EFFECT OF ADHESIVE ON THE SHAPE MEMORY BEHAVIOUR OF THERMOPLASTIC POLYURETHANE

EFFECT OF ADHESIVE ON THE SHAPE MEMORY BEHAVIOUR OF THERMOPLASTIC POLYURETHANE UNDER VARYING CONDITIONS

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LAY ABSTRACT

Nowadays, smart materials in particular shape-memory polymers have been widely used in the industrial and medical applications. Thermoplastic polyurethane (TPU) is one of the significant shape memory polymer groups. The two-phase morphology of a typical TPU gives a unique shape memory behaviour over a defined temperature range. However, this shape memory effect affects the shape fixity of formed TPU. In this study, a special-grade TPU film was laminated to a rigid polymer substrate using selected pressure sensitive adhesives (PSAs). In order to investigate the effect of adhesive layer on the shape memory behaviour of this TPU based laminate, three PSAs with varying properties were applied. The laminate was thermoformed, quenched and processed in a temperature-controlled chamber with a designed recovery measurement method. The shape memory effect was observed at temperatures above the transition temperature of TPU, and this recovery effect was enhanced at higher temperature. Furthermore, the mechanical property of the substrate material was considered as a key factor on the recovery behaviour of the laminate; the recovery of the formed laminate was restricted with a stiffer substrate. The most significant discovery from the recovery results indicated that the shape memory effect was reduced with the adhesive with relatively low adhesion strength, however, the delamination of the laminate occurs with weaker adhesives.

ABSTRACT

Taking advantage of their inherent abrasion resistant, weather resistant, and outstanding mechanical strength, film-grade thermoplastic polyurethanes (TPU) are currently being used as paint protective films but are also being considered for paint replacement within the automotive industry. Special grades of TPU with shape memory behaviour offer an additional feature of self-healing to decorative coatings but there are concerns of shape fixity at service temperatures which are above their glass transition temperature (T_g).

In this study, the shape memory behaviour of a developmental TPU film with T_g around room temperature was investigated. In order to understand the shape memory behaviour, the TPU film was laminated to a rigid polymer substrate of either polypropylene (PP) or acrylonitrile butadiene styrene (ABS). Three different acrylic based pressure sensitive adhesives were tested to bond the film to the substrate, namely a commercial high shear strength transfer tape and two solvent based adhesives of high and low shear strength that were manually cast. The influence of the adhesive was given significant attention as a variable of study in this thesis.

The characterization of all the polymeric films and substrates was based on a series of thermo-mechanical tests (tensile test, stress relaxation test, DSC and DMA). The adhesives were characterized by lap-shear test, peel test, and parallel plate rheometry. The results of material characterization were used to support the analysis and interpretation of shape memory behaviour.

The TPU based laminate was deformed by a matched mold thermoforming process with a pair of arched matched molds. The recovery behaviour of formed samples was quantified with a newly designed measurement method and the results were reported as recovery ratio and recovery rate. During recovery, the surrounding temperature was considered to be an important variable. The recovery behaviour of specimens was investigated in a controlled environment at setpoint temperatures of 15^{o}C, 45^{o}C or 65^{o}C. No shape memory effect was found at 15^{o}C (below TPU's T_g), and yet both recovery ratio and recovery rate increased with temperature, from 45^{o}C to 65^{o}C (both above the TPU's T_g). Since the recovery process was related to the elastic response of the hard segment phase within the TPU, the recovery stress was strongly related to strain conditions. By varying the draw depth into the mold from 6 mm, to 10 mm or 12 mm (8.86%, 15.90% or 19.88% strain, respectively), the recovery measurement results showed that the shape memory effect was weaker with lower strain as less recovery stresses were generated in the TPU film. With the draw depth of 10 mm, the highest recovery ratio and recovery rate were observed, and yet an inexplicable decrease in the recovery ratio and recovery rate occurred as the draw depth increased further from 10mm to 12mm. In regards to the

influence by a substrate, TPU/PP laminate showed a more significant recovery behaviour than TPU/ABS laminates at both 45^{o}C and 65^{o}C. The elastic modulus of the substrate was found to have a key role on the recovery process; the recovery nature of formed laminate decreased with stiffer substrate.

Three adhesives with differing rheological and adhesion properties were tested to bond the TPU film to a substrate. The formed laminates with "strongest" adhesive (transfer tape) in terms of stiffness and adhesion strength showed the highest recovery ratio/rate over laminates made with "weaker" solvent cast adhesives, at both 45^{o}C and 65^{o}C. A finite element analysis (FEA) was employed to simulate the stress transfer within a multilayer structure bonded by a viscoelastic adhesive layer of varying stiffness; the simulated result showed that the relatively low stiffness adhesive could reduce the stress transfer efficiency within layers of a laminate. It suggested that more recovery stresses were transferred from TPU to substrate with a stiffer adhesive layer (transfer tape) and hence increased the recovery ratio and recovery rate. Therefore, adhesive with relatively low stiffness and adhesion strength could be a better choice to reduce the recovery effect of TPU laminate after forming. However, TPU was found to slide at the unsealed edge of formed laminate when the solvent based adhesives were used; the sliding behavior reduced the recovery by releasing stored recovery stress. In the case of HS and LS adhesives at high temperature (65^{o}C), cohesive failure was observed when the edge of specimen was sealed led to a higher bending moment thus increased the recovery ratio over 24 hours investigations. Therefore, adhesives of weaker shear strength do not necessarily overcome the nature of shape recovery by the TPU when formed part shape needs to be preserved.

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ABBREVIATION

TPU	Thermoplastic Polyurethane
SMP	Shape Memory Polymer
PPF	Paint Protective Film
DMA	Dynamic Mechanical Analysis
IMD	In-Mold Forming
FIM	Film Insert Molding
SLV	Standard Liner Viscoelastic Model
CFRML	Carbon-Fiber-Reinforced Metal Laminate
ILSS	Inter-Laminar Shear Strength
TT	Transfer Tape adhesive
HS	High Shear solvent-based adhesive
LS	Low Shear solvent-based adhesive
PP	Polypropylene
ABS	Acrylonitrile Butadiene Styrene
UMTS	Universal Mechanical Testing System
PMMA	Poly(methyl methacrylate)
DSA	Drop Shape Analysis

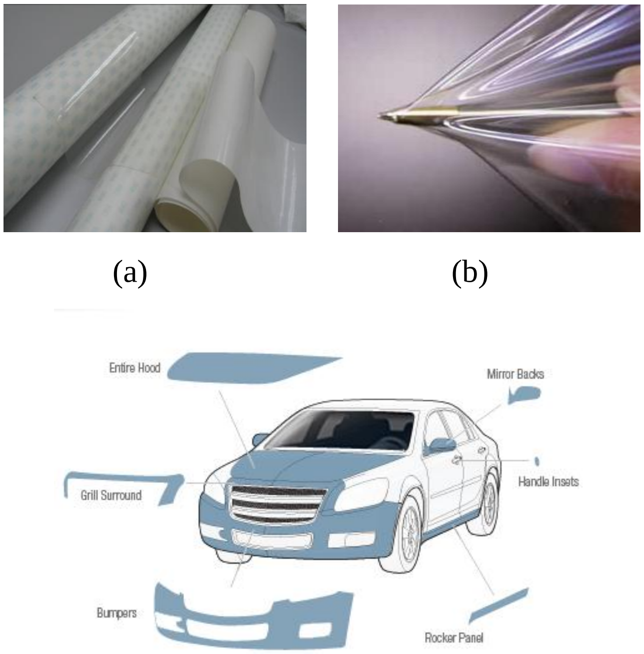
CL	Chord Length
DSC	Differential Scanning Calorimetry

CHAPTER 1 INTRODUCTION

With increased academic and industrial research interest, thermoplastic polyurethane (TPU) has drawn considerable attention and becomes one of the fastest growing polymers in the world today (Tiwari, 2014). Generally, TPU film is manufactured by extrusion and has a chemical structure of linear segmented block copolymers. As one of the most significant application forms of TPU, the film-grade TPU is widely used in the automotive, medical packaging and footwear industries due to its high level strength, abrasion resistant, weather resistant and flexibility (Ohki et al., 2004, Sherman, 2004). From the aspect of substantiality, polyurethane products have long lifetimes, and they are recyclable without disposing toxic or heavy metal waste (Zia et al., 2007). Different physical and mechanical properties of TPU are achieved depending on the chemical structure, with some exhibiting morphology that changes with temperature or other response stimuli which gives it a unique shape memory behaviour. Nowadays, shape memory polymers (SMPs) have a significant role in biomedical, self-healing and smart materials. Among the various SMPs, TPUs are the most popular class of polymers for their easy control of glass transition temperature and excellent shape memory effect (Ohki et al., 2004).

1.1 Application in Automotive Industry

Lightweight, low-cost and sustainable approaches have become the mainstream for entire car design in the automotive industry; there is an increasing amount of plastic materials applied in the production of exterior and interior parts for a car such as door panels, dashboards and headliners. During automobile manufacturing, the painting process is considered as one of the most expensive and time-consuming steps, as well as requiring large floor space and waste disposal systems (Sherman, 2004). Recently, commercial paint protective films (PPF) have been gaining market share such as 3M Scotchgard^{TM}, Xpel Ultimate and Suntek TC series, which are applied onto painted surfaces (Figure 1.1). TPU is the main function component within those film products, providing the ability to self-heal or recover to protect the paint from scratches, rock chips and stains without losing the appearance of the paint (3M_Automotive_Aftermarket&Marine, 2015).



