PERFORMANCE OF COMMERCIAL HOT-MELT ADHESIVES

THE EFFECT OF MATERIAL PROPERTY AND OPEN TIME ON THE PERFORMANCE OF COMMERCIAL HOT-MELT ADHESIVES

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A Thesis Submitted to the School of Graduate Studies in Partial Fulfilment of the Requirements for the Degree Master of Applied Science

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Hot-melt adhesives have been commercially available for a long time and they are used in a wide range of applications. The adhesive performance is governed by the adhesive material property as well as the application conditions for each type of substrate. In order to achieve a good bond between the adhesive and the designated substrate, both wetting ability and open time of the adhesive material have to be considered. Three commercial hot-melts were used in this study in order to examine the relationship between the material property and the adhesive performance. The thermal properties of the materials were obtained through Differential Scanning Calorimetry while Dynamic Analysis (DA) described their viscoelastic behaviour, and the hysteresis loop helped to characterize the flow regime from which the application conditions for the adhesive could be chosen. The adhesive performance was evaluated in term of the force required to break the bond between the adhesive and the substrate through a series of standardized pull-off tests. The effect of the time-temperature trade-off on the adhesive performance by varying the application temperature as well as prolonging the available bond-formation time was also examined. In most cases, the adhesive performance improved with extended open time. However, improved adhesive performance was also shown to be the response of shorter Maxwell characteristic time which was evaluated from the DA data. By providing the characteristic time as a linkage, a relationship between the adhesive performance and the material properties could be established. These results also offer a basis for the formulation of adhesives using structure-property parameters derived from DA.

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LIST OF ABREVIATIONS AND SYMBOLS

DSC – Diffirential Scanning Calorimetry

DA – Dynamic Analysis

G' – Storage modulus

G" – Loss modulus

G* – Complex dynamic modulus

$G_{X\text{-}H}$ – Modulus at cross-over point on the heating curve

$G_{X\text{-}C}$ – Modulus at cross-over point on the cooling curve

$T_{X\text{-}H}$ – Temperature at cross-over point on the heating curve

$T_{X\text{-}C}$ – Temperature at cross-over point on the cooling curve

T_H – Target temperature for the heating cycle

T_C – Target temperature for the cooling cycle

ΔT – Temperature difference

ΔH –Enthalphy

$\Delta H_{recrystal.}$ – Enthalpy corresponded to recrystalization event

ΔH_{melt} – Enthalpy corresponded to melting event

η' – viscosity

ω – Frequency

τ – Characteristic time

δ – Phase angle

De – Deborah number

DECLARATION OF ACADEMIC ACHIEVEMENT

I hereby declare that the results and findings presented in this thesis is solely my own work under the supervision of Dr. David K. Potter. All materials taken from other sources as reference have been appropriately cited within the text.

Introduction

Hot-melt adhesives have been commercially available for a long time and they are used in a wide range of applications from bookbinding, packaging, product assembly, tapes and labels, floor and tile, textile, furniture to specialty adhesive. Evolving from the early use of melted wax for bonding, hot melt adhesives are a one-component system which consists of a non-volatile thermoplastic polymer which is solid at room temperature; has fluid flow characteristics while in the molten state, and solidifies quickly when allowed to cool down (Cagle,1973). The drawbacks for such a system are the limited adhesive strength achieved, and the lack of molten properties such as tack and wetting ability which directly affect the performance of the hot-melt adhesive. In practice, the composition of a hot-melt adhesive usually includes a thermoplastic polymer backbone and a diluent system. Since hot-melt adhesives need to be applied in the molten state, polymers with adequate resistance to heat degradation such as polyethylene, polyvinyl acetate or ethylene-vinyl acetate copolymers are typically used as the backbone polymer (Cagle, 1973). Moreover, high molecular weight polymers are preferred since they provide high viscosity, high (cohesive) strength and good mechanical properties. The diluent system in a hot-melt adhesive can include materials such as wax, tackifier, and plasticizer. By adding these materials accordingly, the properties of hot-melt adhesives can be modified and customized to a specific end usage (Li, 2008). The diluent system can help to lower the viscosity of the molten polymer making it more convenient to apply onto surfaces as well as to increase the wetting ability and adhesive strength; it can also

provide molten tack and modify the physical properties of hot-melt adhesives. However, in order for the diluent system to be effective, the components need to be selected with care to ensure compatibility for the whole system (Tse, 1997; Tse, 1998).

Hot-melt adhesives are solvent-free, a selling point which increases their desirability in potential markets due to the lower health risks associated with using these products. Another advantage is that they have a simple bonding mechanism at a fairly high bonding rate once applied. Hot-melt adhesives are usually water-insoluble therefore insensitive to water (Li, 2008), and they can be used as gap filler in many applications (Cagle, 1973). However, hot-melt adhesives exhibit lower strength and heat resistance compared to conventional liquid adhesives such as epoxies or cyanoacrylate since they are thermoplastic materials that cannot react or cure to form crosslinks; therefore they are not typically used as structural adhesives (Petrie, 2008).

The adhesive performance is governed by the adhesive material property as well as the application conditions for each type of substrate. Therefore, in order to improve the performance of an adhesive, thorough understanding of the material properties and the suitable application conditions for a specific end-use is essential. The performance of an adhesive during and after its application is evaluated differently since different material properties and other parameters are involved. During application, the performance of adhesive will be evaluated in term of its ability to wet the designated substrate and the time available for the adhesive to form a bond with the substrate. After the application

process, adhesive performance will be measured based on the bond strength it exhibits with the designated substrate as well as the cohesive strength of the adhesive material, and the temperature and pressure under which the bond can still sustain before failing. This study will limit to the evaluation of the adhesive performance during application and the parameters involved. Open time and wetting ability are two main factors that govern the performance of adhesive during the application process.

A bond between the hot-melt adhesive and the substrate can be formed only when the adhesive has fully wetted the surface of the substrate. For each hot-melt adhesive, the kinetics of wetting is controlled by temperature and time (Cagle, 1973). The wetting ability of a hot-melt adhesive is governed by the flow property of that adhesive, which is related to the viscosity of adhesive material when it is in the molten state. There are also external parameters that affect the kinetics of wetting of an adhesive such as the surface smoothness of the substrate, the surface tension, and contact angle of the adhesive. Much work was done on examining the kinetic of wetting of hot-melt adhesive on a substrate by following the change in the contact angle of the molten adhesive as a function of time at different temperatures. It was found that the contact angle decreased with increasing time until equilibrium (complete wetting) was reached; and equilibrium was reached in a shorter time at higher temperatures (Kinloch, 1987). A relationship was derived to express wetting of molten adhesive in term of viscosity, contact angle and surface tension, and this relationship can be used as a guideline to determine the time necessary to attain complete wetting and the effect of raising temperature on the kinetics of wetting in

real applications (Kinloch, 1987). When all those parameters are kept in check, the focus is shifted onto the material property that govern the wetting ability of hot melt adhesive, which is essentially the viscosity of the molten adhesive at different temperatures.

Adhesive material with lower viscosity will have more flexibility to flow out, which makes it easier for the adhesive to fully wet the substrate. This provides an opportunity for the adhesive material molecules to orient themselves onto the substrate surface hence forming a bond with the substrate. Adhesive with higher molten viscosity will have a harder time to flow out and completely wet the substrate, hence the adhesive material molecules will have less chance to orient themselves onto the substrate surface to form a bond. Ideally, at application temperature, the viscosity for molten adhesive should stay low long enough for the substrate to be brought into contact and then rise rapidly to set the bond in minimum time (Macosko, 1977). Since viscosity is a temperature-dependent parameter, it follows that for each hot-melt adhesive and application there is a minimum bond-formation temperature below which, complete wetting will not be accomplished and a poor bond with the substrate will be formed (Cagle, 1973).

Open time is an important concept in the adhesive industry. Open time can be defined as the time lapse between applying the molten adhesive onto the substrate and the transformation to the solid state, at which point the hot melt adhesive loses its ability to wet the substrate (Cagle, 1973). On a molecular level, open time can be considered as the time available for the molecules in the adhesive matrix to orient themselves to maximize interaction with the surface to be bonded. Typically, the hot-melt adhesive selected for a

given application must have sufficient open time for that application. Commercial hot-melt adhesives nowadays offer a wide range of open time that can satisfy any type of application demand. In general, the softer and weaker type of hot-melt has longer open time, which means slower setting time, and typically longer compression time and slower machine production speeds (Cagle, 1973). Usually, if extended open time is required in a given production situation, other adhesive systems should be considered to avoid the limitation of hot-melt adhesives. However, in the event that there is a temporary need for longer open time, it is not recommended to change the adhesives system but to extend open time by increasing the operating temperature instead. By increasing the operating temperature, the adhesive is applied at a high temperature, thus it will take a longer time to cool down to eventually reach its solid state. As a result, the material is forced to stay in its molten state for a longer period of time, effectively increasing the time available for the material to adhere onto the substrates, which is essentially the same as extending the open time for the adhesive material. Higher running time prolongs the time available for adhesive to reach the minimum bond-formation temperature as it will also take a longer time for the adhesive to cool down, giving the adhesive more time to form a bond with the substrate. This should result in an improvement in the bond characteristics. Higher running time also means the adhesive is exposed to an elevated temperature for a longer time, suggesting that the adhesive sample will experience a more complete melting event which results in lower viscosity. It allows the adhesive to flow out thus increasing the surface area of the adhesive, consequently increases its cooling surface which means a faster cool for the adhesive (Cagle, 1973). This counters the effect that higher running

time has on the cooling time. On the contrary, when the running temperature is lowered, it will shorten the time available for adhesive to reach the minimum bond-formation temperature. In cases where the bond-formation time is set as fixed due to production timing, lowered running temperature can lead to molten adhesive not reaching the minimum bond-formation temperature, which results in no bond or poor bond being formed between the adhesive and the substrates.

All discussion above is valid only if sufficient amount of adhesive was applied in order to fully wet out the substrate surface and enough to fill the joint between the adherends (Cagle, 1973). When a small amount of adhesive is used, it can lose all its mobility to wet the surface of the substrate due to the heat being lost to the substrate, meaning faster solidification and shorter open time, resulting in poor bond being formed (Cagle, 1973). On the contrary, increasing the amount of adhesive used while at the same time maintaining the initial application conditions provides a greater increase in open time and slower solidification. However, using too much adhesive can have a negative effect on the strength of the bond formed due to the greater contribution of cohesive strength in a thicker adhesive layer, as well as increasing the cost involved by using more adhesive material. It shows that the amount of adhesive used is a strong controlling factor for optimum utilization of hot-melt adhesive as well as the bond quality. Since the amount of adhesive applied affects the time available for the molten hot-melt to be in contact with the substrate surface, it also follows that this parameter also has an influence on the kinetics of wetting for the adhesive material (Cagle, 1973). This wetting

requirement is applied to both surfaces – the one to which the adhesive is applied and the second surface to which the adhesive is bonded. In order to achieve a good bond between the adhesive and the designated substrate, both wetting ability and open time of the adhesive material have to be considered.

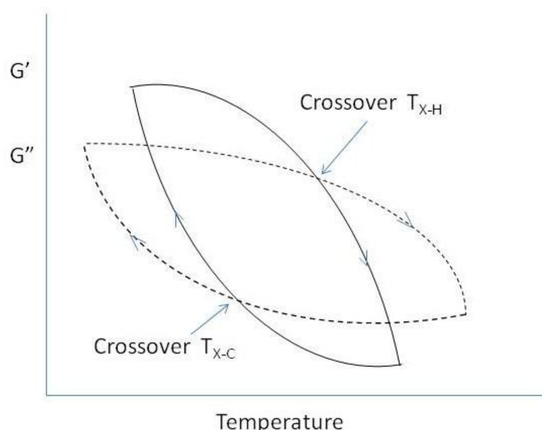
The application conditions for an adhesive system are related to the actual end-use environment and the material properties of the adhesive. In real-life practice, the adhesive application is much different from the scenario portrayed in a research study since the real process is not isothermal; the heating of adhesive to get to its molten state, and the cooling rate of hot melt adhesive are not controlled parameters. Other parameters related to the surrounding enviroment such as ambient temperature can also affect the application process. However, this study only focuses on the effect of open time on the adhesive performance; therefore all other parameters are to be kept consistent all through the course of this study. Prior to this process, the properties of the adhesive material have to be studied. The adhesive material property can be characterized by many different techniques that focus on the thermal and dynamic mechanical behaviours of the material. For a hot-melt adhesive material, its molten state can be defined as its working state during which hot-melt is applied and starts to form a bond with the substrates. Therefore, a thorough understanding of the thermal properties of the adhesive material is necessary in order to study the performance of an adhesive. Thermal behaviour can be examined using methods such as Differential Scanning Calorimetry (DSC). With the aid of DSC, the temperature characteristics of the melting process and relaxation transition can be

determined, as well as the effect of various components of hot-melt adhesive system on its thermal and mechanical properties (Khairullin, 2007).

