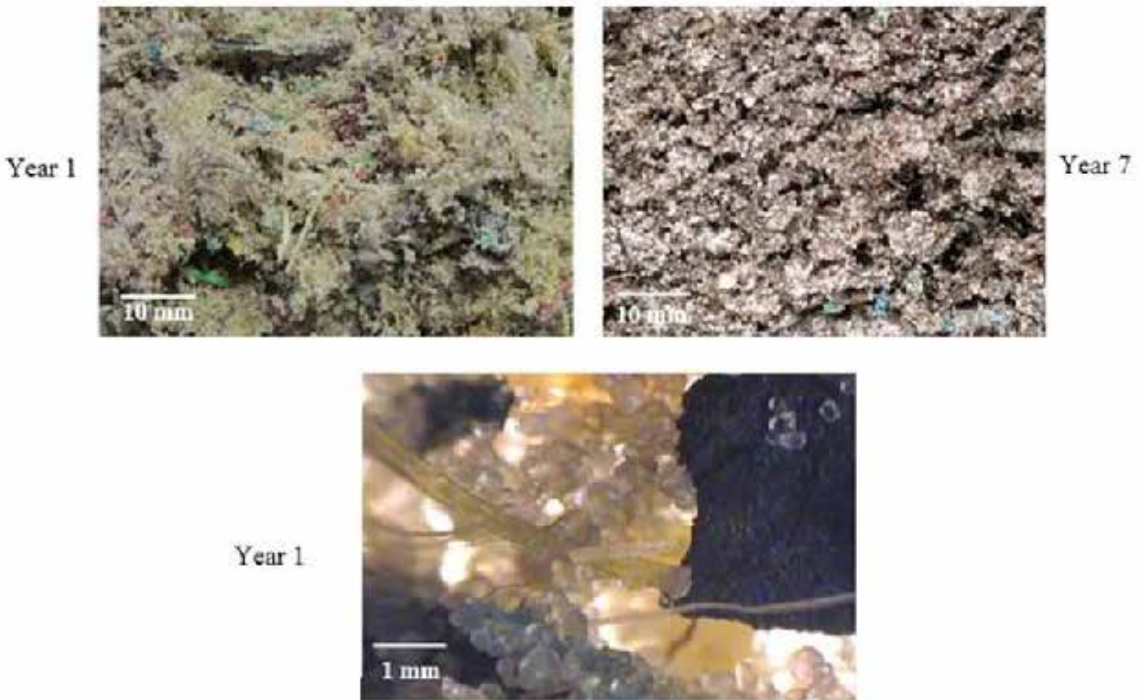
1. Heat from 30 °C to 94 C at 10 °C/min
2. Cool From 94 °C to -30 C at 10 °C/min
3. Hold Temperature for 2 min at -30 °C/min
4. Heat from -30 °C to 94 C at 10 °C/min



**Premature Cracking of Polyurethane Molded Covers Used in Electrical Transformer Housings**

This project involved analyzing the material in an attempt to understand the premature cracking of a polyurethane molded cover used in electrical transformer housings (Figure 6). This material is subject to outdoor environmental exposure. Failure in the original specimen was reported to be occurring near a mounting point of the molded cover. It is to be noted that the area of failure was not tested due to insufficient data on the material. In this experiment, initial interest was in finding the thermal glass transition temperature ( $T_g$ ) value of the polyurethane as well as the melting characteristics. Changing  $T_g$  and melting points can indicate chemical changes to the polymeric structure over time. The aim of this investigation was to determine if the polyurethane cover was the best choice of material for this outdoor applica-

**Figure 4:** An example of hydrocarbon-based binder used in equine sport track surfaces produced from Soxhlet extraction.



**Figure 5:** Photos of hydrocarbon-based binder coated track material taken from Year 1 and Year 7 surface (same track). Silica sand particles are mixed with binder, polypropylene fibers and rubber (black) particles. The darker appearance of the Year 7 sample is attributed to binder oxidation over time. A thin layer of binder covers all components and can cause local clumping of sand particles as seen in the lower magnified photo [8].

tion. Each sample was extracted with a surgical razor blade from the sample show in Figure 6 by shaving off an approximately 10 mg mass sample. There was no specific test specification called out for this application. Only one increasing heating run was involved in each sample run.

