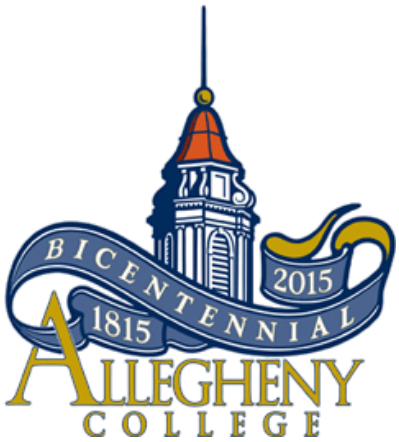
Shape Memory Properties in Flexible Slabstock Polyurethane (PUR) Foam

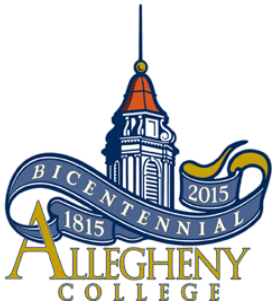


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Senior Project — Spring 2017

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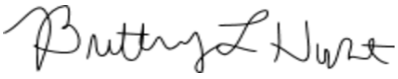
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Dr. P.J. Persichini

I hereby recognize and pledge to fulfill my responsibilities, as defined in the Honor Code, and to maintain the integrity of both myself and the College as a whole.



Brittney L. Hunt

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Abstract

Flexible polyurethane slabstock foam (conventional soft, conventional firm, high resiliency (HR), and viscoelastic memory) obtained from Covestro LLC was used to determine possible shape memory and/or shape recovery properties. DSC was used to determine possible critical temperatures to aid in the production of the procedure for the shape memory/recovery experiments. A spectra of each foam was taken using the FTIR to determine relative amounts of each component within the foams. Scanning electron microscopy (SEM) was used to investigate pore size and structure. SEM and FTIR data was used to determine what factors may or may not be contributing to shape memory/recovery. Pore size and structure for all foams were very similar and therefore had no effect on shape memory/recovery, but was directly related to compressibility. FTIR did not have any useful insight into shape memory/recovery, but provided possible links to compressibility as well.

Introduction

Shape memory polymers (SMP) are exceptionally intelligent materials. Upon heat, compression, and cooling, they are able to deform into a different shape, but subsequently have the ability to recover once heated again.[1] Shape memory is a result of thermomechanical processes and is not an intrinsic property.[2] These materials have been widely studied and are useful for their variety of applications.[3] SMPs have tailorable glass transition temperatures (T_g), and therefore have many diverse conditions they are applicable under.[4] Recently, they have aided in the production of biomedical devices derived from SMPs that have T_gs below body temperature. [3,5,6] Catheters manufactured using SMPs will stay stiff outside of the body, but once inside under warmer conditions, can take on a more flexible shape.[7] Flexible SMP catheters are not only cheaper than rigid ones, they are safer inside the human body and cause less damage in the arteries.

Shape memory polymers also have the ability to be manufactured in the form of foam, otherwise known as shape memory polyurethane (SMPU) foam. While fewer studies have been performed on SMPU foam than basic SMPs, research is growing because this type of foam is so superior due to its high compressibility and low density, amongst many other beneficial properties.[1] SMPU foam has been known to mirror SMPs because they follow the same process when determining if they have shape memory properties.[1,3] The effects of month long compression sequences have been

investigated on polyurethane foam for applications such as the packaging of foam on Earth for its shape to later be recovered in space.[8]

The purpose of this paper is to investigate possible shape memory properties in industrially-relevant, flexible foam. Thermal properties were determined using Differential Scanning Calorimetry (DSC) to serve as a foundation for the creation of the experiments. In the coming weeks, foam will be compressed at varying forces at temperatures above T_g for varying lengths of time. Following decompression, foams will be left to adapt back to free form at room temperature to determine percent recovery and the presence of shape memory properties. All foam was obtained from Covestro LLC, formerly known as BayerMaterialScience, located in Pittsburgh, Pennsylvania.

Polymer Overview

The word *polymer* can be broken down into two parts: *poly*, meaning many, and *mer*, meaning unit. Just like its name suggests, polymers are made up of many single units called monomers. These monomers are covalently bonded into chains and networks to become a polymer, most often made up of carbon and hydrogen. CH_4 is methane, a single monomer in the gaseous form. Hexane, C_6H_{14}, is made up of 6 monomers and can be found in the form of a liquid. $C_{100}H_{202}$ is right around where these monomers transition to a solid polymer. As chain length increases, more secondary bonding is occurring through more Van der Waal interactions. This leads to stronger,

less mobile chains which gives a significant increase in viscosity. The more monomers that are bonded, the more likely the molecule is to act like a polymer.

The length of a chain is often called the degree of polymerization, which can be denoted as *n*. The letter *n* corresponds to the number of monomers that make up the chain. A polymer can not only be defined by the number of chains it has, but by its molecular weight. Since polymer products often yield a wide range of weights, this number is typically can average of all of the known molecular weights.

Polymers come in two forms: amorphous and crystalline. Amorphous polymers are disordered and randomly coiled. The word *amorphous* does not refer to liquid, but rather implies disorder. Amorphous polymers have a glass transition temperature (T_g) where the material goes from a glassy state to a rubber-like one as temperature increases. Crystalline polymers, on the other hand, contain chains that are ordered and are found in the solid phase. These opaque polymers contain a melting temperature (T_m) that occurs when the crystals fall out of line and become disordered. Crystalline polymers are rarely 100% crystalline. Therefore, all crystalline polymers contain an amorphous portion, and have both a T_m and T_g. It is important to note that only the amorphous portion has a T_g and only the crystalline portion has a T_m. Polymers are often described by their *degree of crystallinity* and are considered semi-crystalline structures with a certain % crystallinity based on mass or volume.

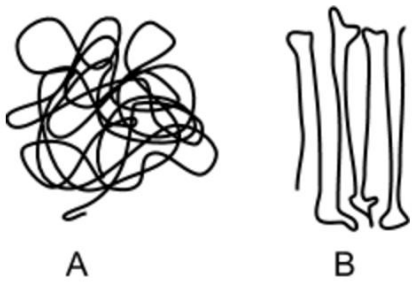


Figure 1. Amorphous (A) and semicrystalline (B) polymer structures

Polymers have endless applications, and are found in just about everything. Playground equipment, garbage bags, automobile parts, and golf clubs are just a few of these applications.

Shape Memory Polymers

Some polymers have been found to exhibit shape memory properties. Shape memory polymers (SMP) are incredibly intelligent materials. SMPs have been widely studied and are useful for their variety of applications. [3] Recently, they have aided in the production of biomedical devices and aerospace engineering.[3,5,6]

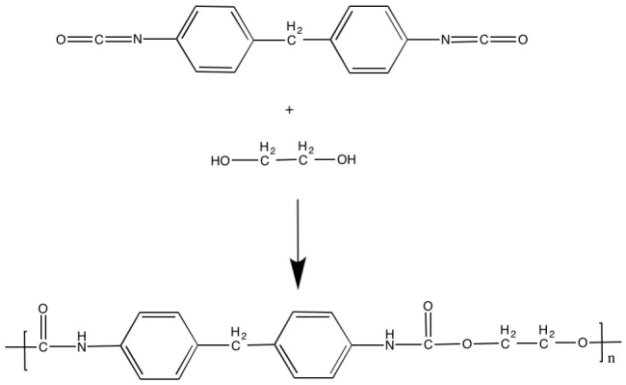
To begin the shape memory process, the polymer must go from its natural state to a distorted state. This process is called programming.[9] Programming most readily takes place when the polymer is in a rubbery, melted state, so it is often heated above T_g to facilitate distortion.[1,10] Programming takes time and energy, but makes the polymers flexible.[10] Once an SMP is programmed on a macromolecular level, it will stay

in its unnatural state until acted upon by outside stimuli such as moisture, light, pH change, heat, or magnetism.[10,11] Their internal properties must be systematically programmed by an external source in order to get from the original state to the distorted state.[12] As a result, shape memory is considered a thermomechanical processes, and is not an intrinsic property.[2] This paper will focus most heavily on temperature acting as the outside stimuli, otherwise known as thermally induced shape memory.[9]