While examining the thermal properties of the adhesive material, even though DSC study can offer a general sketch of the thermal behaviour of the adhesive, it is inadequate in providing a more in-depth quantitative result (Cantor, 2000) due to the inability to capture the profile of the flow property of the material. Moreover, for hot-melt adhesive - as was discussed earlier, flow property is of great importance to understand the kinetics of wetting which has a great contribution on the adhesive performance. At different temperatures, adhesive material may start to melt, but has no flow-ability. In such state, even though the melt starts to take up liquid-like behaviour, it is still not able to flow out and wet the substrate thus forming a bond with the substrate surface; then it fails to perform as a hot-melt adhesive. Therefore we need to utilize another approach to obtain the flow profile of adhesive material in the molten state.

The viscoelastic properties of adhesives can be characterized through Dynamic Analysis (DA). Similar to the Dynamic Mechnical Analysis on a solid sample, DA characterizes the viscoelastic properties of the molten adhesive using the storage modulus G' which measures elastic behaviour and the loss modulus G" which measures the flow behaviour of an adhesive [12]. As temperature increases, the adhesive starts to soften/melt and exhibit liquid-like behaviour, G" starts to dominate G'. This phenomenon can be observed on the heating curve (T_{X-H}) as the first cross-over point. Upon cooling, the

material becomes more solid-like and G' starts to dominate G" which is the second cross-over that can be observed on the cooling curve ($T_{X\text{-}C}$). The temperature difference between the two cross-over temperatures $T_{X\text{-}H}$ and $T_{X\text{-}C}$ can be used to calculate the open time for the adhesive if the heating rate is known and is constant.



Open time is an important performance parameter for adhesive, however in the past it was only roughly evaluated using crude methods. One of the simpler methods used to determine the open time for an adhesive in usual practice is adopted by Glue Machine Corporation as follows. Adhesive is heated in a glass beaker until reaching its melting temperature. One end of a glass rod is immersed in the molten adhesive until equilibrium is reached and the rod has the same temperature as the molten adhesive. A thin layer of adhesive is applied evenly onto a sheet of paper using the glass rod. The test is started by immediately pressing the tip of a finger onto the adhesive film to leave a fingerprint. This action is repeated every second until adhesion is deemed to be minimal. Count the number of finger prints left on the adhesive film, and that is the equivalent open time in second. Since this method only relies on human senses as sensor, the result is only an

estimation of the open time range for an adhesive and only can serve as a general evaluation and may be used for comparison between similar adhesives. It does not intend to provide actual measurement figures.

For research purpose, the modified method for determining the open time of a hot melt adhesive was derived and presented in the US Patent 20090110937A1. For this method, open time was defined to be the time which elapsed between application of hot melt adhesive composition and the point in time at which hot melt adhesive lost its adhesion to the substrate to be joined. Adhesive is melted in a sealed cartridge until complete melting is achieved. Using a nozzle at the end of the cartridge, the molten adhesive is applied as bead onto a cold glass plate at room temperature. The tip of a polyethylene pipette was used for contacting the adhesive bead periodically. This action can be stopped once wetting of the pipette tip by the molten adhesive can not be observed anymore, and the time since the adhesive bead is released until then is recorded as the open time. Even though this method has evolved compared to the previous method, it still relies on observation as validation of the result, therefore the result it offers is just an estimation of the open time for adhesives instead of being accurate measurement that can be related to the fundamental material properties.

These methods provide a crude mean to evaluate and compare the open times of different adhesive materials; they are simple to perform and only require very few apparatus. However, these methods only provide a qualitative estimation, but proved to

be inadequate if a more quantitative analysis that requires accurate measurement such as to be used in formulation is needed. A standard test method for determining the open time of hot-melt adhesives was also derived designated as ASTM D4497-10. The adhesive is heated in a covered glass beaker in an oven, together with a film applicator, until the application temperature is reached. The beaker that contains molten adhesive is removed from the oven and the content is stirred with a metal thermometer to ensure that the molten adhesive is at application temperature. A big sheet of primary substrate is laid on a flat surface. Using the film applicator, the molten adhesive is applied evenly over the surface of the primary substrate. At this point, the timer is started and at 5-second intervals, a secondary substrate strip is laid down on the molten adhesive and a weighted block is used to apply pressure onto the joined area. This action is repeated until the adhesive completely solidifies. The adhesive is allowed to cool down at room temperature for 30-60 minutes before the testing process begins. Testing process involves performing a peel test of the secondary substrate strips. The percentage area of fiber tear for each strip is monitored and for cases where a minimum of 50% fiber tear is achieved, the time at which the strip was laid onto the cooling adhesive is recorded and used to calculate the mean open time. This is a much more sophisticated method that utilizes standardized test and numerical results and statistical mean to obtain the open time for an adhesive.

Probing deeper into the material properties of an adhesive, another approach to evaluate the open time was derived using the viscoelastic data obtained for that adhesive material (Bamborough, Nov 1990). The open time of a hot-melt may be described as

being related to flow and hardness. The hot-melt is considered open when it is capable of flow and can wet out a substrate. Upon cooling, a certain point will be reached when it has achieved certain hardness or viscosity together with cohesive strength, the hot-melt will then no longer be open. This critical point may be determined using viscoelastic parameters. The storage modulus G' describes the hardness and flexibility of the adhesive while tan δ which is defined as the ratio between viscous (G") and elastic (G') contributions of the modulus is a measure of the cohesive strength of the hot-melt adhesive (Bamborough, Nov 1990). A low value of tan δ indicates better cohesive strength of the adhesive but also less flexibility. The critical point at which the adhesive is considered not open is when G' becomes dominant and tan δ reaches 1 upon cooling, or rather it is the cross-over point between G" and G'. Up to this point in the hot-melt cooling curve, the adhesive may be considered as being open. This method provides open time as a temperature value instead of a time value. However, if the cooling rate is known, the open time can be determined in time unit. This method, while being theoretically accurate, lacks the actual physical support. Adhesive performance is influenced by many factors among which some are not material property related, thus cannot be accounted for using only theoretical study and data. For that reason, an ideal approach to evaluate open time of an adhesive should be one that combines the use of material properties relate to physical data that reflects the real situation.

The viscoelastic data (G' and G") is used widely, especially in the field of Pressure Sensitive Adhesive, to predict performance for resin development and for quality

control since the dynamic modulus measurements provide insight into adhesive bond performance (Macosko, 1997). DMA is the most suitable method used to evaluate the solid properties of adhesive material, and adhesive toughness has been quantitatively related to the size of the G" peak in some polymers (Macosko, 1997). The data from DA also reflects the structure-property relationships of polymeric materials. Once adhesive performance can be related back to the DA data, it is possible to manipulate the structure-property characteristics of an adhesive through formulation, using DA measurements as a guide to achieve the desired performance with the reinforcement of the thermal behaviour (Bamborough, 1990). Therefore it is important to study the relationship between adhesive performance and the DA data.

Characteristic time, which reflects the time it takes for the adhesive polymer molecules to return to equilibrium after the polymer chains were relaxed during melting stage, can be determined from the DA data. By definition, this is a material related parameter that can be linked to the fundamental material properties in the flow regime. By establishing a relationship between this parameter and the adhesive performance, it is possible to relate the bond performance to the adhesive material properties.

This project will focus on studying the effect of adhesive material property and open time on the adhesive performance. For this purpose, the experiments will be designed in such a way that they will have consistent application parameters to enable probing of the impact of material properties on product performance. Different commercially available hot-melt adhesives will be used in the experiments to study the

relationship between adhesive performance and dynamic mechanical properties. The material properties of all adhesives will be characterized using DSC and DA, and open time for each adhesive will be evaluated from the DA results. The time-temperature effect on the adhesive performance by varying the application temperature as well as prolonging the available bond-formation time will also be examined. This study will try to relate the adhesive performance to the adhesive material properties. Once a relationship between the adhesive performance and the measureable material properties can be established, it is possible the performance of an adhesive can be modified by changing the material properties through different formulations.

Material and Methodology

Three commercial hot-melt adhesives from the Thermogrip line from Bostik were evaluated. The three materials have different softening/melting ranges according to the manufacturer (Table 1). The manufacturer also indicated that these three materials have different open time as indicated. The materials were purchased as ½" glue sticks. All experiments were completed within the shelf-life time frame and storage conditions as indicated on the material packaging.

Adhesive	Polymer base	Open time	Softening range (ASTM E28)	Melting range
Thermogrip 6330	EVA	Long	67^oC-80^oC	-
Thermogrip 6368	PE	Short	-	99^oC-107^oC
Thermogrip 6390	EVA	Medium	78^oC-88^oC	-

Table 1. Properties of Adhesives evaluated as supplied by manufacturer

Thermal property by Differential Scanning Calorimetry:

Differential Scanning Calorimetry (DSC) was used to assess the thermal characteristics of the adhesives. The experiments were performed on a TA Q200 DSC using standard Aluminum pans and lids. The cell environment is purged with nitrogen.

The testing specimen was exposed to a heating-cooling-heating treatment cycle at a rate of 10^oC/min, and the heat flow was monitored as temperature changed. The first heating treatment removed the material's processing history; recrystallization and melting temperatures were evaluated from the heat flow signals observed during the cooling and second heating cycle respectively.

Viscoelastic property by Dynamic Analysis:

The viscoelastic behaviour of the molten adhesives was studied using Dynamic Analysis (DA). A parallel-plate rheometer, Rheometric Scientific ARES, was used for these experiments.

For each material, adhesive had to be made into a round disk with a diameter similar to that of the plates used for testing. This was done in a small hand-operated hotpress with controlled temperature using an Aluminum mold prepared specially for each plate size. The two parameters that are measured by the machine are torque and phase angle. Depending on the viscosity of each material, the torque signal transmitted would be either too low that it fell out of the allowable limit; or too high that it overloaded the transducer of the machine; therefore the plate geometry has to be changed for each adhesive material in order to get good signal – meaning the signal received would have to stay within the sensitivity limit of the machine to guarantee that the signal was "true". It was found that Thermogrip 6330 and 6390 had good signal when tested on 12mm plates and 6368 had good signal on 25mm plates.

Special care was paid to the loading sample procedure to ensure that the material was in total relaxed state prior to the actual test as well as to prevent slipping problems- that the adhesive disk had adhered onto the Aluminum testing surface. A sinusoidal oscillation was applied to the material placed in between the parallel plates while the material went through a heating-cooling treatment. In this Dynamic analysis, adhesive materials were introduced to a heating/cooling cycle at a controlled rate of 10°C/min so that the results obtained would be at a comparable heating rate from DSC.

Table 2. Testing parameters for Dynamic Analysis with T_H as target temperature for the heating cycle, and T_C as target temperature for the cooling cycle

Material	Strain (%)	Frequency (rad/s)	Start temp. (°C)	T_H (°C)	T_C (°C)
Thermogrip 6330	2.5-15	1	40	80	30
Thermogrip 6368	2.5-15	1	50	110	40
Thermogrip 6390	2.5-15	1	40	100	35

Table 2 showed the testing parameters for the DA for each material. Prior to the dynamic mechanical test, Strain Sweep for each material were conducted to determine the appropriate strain needed where adhesive materials are in linear viscoelastic region for the dynamic mechanical test. The Strain Sweep was also conducted at different frequency to evaluate the advantage of running the test at higher frequency in hope to obtain better signal at lower strain [refer to Appendix A]. However, it was shown that at different frequency, the viscoelastic region for each material was characterized by similar strain values. Therefore, a standard frequency of 1 rad/s was used for all experiments conducted.