#### Test Method Applied:

1. Heat from -20 °C to 120 °C at 10 C/min
2. Calculate transition temperatures and melting enthalpy



**Figure 6:** A sample of the polyurethane molded cover used in electrical transformer housings.

### Determination and Characterization of an Unknown Polymer Used in High-Temperature Fluid Filtration Systems

This project involved the identification of an unknown polymer used in high-temperature fluid filtration systems (Figure 7). The goal for this project was to determine the melting point temperature ( $T_m$ ) value and compare with known values of adhesives used in similar high temperature fluid filtration applications. Each sample was prepared by cutting the adhesive used as the base of the filter membrane. The remaining fibers on the adhesive were carefully extracted by further cutting and filing. Once all fibers were successfully removed from a strip of adhesive, approximately 10 mg samples were cut and placed into the aluminum sample pans. All runs performed on the material were performed in accordance to the ASTM D3148

specification (ASTM D3148, 2003).

#### Test Method Applied:

1. Heat from 120 °C to 250 °C at 10 °C/min
2. Hold for 5 min at 250 °C
3. Cool from 250 °C to 120 °C at 10 /min
4. Hold for 5 min at 120 °C
5. Heat from 120 °C to 250 °C at 10 °C/min



**Figure 7:** The unknown polymer in filter membrane. The membrane fibers were removed with a file to analyze the unknown polymer in the DSC.

### Poly Vinyl-Acetate Polymer Comparisons

This last example involved comparisons of three separate poly vinyl-acetate adhesives that showed various degrees of ductility (Figure 8). This was accomplished by determining the thermal glass transition temperature  $T_g$  of each sample. The goal was to determine differences in the three materials, and if a potential replacement material possessed a suitable  $T_g$  and adequate thermal characteristics for the given application. The  $T_g$  values were determined from the DSC by deducing the midpoint temperature per ASTM Standard E1356 (ASTM E1356, 2008). Each sample was prepared by cutting an approximately 10 mg sample and placing them into the aluminum sample pans.

#### Test Method Applied:

1. Cool from 20 °C to -20 °C at 10 °C/min
2. Hold for 1 min at -20 °C
3. Heat from -20 °C to 60 C at 10 °C/min



**Figure 8:** Oven Cured 7g Samples. Samples 1-3 are laid out from left to right. Sample 1 was bent over to show ease of deformation. Samples 2 and 3 show cracking and were brittle.