(a) (b)

(c)

Figure 1.1: (a) Commercial paint protection film from 3M Scotchgard^{TM} (b) Demonstration of high level strength of TPU film products (c) Suggested painted surfaces with PPF (3M_Automotive_Aftermarket&Marine, 2015)

However, the application of PPF requires manual,cautious installation by professionals, which directly affects the budget of clients. To improve the performance of TPU films and avoid the cost of installation, an idea of paint replacement raised by substituting the plastic parts of a vehicle with unibody plastics with coloured protective film coating (Fuchs, 2014, Rotheiser, 2000). With the technique of In-mold decoration (IMD) or direct thermoforming, the coated plastic part can be produced as a single unit.

1.2 In-Mold Decoration

In-mold decoration (IMD) has become one of the main manufacturing processes for plastic decoration in the automotive and electronics industries. Although IMD is not excepted to replace the paint line of an assembly plant in the near future, with the progress made in IMD technology today, large 3D parts such as entire dashboards, bumpers, roofs and even hoods for vehicles are able to be produced with high-level finishes (Rotheiser, 2000, Sherman, 2004). To broaden the application of IMD, a specific process known as film insert molding (FIM) is designed to provide the method of producing components with functional films such as TPU. The insert molding process starts with the lamination of a functional film onto a rigid substrate, and the laminate is thermoformed to a mold shape with pressure, vacuum or matched metal dies. The thin substrate is selected to provide sufficient structural support to fix the shape of formed laminate and a thin adhesive layer, possibly an acrylic-based pressure sensitive adhesive (PSA), is applied between the film and substrate (Figure 1.2).

Figure 1.2: Multiple layers structure of laminate with shape memory film

With easy machining and replacement of molds, even for large scale parts (Senthil, 2012), thermoforming provides more possibilities of complex contoured part design for the preformed laminate. In this way, the laminate is preformed, trimmed and inserted into the mold for the injection process. The compatible plastic is injected into the mold behind the insert and it becomes part of the plastic unit (Figure 1.3) (Nissha Printing Co., 2015, Rotheiser, 2000).

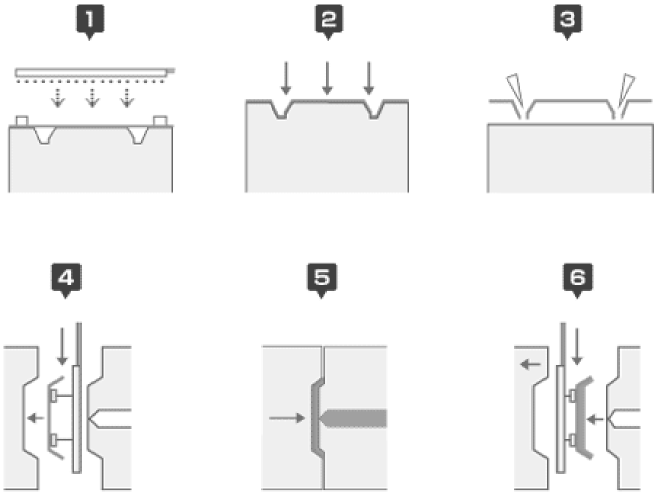


Figure 1.3: Schematic diagram of film insert molding (FIM) process by Nissha Printing Co.,Ltd. (Nissha Printing Co., 2015)

1.3 Motivation of Work

Laminates with shape memory TPU film have the benefits of abrasion resistance and self-healing properties; however, the shape memory behaviour can also affect shape fixity of a formed part (Tobushi et al., 1998). Due to the fact that the glass transition temperatures of some TPUs are around room temperature (Ohki et al., 2004), the formed laminate may experience recovery deformation during transportation or storage. This unexpected recovery behaviour will limit the practical applications of this smart material. With consideration of the potential factors such as environmental temperature, adhesive and substrate layer, research on the shape memory effect of TPU film laminate can help in understanding how to form parts with this film type and hence expand its applications.

1.4 Objectives

In this study, we focus on the recovery behaviour of thermoformed TPU film laminate. The specific objectives of this research were:

- To design a shape recovery evaluation method that replicates, in part, the stretch-bending deformation indicative of thermoforming.
- To investigate the failure mode of adhesive during the forming process and recovery observations of the laminate.
- To study the effect of shear adhesive strength on the recovery behaviour of a laminate with different substrates.
- Devise a numerical model to simulate the forming process and recovery behaviour.

CHAPTER 2 LITERATURE REVIEW

2.1 Shape Memory Polyurethane

The ‘shape memory’ effect was first discovered in a metallic alloy consisting of nickel and titanium in the 1960s (Lin and Chen, 1998a). That investigation promoted research of shape memory behaviour in polymeric materials (Lendlein and Kelch, 2002, Leng et al., 2011, Lin and Chen, 1998b, Lin and Chen, 1998a). Generally, a polymeric material is classified as a shape memory polymer if it can maintain a deformed shape yet recover its original shape without external loading (Lendlein and Kelch, 2002, Liang et al., 1997, Lin and Chen, 1998b, Lin and Chen, 1998a, Ohki et al., 2004, Takahashi et al., 1996, Lin and Chen, 1999b). In 1984, a polynorborane type shape memory polymer (SMP) was introduced by Nippon Zeon Company, followed by various forms of SMP including poly(isoprene-butadiene-styrene), polyurethane and polystyrene series (Yang et al., 2003). Compared to shape memory metal alloy (SMA), SMP has the advantage of low density (1.0-1.3 g/cm^3), low manufacturing ratio, high shape recovery ratio and easy processing (Lee et al., 2001, Liang et al., 1997, Ohki et al., 2004, Tobushi et al., 1997). The most common SMPs respond to thermal changes to initiate recovery to their initial shape, which is the class focused on in this review.

2.1.1 Structure and Thermo-mechanical Properties of Shape Memory Polyurethane

Among the class of thermoplastic SMPs, segmented polyurethanes have drawn the most attention because of their high shape recoverability (maximum recoverable strain >400%), a wide range of shape memory temperature (from -30 to 70^{o}C), and better processing ability (Liang et al., 1997). A great number of studies have been carried out on their morphology, thermo-mechanical behaviour and rheological properties (Lin and Chen, 1999b, Takahashi et al., 1996). In 1988, a shape memory polyurethane was created by Nagoya Research and Mitsubishi Company with a separated micro-phase structure (Lee et al., 2001, Yang et al., 2003). Due to the thermodynamic immiscibility of the constituent segments, the morphology of typical shape-memory PUs should contain two phases, which are a reversible soft-segment phase and fixed hard-segment phase. The thermally reversible phase is usually designed to exhibit a significant drop in elastic modulus as the temperature changes over its phase-transition temperature (normally its glass transition temperature, T_g). However, the fixed hard segment has a higher transition temperature which allows the hard segment to remain in its glassy state or crystalline state in the range of operating temperature, thus the fixed phase would always present an elastic response to the deformation and be driven to recover its original shape (Jeong et al., 2000, Lin and Chen, 1998b, Lin and Chen, 1999b, Ohki et al., 2004, Takahashi et al., 1996, Tobushi et al., 1998). Figure 2.1 indicates the schematic diagram of shape memory behaviour.

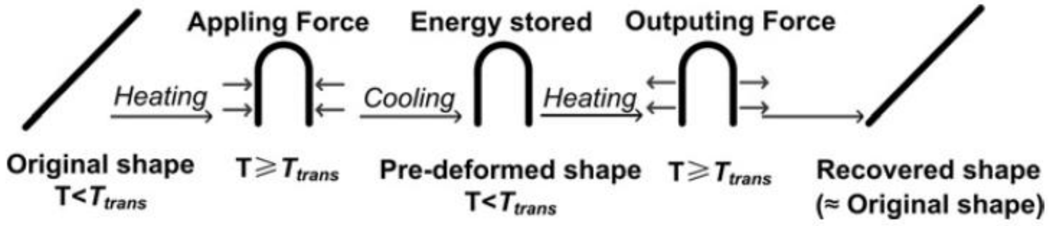


Figure 2.1: Schematic of shape-memory effect during a thermo-mechanical cycle (Leng et al., 2011)

In the scheme above, external loading is applied when an SMP specimen has been heated above the T_g of the reversible phase whereby the material is treated as elastomer with high mobility. Then, the deformation is fixed by quenching to a temperature below T_g. Because of the phase transition in the soft segment from amorphous to glass state, resistance to counter the recovery force of the hard segment is possible. Once the polyurethane material is heated up again, the soft segment losses its strength for temperatures above T_g. The specimen attempts to recover to its original shape because of the elastic response of the hard segments (Leng et al., 2011).

2.1.2 Constitutive Model

In order to better design SMP components, a constitutive model that describes thermo-mechanical properties of SMPs is necessary. It is also important to develop the constitutive model in respect of finite element analysis of SMPs (Lin and Chen, 1999b, Tobushi et al., 1997, Leng et al., 2011). Generally, the thermo-mechanical constitutive model for shape-memory TPUs is expressed based on the viscoelastic behaviour of polymer, where spring and dashpot elements are commonly used for representing the elastic and viscous properties of a polymer (Leng et al., 2011). In the study by *Tobushi et al* in 1997, a constitutive model describing thermo-mechanical properties in TPUs was developed as an improved form of the standard linear viscoelastic model (SLV) (Tobushi et al., 1997). The SLV model is frequently used in deformation modeling of viscoelastic materials.