There is no set material property that a polymer must obtain to exhibit shape memory effects (SME). It is a combination of the chemical structure and morphology, or in other words the chain's ability to arrange itself at a microscopic level. The chemical structure and morphology is paired with the externally programming that dictates whether or not the polymer will exhibit SME.[9] Many polymers that have significant differences in chemical compositions may all recover their shape following external stimuli. The way a shape memory polymer works begins with the heating and distortion of the polymer. In this stage, chains are rearranged and realigned, and as the material cools and the crosslinks solidify, it takes on a different shape. This is how one would expect a typical polymer to behave; once it is deformed it does not go back. It is upon the next heating and cooling process that the SME comes into play. When the polymer is reheated, the stored energy of the chains is released and, upon cooling, the material takes back on its original shape.

Polyurethane (PUR) Foam

Polyurethanes were invented in the 1930s by Professor Dr. Otto Bayer, otherwise known as the “father” of polyurethanes. Chemically, a polyurethane is a polymer containing organic molecules connected by urethane links. Polyurethanes are produced by mixing an isocyanate with a polyol (Scheme 1). Other materials such as catalysts and blowing agents vary depending on the type of polyurethane that is desired.



Scheme 1. Synthesis of a polyurethane from a diisocyanate and a polyol

Polyurethanes have numerous applications that are dictated by the physical and chemical properties of the urethanes, specifically their R groups. Polyurethane coatings have revolutionized lifespan and appearance of many materials in the automobile and housing industry.[13] PUR coated cars have increased resistance to scratches and corrosion, while PUR coated concrete supports in homes are durable in undesirable weather conditions. Certain polyurethanes are also contain biostability, withstanding

conditions within the human body.[14] These are just a few examples that display the variety of properties and applications that polyurethanes possess.

In the 1940's, polyurethanes began to be produced on an industrial scale. It was not until 1952 that isocyanates became commercially available, revealing the elastomeric improvements that polyurethanes had made.[13] Not long after in 1954, a unique polyurethane was created: polyurethane (PUR) foam. PUR foam can be rigid or flexible, both having different chemical properties and applications. Rigid foams are considered “closed-cell” and have longer polymer chains, more isocyanate groups (hard segments), and higher molecular weights. They are often used for insulating purposes in houses and refrigerators. Contrarily, flexible foams have “open-cells,” and have shorter polymer chains, more polyol groups (soft segments), and lower molecular weights. Flexible foams are often used in carpet cushioning, bedding, and furniture.

PUR foam differs slightly from other polyurethane polymers in the manufacturing industry. Most polymers, such as poly(ethylene) and poly(propylene), are manufactured as powders, films, etc. These forms are then heated, pressurized, and cooled into the desired product. It can be said that the final product is dependent on the original polymer. Contrarily, PUR foams are most often manufactured directly into the final product. They are produced into large blocks and are then cut into the desired shape.

Like all polymers, PUR foam contains a glass transition temperature (T_g). Above and below this temperature, the molecules have different relaxation times which are what gives rise to the shape memory properties.[3] This temperature region occurs where

the foam transitions from a stiff, glass like material to a softer, more rubbery material. When the foam is heated above the T_g, all present molecules are in the same rubbery state and the foam can be compressed. Following compression, the sample is returned back to room temperature in its compressed state. After a given amount of time, the foam is released from compression. If it does not return to its normal shape at room temperature, shape memory properties are present. If the foam does return to original shape, it can be concluded that no shape memory properties are present (Figure 3).[8,16]

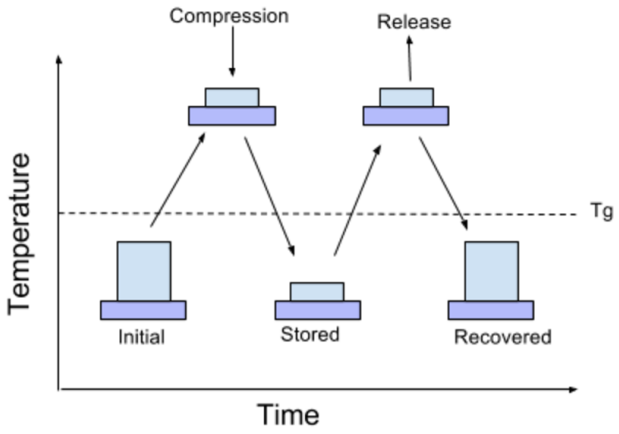


Figure 2. Process for determining possible shape memory effects. Redrawn according to Ref 15

Because of their versatility, they have been known to exhibit shape memory properties following thermochemical and mechanical stressors.[1,3,15] It is not uncommon for experiments investigating the shape memory properties of foam to first synthesize the foam in the lab to have control over concentrations, and to simply know the chemical structure of the foam.[1,17] It has been found that with an increase in gelling

catalyst and decrease in polyol molecular weight, shape fixability of PUR foam is higher.[17]

Shape memory studies have also been done using pre-manufactured foam.[8] It has been found that SMP foams act the same as SPMs in the sense that they must be cooled down to recover their original shape after deformation.[1,3] If the original foam is heated, compressed, cooled, and heated again, it will not return to its original shape, therefore the last cooling process is critical (Figure 2). Due to the time constraints, flexible foam was not able to be synthesized for this experiment. Different flexible foams obtained from Covestro LLC will be used to investigate shape memory properties.

Previous studies have shown that fixable polyurethane foams with high densities have 99% recovery following compression.[18] According to Lee, shape fixicity is dependent on the density and the glass modulus. The lower molecular weight of polyol and higher amount of glass modulus, the higher the fixicity. The chains are fixed in the cooling process in their glassy state, which can back up this claim. Fabrizio found similar results with polycaprolactone (PCL) foams in that 100% recovery was acquired when the sample was compressed at a 30% maximum.

While shape memory is important to customers and the effectiveness of the foam, it is also important for transportation purposes. Manufacturers have to be aware of the temperature, duration/degree of compression, and other stressful conditions that the foam will encounter in its transportation route.[17]

Analysis Techniques

Differential Scanning Calorimetry (DSC)

DSC is useful in determining the heat needed to raise the temperature of a given sample 1^{o} C. The DSC measures enthalpy of transition as a function of temperature. Since temperature is changing and is not held constant, the resulting graphs yield peaks rather than straight lines. The top of the peaks tell polymer scientists critical temperatures such as the melting temperature (T_m) and crystallization temperature (T_c). The areas beneath the peaks found at these temperatures are equal to the enthalpy of transition. In other words, since the temperature is changing, the areas under the curves show how much heat is needed to melt or crystallize a given sample. This area can either be positive or negative. A positive area means that there is a positive enthalpy, and the transition, such as melting, is endothermic. Contrarily, if the area under the curve is shown as negative, the process, such as crystallization, released energy and is considered exothermic.