## Results and Discussion

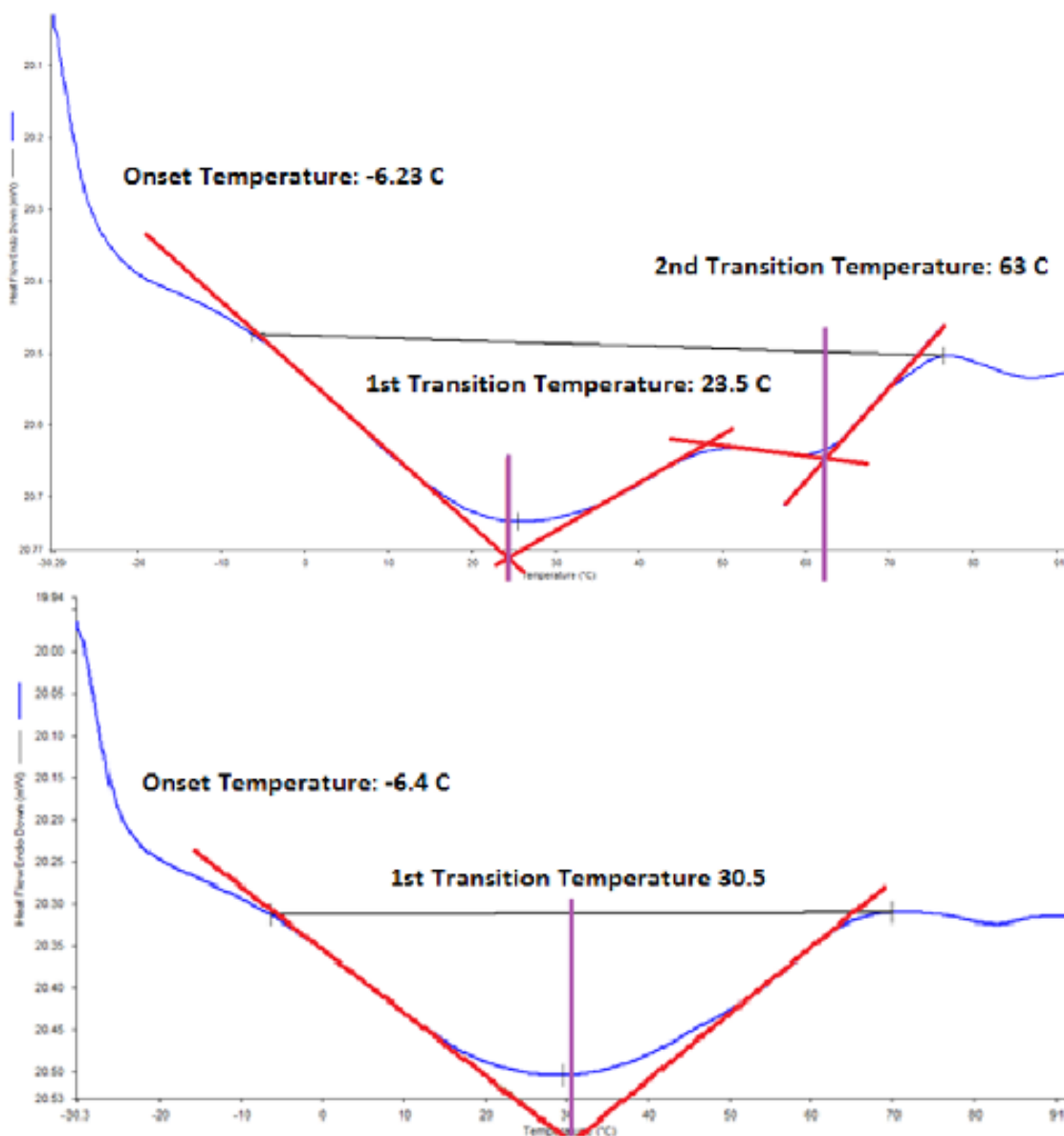
### The Oxidative Degradation in Hydrocarbon-Based Binders Used in Equine Sport Track Surfaces Results

Figure 9 below shows two DSC curves of the wax binder extracted from the same thoroughbred horse racetrack but 6 years apart. This hydrocarbon-based binder is used in many equine sport track surfaces and is suspected to degrade over time. Note per Figure 9 that during the first year when the surface was first installed, the binder melting enthalpy was found to be 7.7 Joules per gram (J/g), the first transition temperature 23.5 °C, and the second transition temperature 63 °C. Six years later, after exposure to factors such as racing, track harrowing, and weather, the enthalpy decreased 34% to 5.1 J/g suggesting a decrease in crystallinity over time. It is also worth noting that the second temperature transition peak at approximately 63°C fades away over the seven-year period. This second transition region correlates to higher molecular weight hydrocarbon-based molecules that have higher melting temperatures (Bridge, 2015) In conjunction with other analytical testing methods such as gas chromatography, the results are consistent with decreasing crystallinity as hydrocarbon chains scission (Bridge, 2016). Testing at UW Bothell

enabled the hypothesis that oxidation is the primary degradation mechanism in the composite binder and is most likely due to ultra violet (UV) radiation. Future testing will be conducted after artificially exposing a first-year stockpile of the hydrocarbon-based binder with UV radiation to mimic the effects of accelerated weathering.

### The Premature Cracking of Polyurethane Molded Covers Used in Electrical Transformer Housings Results

As shown on the DSC scan in Figure 10, the thermal glass transition temperature was approximately 29.2 °C. Thus, temperatures greater than 29.2°C will result in changes to the polyurethane's mechanical properties, such as unexpected softening, which can result in reduced load-carrying capability or reduced sealing performance which would be of a concern in an outside environment. Other concerns are related to ductility or lack of, different coefficients of expansion, and accelerated aging. Additional failure considerations that DSC can help detect in this application include incomplete mixing of the polymer components, incomplete curing, or both during manufacturing.



**Figure 9:** Comparison of DSC curves of wax binder extracted from same track surface of year 1 (top) vs. year 7 (bottom).