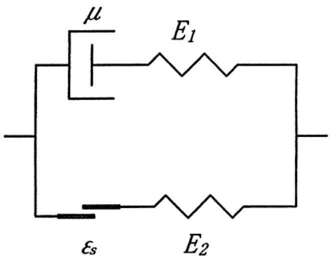


Figure 2.2: Four-element model (Tobushi et al., 1997)

In this thesis, the stress-strain-temperature relationship of a shape memory polyurethane in a four-element model shown in Figure 2.2 was expressed as:

$$\begin{cases} \dot{\varepsilon} = \dfrac{\dot{\sigma}}{E} + \dfrac{\sigma}{\mu} - \dfrac{\varepsilon - \varepsilon_s}{\lambda} + \alpha \dot{T} \\ \varepsilon_s = C(\varepsilon_C - \varepsilon_l) \end{cases} \tag{1}$$

where σ, ε and T represent stress, strain and temperature, respectively and ε_s was the irrecoverable strain. $E_{1,2}$, μ and λ denote the elastic modulus, viscosity and retardation time, respectively. These three variables as well as the temperature-dependent constants C and ε_l were expressed as a function of temperature:

$$f(T) = f(T_g)\exp[a(\frac{T_g}{T} - 1)] \tag{2}$$

where T_g is the glass transition temperature and a is assumed to be constant temperature coefficient. Through fitting to thermo-mechanical characterization data (DMA, creep test, stress relaxation test, recovery stress test, etc), the proposed theoretical model is known to express well the thermo-mechanical properties of TPU and is able to predict shape memory behaviours such as shape fixity, shape recovery and recovery stress.

To date, there are only a few constitutive models for shape-memory TPUs based on viscoelasticity which have been developed to describe thermo-mechanical behaviours (Lin and Chen, 1999a, Nguyen et al., 2008, Abrahamson et al., 2003). The application of a constitutive model is necessary in understanding thermo-mechanical responses of a TPU within a numerical simulation.

2.1.3 Characterizations of Shape Memory TPUs

Because of the complexity of non-linear shape memory behaviour, there is no standard characterization method to quantify the degree of shape recovery. The thermo-mechanical cycle test is frequently used to investigate the shape memory effect of SMPs (Tobushi et al., 1997, Ohki et al., 2004, Tobushi et al., 1998, Hu et al., 2005). There are four steps in a single cycle of thermo-mechanical cycle test as illustrated in Figure 2.3.

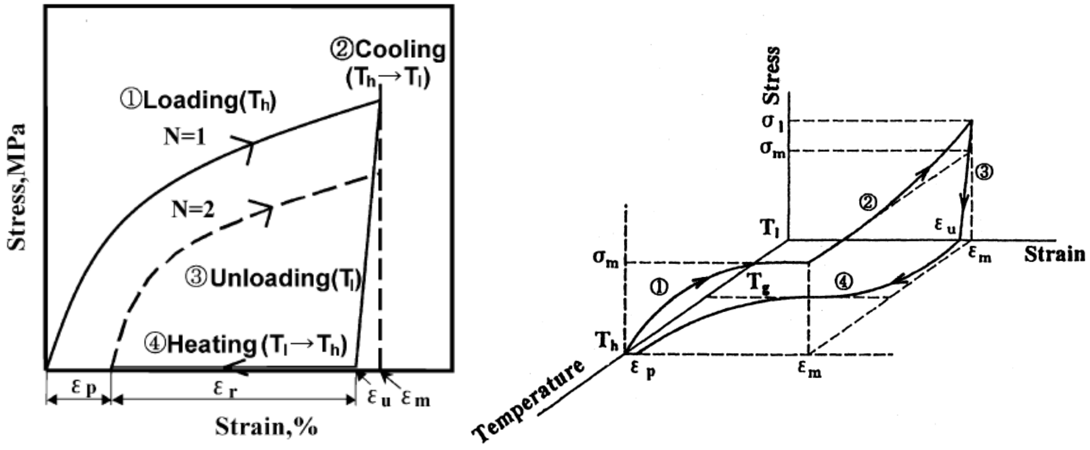
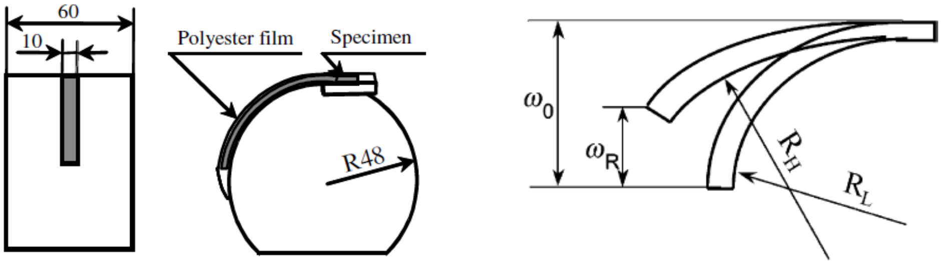


Figure 2.3: Schematic representation of the thermomechanical cycle (Ohki et al., 2004, Tobushi et al., 1998)

In the study of shape memory behaviour by *Ohki et al* in 2002 (Ohki et al., 2004), specimens were uniaxially loaded to strain ε_m at a crosshead speed of 5 mm/min while at temperature T_h which was higher than the glass transition temperature of the soft phase (Process 1). The deformed specimen was then quenched to temperature T_l ($T_l < T_g$) while under load to hold the strain (Process 2). When the temperature of specimen reached T_l for 5 minutes, the load was removed and the remaining strain ε_u was recorded (Process 3). Finally, the specimen was heated up to T_h again without load (Process 4). The authors repeated five cycles in their research. The strain recovery ratio was then defined by the value of $\varepsilon_r / \varepsilon_m$, recovered strain over the designed strain, and the shape fixity was calculated by $\varepsilon_u / \varepsilon_m$. Results indicated that the shape recovery ratio and shape fixity were affected by the recovery temperature and number of cycles on the materials. Both of recovery ratio and fixity decreased with increased number of cycles. In this study, author conducted the tests at three different temperatures (338 K, 358 K and 373 K), and the result showed that the recovery ratio increased as the temperature increased. Since the thermo-mechanical deformation of shape-memory polyurethane was produced by Brownian motion within the amorphous phase, the recovery speed was influenced by the recovery temperature (Jeong et al., 2000). Through this thermo-mechanical test, the shape memory behaviour could be quantified and the effect of variables such as elastic modulus of material, recovery temperature, pre-strain deformation, etc can be investigated.

Another characterization method, the bending recovery test of shape memory behaviour for TPUs and their composites was studied by *Zheng et al* in 2005 (Zhang and Ni, 2007). SMP based laminates were bent at a specified angle with the jig as shown in Figure 2.4(a). Then the whole system was placed into an environmental chamber at 65^{o}C (above T_g) for 1 hour, and one end of specimen was fixed on the jig. The specimen with fixed bending angle was cooled down to 15^{o}C which was below T_g of TPU, and the specimens were heated back to 65^{o}C. The investigation of shape memory effect of samples was conducted under varying recovery times at 65^{o}C (5 min, 10 min, 15 min and 20 min).



(a) (b)

Figure 2.4: (a) The jig for fixing specimen shape; (b) The definition of bending recovery ratio (Zhang and Ni, 2007)

The recoverability was measured as bending recovery ratio defined by the parameter, $R = \omega_R / \omega_0$ where ω_R and ω_0 are the recovery and initial deflection, respectively as indicated in Figure 2.4(b). In that study, the bending shape memory effect of TPU based laminates with carbon fiber fabric was investigated by changing recovery time. The results indicated that the bending recovery ratio was significantly increased with the increment of recovery time, and the presence of carbon fiber fabric would improve the bending recovery property of SMP materials. These two existing characterization methods provided practical ways to quantify the shape memory effect of SMP materials.

2.2 Adhesive Layer

Adhesive bonded joints are widely used in the preparation of composite structures based on metal, concrete, wood and polymeric materials. Adhesives are regarded as polymeric substances with viscoelastic behaviour, capable of producing a physical or chemical bond to hold the adherends together without separating (Balden, 2004).

Depending on an application, they exist in forms of hot melts adhesives, pressure sensitive adhesives, solvent-based adhesives etc. In comparison with mechanically fastened and riveted joints, adhesive bonds offer the advantages of time and cost savings, corrosion and fatigue resistance, lower stress concentration (no drilled holes required), higher strength to weight ratios, and so on (Balden, 2004, Tsai and Morton, 1995). However, the disadvantages are inherent material heterogeneity, relatively low transverse strength and shear stiffness, and free edge effects, which will influence the mechanical performance of laminates (Tsai and Morton, 1995). To date, a large number of studies on the adhesive mechanism have been performed theoretically, experimentally and numerically (Asloun et al., 1989, Roberts, 1989, Yuan et al., 2001). The mechanical properties, thermal properties, surface texture, thickness of adhesives were reported as important roles on the mechanical behaviour of laminated structure (Asloun et al., 1989, Balamurugan et al., 2013, Le and Nairn, 2014, Roberts, 1989).