The thermal profiles obtained from DSC results which provided the melting temperature range and recrystallization temperature range for each material were used to construct the temperature parameters for the DA. These temperature parameters include the starting temperature, the target temperature T_H for the heating cycle at which material starts to go through a state transition to adopt liquid-like behaviour, and the target

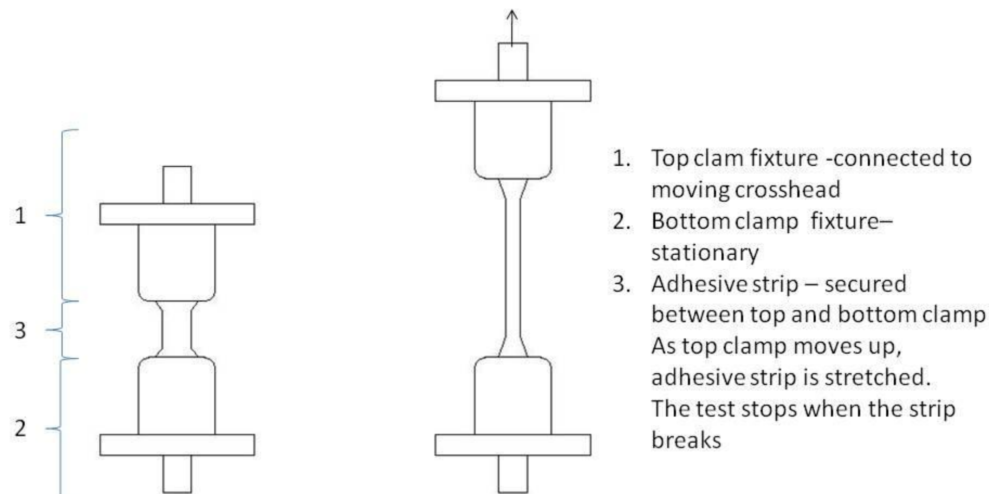
temperature T_C for the cooling cycle at which material starts to transform back to solid state. T_H was chosen within the melting temperature range and T_C was chosen within the recrystallization temperature range of each materials.

Upon heating, hot-melt adhesives changed from solid state to liquid state, and the temperature at which adhesives started to assume liquid-like behavior was observed as a cross-over point of the storage and loss modulus. Similarly, the temperature at which adhesives start to assume solid-like behavior upon cooling is characterized by a similar cross-over point.

Mechanical property through tensile tests:

Adhesive mechanical properties were characterized using tensile tests according to ASTM standard D-638. Test specimens were prepared at elevated temperature for all three materials by compression molding the adhesive material into dumbbell shape.

Testing was done at room temperature on a TA Instron Series IX/s with a 500N load cell at 3.5 mm/min crosshead speed for all samples. For each adhesive material, an average of all tested samples was taken as the recorded result. The mechanical property testing set up can be seen in Scheme 1.



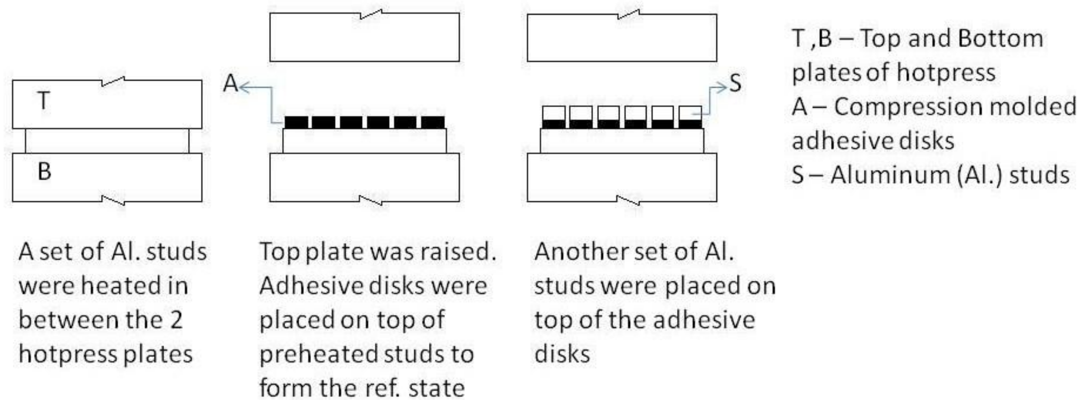
Scheme 1. Mechanical property testing set up

Adhesive performance through pull-off tests:

The adhesive properties of the materials were studied through pull-off tests. The testing procedure developed in this project was implemented to follow ASTM D 4541-02. The objective of this test was to evaluate the bond between adhesive material and Aluminum substrate under different conditions. Aluminum was chosen for its convenience in practice. Aluminum is a metal that can be easily obtained and processed. Moreover, using Aluminum substrate would provide consistency among the test results, since Aluminum was also used for the parallel plates used in DMA, as well as the pans and lids used in DSC.

Test specimen preparation: [refer to Scheme 2]

The adhesive materials were compression molded into 12.5mm diameter round disks with thickness of 2mm for around 2 minutes at 140°C for Thermogrip 6368, 120°C for Thermogrip 6390 and 100°C for Thermogrip 6330 respectively.



Scheme 2. Specimen preparation for pull-off test

Aluminum studs with a diameter of 12.5mm were preheated in a temperature controlled environment until targeted temperature – which was chosen to be 20°C above the melting temperature of each material was reached (140°C for Thermogrip 6368, 120°C for Thermogrip 6390 and 100°C for Thermogrip 6330). At such high temperatures, the materials can flow freely hence can be easily molded into any desirable shape; moreover, all processing history of the materials will be erased so that all the test results obtained will only reflect the heat treatment that each sample goes through during the sample preparation process. Adhesive disks were then quickly placed on these studs. Studs with adhesive were allowed to stay at that elevated temperature for 10 minutes

before being removed from all heat sources and allowed to cool down to room temperature. These studs were marked as the reference state. Aluminum studs were preheated in a temperature controlled environment until targeted temperature was reached. Adhesive disks were then quickly placed on these studs. Studs with adhesive were allowed to stay at that elevated temperature for different time periods before being removed from all heat sources and allowed to cool down to room temperature.

While waiting for the set of reference studs to cool down, a new set of Aluminum studs were preheated in a temperature controlled environment until targeted temperature was reached. The reference studs were then quickly placed up side down on these new studs, so that the adhesive disk would be in between 2 Aluminum studs. These samples were allowed to stay at that elevated temperature for different time periods [refer to Table 3] before being removed from all heat sources and allowed to cool down to room temperature. At this point, the specimen preparation was completed.

It should be noted that the time during which samples were allowed to stay at elevated temperature will also be referred to as the allowed bond-formation time, or conditioned open time.

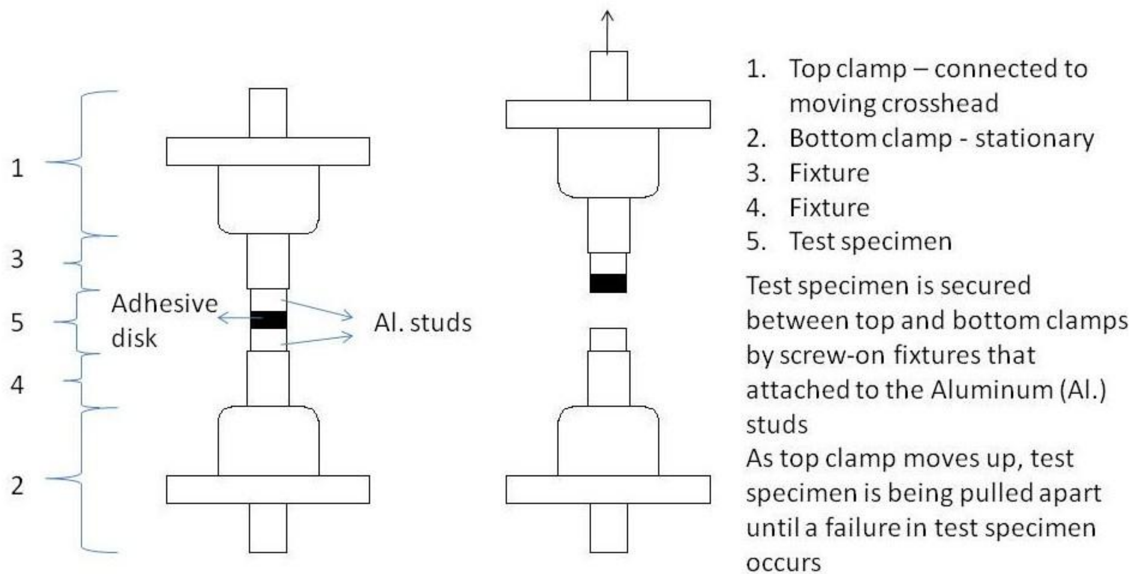
Table 3. List of experiments conducted to evaluate adhesive properties for three materials

	70°C	80°C	90°C	100°C	110°C	120°C
Thermogrip 6330	1,3,5 mins	1,3,5 mins	1,3,5 mins			
Thermogrip 6368				1,3,5 mins	1,3,5 mins	1,3,5 mins
Thermogrip 6390		1,3,5 mins	1,3,5 mins	1,3,5 mins		

Test procedure:

Testing was done on a TA Instron Series IX/s with a 500N load cell at 3.5 mm/min crosshead speed at room temperature for all samples. Each end of the sample specimen would be attached to the Instron sample clamp through an extension [refer to Scheme 3].

The force required to break the samples as well as the extension at failure of samples was monitored and recorded. From here, the apparent stress and strain, and other mechanical properties for the adhesive samples could be calculated.



Scheme 3. Adhesive perforamnce testing set up

Result and Discussion

Through DSC, the adhesive samples were exposed to a heating/cooling/heating cycle, and the corresponding heat flow in response to the change in temperature was monitored and presented in Figure 1 below.

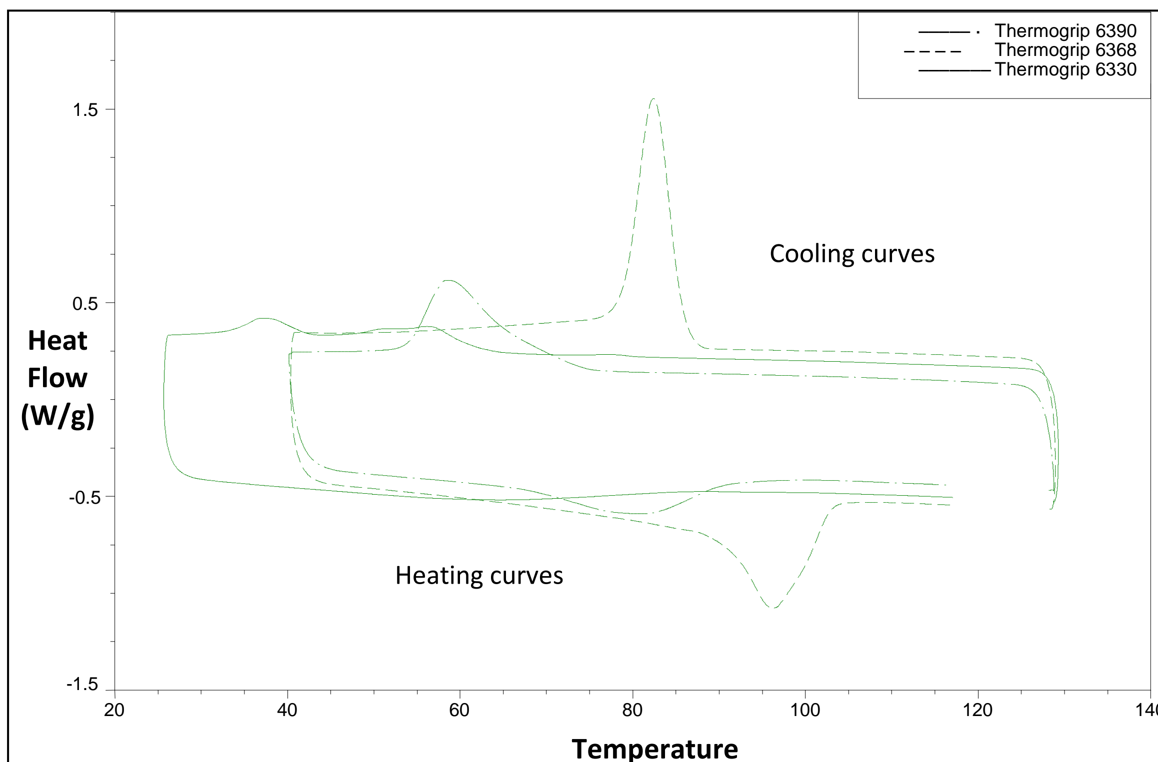


Figure 1. Heat flow vs. temperature curve for 3 materials: Thermogrip 6330, 6368 and 6390 obtained through DSC, with heating/cooling rate of 10°C/min

The peaks observed on the heating curve corresponded to the melting event, while the peaks observed on the cooling curve corresponded to the recrystallization event. It can be seen that all three materials had different thermal behaviours from each other. The

melting endotherms and the recrystallization exotherms happened over different temperature spans for all three materials. Thermogrip 6368 gave sharp peaks on both heating/cooling curves, indicating that the thermal events occurred in a short temperature span, as opposed to material Thermogrip 6339 and 6390 which had broader peaks. In particular, Thermogrip 6330 gave shallow and broad peaks on both heating/cooling curves, indicating that the thermal events occurred in a long temperature span compared to the other materials. It seemed that under the same heating/cooling rate of 10°C/min, the thermal transformation of Thermogrip 6330 material happened gradually while Thermogrip 6390 and 6368 underwent the state transformation at a faster pace. It should also be noted that the width and height of the peaks observed from the heat flow curves of the three materials seemed to reflect the open time range suggested for each adhesive by the supplier: Thermogrip 6368 was deemed to have short open time, thus the sharp and tall peaks; Thermogrip 6330 gave the broadest and most shallow peaks, and this material is supposed to have long open time. Thermogrip 6390 is supposed to have medium open time, which reflected in the medium peaks' width and height as can be seen from Figure 1. The difference in intensity of the peaks suggested that the amount of crystalline material presented in the three samples were not the same.