### Section 3.3 Determination and Characterization of an Unknown Polymer Used in High Temperature Fluid Filtration Systems Results

As shown in Figure 11, the melting point temperature ( $T_m$ ) was found to be 164.7 °C. This melting point value was compared against known values of adhesives used in similar high temperature fluid filtration applications. Polyamide resins have different thermal prop-

erties depending on the monomers used in the formation of the polymer. Melting points can range from between 150 and 240 °C based on the carbon chain lengths and amide functional groups (CRC, 1978). When coupled with Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) the unknown polymer was confirmed to be a polyamide.

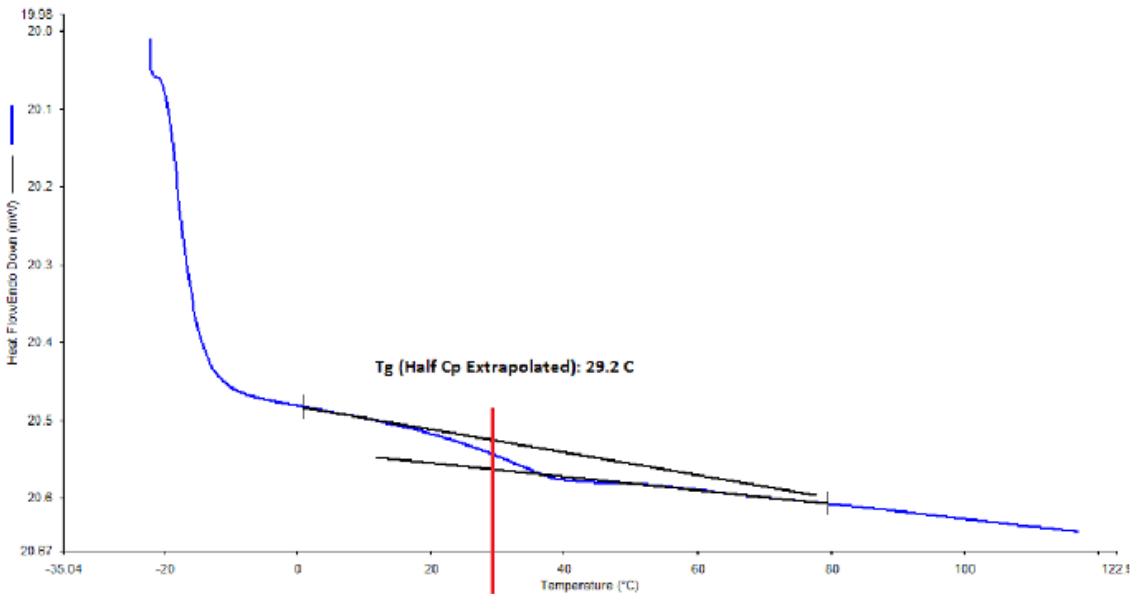


Figure 10: The Differential Scanning Calorimetry curve generated after performing a run on the polyurethane molded cover used in electrical transformer housings.

### Poly Vinyl-Acetate Comparison Results

In Figure 12 that follows, the differences in thermal glass transition temperature ( $T_g$ ) values of three poly vinyl-acetate samples are shown. The  $T_g$  values were 12.71 °C, 21.56 °C, and 21.55 °C respectively. Sample 1 showed a clear difference in  $T_g$  when compared to the other two. The result of Sample 1 having a  $T_g$  value lower than room temperature was expected due to the easy deformability of the material as evident in Figure 8. Samples 2 and 3 were observed to be brittle at room temperature. After coupling the DSC runs with FTIR, it was concluded that at moderate temperatures, the tested poly-vinyl acetates will show differences in performance and affect the stability of each in their given application.