2.2.1 Adhesive Effect on the Mechanical Properties of Laminate

In the practical application of composite structures, laminates are designed to bear different kinds of loading conditions. Especially in the processing of polymer laminates such as by thermoforming, large deflections are frequently applied. Thus, it is important to understand the interfacial stress transfer behaviour of a laminate. As pointed out by

Lapique and Redford, the mechanical properties of the adhesive layer should affect the stress transfer across its interfaces hence change the results of mechanical testing (Lapique and Redford, 2002). In the study of *Le et al* on measuring interfacial stiffness of adhesively-bonded composite, the adhesive stiffness was also considered as a significant role in the properties of composite (Le and Nairn, 2014). They pointed out that a stiffer interface will transfer stresses faster between each element while a relatively weak adhesion will lead to a slower stress transfer and reduce the mechanical properties of composite. In 1997, *Lawcock et al* published their work on the effect of adhesive bonding on the mechanical properties of carbon-fiber-reinforced metal laminates (CFRMLs) (Lawcock et al., 1997). Adhesion was produced by using two different aluminum surface treatments. Through the three-point and five-point bend tests, the laminated samples with different adhesive properties were tested to investigate the difference in inter-laminar shear strength (ILSS). The results indicated that the ILSS was reduced by approximately 10% with lower strength adhesion compared to the ILSS with stiffer bonding. Therefore, it is agreed that the strength of adhesion would have a strong influence on the mechanical properties of laminate.

2.2.2 Delamination and Stress Distribution of Adhesive

Polymer laminates are widely used in engineering industry, particular in aerospace and automotive industries, large deflection or impact may be applied to the materials during the manufacturing or application. The resultant stress developed in the bond line may lead to the adhesion failure and hence reduce the strength of the laminate (Amaro et al., 2011, Balden, 2004, Hansen and Spies, 1997). The delamination effect on bending behaviour in carbon-epoxy laminate was studied by *Amaro et al* (Amaro et al., 2011). The laminate was prepared with delamination located at different positions along the laminate thickness, and its bending behaviour was investigated experimentally and numerically by a three-point bending test. Compared to the undamaged case, samples with defects showed a lower load responded to the change of displacement, up to an average reduction of 24.4% was obtained by the sample with delamination occurred at half thickness; and the numerical results also indicated that more shear stress would be concentrated at the delaminating locations.

Due to the significant effect of adhesive delamination on mechanical properties of laminated structures, it is important to understand the stress distribution within the adhesive layer. However, since it is impractical to experimentally investigate the stress distribution in adhesive layer, a good theoretical or numerical model can be beneficial to analyze the mechanical properties of adhesives (Roberts, 1989).

2.2.3 Damping Effect of Adhesive Layer

Due to the fact that the adhesive is derived from polymeric materials, the viscoelastic property of adhesive could contribute a damping effect in the laminated structure (Bai and Sun, 1995, Hansen and Spies, 1997). Many researchers reported that the viscoelastic adhesive layer allowed the shearing strain caused by the flexural vibration to dissipates energy and hence reduce vibrations (Bai and Sun, 1995, Fujii, 1993, Ghinet and Atalla, 2007, Johnson and Kienholz, 1982, Miles and Reinhall, 1986). The dynamic response of laminated structure with adhesive damping layer was studied by *Fujii* in 1993 (Fujii, 1993).

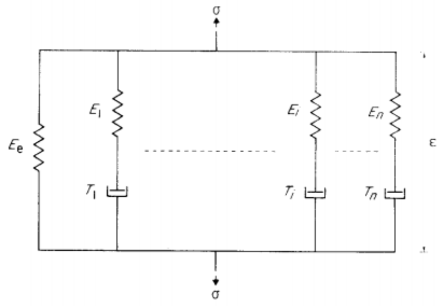


Figure 2.5: Generalized Maxwell Model (Fujii, 1993)

Based on the generalized Maxwell model shown in Figure 2.5, the time-stress-strain relationship of adhesive damping layer was expressed as

$$\Delta\sigma = E^{*}\Delta\varepsilon + \sigma_0(t) \tag{3}$$

where

$$E^{*} = \sum_i \frac{E_i}{[1+(\Delta t/2T_i)]} + E_e\,; \quad \sigma_0(t) = -\sum_i \frac{\Delta t}{[1+(\Delta t/2T_i)T_i}\sigma_i(t) \tag{4\&5}$$

where $\Delta\sigma$ and $\Delta\varepsilon$ donate the stress and strain increment with a time increment Δt, respectively. The elastic modulus (spring element) and relaxation time (damping element) in the Maxwell model were expressed as E_i and T_i, respectively. A similar constitutive equation was also assigned to the relation between shear stress, strain and time,

$$\Delta\tau = G^{*}\Delta\gamma + \tau_0(t) \tag{6}$$

where $\Delta\tau$ and $\Delta\gamma$ donate the shear stress and strain increment, and G represented the shear modulus of adhesives. A finite element analysis based on this generalized Maxwell model indicated a good fit to experimental results in their testing of dynamic response by laminated beams. In 2009, *Miles et al* devised an analytical model for the vibration of laminated beams with adhesive layer (Miles and Reinhall, 1986); they concluded that if the adhesive is very soft compared to one of the adherends in bending, then the thickness deformation in the adhesive can become the dominant damping mechanism. Thus, the adhesive layer is not only the bonding agent of two materials, but also plays a significant role in the overall performance of the laminate. Particularly, in the project with TPU based polymer laminates, a simple material model based on the generalized Maxwell model by *Fujii* (Fujii, 1993) was introduced in the finite element analysis as suggested in the introduction chapter.

CHAPTER 3 EXPERIMENTAL

3.1 Sample preparation

3.1.1 Materials

A developmental shape memory thermoplastic polyurethane (TPU) film with thickness of 200μm was supplied by 3M Canada (London, ON), having black, leather-like surface on both sides; according to our interactions with 3M Canada this film is known as TPU-high referring to its modulus but in this thesis it will simply be referred to as TPU film. To study the effects of the adhesive layer on the deformation behavior of shape memory laminates, three different types of pressure sensitive adhesives (PSAs) were examined with varying adhesion properties: adhesive Transfer Tape 468MP (TT) with a thickness of 0.125mm (3M Canada); and two liquid-type adhesives. The two polyacrylate solutions, namely *RD-1295 MC-874 RD-2839 RD-2909 RD-1810* (HS = high shear strength) and *RD-1291 MC-1445 R-27095 RD-1367* (LS = low shear strength) supplied by 3M Canada were supplied in heptane. For lamination, two commonly used substrates were examined in the trials as 0.5 mm thickness sheets: black DuPont polypropylene (PP) with maleated coating on one side (provided by 3M Canada) and semi-clear beige acrylonitrile butadiene styrene (ABS) purchased from McMaster-CARR.

3.1.2 Adhesive Preparation

Before transferring the adhesives to film specimens, dry adhesive layers were first prepared on release liners. A laboratory drawdown coater (Model LC-100, Chemsultants International, Cincinnati, OH) was used to evenly apply the liquid adhesive onto the release liner at appropriate thickness. The release liner used featured a micro-pattern of micro-square blocks described in a recent publication and found to be well suited to high temperature molding operations (Balamurugan et al., 2013). Liquid adhesive was applied from the coater reservoir onto the surface of release liner at an angle of 45 degrees from the horizontal plane, as shown in Figure 3.1.

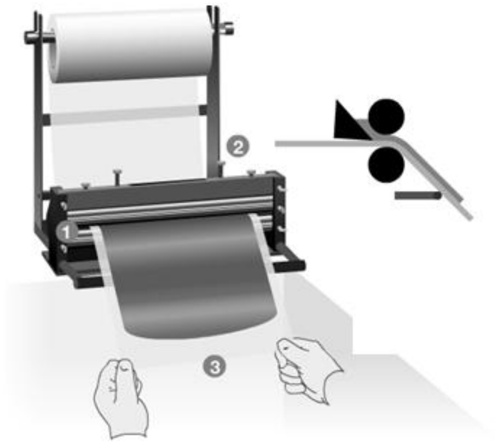


Figure 3.1: Schematic diagram of adhesive preparation by using the draw-down coater

The thickness of dried adhesive layers was controlled to be 0.13 mm with a variance of 0.02 mm by setting the gap distance of 0.34 mm. The solvent of coated liner was allowed to dry and ultimately heated under a radiant heater set to 60^{o}C for 4 hours until the solvent was fully eliminated. Final adhesive layer thicknesses by this method were 0.143 mm and 0.120 mm after preparation, for the HS adhesive and LS adhesive, respectively.

3.1.3 Film Lamination

Two steps were necessary to prepare the TPU laminates. Firstly, the dried adhesive layers on release liners and the transfer tape (also supplied on a release liner but without micropattern) were laminated to the TPU film using a HL-100 hot roll laminator (Chemsultants International, Cincinnati, OH, USA) equipped with a top metal roller and a lower rubber roller. A compression ratio (laminate thickness/nip gap opening) of 0.9 and holding line pressure of 270 kPa was suggested for all laminations. The laminator was operated at 23^{o}C and a roller speed of 2 RPM. Then, the release liners were removed and the now-coated TPU film with differing adhesive layers was adhered to the substrates. The TPU film laminates were placed on a flat surface for 72 hours to allow curing before further characterization and testing.

3.2 Thermoforming and Recovery Observation

3.2.1 Thermoforming Process

Matched-mold thermoforming was selected to stretch/bend the TPU laminate to the desired arched shape. A set of conforming die plates were made with an arched radius of

26 mm and peak height of 11 mm, and an additional female mold with 15 mm peak height was made for thermoforming with varying depths between 11 mm to 15 mm; the dies could mold three samples simultaneously for the purposes of assessing experimental uncertainty. The laminate specimens were cut from the prepared sheets as strips (152.4 mm by 25.4 mm) with a dumbbell shape to produce a gauge length of 40 mm and gauge width of 12.7 mm. The dumbbell shape was chosen so that deformation during testing would occur at the desired middle section of sample without drawing materials from the two ends during thermoforming. The thermoforming was conducted inside a controlled environmental chamber attached to a 10 kN universal mechanical testing system (UMTS) supplied by Instron Corporation (Canton, MA, USA) fitted with a 5 kN load cell. As shown in Figure 3.2, when the samples were heated up to 160^{o}C (using an oven setting of 180^{o}C), the forming process was started with a controlled out-of-plane deformation rate of 12 mm/min to a certain depth which gave the sample a desired strain for recovery observations.