The enthalpy (ΔH) for each thermal event was calculated and presented in Table 4. The energy associated with the melting event for each material was noted as ΔH_{melt} while the energy associated with the recrystallization event for each material was noted as $\Delta H_{recrystal.}$ For all material, there was a slight difference between the enthalpy associated

with melting and recrystallization; however they remained within the same magnitude compared to the other two materials.

Material	ΔH_{melt} (J/g)	$\Delta H_{recrystal.}$ (J/g)
Thermogrip 6330	11.44	12.32
Thermogrip 6368	42.42	39.19
Thermogrip 6390	21.67	22.0

Table 4. Enthalpy for peaks observed for Thermogrip 6330, 6368, and 6390 from DSC data

Thermogrip 6330 had the lowest ΔH_{melt} among the three materials, indicating that less crystalline material was present per weight of sample compared to that of Thermogrip 6368 and 6390. The lower energy associated with the melting event was also spread out over a broad temperature range. This result implies that different populations of crystals with different melting temperatures are undergoing the melting transformation over a wide temperature range.

The same analogy could be applied for Thermogrip 6368 and 6390. Thermogrip 6368 had the highest ΔH_{melt} and $\Delta H_{recrystal,}$ indicating that more crystalline material was present per weight of sample compared to that of other materials. The higher energy associated with the melting event was spread out over a narrow temperature range implying that a large portion of the adhesive matrix underwent the melting transformation and recrystallization transformation in a short time frame resulting in, if possible, a small window where the adhesive matrix as a whole would behave like a liquid and forming a bond with the substrate.

Thermogrip 6390 had a moderate ΔH_{melt} and $\Delta H_{recrystal.}$ compared to Thermogrip 6330 and 6368, and the temperature range over which the thermal transitions occurred was also in between that of the other two materials indicating that a moderate amount of crystalline material was present in the sample that underwent the melting and recrystallization transformation.

However, it is impossible to draw a conclusion from this data whether the adhesive matrix as a whole would behave as a liquid that is capable of wetting out a substrate to which the material is applied. It is necessary to examine the flow properties of the adhesive materials.

The result of the Dynamic Analysis performed on material Thermogrip 6330 at specified conditions was shown in Figure 2 below. The viscoelastic properties of the adhesive material were characterized using the storage modulus G' which is a measure of the energy stored elastically during material deformation, and the loss modulus G" which is a measure of the energy dissipated in flow during material deformation (Ferry, 1980). As the temperature increases, the adhesive starts to flow and exhibit liquid-like behaviour, G" starts to dominate G'. This was the first cross-over point observed on the heating curve ($T_{X\text{-}H}$), which is also called the heating cross-over point. Upon cooling, the material becomes more solid-like and G' starts to dominate G" which is the second cross-over observed on the cooling curve ($T_{X\text{-}C}$), also known as the cooling cross-over point. The cross-over points for the storage and loss modulus are of real interest in this experiment,

since they represent the change in material property between liquid-like behaviour and solid-like behaviour and characterize when the adhesive is able to wet a substrate.

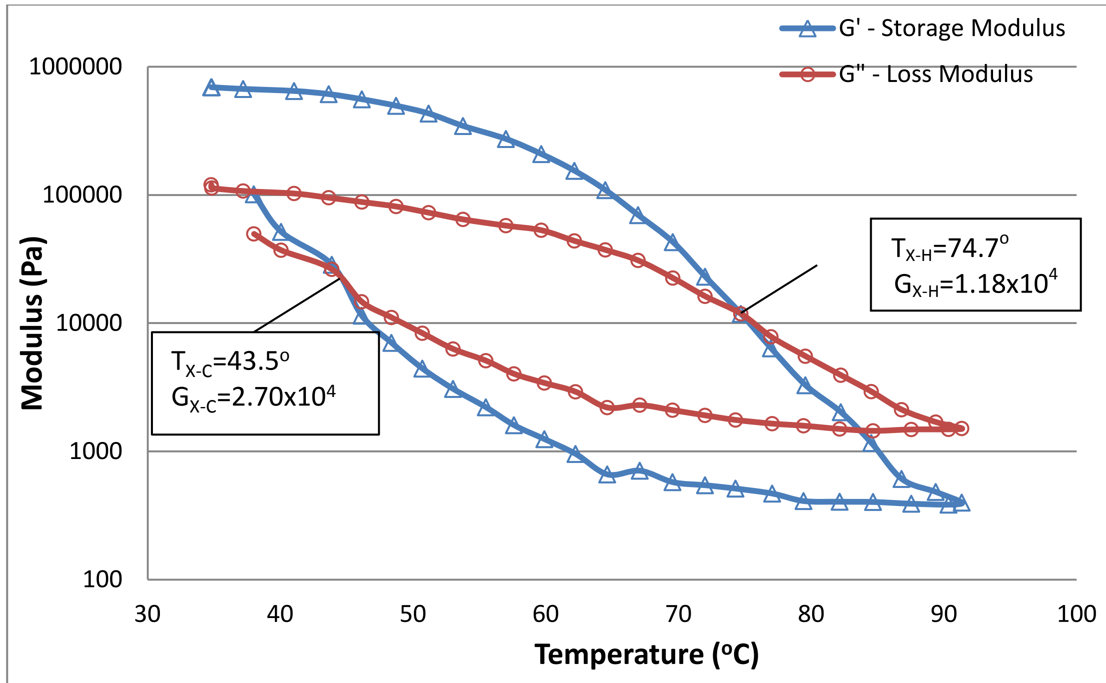


Figure 2. Dynamic Analysis hysteresis loop for Thermogrip 6330 at 1.0% strain, 1 rad/sec frequency, and with a heating/cooling rate of 10°C/min

When the test started, the adhesive sample was at solid state behaviour. The first cross-over point happened at 74.7°C signifying that the material started to exhibit liquid-like behaviour since G" started to dominate G' as can be seen in Figure 2. In this state, the hot melt adhesive is ready to wet the substrate that would be bonded. The second cross-over point happened on the cooling curve at 43.5°C. Moving on to this state, the material was cooled down, thus given the polymer chains in the material an opportunity to start recrystallizing and resuming their structure and solid-like behaviour. During the transition

of material in between these two crossover points, the material sample was in the liquid state - in other words, material could flow- which allowed the material to re-arrange its structure and bond with the substrate surface.

The first cross-over point (T_{X-H}) obtained from the DA data laid toward the end of the peak on the heating curve in the DSC data rather than being at the front of the peak. From this observation, it can be suggested that when temperature reaches the peak of the heating curve, the majority of the sample has melted; however, a complete melting state where the material starts assuming liquid-like behaviour can only be achieved at higher temperature such as T_{X-H} or above.

DA for materials Thermogrip 6368 and 6390 were conducted under similar conditions as Thermogrip 6330 and can be found in Appendix B. The hysteresis loops obtained for these two materials also exhibited similar behaviour to that of Thermogrip 6330 as shown in Figure 2. For Thermogrip 6368, the first cross-over point happened at 109°C, a temperature which located toward the end of the peak on the heating curve in the DSC data; and the second cross-over point happened on the cooling curve at 74.3^{o}C. For Thermogrip 6390, the first cross-over point happened at 93°C, the temperature that corresponded to the end of the peak on the heating curve in the DSC data, with a second cross-over point happened at 57°C. A summary of the cross-over points for all three materials were presented in Table 5 below.

Material	Heating G'/G" cross-over		Cooling G'/G" cross-over		ΔT
	T_{X-H} (°C)	G_{X-H} (Pa)	T_{X-C} (°C)	G_{X-C} (Pa)	(°C)
Thermogrip 6330	74.7	1.18E+04	43.5	2.70E+04	31.2
Thermogrip 6368	109	2.46E+03	74.3	1.91E+04	34.7
Thermogrip 6390	93.0	3.55E+03	57.0	6.09E+03	36

Table 5. Summary of Dynamic Analysis for Thermogrip 6330.6368. and 6390

The temperature difference (ΔT) between the two cross-over points can be used to calculate the open time for each material assuming a constant heating/cooling rate of 10°C/min. In that case, all three materials should have a theoretical open time of around 3 minutes. However, in the real world application of adhesives, the cooling rate of an adhesive application would be varied due to external factors such as environment. Moreover, cooling rate is not a constant parameter; while being exposed to ambient air the molten adhesive will cool down at a different rate compared to when it has come into contact with the substrate surface, and it also varies for different types of substrate due to the different heat transfer coefficient for each material. Therefore, the open time referred to in these experiments only serve as a benchmark for characterizing adhesive performance.

Looking at the data from Table 5, it should be noted that the modulus G_{X-H}, which represents both G' and G" at the heating cross-over point, for all three materials are different from one another. And since G" is a function of the viscosity η' and the frequency ω:

$$G'' = \frac{\eta'}{\omega} \qquad \text{(Ferry, 1980)}$$

with frequency ω being constant for all tests, G" then reflected the viscosity η' of the material. During the course of the test, the value for G" changed as can be seen in Figure 2, indicating that the mobility of molecules to orient to the substrate was not the same at all times. The difference in the viscosity of the materials influence its ability to flow out to wet the substrate, hence resulted in different open times for the three materials, even though they should have had similar open time value based on the ΔT obtained from Table 5, with heating/cooling rate being controlled and similar for all cases. From the G_{X-H} for the three materials, it was clear that Thermogrip 6330 would need to be maintained at an elevated temperature for a longer period of time in order to achieve wetting. The high viscosity in the adhesive's molten state reduces the rate at which molecules can conform to the substrate, requiring a longer time for the material to fully wet the substrate and form a bond. Respectively, Thermogrip 6390 material would need medium period of time to achieve wetting; and Thermogrip 6368 material would only need a short time period to achieve wetting due to the low viscosity in its molten state.

Moreover, there was a difference in the modulus G_{X-H} and G_{X-C} for all materials. This happened due to the difference between the kinetics of melting and recrystallization of material molecules. In the event of melting, as temperature heats up, the polymer network starts to relax, and molecules start to slide past each other in a random fashion, which explains the flow-ability of the material in its molten state. However, in the event

of recrystallization, molecules have to orient themselves in a certain way in order to form the crystal structure; the G_{X-C} values from Table 5 are higher compare to G_{X-H} which supports the fact that as the material starts to recrystallize and takes up more solid-like behaviour, its viscosity will be higher than when the material is in its liquid-like state.

The partial enthalpy of fusion from DSC data for the materials marked by temperature T_{X-H} and T_{X-C} were calculated and presented in Table 6.

Material	ΔH_{melt} (J/g)	ΔH_{melt} at T_{X-H} (J/g)	%	$\Delta H_{recrystal.}$ (J/g)	$\Delta H_{recrystal.}$ at T_{X-C} (J/g)	%
Thermogrip 6330	11.44	5.581	48.8	12.32	4.663	37.8
Thermogrip 6368	42.59	42.64	100.0	44.56	29.17	65.5
Thermogrip 6390	21.67	19.32	89.1	22.0	7.864	35.7

Table 6. Enthalpies for the peaks observed from DSC data for Thermogrip 6330, 6368, and 6390 and the percentage of melted sample at the cross-over point T_{X-H} and T_{X-C}

It is clear that each material entered a different stage of their melting transition corresponding to their respective T_{X-H}. For Thermogrip 6330, at the heating cross-over point, only about 50% of the material sample has melted, while for Thermogrip 6368, all the sample has been melted at the heating cross-over point, thus showed that there was no basis for calculating and comparing the open time for the three materials using DSC data alone. The DSC data was not sufficient in order to characterize the material flow property which was essential in determining the open time for an adhesive material. Therefore it is

impossible to evaluate the open time for the adhesive material with only the DSC data; the use of DA is necessary.