This is important for testing the shape memory of foam because of the critical temperatures that are obtained from the foam samples. For shape memory to be exhibited, it is sometimes necessary that a sample must be heated above and below the critical temperatures to take on different shapes. This is helpful in knowing which temperatures the foam transitions because it allows a foundation when designing the conditions under which the foam is compressed. When dealing with foam, T_g is the most relevant critical temperature because it reveals the temperature at which the flexibility of

the foam changes due to chain mobility. T_g is not shown at a distinct peak, but can be estimated in the middle of the incline (Figure 3).

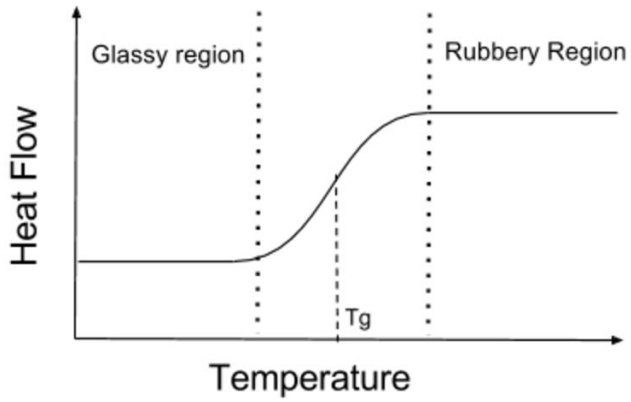


Figure 3. Glass transition temperature as shown on a DSC

Fourier Transform Infrared Spectroscopy (IR)

FTIR is a form of Infrared Spectroscopy (IR). Just like other forms of IR, infrared light is passed through a sample, and absorbance is measured as a function of wavelength. While some of the light is absorbed by the sample, some is passed through (transmitted). The result is a molecular fingerprint of the sample, showing absorbance and transmittance. The absorption bands correspond to frequencies of vibration between the atoms and bonds in a given sample. This not only helps identify unknown components in samples, the size of the peaks give information on how much of one functional group is present.

Frequencies of bonds vary depending on the state of the material. FTIR is useful in this experiment because it allows the foam to be characterized by its bond

frequencies. Secondary bonding that may be present in a stressed form may not be present in the free form, or different secondary bonds could be present at different temperatures.

Scanning Electron Microscope (SEM)

An SEM is a type of microscope that scans samples using a beam of electrons. Signals are produced by interaction derived from the atoms in the sample interacting with the electrons. The result is an image that contains information about the sample's immediate surface and composition. In this experiment, an SEM is particularly useful for analyzing the foam's pore sizes before and after compression.

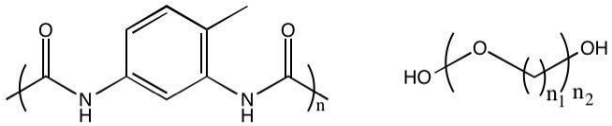
This Study

The intention of this experiment is to analyze possible shape memory effects in conventional (soft and firm), high resiliency (HR), and viscoelastic memory flexible foam obtained from Covestro LLC. For all four types of flexible foam, T_g will be found using the Differential Scanning Calorimetry (DSC) to determine how high each sample needs to be heated before compression. Samples will then be compressed under multiple forces for varying time spans above their T_g temperature. They will then be cooled under stressed conditions for the crosslinks to solidify. In stress free conditions at room temperature, if the sample holds the deformed shape, it will then be heated above the T_g to examine its percent recovery and shape memory capability.

Experimental

Materials

Polyurethane conventional (soft and firm), high resiliency (HR), and viscoelastic memory flexible slabstock foam were obtained from Covestro LLC. All foams were made with toluene diisocyanates (hard segments), polyether polyol(s) (soft segments), catalysts, surfactant, and water (Figure 4). Exact details are unknown due to confidentiality agreements.



A B

Figure 4. Toluene diisocyanate monomer unit (A) and polyether polyol(s) additive (B)

DSC Methods

A PerkinElmer DSC 8500 was used to perform DSC analysis. Foam samples ranging from 5 - 10 mg were placed in aluminum sample pans that were ± 0.1 mg difference from the reference pan. Samples were heated from -10^{o}C to 175^{o}C at 30^{o}C/min to erase thermal history. Upon holding for 2 minutes at 175^{o}C, samples were cooled from 175^{o}C to -70^{o}C at 10^{o}C/min and held at -70^{o}C for 1 minute. The final process heated the sample from -70^{o}C back to 175^{o}C.

Shape Memory Methods

Foam heights, x_o, and cross sectional areas, a, were measured in free form at room temperature prior to compression. Both conventional foams were heated to 130^{o}C, and

HR and viscoelastic memory were heated to 100^{o}C for 30 minutes. Foams were compressed with a mass, *m*, at high temperatures for time, *t*. The new height, x, was measured to calculate strain (ε). Following compression time, *t*, foams were removed from oven to let cool at room temperature for 30 minutes with mass, *m*, still on. Masses were removed and the new height, z_1 was taken. After 30 more minutes, an additional height measurement was taken, z_2, to measure shape memory. All foams were placed back in the oven for 3 hours and taken out one last time to measure the final height, *y*, for shape recovery calculations.

Results and Discussion

For confidentiality purposes, no phase transition temperatures were included with any of the foam samples provided by Covestro. Since the DSC yields peaks corresponding to important phase transitions such as T_g, T_c, and T_m, this instrument was used to determine phase transitions for conventional firm, conventional soft, high resiliency, and viscoelastic memory flexible foam. DSC has been proven to yield phase transition temperatures for polyurethane foam.[19-21] Additionally, values are excluded from the y-axis in Figures 5, 7, and 8 because the exact heat flow change is not of interest, and for these values to be usable the baseline must be calibrated to a much higher degree than it presently is. Fortunately for this experiment phase transition temperatures are the only relevant DSC data. Figure 5 shows the DSC cooling curves for three of the Covestro foams: conventional firm, conventional soft, and high resiliency. Conventional soft showed exothermic peaks in a range from 65 – 5^{o}C, conventional firm at 82 – 25^{o}C, and high resiliency (HR) 82 – 5^{o}C. These peaks should represent crystallization processes in the material. Details of the crystallization are unknown due to ambiguity regarding the foam composition. Consecutive DSC runs did not yield reproducible melting and crystallization peaks for each trial. Fortunately, for the sake of this study, it is not crucial to know the exact temperature that each component melts or crystallizes at, but rather the range over which these occurrences happen. The DSC trials for the viscoelastic foam showed no melting/crystallization peaks or glass transitions.

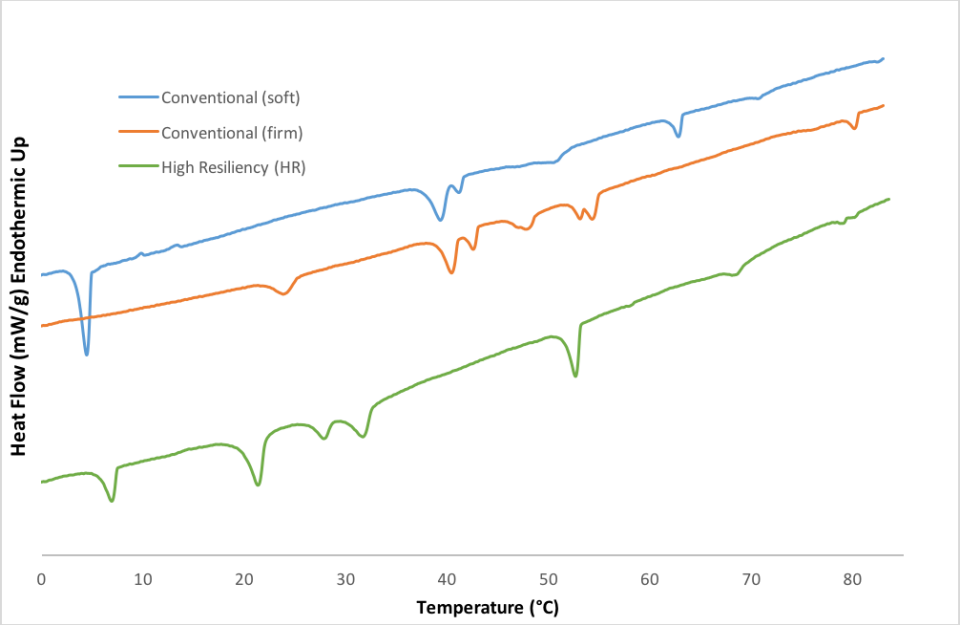
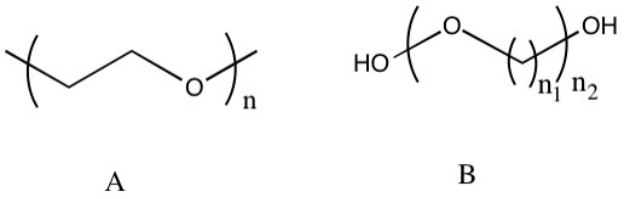