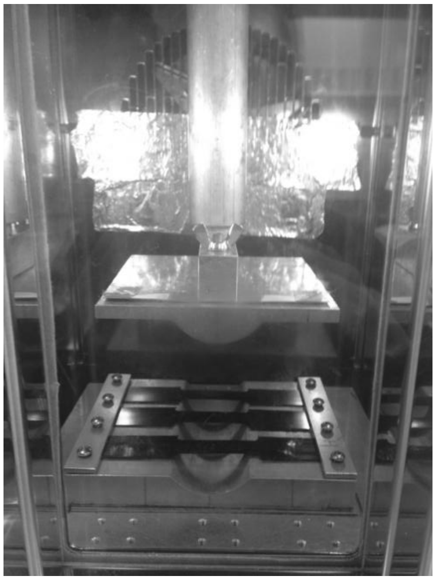


Figure 3.2: Photograph of the thermoforming process within the UMTS system seen through the window of the environmental chamber

After the specimens were deformed to the chosen out-of-plane strain, both mold and samples were then immediately moved to a deep freezer (Rototron Corporation, NY, USA) with an ambient temperature of -40°C. Once cooled down to 10°C over a span of 20 minutes, the upper male-half of the mold was raised and the three specimens were trimmed, and then removed. One end of formed sample was trimmed along the edge of gauge region, and the other end of sample was cut at the shoulder section with 1 mm distance beyond the reduced section for clamping. The trimmed sample was fixed into a PMMA clamp, while the free end was sealed with epoxy adhesive to minimize delamination. Minimal direct contact with the specimen occurred during these steps in order to minimize any rise in temperature till the recovery test could be started.

3.2.2 Recovery Measurement

The clamped laminate samples, noted in the last section, were moved into a plastic chamber made of poly(methyl methacrylate) (PMMA) with top opening and placed into a Model 1157P circulating temperature bath (VWR International, PA, USA). The laminate samples remained dry while the bath controlled the ambient temperature during the recovery test. The ambient recovery temperature was set with the digital controller of the circulating bath; three ambient temperatures were examined in this project: 10^{o}C, 45^{o}C and 65^{o}C. Calculation of recovery angle were based on the assumptions that the arc length of the formed laminates remained constant during recovery and that the recovering sample traversed a circular arc with decreasing central angles, as shown in Figure 3.3; the arc was determined in the numerical computing software MATLAB.

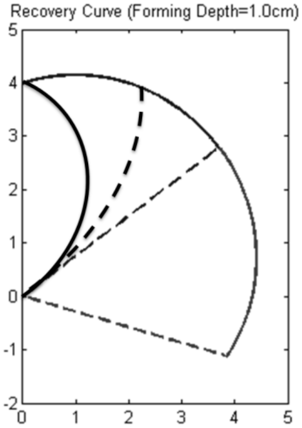


Figure 3.3: Recovery curve computed by MATLAB showing the recovery path of formed laminates after deformed by 10 mm out of plane.

Three samples were tested simultaneously. Three digital timer-operated cameras were placed on a transparent PMMA lid on top of the chamber and the recovery behaviors of samples were recorded individually. The photo capture interval was set to be 15 seconds for first 30 minutes and 1 minute for the next 30 minutes, and 10 minutes for 1 hour of recovery time. The final angle was recorded after 24 hours of recovery. The recovery behavior of thermoformed TPU laminate was quantified and reported as two values: Angle recovery ratio ($R_a(t)$, %) and Recovery rate (R', %/h). Angle recovery ratio was defined as:

$$R_a(t) = \frac{\alpha_0 - \alpha_t}{\alpha_0} \times 100\% \tag{7}$$

where α_0 is the initial central angle of formed laminate and α_t is the central angle at a certain time *t*. The other quantified value, recovery rate, was determined by finding the secant slope of the recovery ratio curve over the first 5 minutes.

3.3 Characterization

3.3.1 Water Contact Angle Measurement

The water contact angles of all the contacting surfaces including TPU film, adhesive layers and substrates were measured using a Drop Shape Analysis System DSA10 (KRÜSS GmbH, Hamburg, Germany). The contact angle was determined from analyzing the image of the sessile drop for an elapsed time interval of one minute by the software DSA, KRÜSS GmbH (registered version).

3.3.2 Lap Shear Test

The shear strengths of adhesives under varying temperature were obtained by the lap shear test according to ASTM-D1002. Two 101.6 mm x 25.4 mm steel strips were bonded together with an overlap length of 12.7 mm with two washers attached on both end of testing sample to prevent misplacement. A test specimen was mounted in the clamps attach to a universal mechanical testing system (UMTS) and housed within an environmental chamber with set temperatures of 45 ^{o}C, 65 ^{o}C, or 160 ^{o}C. The tests used a crosshead speed of 12 mm/min until the two testing panels detached completely.

Similar testing was done replacing the metal strips with polypropylene (PP) strips.

3.3.3 180^{o} Peel Test

The adhesion strength of the TPU laminates was evaluated by an 180^{o} peel test according to ASTM D903-98. Laminate specimens were prepared with 127 mm x 25.4 mm rectangular shape. The substrate side was bonded on a 127 mm x 25.4 mm steel panel of 1.5mm thickness to avoid flexural deformation during peeling, while the thin TPU film was taped with aluminum foil to reinforce the tensile strength of the TPU film. The reinforced TPU film was manually peeled from the substrate till only 25.4 mm of its bonded length was left. The free end of TPU film was pulled at 180 degree from its original position and clamped into the movable grip of the UMTS. A thermocouple was attached on the specimen to detect the surface temperature and the test temperature variation was achieved by the controllable environmental chamber. The peeling rate was set as 12 mm/min by the crosshead speed.

3.3.4 Differential Scanning Calorimetry

The thermal transitions of the TPU film were obtained by a Q200 differential scanning calorimeter (DSC) supplied by TA Instruments (New Castle, DE, USA). The Heat/Cool/Heat method was used for a temperature range of -45^{o}C to 250^{o}C with a heating rate of 10 ^{o}C/min and cooling rate of 10^{o}C/min under nitrogen purge.

3.3.5 Dynamic Mechanical Analysis

The viscoelastic behavior of the TPU film as well as PP and ABS substrates was characterized by dynamic mechanical analysis (DMA) using a Model 2980 dynamic mechanical analyzer supplied by TA Instruments (New Castle, DE, USA). The method of Temp Ramp/Single frequency was chosen for all three specimens. The TPU film was examined with a frequency of 10 Hz and amplitude of 100 μm over a temperature range of -25^{o}C to 110^{o}C, while the substrates were tested with a frequency and amplitude of 50 Hz and 15 μm, respectively from -25^{o}C to 175^{o}C (PP) and -30^{o}C to 160^{o}C (ABS).

3.3.6 Tensile Test

The mechanical behavior of the TPU film as well as PP and ABS substrates under axial tensile load was done in the UMTS under varying temperatures: 21^{o}C, 45^{o}C and 65^{o}C. The polymer tensile dogbone specimens were prepared with gauge length of 40 mm and 12.7 mm width. The test followed the procedure described in ASTM D638-14 with a crosshead speed of 12 mm/min.

3.3.7 Rheological Measurement

Rheological properties of the three adhesives were characterized using an ARES Rheometer supplied by TA Instruments (New Castle, DE, USA). Samples were prepared as circular specimens of 25 mm diameter and 1.05 mm (±10%) thickness. Dynamic strain sweep tests were firstly conducted to determine the linear viscoelastic region for each adhesive at 25^{o}C. The oscillation frequency was selected to be 1Hz, in the linear region, since the deformation rate was relatively slow more closely corresponding to the thermoforming process. Dynamic temperature sweep tests were performed based on this strain value with temperature varying from 25^{o}C to 185^{o}C with an increment of 5^{o}C and 25 seconds of soak time. After the tests, the results were reported as shear storage and loss moduli, *G'* and *G''*.

CHAPTER 4 CHARACTERIZATION

4.1 Water Contact Angle Measurement

After one-minute observation of the sessile drop on the different test surfaces, the images were analyzed and water contact angle was determined in units of degrees. Materials were classified as hydrophilic or hydrophobic surfaces based on a threshold value of 90^o. Figure 4.1 shows the average of three water contact angle measurements for all of the contacting surfaces with the error bars representing one standard deviation. The surfaces of the TPU film, as well as PP and ABS substrates were regarded as hydrophilic since their water contact angles are less than 90^o while all the adhesive layers were hydrophobic with water contact angles higher than 90^o.