The pull-off tests on all adhesive materials were carried out in order to examine how the adhesive material behave on Aluminum substrate under varied application conditions (temperature, time- refer to Table 3), consequently varying the open time. The hypothesis suggested for this study was that at higher temperature, or given longer time at a temperature, the bond formed between adhesive and the substrate would be stronger, therefore the force required to break this bond would be higher. The experiments in this study were also designed to provide some indications for the time-temperature trade-off in bond formation between adhesive and substrate, to see whether samples that were prepared at higher temperature for a short time period would have the same bond strength as samples that were prepared at lower temperature for a longer time period.

After Aluminum substrates were preheated to achieved the target temperature (that was referred to in the results), the adhesive disks were placed onto the substrate and allowed to stay there for a period of time in order to form a bond with the substrates before they were removed from all heat sources and allowed to cool down to room temperature. The 3 temperatures were chosen with reference to $T_{X-H;}$ one temperature to be around the melting region of the material – around T_{X-H}, one temperature well above T_{X-H} and one temperature below T_{X-H}.

The pull-off tests were carried out, and the maximum stress required to break the bond formed between the adhesive and the substrate were recorded against the sample preparation conditions and presented in Figure 3.

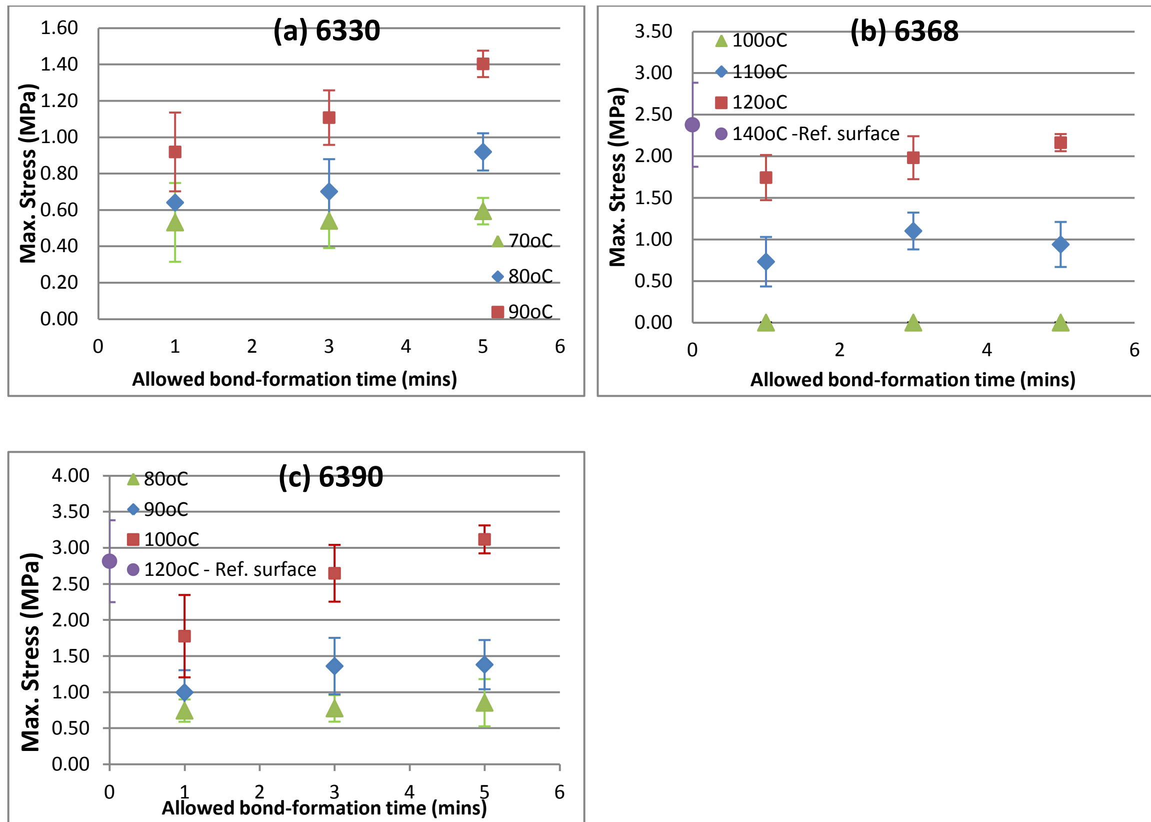


Figure 3. Pull-off test result for Thermogrip materials (a) 6330 (b) 6368 (c) 6390, with a crosshead speed of 3.5mm/min and load cell of 500N

All Thermogrip 6330 samples failed adhesively at the testing surface. At 70°C, which is about 5°C below the heating cross-over point for this material, the bond strength was inferior to that formed at higher temperatures, reflected in the low stress required to break the bond compared to that formed at higher temperatures as shown in Figure 3a. At

temperatures below the heating cross-over point, the adhesive was not expected to adhere properly onto the substrate surface since the material still did not assume liquid-like behaviour as can be seen by the characteristic G' and G" from the DA data. By increasing the time the adhesive was allowed to stay in contact with the heated substrate surface did not help much in improving the adhesion, resulting in the similar stress required to break the bond formed between the adhesive and the substrate for all samples prepared at 70°C. At 80°C, which is about 5°C above the heating cross-over point, the material had assumed liquid-like behaviour. By increasing the time the adhesive was allowed to stay in contact with the heated substrate surface, the adhesion was improved - slightly at first as can be seen by a small change in the magnitude of the stress required between 1-min and 3-min samples; and the change became larger as the time allowed increased to 5 minutes . At 90°C, which is about 15°C above the heating cross-over point for this material, the bond formed between the adhesive and the substrate were stronger than that of the bond formed at lower temperatures reflected by the higher stress required to break them as shown in Figure 3a. The adhesion was greatly improved by increasing the time the adhesive was allowed to stay in contact with the heated substrate surface based on the large increase in magnitude of the stress required with respect to time for samples at 90°C. By letting the adhesive bond to the substrate at such high temperature, the material was given more time to wet and adhere onto the substrate surface thus resulting in better adhesion.

It could be seen that the time-temperature trade-off phenomenon occurred in this set of data. Within the standard deviation limits, it could be said that the stress required to break the bond formed at 80°C-1min was similar to that at 70°C-5min, or the strength of

the bond formed at those conditions were similar. This was also the case for 90°C-1min and 80°C-5min conditions. These data demonstrated that the same bond strength created at a high temperature for a short time period could be achieved by lowering the temperature and increasing the time period allowed for the adhesive and the substrate to stay in contact.

The pull-off test results for Thermogrip 6368 were presented in Figure 3b, and all samples failed adhesively. At 100°C, which is 9°C below the heating cross-over point for this material, all samples broke as soon as a very small stress was applied, indicating that the adhesive did not adhere onto the substrate surface at this temperature, regardless of the time it was allowed to stay in contact with the heated substrate. At 110°C which is about the same as the heating cross-over temperature of this material, the adhesive adhered better to the substrate indicated by the higher magnitude in the stress required to break the bond formed. By increasing the time the adhesive was allowed to stay in contact with the heated substrate, the bond strength seemed to increase – greatly at first as indicated by the large change in the magnitude of the stress required for 1-minute and 3-minute samples; but the change came to a an invariant point as could be seen by the similar value for the stress required between 3-minute and 5-minute samples, within standard deviation limits. At 120°C, which is about 11°C above the heating cross-over point for this material, the bond created had much greater strength compared to bonds formed at lower temperature as could be seen by the higher magnitude of the stress required to break the bond from Figure 3b. The bond strength continued to increase as the

adhesive was allowed to stay in contact with the heated substrate for a longer time period reflecting in the increasing values for the maximum stress required with respect to time at this temperature.

It should be noted that for samples prepared at the 120°C-5minute condition, the specimens simultaneously failed at both the testing and reference surface, indicating that the maximum bond strength has been achieved at the stated condition, therefore it would be similar to the bond created at the reference condition, which was 140°C-10minute. Once the maximum bond has been achieved, it became independent on time and temperature. There was also no evidence to support the time-temperature trade-off phenomenon in this data set.

The pull-off test results for Thermogrip 6390 could be seen in Figure 3c, and all samples also failed adhesively as the case of Thermogrip 6330 and 6368. At 80°C, which is 13°C below the heating cross-over point for this material, the bond formed between the adhesive and substrate were weaker, indicating by the low stress required compared to that at higher temperatures. No change in the bond strength could be observed even when the time that the adhesive was allowed to stay in contact with the heated substrate was increased, resulting in similar stress required value for all samples prepared at this temperature. At 90°C, which is 3°C below the cross-over temperature, the adhesion of the material onto the substrate improved as could be seen by the higher magnitude of the stress required. As similar to the case of Thermogrip 6368 material at its heating cross-over temperature, increasing the time that the adhesive and the heated substrates were

allowed to stay connected helped to improve the bond strength created at first, but then the change became invariant, as reflected in the similar stress required value for 3-minute and 5-minute samples at this temperature. At 100°C, which is 7°C above the heating cross-over temperature for this material, the bond strength has increased greatly compared to that formed at lower temperatures based on the much higher stress required to break the bond showed in Figure 3c. Compared to the samples prepared at lower temperatures, the adhesive material fully assumed liquid-like behaviour at this temperature, and this influenced the adhesion of the material onto the substrate. By increasing the time that the adhesive and the substrate stayed connected, the adhesion improved greatly as shown by the large change in the magnitude of the stress required with respect to time.

The time-temperature trade-off could only be seen in the case of samples prepared at 90°C-1minute and 80°C-5minute indicating that the strength of the bonds created at these condition were similar. It should also be noted that for samples prepared at 100°C-5minute, the specimens simultaneously broke at the testing and reference surface indicating that the maximum bond strength has been achieved at this condition, and it rivalled the bond strength created at the reference condition which is 120°C-10minute.

Between the three materials, Thermogrip 6390 seemed to have the best performance; the maximum bond strength achieved required a stress magnitude of around 3.20 MPa to break it, while for Thermogrip 6368, a stress magnitude of around 2.20 MPa was required to break the maximum bond strength achieved, and for Thermogrip 6330, a stress magnitude of around 1.40 MPa was required. In general, the majority of the data

obtained supported the proposed hypothesis that at higher temperature, or given longer time at a temperature, the bond formed between adhesive and the substrate would be stronger, therefore the force required to break this bond would be higher. It seemed that when the material was forced to be "open" for a longer time period, better adhesion could be achieved between the adhesive and the substrate.

It should be noted that the result obtained from the pull-off test is both influenced by the adhesive property of the material as well the mechanical property. Even though all pull-off samples failed adhesively, the result might still be affected by the change in mechanical property of the adhesive material when being exposed to different thermal treatments. In order to validate the pull-off results obtained with respect to the adhesive property of the material, we need to observe how the material property of the adhesive changes after undergoing different thermal treatments. To verify the change in material property, or more specifically, the change in crystallinity, DSC test was done for samples that were compression molded at different temperature/time (refer to Table 3) and the results are shown in Figure 4.

The heat flow versus temperature curves for different Thermogrip 6330 samples were presented in Figure 4. The curves shown in the above figure all had similar shape; however, there were small differences between samples prepared at different temperatures.