Figure 5. Crystallization peaks for conventional soft (blue), conventional firm (orange), and HR (green) foams.

Polyurethane foam's internal properties are slightly heterogeneous.[22] Since each foam had multiple trial runs, each containing a different sample of foam, it is thought that the foam's inhomogeniety caused the inconsistent DSC data. While the individual peaks were inconsistent, the range at which the peaks occurred remained the same for each trial. Conventional soft had a range of crystallization peaks that occur lower than conventional firm. Since the makeup of the foam is not entirely known, the reasoning behind this is inconclusive. It can be hypothesized that the since the conventional firm is more rigid, the chains are more tightly packed and have an incentive to crystallize sooner; whereas, the conventional soft crystallizes later as evidenced by its softer state at room temperature. Additionally, all of the foams have different make-ups (densities,

hard/soft segment composition, etc.), so crystallization should not occur at the same time for each foam, which it did not. Since the viscoelastic foam showed zero peaks, the hard to soft ratio of its makeup may be vastly different than the conventional and high resiliency.

Toluene diisocyanate is known to have a T_g at 47°C.[23] This was not able to be seen in any of the trial runs. It is possible that one of the "crystallization" peaks is actually a glass transition, or there are so many components crystallizing that the T_g is masked by them. Additionally, the DSC needed recalibrated due to the upward trending baseline and somewhat unsteady lines, which was thought to be masking the T_g of interest. Recalibration was done using the Perkin Elmer SmartScan program with a standard indium sample that contains known enthalpy and phase transitions. Upon similar trials following DSC recalibration, the toluene diisocyanate T_g was unable to be seen. Therefore, the literature T_g of 47°C will be used when heating the samples for all shape memory/ recovery experiments.. The same DSC runs also showed glass transition temperatures below -60°C for conventional soft, firm, and high resiliency foam. It can be expected that this transition temperature belongs to the polyether polyol(s) groups due to its structural similarities to poly(ethylene oxide) (PEO), shown in Figure 6, which has a T_g of about –60°C.[24] The polyether polyol T_g is far too low to work with in this study since temperatures of –60°C cannot realistically be reached. For now, the upper temperature of the crystallization range will be used instead of the glass transition temperatures to study the mechanical behavior.



A B

Figure 6. PEO (A) and polyether polyol (B)

The cooling process discussed above is specifically useful in determining critical phase transitions for shape memory purposes, but that does not go without saying that the heating processes do not yield valuable information as well. For the initial heating of the foam, a large exothermic process takes place around 75^{o}C. Figure 7 shows the thermograms for this process. Following cooling and the second round of heating, the same behavior is not present. It was initially hypothesized that following an initial heating, the foam's internal structure is permanently modified due to the foam releasing small residual molecules that evaporate due to an increase in temperature. Crystallization peaks seen in Figure 5 could be these evaporating oils forming into crystal structures. It was also thought that there was residual stress present that was imposed during the foam production caused by the blowing agents (water) and other materials. If this was the case, it would make sense that since the chains were pulled tight with a low entropy, they would want to come apart upon heating and become more disordered. If the initial heating does permanently distort the foam, it is important to know from a manufacturing standpoint so this foam does not exceed those temperatures and lose its application, therefore, becoming useless to the customer.

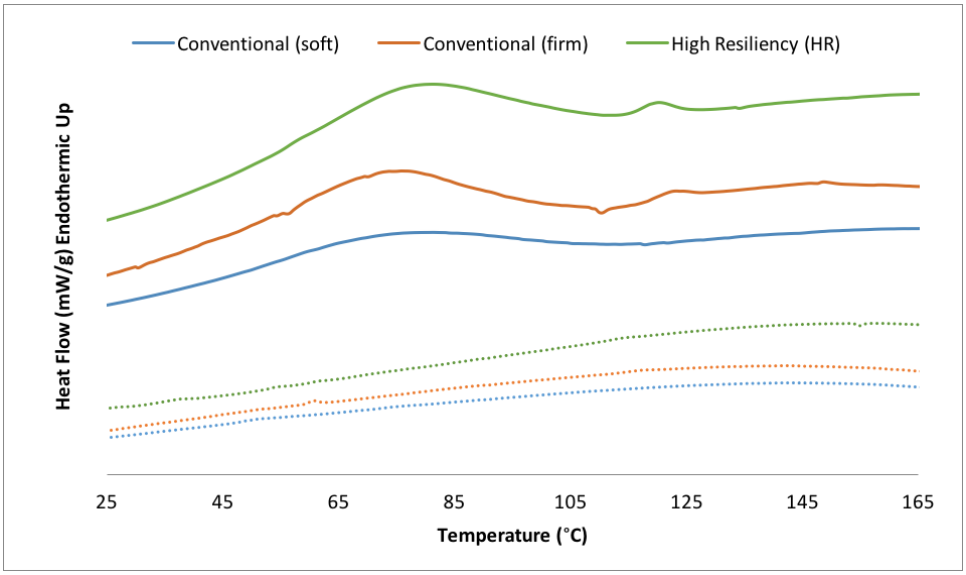


Figure 7. Initial (solid lines) and second (dotted lines) round of heating foam

To investigate the initial change in enthalpy, the foam was heated in the oven to 135^{o}C before running the DSC trials. This method was based on the hypothesis that the enthalpy change was due to the inititial heating of the foam causing the blowing agents to evaporate. Theoretically, heating it in the oven would cause the residual stress imposed by the blowing agents to evaporate and relieve any residual stress that the foam held. This method proved unsuccessful, and the trials produced graphs similar to the ones seen in Figure 7**.** It can be concluded that the large initial change in enthalpy was not due to small molecule evaporation and the residual stress imposed by the foam's blowing agents. This is a positive result from a manufacturing standpoint because it can be confirmed that increasing the foam to high temperatures does not cause the foam to lose its fundamental application.

It then was thought that the change could be due to stress imposed by the DSC pan rather than the blowing agents. When the samples from Figure 7 were prepared, they had to be packed into the pan because their standing volume exceeded that of the pan itself. The packing was thought to have stressed the foam in the pan. To minimize the force imposed by the pan, it is desirable to have minimal compression force on the foam. To minimize the compression force, foam samples were diced into very small pieces before preparing the sample in the pan. This allowed the samples to lay better in the pan and minimize the compression that had to be done. The DSC trials that followed this sample preparation method were shown to have a reduced initial enthalpy change, proving this method to be successful (Figure 8). While the change is still slightly present, dicing the foam greatly reduced it. It can be hypothesized that if the foam was able to be diced even smaller with more advanced tools, the initial heating line would be flat and the change would not be present at all. To conclude, the lack of an endotherm in subsequent heating is due to a release of residual stress from compression in the pan before heating.