### Conclusions

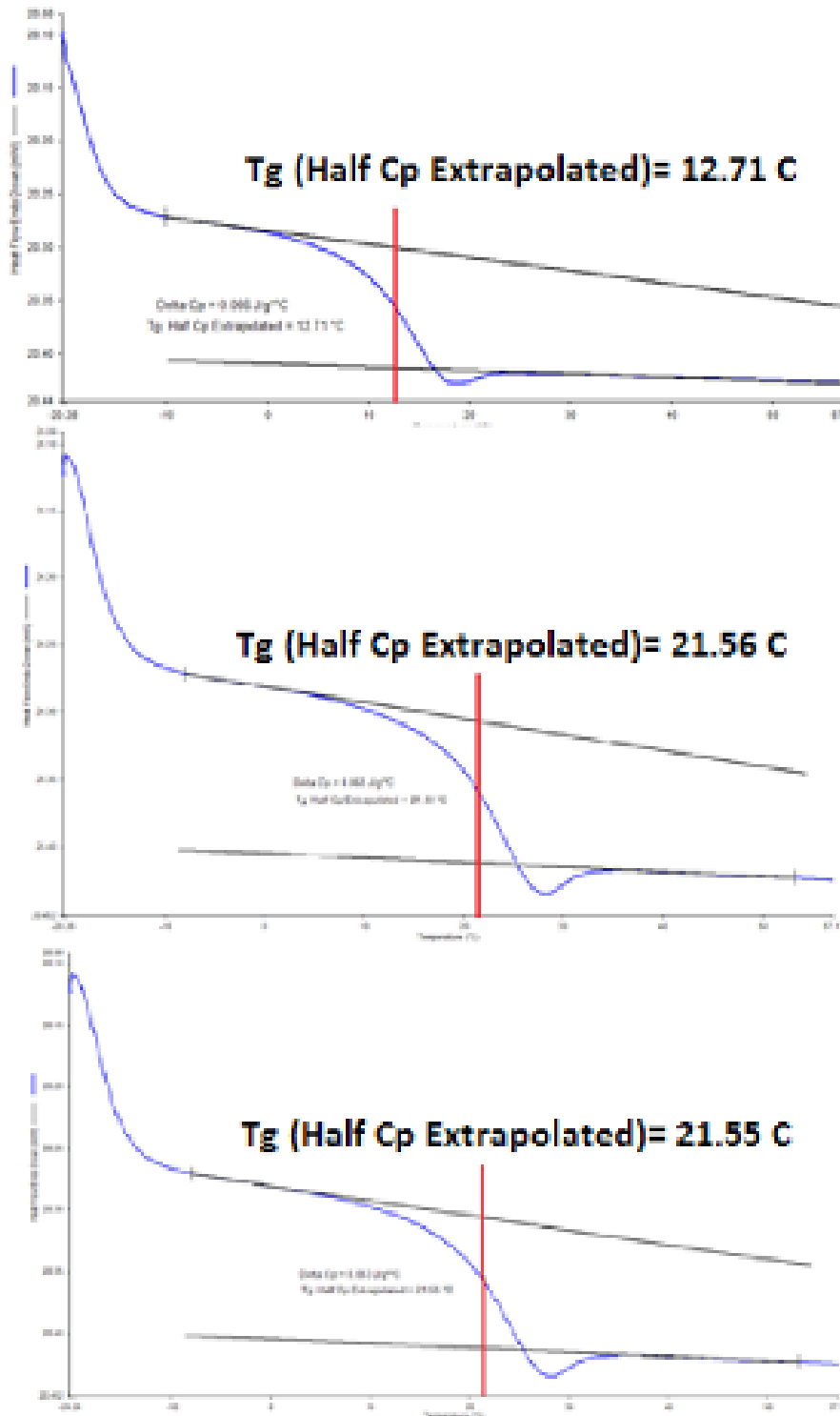
Differential Scanning Calorimetry is powerful analytical tool used to examine the thermal properties of polymeric materials found in a myriad of engineering materials. The thermal information provided from the generated heat flow curves of a test sample allow for a material's properties to be characterized and or

compared. These properties can include glass transition temperatures, melting points, and melting enthalpies as shown in each of the four application examples of the DSC. When used in conjunction with other analytical techniques such as Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography (GC), useful mechanical and thermal performance of polymeric materials may be attained. The hands-on testing of polymers used in real-world applications provides valuable experience for undergraduate students who will find themselves working with similar materials in their engineering careers. These experiences will also aid them when selecting engineering plastics with optimized mechanical properties for specific applications.

### Acknowledgement

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**Figure 12:** The DSC-analyzed Scanning Calorimetry curves generated for Sample 1 (Top), Sample 2 (Middle), Sample 3 (Bottom) of the Poly-Vinyl Acetate. The vertical line created from the Temperature axis represents the T<sub>g</sub> value of each sample.

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