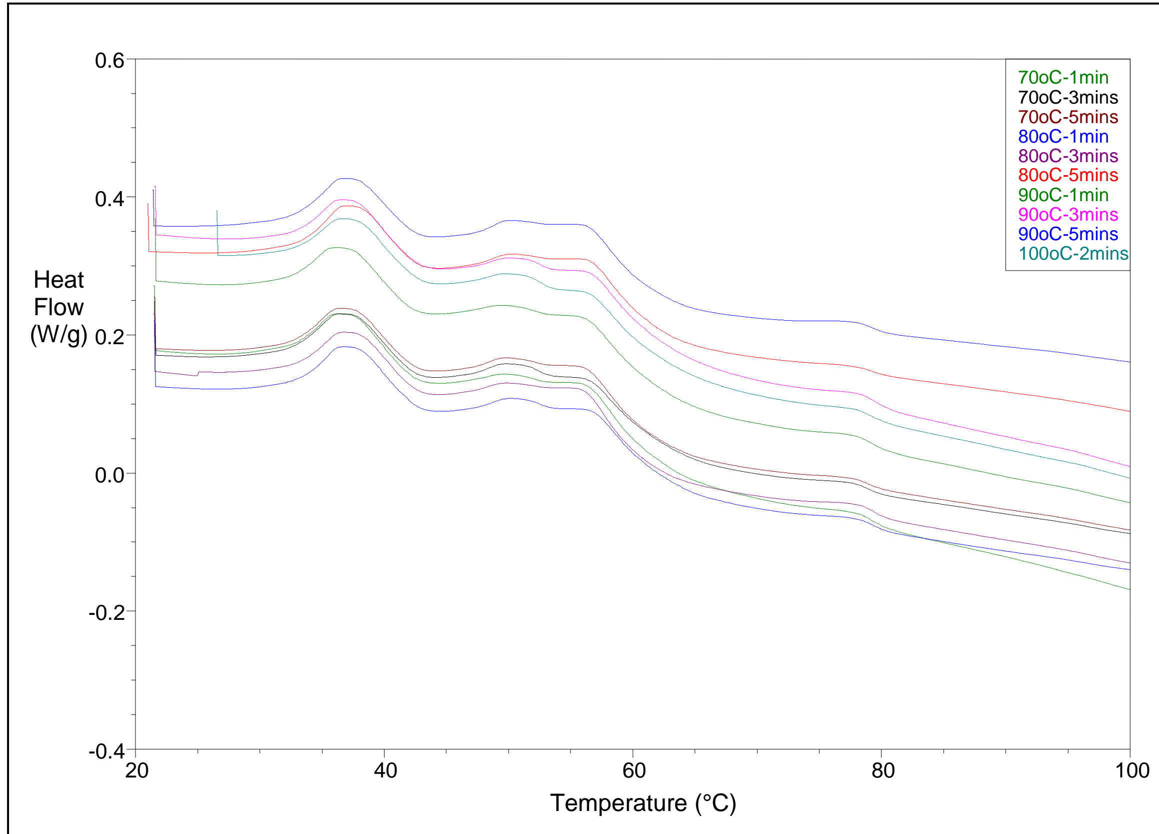


Figure 4. DSC results for Thermogrip 6330 samples compression molded at different temperature/time conditions

It could be seen that the curves for samples at 70°C-1minute and 70°C-3minute had the same shape, while sample at 70°C-5minute had the same shape with all samples at 80°C; and all samples at 90°C had the same shape. Even though there was a change in the shape of the curves, the change was small enough to be negligible. It could be seen that there was a difference in the heat flow magnitude for all the samples, and this was a result of the difference in the thermal diffusion due to varied sample thickness. The same tests were carried out for Thermogrip 6368 and 6390 and the results obtained were similar to that of Thermogrip 6330 [refer to Appendix C]. Since there was only a slight difference in

the shape of curve and the peak height, the curves could be considered to be the same. This implied that the material property of the adhesive sample stayed the same after experiencing different thermal treatments.

In order to verify the argument made above, the mechanical property for samples that underwent different thermal treatment similar to that performed in the previous DSC test would be examined. Dumbbell shape samples were prepared at the conditions indicated in Table 3, and tensile tests were carried out with their results shown in Figure 5 below for the three materials.

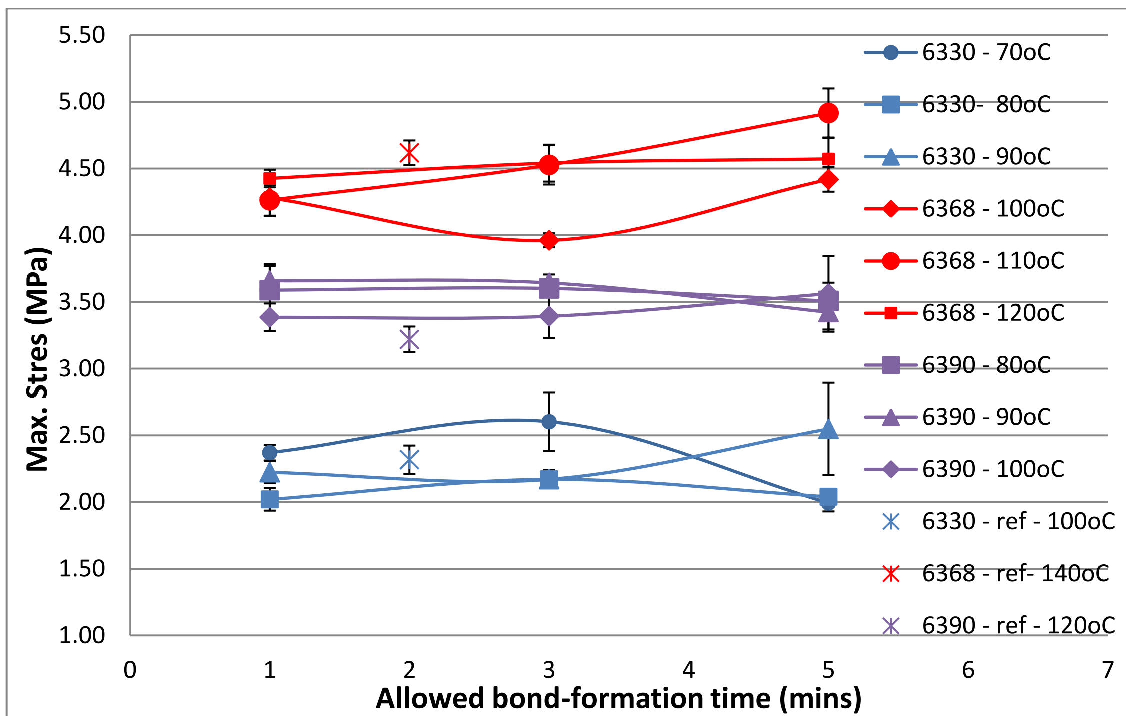


Figure 5. Tensile results for Thermogrip 6330, 6368, and 6390 samples that were prepared at different temperature/time conditions

The result for samples at 100°C-2minute was the reference for all other Thermogrip 6330 samples. While all samples at 80°C had similar maximum stress required, there was a slight decrease for samples at 70°C as opposed to a slight increase for samples at 90°C. However the magnitude of the difference in the stress required for this tensile test was small compared to that observed from the pull-off test of the same material under similar test conditions. Within the standard deviation limits, the maximum stress required for all samples were deemed to be similar and close to the result for the reference samples.

The result for samples at 140°C-2minute was the reference for all other Thermogrip 6368 samples. All samples at 110°C and 120°C seemed to yield similar maximum stress while there was a slight difference for samples at 100°C. Within the standard deviation limits, it seemed that most samples had similar maximum stress required as the reference sample. It was clear that the trend observed in this tensile test was different than that observed in the pull-off test for the same material which show a clear increase in the stress required to break the samples in response to the increased sample preparation time. Moreover, the maximum stress required values in the two tests were at different magnitudes.

The result for samples at 120°C-2minute was the reference for all other Thermogrip 6390 samples. Within the standard deviation limits, it seems all samples at different compression molding time for Thermogrip 6390 had similar maximum stress

required. This result was much different compared to the pull-off test result for the same material.

It could be concluded that even though there was a small change in the mechanical strength of the materials that underwent different thermal treatments, the change was small with regard to the magnitude of the stress required; therefore in this scope of study, the mechanical strength of the materials could be considered to stay the same, which agreed with the DSC results. And the trends shown in these tensile results as well as the magnitude of the maximum stress required were different than that observed from the pull-off data for the same material, indicating that the pull-off results were independent of the result obtained from the tensile test. Hence, the pull-off results was the reflection of the adhesive-substrate bond strength , and was not influenced by the change in the mechanical property as materials underwent different thermal treatments.

Characteristic time τ, or relaxation time, is defined by the equation:

$$\tau = \frac{\eta'}{G^*} \quad \text{(Ferry, 1980)}$$

It is a measure of the time it takes for the adhesive polymer molecules to return to equilibrium after the chained were relaxed during melting stage. In other words, characteristic time reflects the time needed for the adhesive molecules to re-orient themselves after undergoing a deformation. It follows that if the conditioned open time – which is the same as the allowed bond-formation time- for the adhesive is less than the characteristic time for the material in similar condition, it means the adhesive does not

have enough time for its molecules to re-orient themselves to form a bond with the substrate surface, or that the adhesive will not adhere well to the substrate. In the case where the conditioned open time exceeds that of the characteristic time in similar condition, it is possible for the adhesive material to adhere to the substrate surface (Novikov, 2008).

Alternatively, characteristic time can also be expressed in term of:

$$tan\delta = 1/\omega\tau \quad \text{(Ferry, 1980)}$$

From the DMA data obtained for the three materials Thermogrip 6330, 6368 and 6390, the characteristic times τ corresponded to the running temperature were calculated using the equation above and the results are shown in Table 7-9. The Deborah number (De), which is a dimensionless parameter that reflects the "fluidity" of a material, can be expressed as the ratio between the response time of the material and the time scale of the process (Rudin, 1999), or in this case the ratio between the characteristic time and the conditioned open time for each material sample. The De values for all samples were also calculated and presented in Table 7-9 below.

Material	**6330**								
Temperature (^{o}C)	**70**			**80**			**90**		
Process. Time (min)	1	3	5	1	3	5	1	3	5
τ (s)	1.84	1.84	1.84	0.58	0.58	0.58	0.28	0.28	0.28
De	0.0307	0.0102	0.0061	0.0097	0.0032	0.0019	0.0047	0.0016	0.0009
Stress for pull-off test (MPa)	0.53	0.54	0.59	0.64	0.70	0.92	0.92	1.11	1.40

Table 7. Characteristic time and Deborah number for Thermogrip 6330

Material	6368					
Temperature (^{o}C)	100			110		
Process. Time (min)	1	3	5	1	3	5
τ (s)	5.99	5.99	5.99	0.54	0.54	0.54
De	0.0998	0.0333	0.0200	0.0090	0.0030	0.0018
Stress for pull-off test (MPa)	0	0	0	0.73	1.10	0.94

Table 8. Characteristic time and Deborah number for Thermogrip 6368

Material	6390								
Temperature (^{o}C)	80			90			100		
Process. Time (min)	1	3	5	1	3	5	1	3	5
τ (s)	4.42	4.42	4.42	2.12	2.12	2.12	0.23	0.23	0.23
De	0.0736	0.0245	0.0147	0.0354	0.0118	0.0071	0.0039	0.0013	0.0008
Stress for pull-off test (MPa)	0.75	0.78	0.86	1.00	1.28	1.38	1.78	2.65	3.12

Table 9. Characteristic time and Deborah number for Thermogrip 6390

It is important to remember that although these τ values are a measure of the relaxation time for the adhesive, it is not an absolute measurement of the material relaxation time. The relative behaviour of the materials with respect to this is interesting because this characteristic time can be directly related to the structure-property relationships for the materials via the Dynamic analysis.

As seen in Table 7, τ values for Thermogrip 6330 material varied from around 1.8 to 0.3 second as temperature increased from 70°C to 90°C. At each temperature, an increase in allowed bond-formation time results in a decrease in De values and an increase in the stress at pull-off. Since De reflects the "fluidity" of the material, a lower

De value signifies increasing flow-ability of the adhesive material which provides a chance for a good bond to form between adhesive material and the substrate. As a result, higher stress is needed to break the bond. This result is in agreement with the result obtained from the pull-off tets which suggested that stronger bond formed in correspond to an increase in allowed bond-formation time.

Table 8 showed the results for characteristic time τ for Thermogrip 6368 which ranged from around 6 to 0.5 second as temperature went from 100^oC to 110^oC. Similarly to the case of Thermogrip 6330, an increase in allowed bond-formation time resulted in a decrease in De as well as an increase in the stress at pull-off for samples at each running temperature, signifying a stronger bond was formed between adhesive and substrate as allowed bond-formation time and running temperature increased. Thermogrip 6368 exhibits the largest difference in τ values for two consecutive processing temperatures which reflects in the large difference in the stress required to break the samples prepared at these temperatures.

The magnitude of characteristic time τ for Thermogrip 6390 ranged from 4.5 to 0.2 second as can be seen in Table 9. Thermogrip 6390 also behaved in a similar manner to that of the other two materials. At each running temperature, other than the decreasingτ, an increase in allowed bond-formation time brought about a decrease in De as well as a large increase in the magnitude of the stress at pull-off.

The characteristic time τ was plotted against the slope of the maximum stress required vs. the allowed bond-formation time curve and shown in Figure 6. This plot can be viewed as a characteristic time versus running temperature plot for all adhesive material.