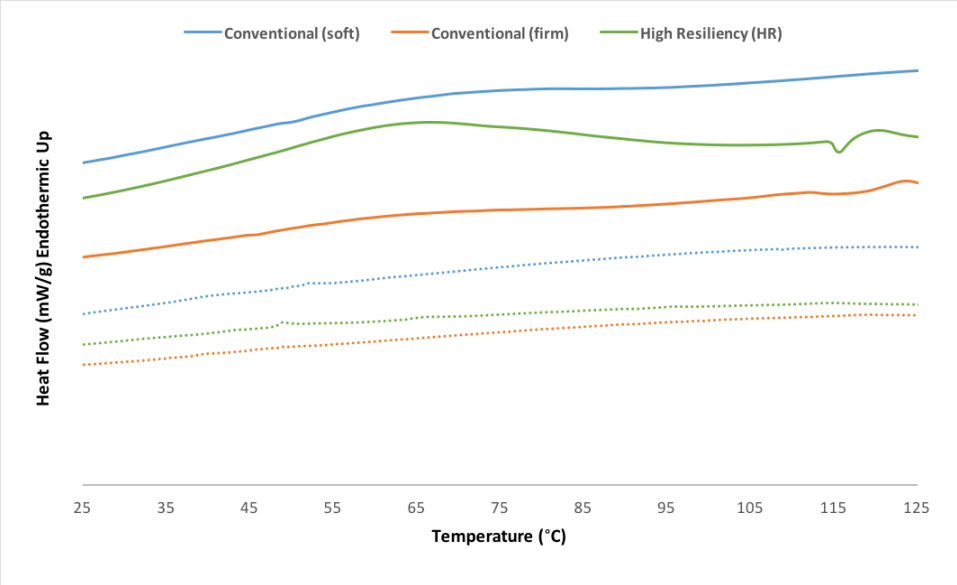


Figure 8. Initial (solid lines) and second (dotted lines) round of heating diced foam

As seen in Figure 2, materials must be heated above the T_g in order to determine shape memory properties. To confirm this, all types of foam were compressed at room temperature for 1 – 2 days. It was shown that following compression, each foam exhibited 100% shape recovery and no shape memory. Without heating above the T_g, the chains within the foam are unable to take on a different shape to allow the foam to stay in its compressed form once the weights had been released. All additional trials were done in the presence of temperatures exceeding the T_g as suggested by the literature.[15]

To begin the shape memory experiments, all foams were heated to 130^{o}C and compressed with arbitrary amounts of weights for 1 – 2 days to test responsiveness to such high temperatures. Once they were cooled back to room temperature and heated back to 130^{o}C, both conventional foams showed shape memory/recovery but high

resiliency and viscoelastic memory showed shape memory but did not recover at all. The same process was repeated with the latter two foams at 100^{o}C and both showed shape memory as well as shape recovery. Due to these results, all shape memory experiments for both conventionals were done at 130^{o}C and high resiliency/viscoelastic memory were done at 100^{o}C.

All foams were compressed with traditional lab masses. The compressive force of each mass was calculated using Equation (1). The force then was used to find the compressive stress applied to each foam with Equation (2). It is important to find this variable because the mass is not enough to quantify the amount of compression. If an arbitrary mass is applied to a small piece of foam, it is important to note that the force of the mass will have a larger effect on the small piece of foam than a piece of foam double its size.

$$F = m \times g \qquad (1)$$

$$\sigma = \frac{F}{a} \qquad (2)$$

Where force (F) is calculated by multiplying the mass of the weight (m) times the acceleration due to gravity (g) and compressive stress (σ) is equal to force (F) divided by the cross sectional area (a).

Equation (3) was used to calculate the strain on each foam to create a stress vs. strain curve in order to identify the compressibility of each foam. Because x is smaller than x_o, the strain is considered compressive, and Equation (3) yields a negative number. Contrarily, if the foam was being stretched, x would be larger than x_o, and the

strain would be considered tensile, yielding a positive number for strain. Compressive strain was used in this experiment, but despite the strain being negative in value, it will be shown as positive on all graphs because the sign is only providing directionality.

$$\varepsilon = \frac{(x-xo)}{xo} \qquad (3)$$

Where ε is the strain imposed on the foam, x is the foam's compressed height, and x_o is the height in its free form.

Two additional equations were used in the data analysis of this experiment (Equations 4 and 5). Percent recovery looks at how well the foam returned back to its original shape following the shape memory processes shown in Figure 2. X_o was measured when the foam was free standing at room temperature, and y was measured at room temperature once the shape memory process was completed. Like previously stated, this component is crucial in the transportation industry. If foam is being packaged and shipped, it is important to know that it will return to its original shape upon the customer's acquisition. Therefore, a percent recovery close to 100% is desired.

Percent shape memory describes how well each foam held its compressed shape. Initially, Equation (6) was going to be used to calculate this value, but z_1 turned out to be a useless variable. It was deemed useless because it was taken immediately after the weights had been removed following the initial heating. From the time the weight had been removed to the time the measurement was taken, it is possible that there was shape recovery that had not been accounted for. A measurement of the foam's height would have been taken upon removal from the oven with the weight still

on, but it was too difficult to get an accurate measurement considering the temperature of the metal weight itself and the scale of the experiment. Everything was measured in millimeters so accuracy was important. Due to the data collection limiting factors above, *x* was the variable that appeared to be a most accurate representative for the initial shape of interest, and shape memory was calculated using Equation (5). With access to better equipment, z_1 could be measured, allowing Equation (6) to be used to calculate a more accurate percent shape memory.

$$\% \, Recovery = \frac{y}{xo} \text{ x } 100 \quad (4)$$

$$\% \, Shape \, Memory = \frac{x}{z2} \text{ x } 100 \quad (5)$$

$$\% \, Shape \, Memory = \frac{z1}{z2} \text{ x } 100 \quad (6)$$

Shape memory/recovery experiments were conducted for *t* = 1 day and *t* = 1 week. Initial trial runs for all four foams were done at 130^{o}C. While this temperature proved sufficient for conventional soft and firm, it was too high for high resiliency and viscoelastic memory. Trials were done on the latter two at a lower 100^{o}C and were more responsive to compression. This was investigated and will be discussed later on. All of the following shape memory experiments were done at 130^{o}C for conventionals and 100^{o}C for HR and viscoelastic memory.

For the week long compression, all four foams retained 100% of their post compression shape, exhibiting excellent shape memory properties. For any further shape memory experiments, it is not necessary to exceed *t* = 1 week because anything longer than this should yield 100% shape memory as well. For percent recovery, there

was a somewhat steady decrease as compressive stress and strain increased (Figure 9). While HR and viscoelastic memory had a relatively linear decrease, both conventionals seemed to drop off faster. This would suggest that they would reach 0% recovery faster than the other two, and should be more closely monitored when shipping for long periods of time. As previously stated, the lower the shape recovery, the farther away from full function the foam is, which is not desirable to the customer.