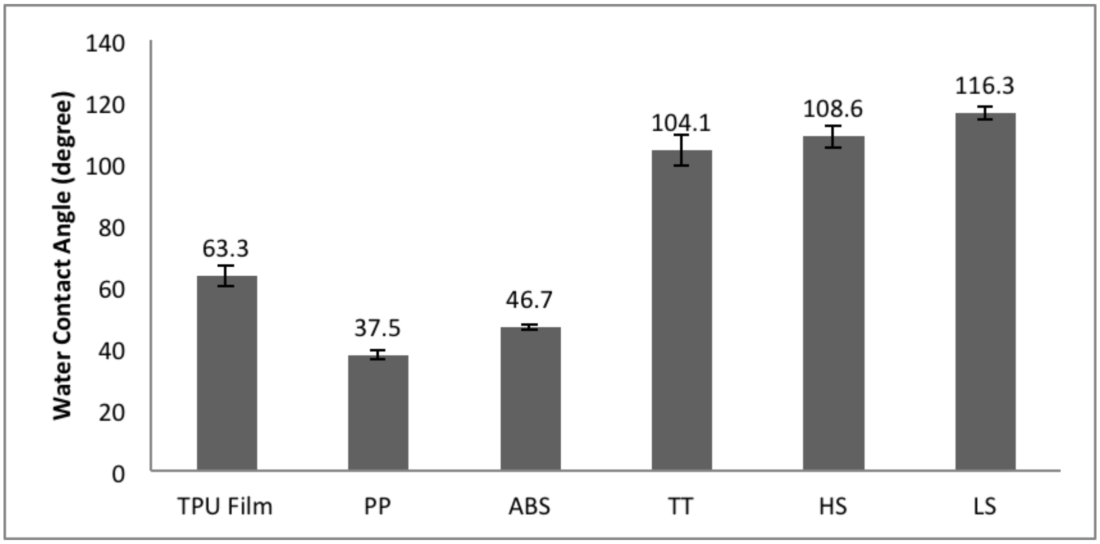
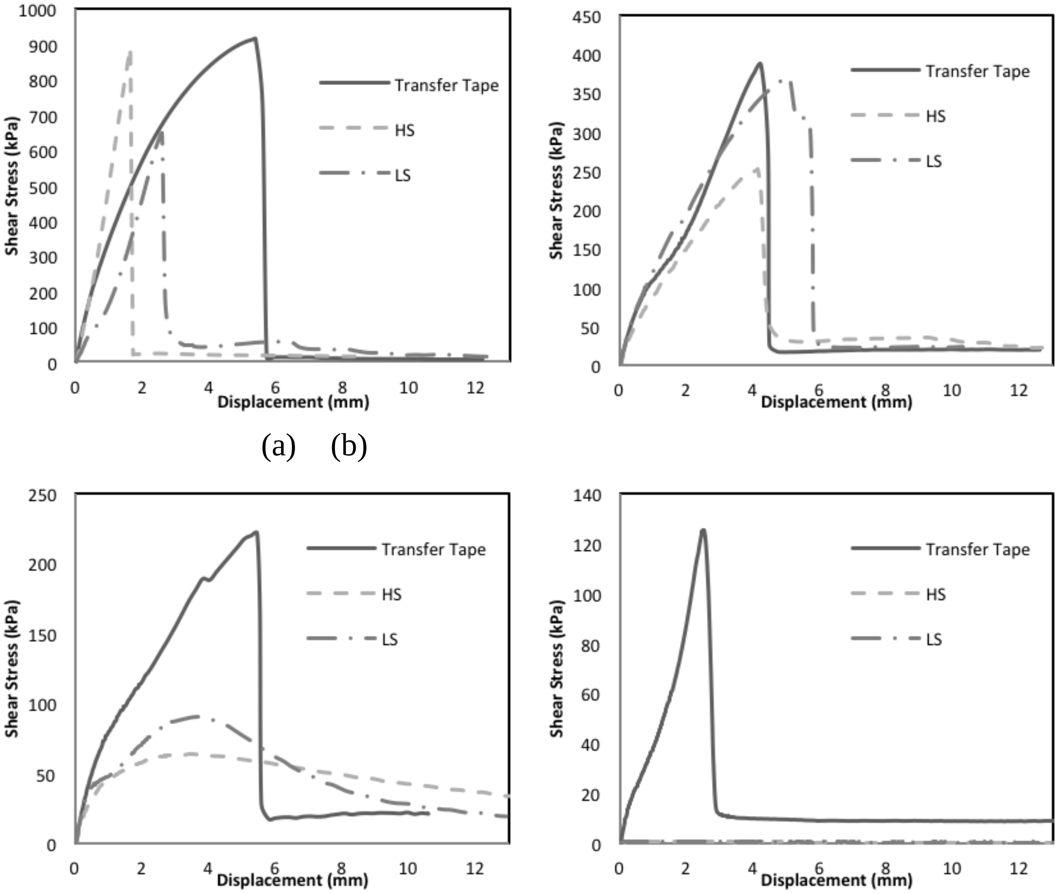


Figure 4.1: Water contact angles for the contact surfaces of laminates (TPU film, adhesives and substrates)

Compared to the other two polymer films, PP showed better hydrophilicity with a mean value of 37.5^{o}. In terms of adhesive layers, there were no differences between transfer tape and HS adhesives for water contact angle, while the LS adhesive layer indicated a higher hydrophobicity.

4.2 Lap Shear Test

The adhesion strength of the adhesive layer at the substrate-adhesive interfaces corresponding to shear deformation was examined by the lap shear test. The shear stresses responding to shear deformation of the overlapping adhesive layer between PP substrate layers is shown in Figure 4.2(a)-(c) for the temperatures used in the subsequent recovery trials. The test with adhesive between metal plates at 160 ^{o}C is shown in Figure 4.2(d). The shape of the stress-stain curve indicates the nature of the adhesive while deforming. At room temperature, the sharp linear rise of HS and LS adhesives shows an elastic response under the stain deformation, and the slopes of the linear region indicate the shear modulus of adhesives – for which both transfer tape and HS adhesive had similar values but the LS adhesive was lower. The total area of the stress-displacement curve represents the overall adhesion energy during the test. As shown in Figure 4.2(a) and (c), the adhesion energy of the transfer tape was significantly higher than HS or LS, at room temperature and 65^{o}C. Compared to HS adhesive, the adhesion strength of LS adhesive was less sensitive to increasing temperature, as shown in the results of the high temperature tests at 45^{o}C and 65^{o}C, Figure 4.2(b) and (c).



(a) (b)

(c) (d)

Figure 4.2: Lap shear test curves for PP substrates bonded with Transfer tape, HS and LS adhesives under varying temperature (a) Room temperature, 21^{o}C (b) 45^{o}C (c) 65^{o}C and (d) 160 ^{o}C for metal panels bonded adhesion

The peak values of each shear stress curve measured the shear strength of the adhesive during deformation under certain temperature (21^{o}C, 45^{o}C and 65^{o}C for bonding with PP and 160 ^{o}C for bonding with metal), summarized in Table 4.1

Table 4.1: Shear strength of adhesives under varying temperature

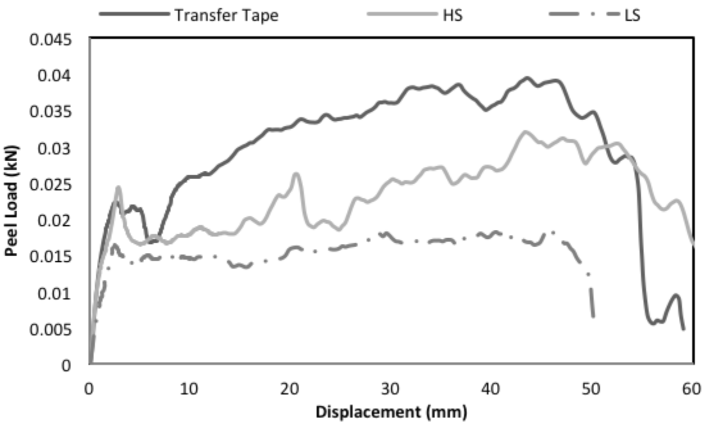
Temperature (^oC)	Shear Strength (kPa)		
	Transfer Tape	HS	LS
21 (Bonded with PP)	946.7 ±65.1	881.0 ±100.6	679.4 ±108.5
45 (Bonded with PP)	386.0 ±29.9	253.0 ±20.1	369.1 ±13.8
65 (Bonded with PP)	221.6 ±4.0	63.8 ±4.4	90.8 ±15.3
160 (Bonded with Stainless Steel)	120.0 ±32.0	0.8 ±0.3	0.8 ±0.1

The shear strengths of all adhesives decreased with increasing temperature, as indicated in Table 4.1. For all temperatures, the shear strength of the transfer tape remained the highest. At room temperature, the HS layer exhibited higher strength than the LS layer, as anticipated based on their grades of adhesive. However, at 45^oC and 65^oC, the LS adhesive exhibited higher strength than the HS adhesive. At 160^oC which relates to the thermoforming temperature, the transfer tape still exhibited significant shear strength with an averaged value of 120.02 kPa while both HS and LS adhesives were considered as fluids with near complete loss of adhesion strength. After the tests, the failure modes were noted by observation of the surfaces of the separated plates. The transfer tape presented an adhesive failure in all tests; while at both temperatures of 21^oC and 45^oC, the HS adhesive and LS adhesive showed cohesive failure and adhesive failure, respectively. For tests at 65^oC, the HS and LS adhesives showed a mixed-mode failure.

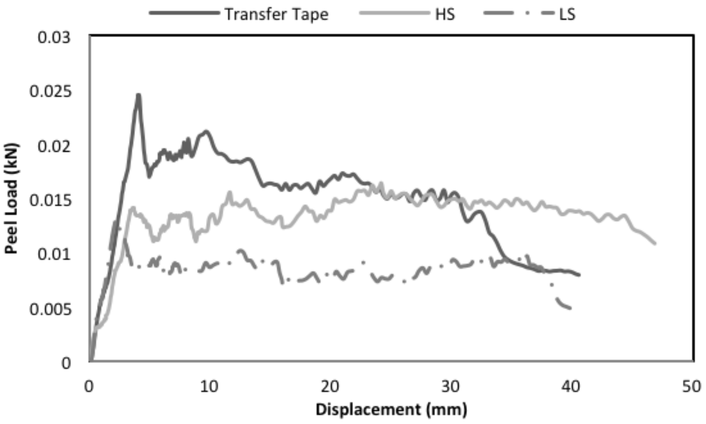
Compared to the transfer tape and LS adhesive, more cohesive failure was more often found with the HS adhesive. For the out-plane deep drawing indicative of the thermoforming process, the adhesive layer will experience both in-plane and shear deformation modes. The analysis of shear strength will help in the discussion of adhesion failure during the thermoforming process and subsequent recovery of the laminated structures in the next chapter.