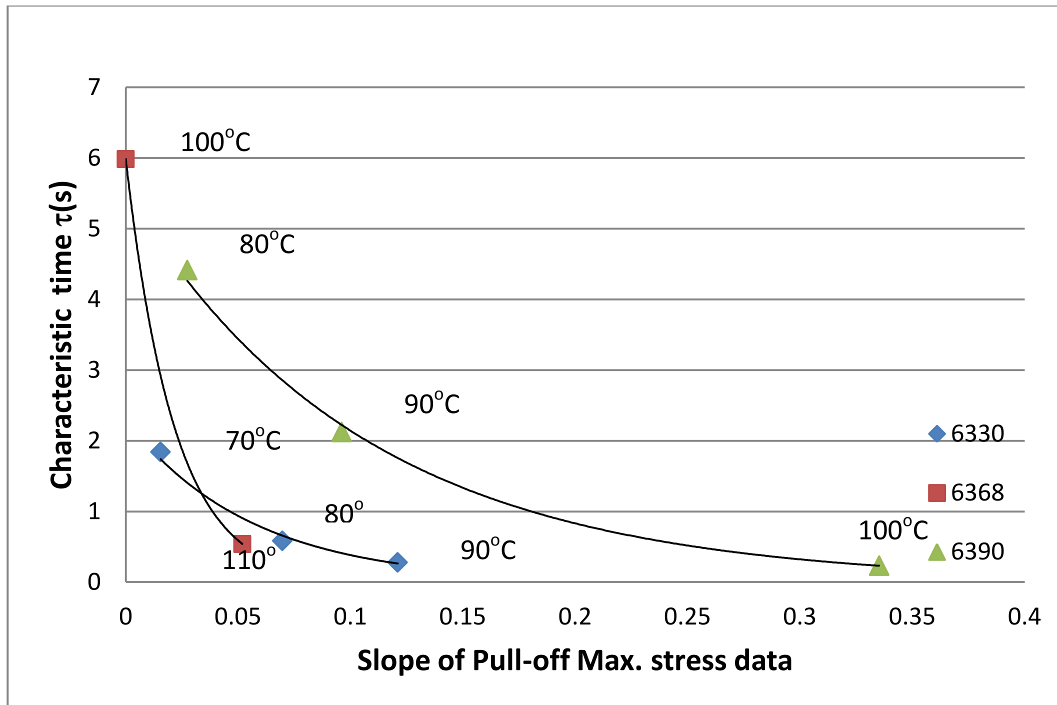


Figure 6. Characteristic time vs. slope of the [max. stress versus allowed bond-formation time] curve for all experiments of 3 materials

As can be seen in Figure 6, there is a negative relationship between the characteristic time τ and the slope of the pull off stress development time curve, as well as a negative relationship between τ and the running temperature. As running temperature increased, the value for τ decreased while the slope for the maximum stress required vs. the allowed bond-formation time curve increased which indicated that the effect of the

increasing bond-formation time on the adhesive performance was more pronounced. Based on the slope of the curves shown in Figure 6, it seemed that τ had the greatest effect on the open time and adhesive performance of Thermogrip 6330 and Thermogrip 6390, while it appeared to have very small effect on the performance of Thermogrip 6368 indicating by the very steep slope. The steep slope for Thermogrip 6368 suggested that a large difference in magnitude of the characteristic time τ would only produce a small change in the pull-off test result which implied only a slight difference in the adhesive performance. It is likely that this adhesive does not inherently bond well to aluminum. At the same time, the shallow slope for Thermogrip 6330 and 6390, especially at higher running temperature suggested that with only a small change in the magnitude of τ would result in a large difference in the adhesive performance, indicating the great effect of increasing bond-formation time on the adhesive performance for these two materials. Similarly, increasing bond-formation time seemed to have small effect on the performance of Thermogrip 6368 reflected in the small slope values. Despite the difference in the level of effect that τ has on each material, it can be seen that as τ decreases, the effect of the bond-formation time on adhesive performance becomes more significant as evidenced by the increasing slope of the time vs. pull-off stress curve. This observation implies that for a similar increase in bond-formation time, the case with shorter τ can yield greater improvement in the adhesive performance compare to the case with a longer τ. Therefore, in order to effectively enhance the adhesive performance by increasing the bond-formation time, shorter τ is preferred.

Using characteristic time to evaluate the open time and adhesive performance has an advantage over using the open time which was determined from the hysteresis loop data to evaluate the adhesive performance. This open time was specific to each case run; therefore it could not correlate with a change in running temperature. Therefore, the problem with using open time determined from the hysteresis loop is that it did not take into consideration the change in viscosity of the material through out the process. By making this assumption, the estimation of open time is less accurate for the dynamic of the system. Characteristic time, on the other hand, is a parameter that is closely tied to the running temperature which has a big influence on the adhesive performance. In this way, it is a more flexible approach which can also be related to the material properties, thus providing a connection between the material properties and the adhesive performance.

Conclusion

The material properties and adhesive performance of three commercial hot-melt adhesives were characterized by DSC, DA and standardized testing methods. The thermal performance of the adhesives could be obtained through DSC while DA helped to describe their viscoelastic behaviours. It is concluded that adhesive performance cannot be characterized using DSC data only since it is not capable of capturing the flow behaviour of the material which plays an important role in the wetting kinetics of the adhesive material.

Dynamic analysis was used to capture the hysteresis in material flow properties as a function of temperature. The hysteresis loop provided a basis for choosing the application conditions for the adhesive. The adhesive performance under these conditions was evaluated in term of the force required to break the bond through a series of pull-off tests. Expected processing trade-offs between time and temperature parameters were observed and were compared to the parameters generated dynamic mechanically.

The Maxwell characteristic time was estimated from the DA data and compared with the rate of adhesive bond formation data from pull-off tests. Shorter characteristic times were observed to correspond to stronger bond formation kinetics although the data is insufficient to test the relationship statistically. This result suggests that further research into the characterization of adhesive open time using the Maxwell characteristic time is warranted. The results also provide a basis for the formulation of adhesives using structure-property parameters derived from dynamic analysis.

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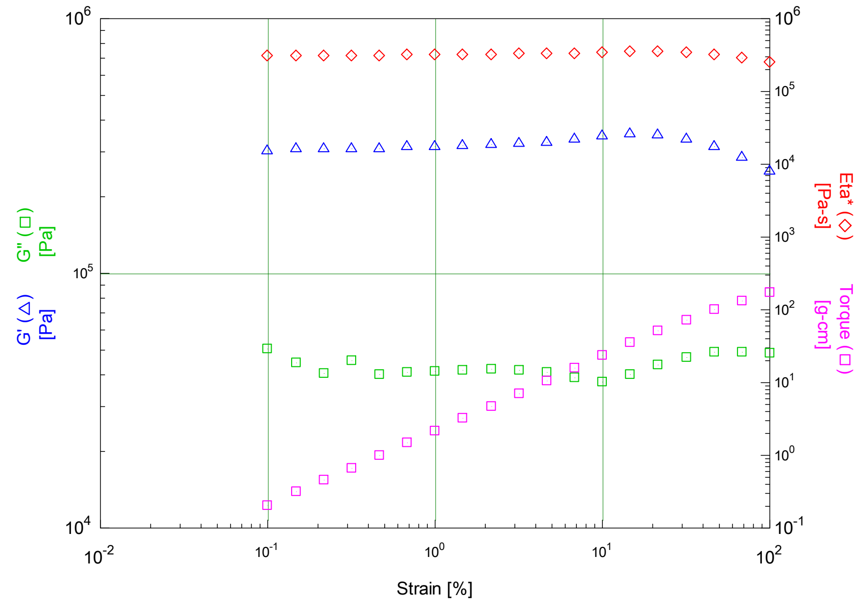
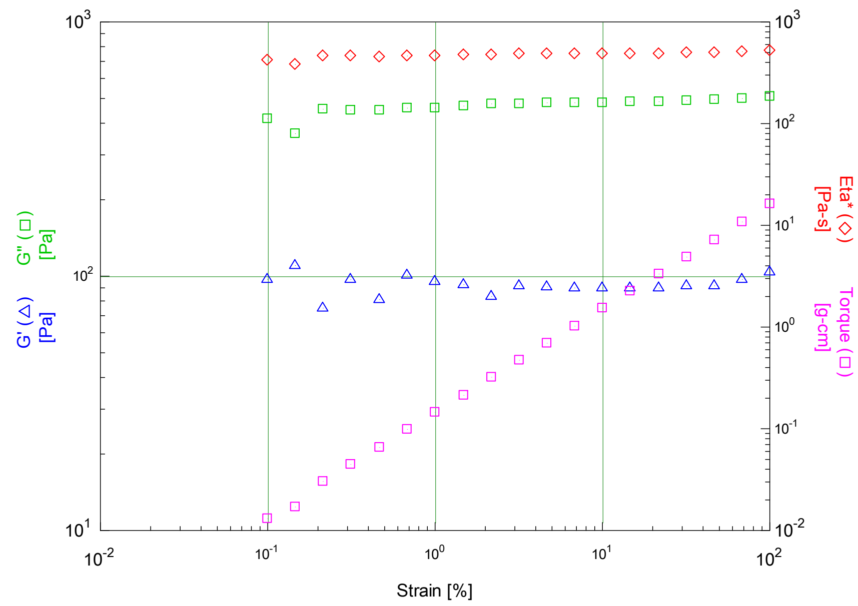
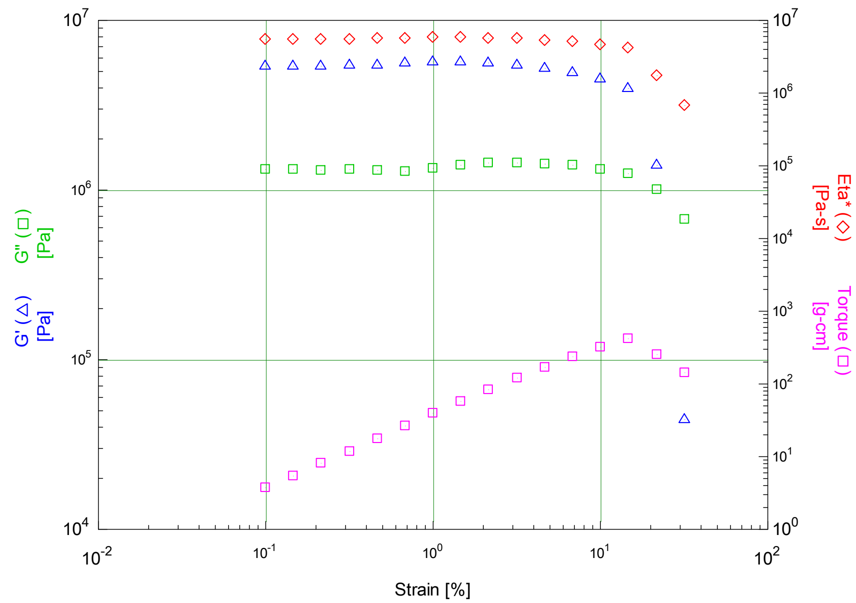
Appendix A – Strain Sweep tests

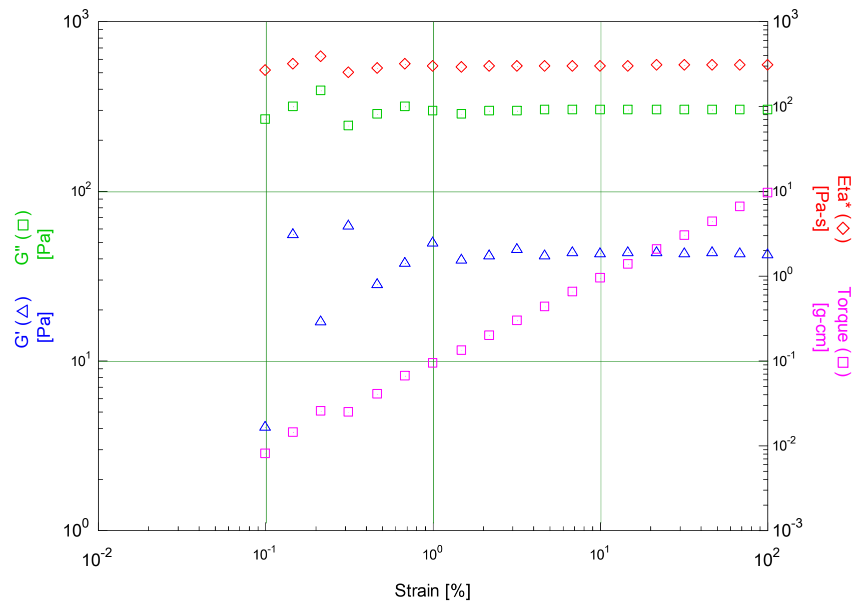
6330 - Strain Sweep at 40oC, frequency 1 rad/s