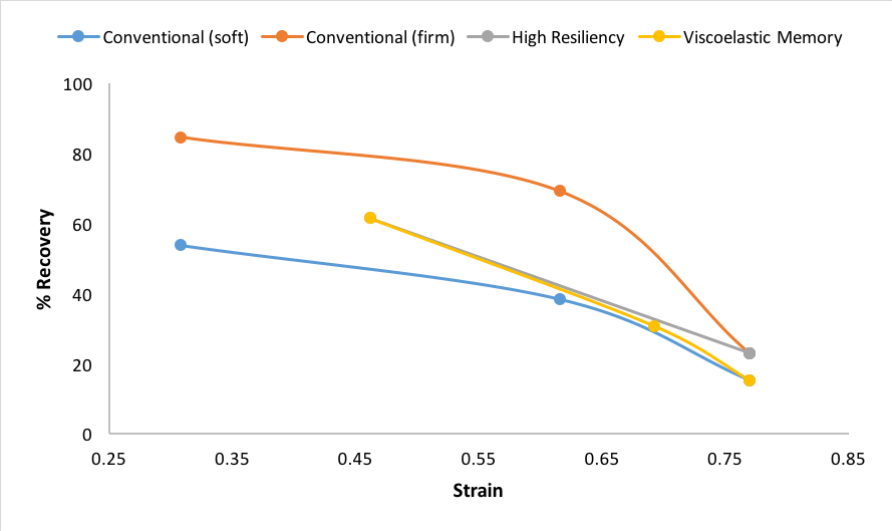


Figure 9. Percent recovery plotted against strain for the week long compression

The day long compression that was done yielded similar trends to that of the week long compression but had an incongruence with the high resiliency. As seen in Figure 9, HR reaches a maximum strain. This asymptotic behavior yielded questionable percent recovery. With equal strain, one sample had a higher recovery than the other, when one would think that equal strain may yield equal percent recovery (Figure 10). The reasons are unknown until Figure 11 is presented and depicts the compressive stress against percent recovery. Here, it is shown that different stresses yield different

percent recoveries, and the asymptotic behavior seen in Figure 10 is not present. Comparing both graphs, one can conclude that compressive stress has a more defining role in shape recovery than that of strain.

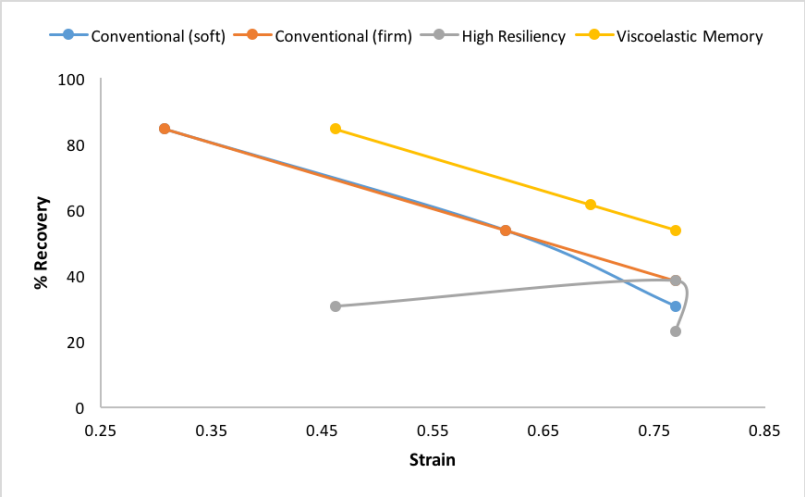


Figure 10. Percent recovery plotted against strain for the day long compression

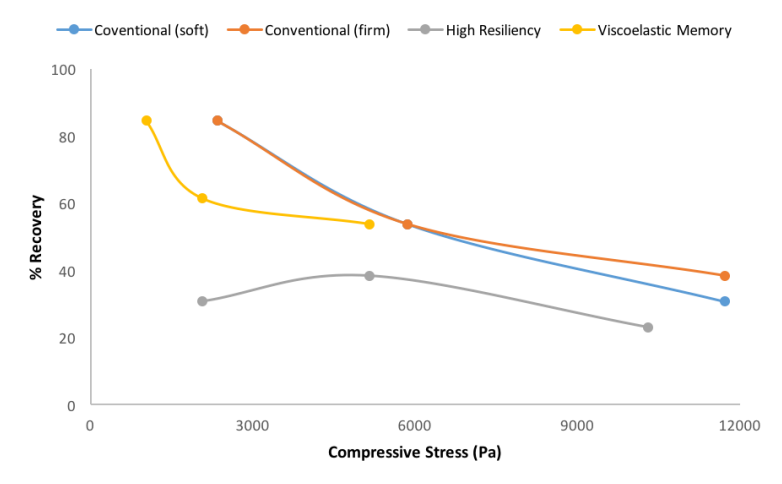


Figure 11. Percent recovery plotted against compressive stress for the day long compression

It would be intuitive to think that with an increase in stress, percent recovery would go down, just as it did with the week long compression. This was not the case with the day long compression in regards to the high resiliency foam (Figure 11). The sample compressed with the second largest amount of stress has a larger percent recovery than the sample with the smallest compression. This could be due to the lack of highly technical equipment that was accessible for this experiment. When the foams were compressed with the masses, the mass would tilt at times, not always distributing the force evenly. This could have been due to the fact that the foam was cut by hand and may not have had perfectly straight sides, causing the weight to be more distributed on the side closer to the base. So it is possible that the side of the HR sample that was being measured under the second largest weight was not compressed as much as it should have been, and the majority of the weight was on the other side. It would have been helpful to have the foam manufactured in smaller cubes to ensure all edges were straight, rather than cutting small cubes from a large piece of foam by hand. The experiment would also be more accurate with machinery that is able to hold the foam in place and compress it for programmed lengths of time. The only compressive equipment that was available for this experiment was traditional masses that were very difficult to balance on the pieces of hand cut foams. To take away, there is an inconsistency seen with the high resielency's percent recovery in Figure 11 can be attributed to human error and lack of precise equipment.

Figure 9 displays the stress vs. strain curve for conventional soft, conventional firm, high resiliency, and viscoelastic memory foam. Figure 9 yields important information for each type of foam: compressibility. Compressibility can be directly related to how much strain is imposed for a given amount of stress. While it is easy to determine compressibility by simply squeezing the foam, it is important to be able to quantify data that yields the compressibility of a specific type of foam in comparison to the others.

The blue conventional soft line cannot be seen because it is hidden behind the orange conventional firm line. The identical lines imply that the two conventional foams have the same, and lowest compressibility because they had the lowest amount of strain for every amount of stress. The viscoelastic memory foam has the highest compressibility due to the increased strain in comparison to its counterparts. For each given amount of stress, it has the largest amount of strain. High resiliency exhibits interesting asymptotic behavior when higher stress is imposed. For the higher two stresses, the foam exhibits the same strain. The two lowest amounts of stress appear to have a linear increase with strain, but the third point yields the same strain value, meaning HR had already reach maximum strain with a low amount of stress. Conventional soft, conventional firm, and viscoelastic memory foam all seem to be approaching a similar strain asymptote, but have not yet done so with the stress imposed. Future experiments could be done to examine when each foam reaches

maximum strain. For now, it can be concluded that high resiliency reaches maximum strain before the rest.