4.3 180^o Peel Test

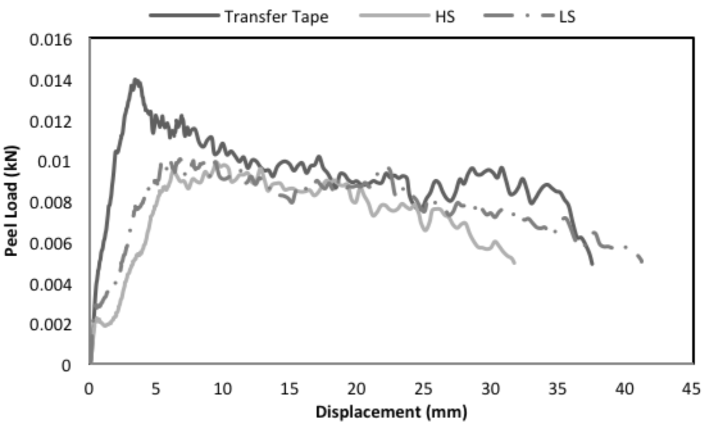
In the 180^o peel tests under varying temperatures, peel load was determined by the averaged loads within the steady region of the peel curves (normally corresponding to displacements in the range of 15 mm to 35 mm). Figure 4.3 shows that the peel strength of all three adhesives decreased with increasing temperature. At all testing temperatures, adhesion with transfer tape required the highest peel energy as indicated from the covered area of peel load curves. At room temperature, the peel loads of HS and LS adhesives remained steady beyond the peak load which could be interpreted as demonstrating adhesive failure mode – an observation consistent with visual determination. For the transfer tape at room temperature, peel load was increased as the increasing of with displacement, and the adhesive failure mode was observed based on the clear surface of the substrate. For the tests at 45^{o}C, mixed-mode failure was observed for all three adhesives, while more presence of interfacial failure on the transfer tape adhesion and more cohesive failure was observed with the HS and LS adhesives. The cohesive failure mode was obtained for HS and LS adhesives at the highest peeling temperature (65°C), while the transfer tape maintained the mix-mode failure.



(a)



(b)



(c)

Figure 4.3: Peel load curves for TPU/PP laminates with Transfer tape, HS and LS adhesives under varying temperature (a) Room temperature, 21°C (b) 45°C and (c) 65°C

The transfer tape exhibited the strongest adhesion for all three temperatures (21°C, 45°C and 65°C), consistent with the lap shear strength test. The HS adhesive had a higher peel strength at both 21°C and 45°C compared to the LS adhesive, while the results were similar for HS and LS adhesives for 65°C, as indicated in Table 4.2.

Table 4.2: Average peel strength of adhesives under varying temperature in 180° peel tests

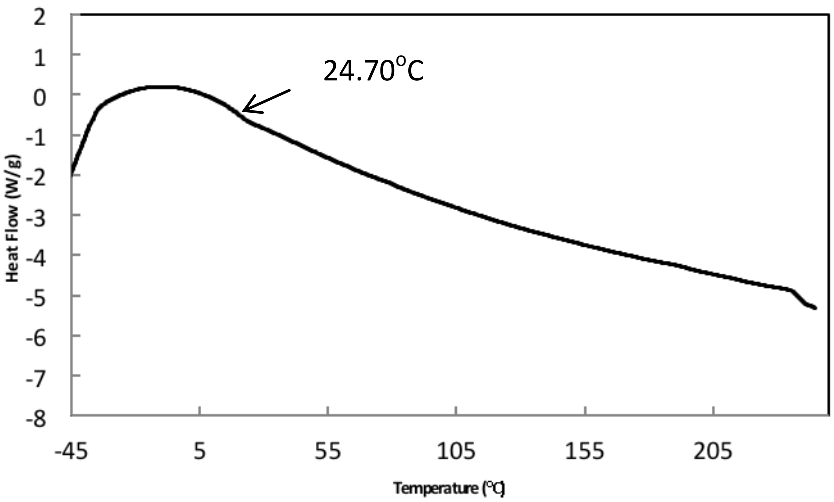
Average peel load (N)	Transfer Tape	HS	LS
21°C	1413 ± 83	1086 ± 196	590 ± 4
45°C	662 ± 21	500 ± 60	334 ± 34
65°C	368 ± 61	290 ± 25	330 ± 13

The peel strength of adhesive represented the adhesive resistance to debond against normal force. As mentioned, in the peeling test at 45°C and 65°C, cohesive failure was observed for both the HS and LS adhesives indicating weak bonding at high temperatures.

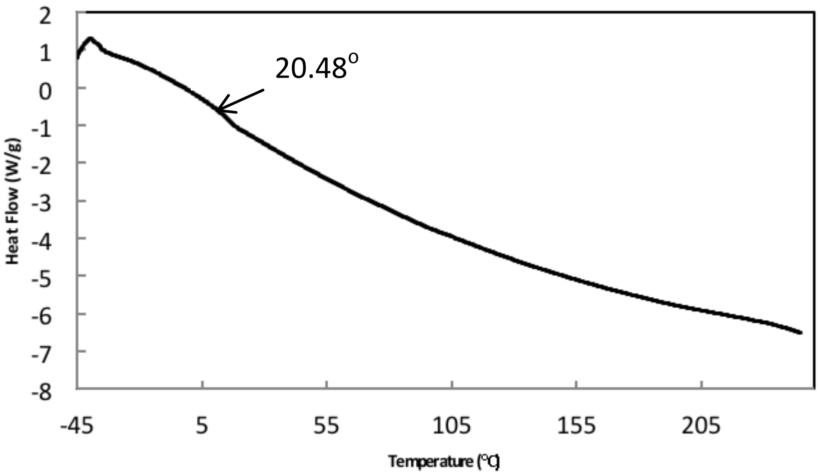
This is consistent with later discussions denoting the appearance of de-lamination during the recovery of deformed TPU laminates.

4.4 Differential Scanning Calorimetry

The thermograms corresponding to the change of temperature for two complete cycles are shown in Figure 4.4. The TPU material showed a glass transition temperature at 24.70°C in the first heating cycle, and 20.48°C during the second heating cycle upon elimination of thermal and processing history effects imposed on the specimen. The glass-transition temperature found was thought to correspond to the soft-segments of the polyurethane, and no higher transitions were found up to the scanned limit of 250°C.



(a)



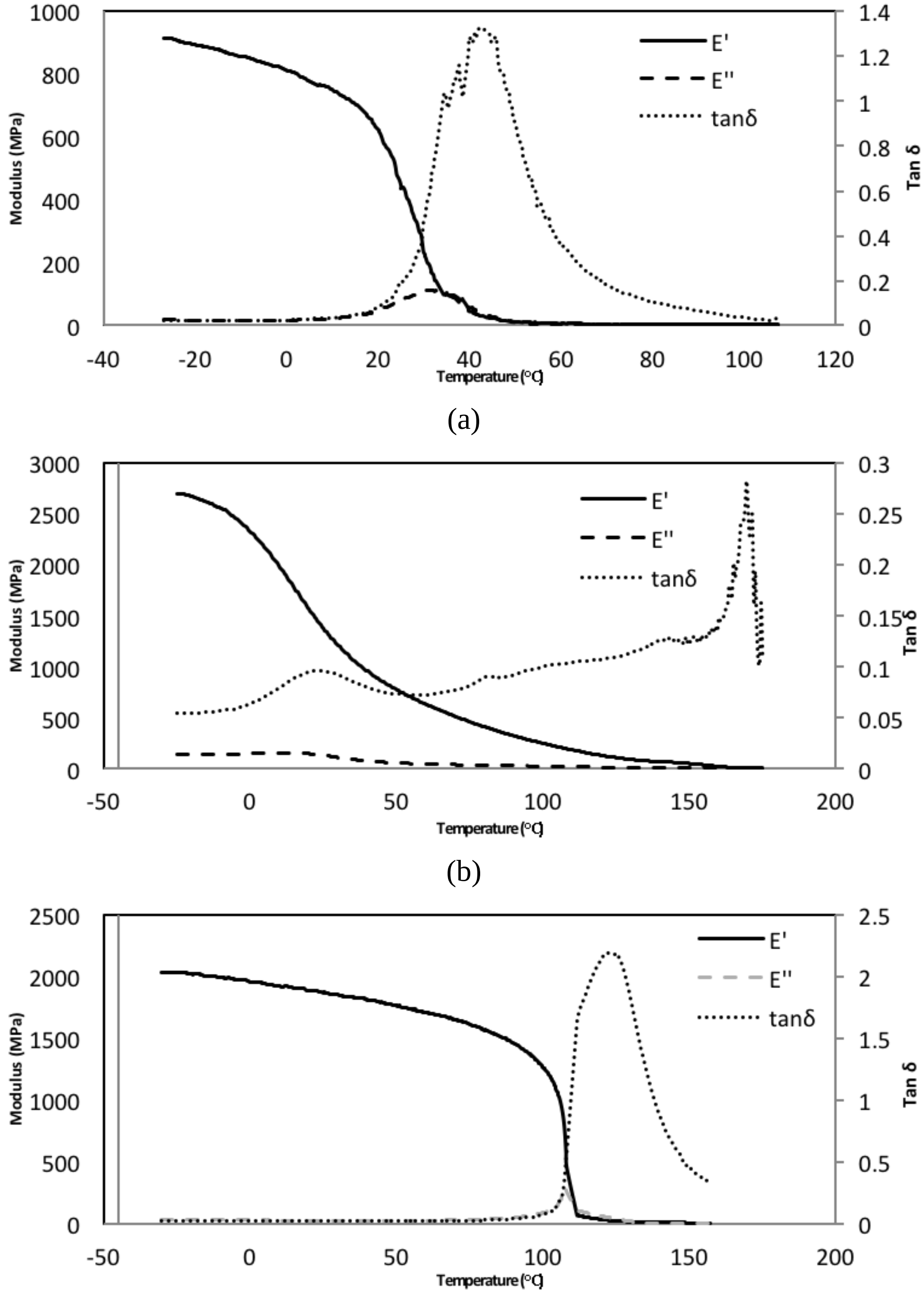
(b)