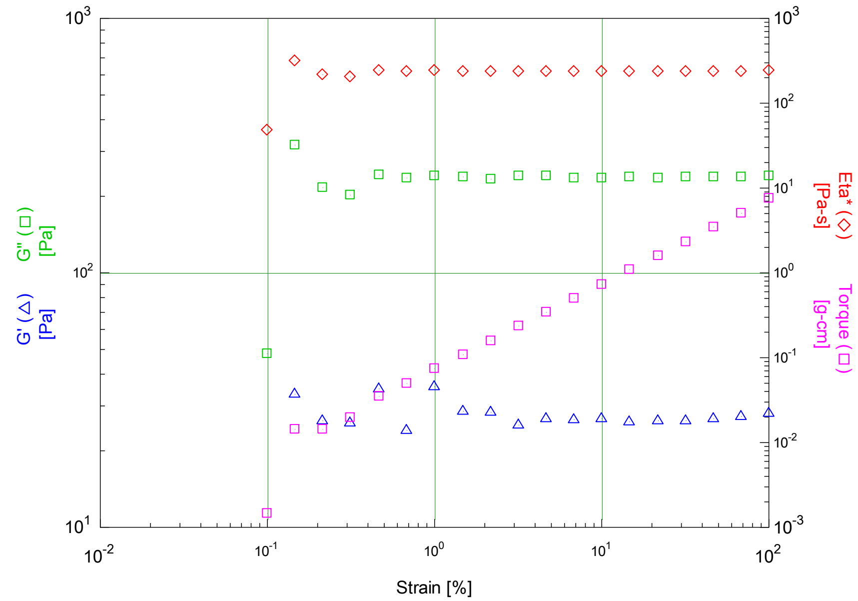


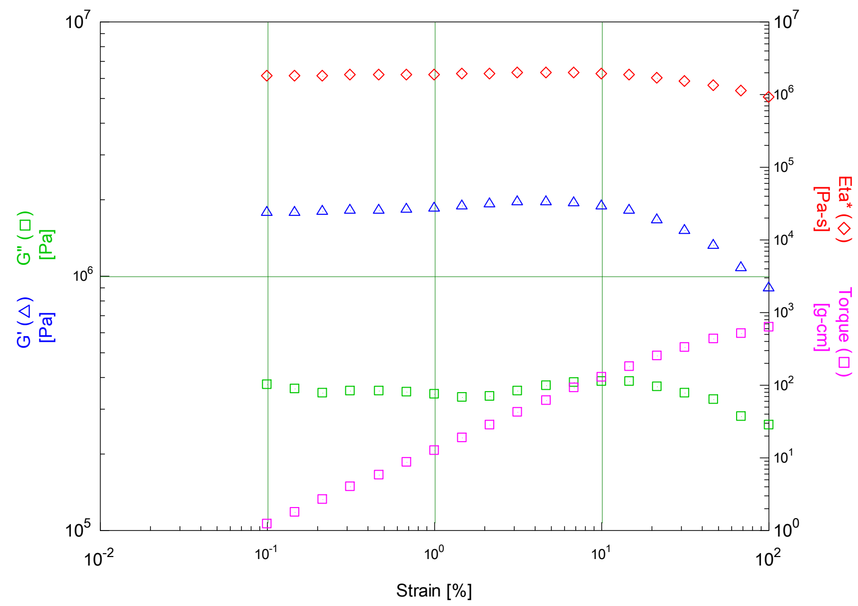
6330- Strain Sweep at 90oC, frequency 1 rad/s



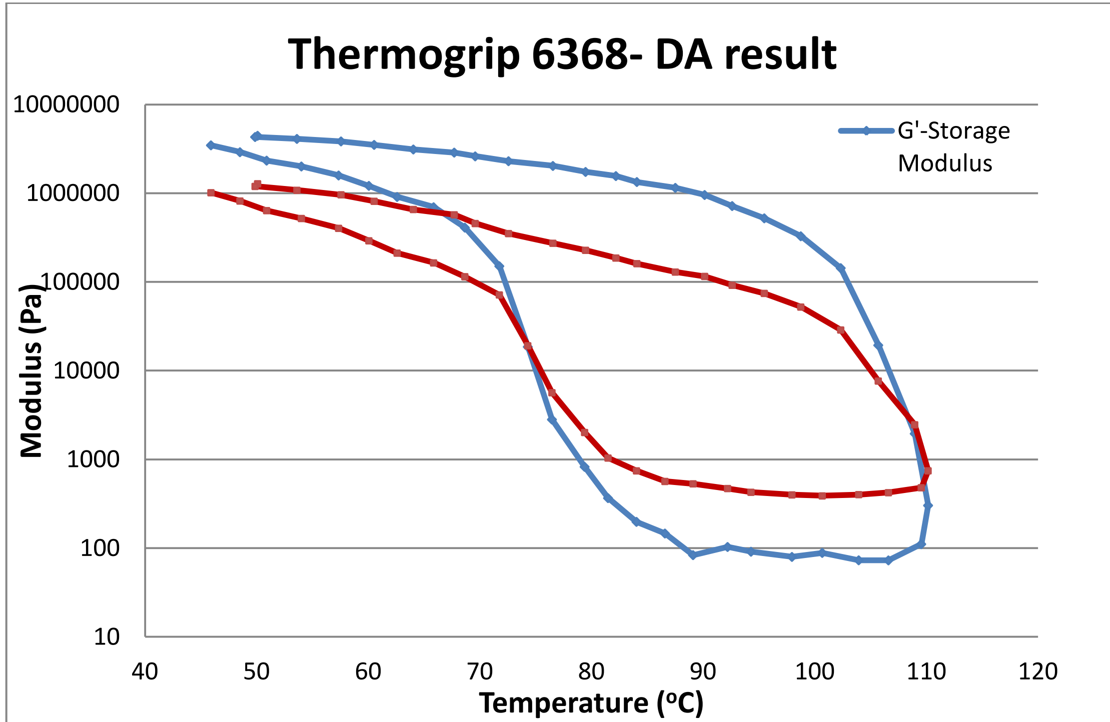

6368- Strain sweep 50oC. frequency 1 rad/s
G' (△) [Pa]
G'' (□) [Pa]
Eta* (◇) [Pa-s]
Torque (□) [g-cm]
Strain [%]

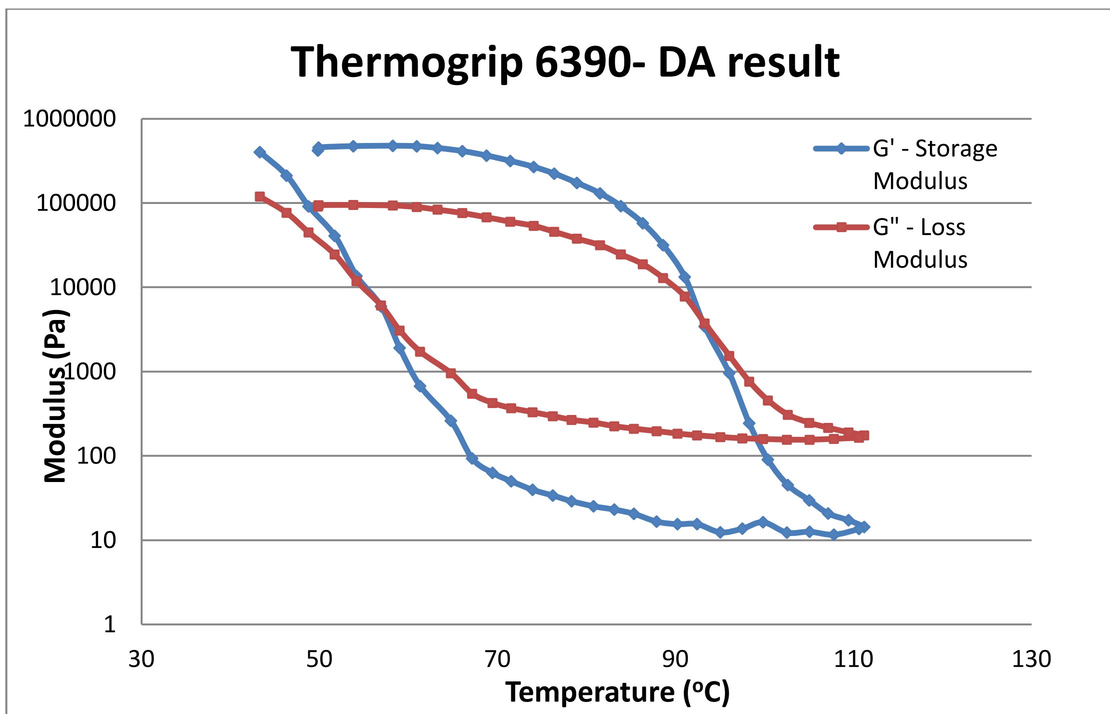

6368- Strain Sweep at 110oC, frequency 1 rad/s
G' (△) [Pa]
G'' (□) [Pa]
Eta* (◇) [Pa-s]
Torque (□) [g-cm]
Strain [%]


6390- Strain Sweep at 90oC, frequency 1 rad/s
G' (△) [Pa]
G'' (□) [Pa]
Eta* (◇) [Pa-s]
Torque (□) [g-cm]
Strain [%]


6390 - Strain Sweep at 40oC, frequency 1 rad/s
G' (△) [Pa]
G'' (□) [Pa]
Eta* (◇) [Pa-s]
Torque (□) [g-cm]
Strain [%]

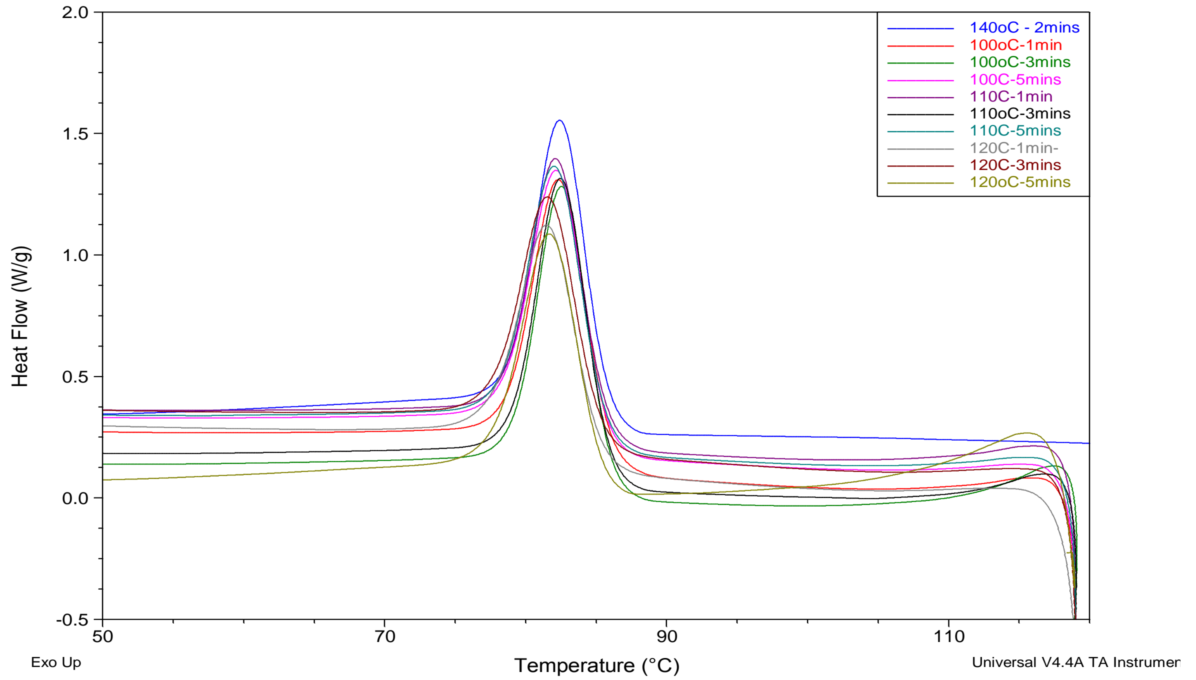
Appendix B – DA results - hysteresis loops





Appendix C – DSC overlay

Cooling curves for Thermogrip 6368



Cooling curves for Thermogrip 6390