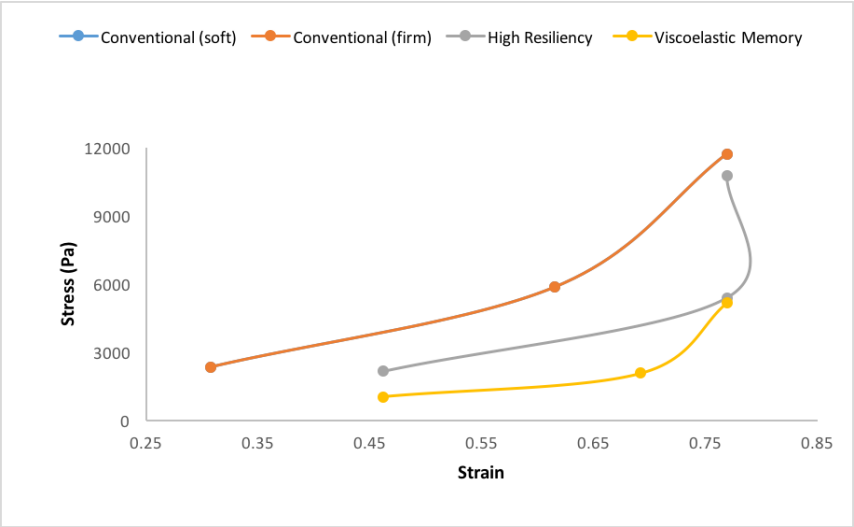


Figure 12. Stress plotted against strain for all four foam types

SEM images were taken for all four types of foam (Figure 13). In contrast to rigid foams that have closed cells, each image displays open cells, confirming that this foam is flexible.[25] Conventional firm and soft appear to have larger cell sizes in comparison to the high resiliency and viscoelastic memory. While the viscoelastic memory foam appears to have smaller pore sizes, there is more material per unit volume present. Regardless of this slight differences, all of the foams have circular, open pores and share the same general cell structure. Since the microscopic structure of each foam is similar in appearance, it can be assumed that the cell structure likely has no effect on shape memory or shape recovery.

While SEM images portray many similarities in the foams, specific attention should be directed toward conventional soft and firm foam. These two images are

nearly identical in pore size and cell structure, while HR and viscoelastic appear slightly different. Both conventional foams also have identical compressibility properties (Figure 12). From this data, one can deduce that cell structure and size can be directly related to compressibility.

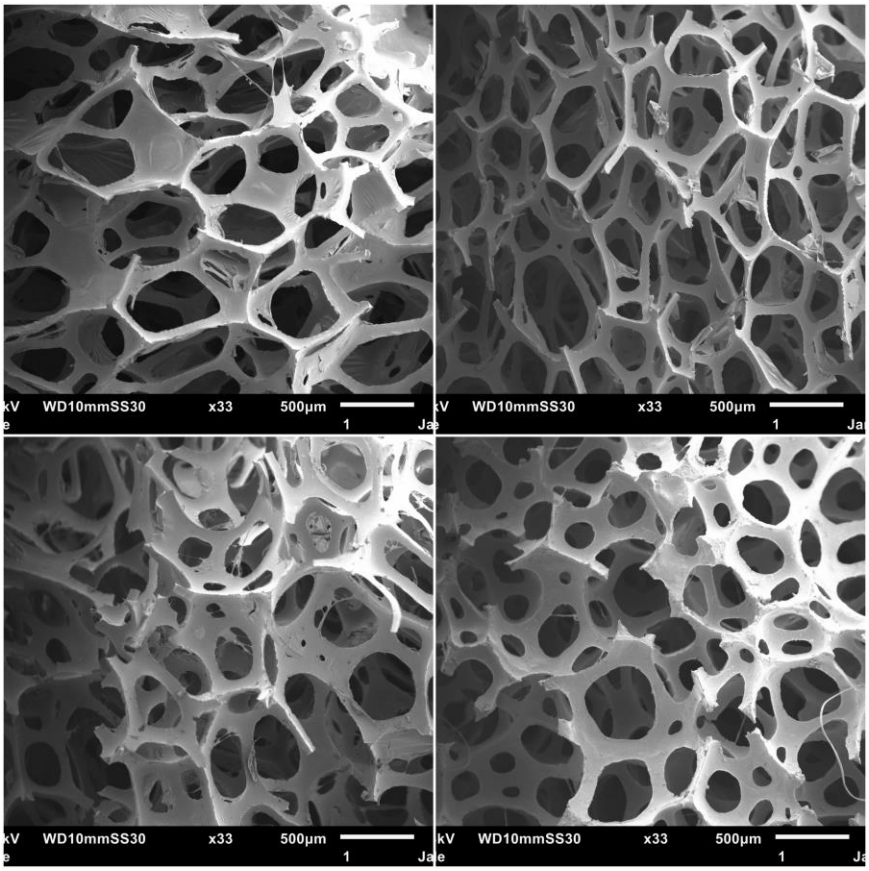


Figure 13. SEM images of conventional soft (top left), conventional hard (top right), high resiliency (bottom left), and viscoelastic memory (bottom right)

The FTIR was used to confirm the make up of each foam. Covestro stated that each foam contained polyether polyols and diisocyanates. The FTIR data confirms the information provided by Covestro. Figure 14 gives an overlay of each foam's spectra. While the foams' make-ups were provided upon receiving the foam, the amount of each

component was not. The FTIR data gives insight on how much of each component is in the foam relative to the rest. Viscoelastic memory foam contains the highest polyether component by a large margin (Figure 14). Additionally, it has the highest compressibility and, according to the SEM, contains the most material per unit volume (Figure 9 and 14). The SEM and FTIR are complementary to confirm that the amount of material present in the foam is directly related to compressibility. The FTIR suggests that polyethers have the highest contributing factor.

Looking back at Figure 12, compressibility can be ranked as follows: viscoelastic memory > HR > conventional soft = conventional firm. Close examination of the FTIR spectra shows that only the polyol portion mimics this trend. The viscoelastic memory has the highest, followed by HR, and both conventional lines are overlapping which suggest they have the lowest/same. This somewhat contradicts what was previously stated regarding the polyether components being directly related to compressibility since this observation suggests that only polyols are related. While the trend for the polyol portions from the FTIR does technically match what was taken from the stress vs strain curve, the margin is very small. There are very little polyol groups in comparison to the polyethers. With this in mind, it is inconclusive what, if any, components as seen on the FTIR relate back to compressibility.

Like previously stated, reacted monomers results in polymers. Scheme 1 shows how the polyether polyol monomer reacts with the diisocyanate monomer. Figure 14 serves as validation that the polyol did react with the isocyanate. First, close attention

must be brought to the absorbances of the ethers and alcohol groups. If no reaction had happened, there would be a much larger portion of alcohol groups, which is not seen. It clearly shows that there is much more polyether than alcohol groups (Figure 14). The same is true for the isocyanate and the amide absorbances. There are far more amide bonds than isocyanates (Figure 14). If no reaction would have happened, the isocyanate absorbance would be much larger. Scheme 1 shows no explicit alcohol or isocyanate groups in the product, but the FTIR data shows that some are present. The small amounts of the polyol and isocyanate can be attributed to the unreacted monomers in the foam's content.

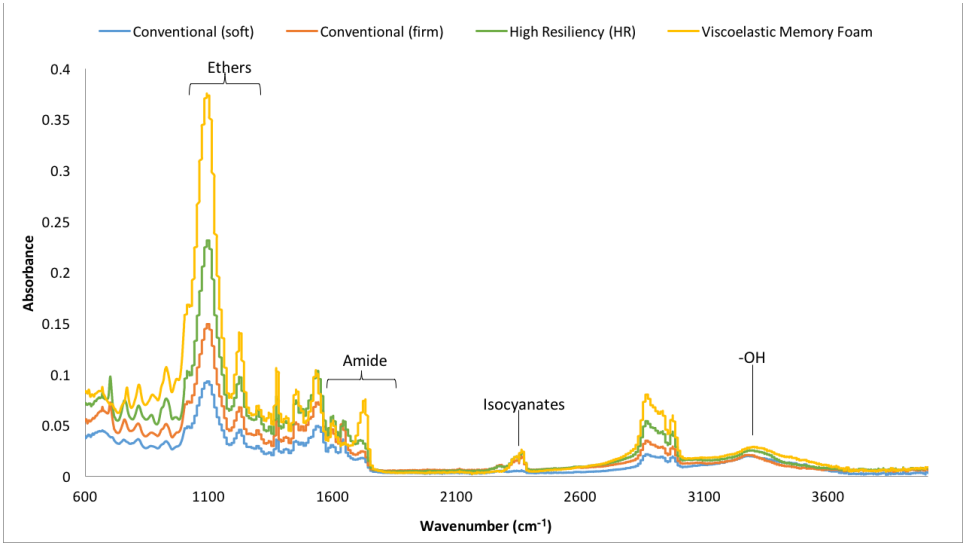


Figure 14. FTIR readings of foams with identified peaks[26]

Like previously stated, it initially appeared that high resiliency (HR) and viscoelastic memory foam did not recover well at 130^{o}C but both conventional soft and firm did. If at 130^{o}C HR and viscoelastic were not responsive and at 100^{o}C they were, it

seemed logical that there would be a maximum temperature in between the two at which they would switch from exhibiting shape recovery to not exhibiting shape recovery. In trying to find this temperature, additional shape memory experiments were done at 110^{o}C and 120^{o}C for HR and viscoelastic memory. Identical forces with corresponding shape recovery percentages can be found in Figures 15 and 16. It can be seen that with the HR, a temperature of 110^{o}C yields the best recovery and 100 and 120^{o}C exhibit the same shape recovery (Figure 15). Contrarily, the viscoelastic memory showed the least recovery at 110^{o}C and 100 and 120^{o}C exhibited, this time, better and again same recovery. Unfortunately, a trend could not be determined from the data collected that would yield a turning point temperature (Figures 15 and 16). It would have been expected that the lowest temperatures would have exhibited the best shape recovery since at room temperature there was 100% recovery and at 130^{o}C there was very little.

With no solid trend, it could be thought that temperature does not have an effect on shape recovery. This cannot be true though seeing as different temperatures did yield different amounts of shape recovery, so temperature must play a factor. It is possible that human error and lack of precision equipment can be held responsible for the lack of trend. Like previously stated, this experiment was not done with the most technical of equipment. The oven that was used for 110^{o}C trial was adjusted using a dial. Where the dial was adjusted as close as possible to get to the desired temperature, it would not be unreasonable to think that the temperature was above or below the

desired temperature. It does not go without saying that the oven used was a contributing factor in the inconsistent trend. Also, this was done on a millimeter scale using a ruler, making it difficult to obtain exact measurements. With access to more accurate ovens and more technical measuring equipment, it is possible that the temperature at which they become unresponsive would be determinable.

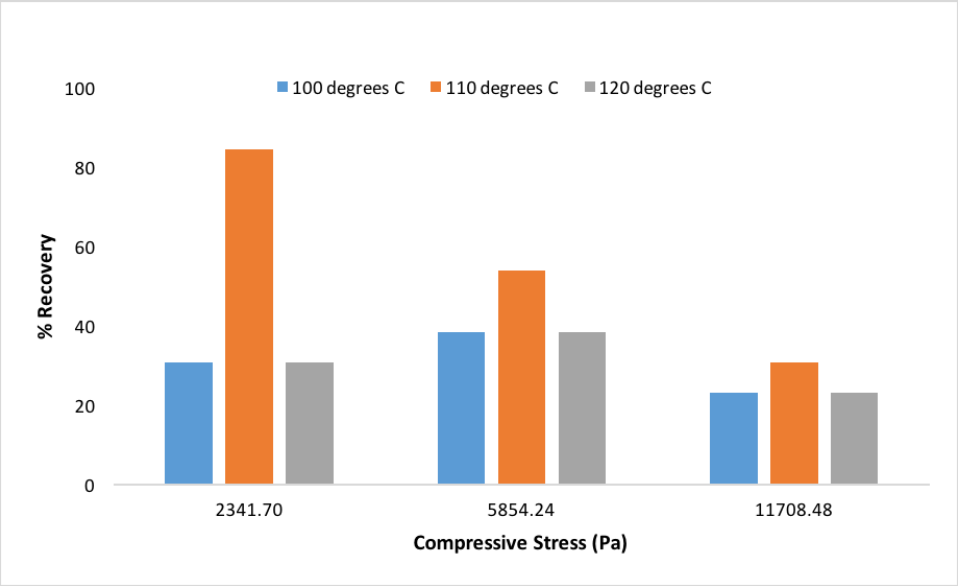


Figure 15. High resiliency (HR) foam tested at various temperatures

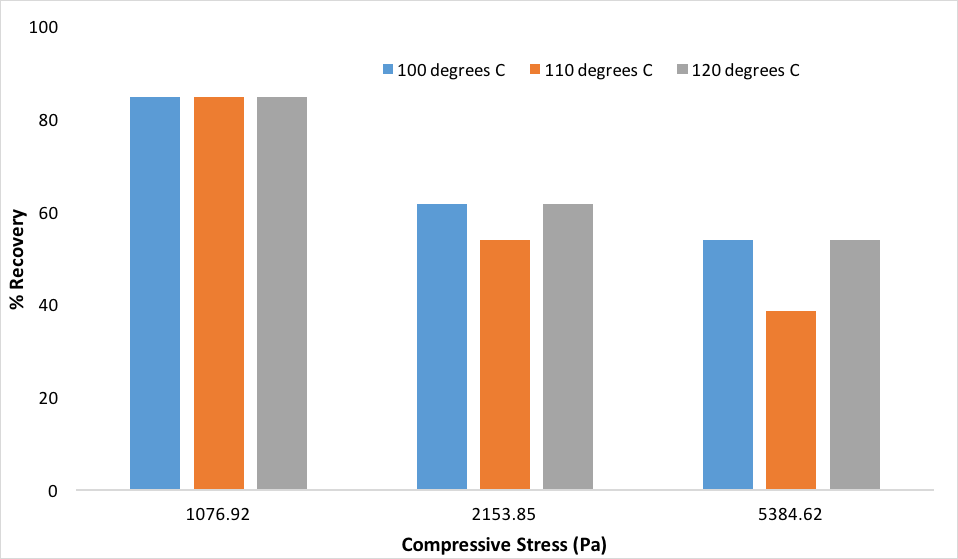


Figure 16. Viscoelastic memory foam tested at various temperatures

Conclusion

Flexible polyurethane foams (conventional soft, conventional firm, high resiliency, and viscoelastic memory foam) exhibited excellent shape memory properties and some shape recovery properties. DSC readings did not give concrete glass transition temperatures, so the literature was used to determine what temperature all foams needed to be heated above to determine the shape memory/ recovery procedure. Shape recovery tended to decrease with increasing compressive stress as well as length of compression. FTIR spectra of each foam was able to assist in supporting shape memory/ recovery findings. It helped to prove that the isocyanate did react with the polyether polyol, leaving behind monomer units, to create a polyurethane. Each foam was able to be defined by its compressibility using a stress vs. strain curve.

Human error and lack of precise equipment were large contributing factors in this experiment. Both caused inconsistencies in shape recovery and accounted for lack of trends when varying temperatures. If this experiment is to ever be continued, it would be recommended that more technical equipment is used to eliminate these obstacles.

It was proven that varying compressive stress and length of compression did yield different shape memory and shape recovery. With this is mind, it is a valuable experiment to look at because recovery is important from a manufacturing standpoint. Like previously stated, with more precise equipment, it is likely that more concrete results could be found.

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