Figure 4.4: Heat flow curves obtained from DSC for a temperature range of -45°C to 250°C in (a) First heating cycle, (b) second heating cycle

The thermally defined T_g from DSC indicated the temperature that the soft-segments of TPU material started to exhibit higher mobility. Above this temperature the stresses fixed in the film by its deformed shape are lost, and the recovery phenomenon occurs as the elastic behavior of hard-segments of polymer became dominated. Based on the DSC results, the surrounding conditions for the designed recovery measurements were selected to be 15°C, 45°C and 65°C.

4.5 Dynamic Mechanical Analysis

The dynamic mechanical properties of the TPU film as well as the PP and ABS substrates were characterized by DMA. Figure 4.5 shows the dynamic tensile moduli E', E'' and Tan δ for TPU film, PP substrate and ABS substrates with respect to temperature.



(a)

(b)

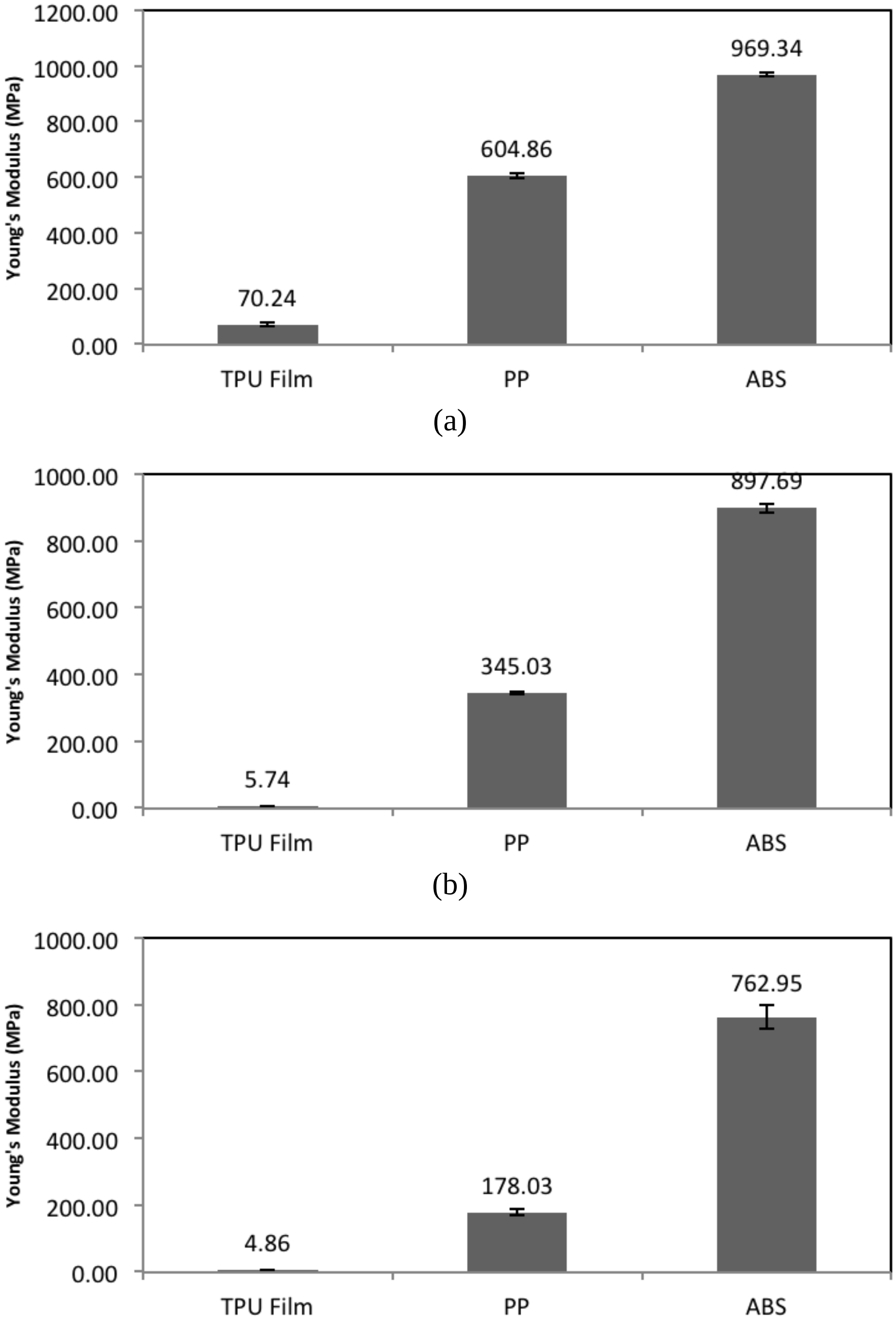
(c)

Figure 4.5: Dynamic tensile storage modulus (E'), loss modulus (E") and Tan δ for (a) TPU film from -25°C to 110°C (b) PP substrate from -25°C to 175°C (c) ABS substrate from -30°C to 160°C

The glass transition temperature of TPU was found at 42.18°C where the peak value of tangent delta appeared. This mechanically defined T_g was almost 20^{o}C higher than the T_g found by DSC. The tensile modulus of the TPU experienced a significant drop starting near 20^{o}C (DSC Tg) and plateaued at its lowest value by 60^{o}C. In terms of the substrate, the elastic stiffness of PP was consistently decreasing with increasing temperature while the ABS substrate exhibited a significant decreasing around 100^{o}C. The melting points of PP and ABS were defined as 169.5^{o}C and 125.7^{o}C, respectively. The tensile properties of TPU film and two substrates were also examined in tensile tests (Sec. 4.6) under different temperature environment (21^{o}C, 45^{o}C and 65^{o}C)

4.6 Tensile Test

The tensile testing of TPU, PP and ABS were performed with 21^{o}C, 45^{o}C and 65^{o}C to define the elastic stiffness. The results were reported as the Young's modulus (E) as indicated in Figure 4.6.



(a)

(b)

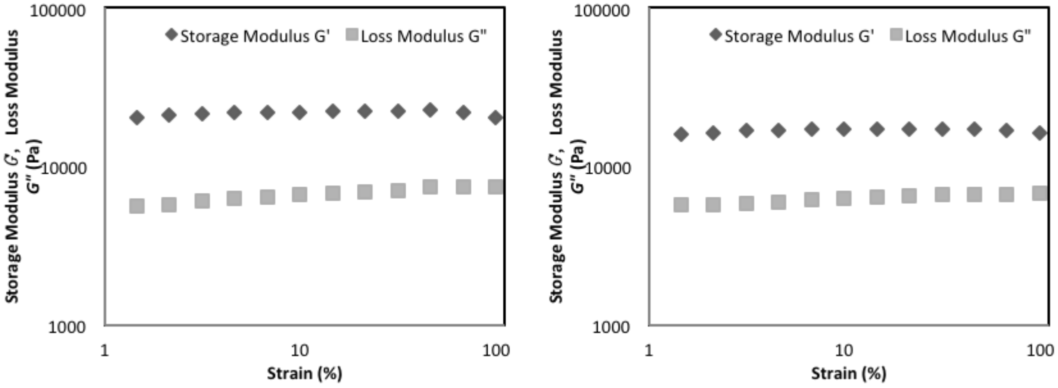
(c)

Figure 4.6: Young's modulus of TPU film, PP and ABS substrates under (a) 21°C, (b) 45°C and (c) 65°C by tensile test

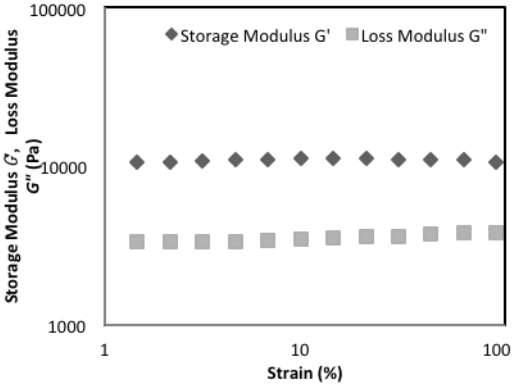
The tensile moduli exhibited by these three materials were in order of ABS, PP and lowest being TPU film. The elastic stiffness of TPU film was similar at 45^{o}C and 65^{o}C, which corresponded to the results of DMA. Meanwhile, the reducing tensile modulus of the PP substrate was much more significant (48.4%) compared to that of TPU film (15.3%). There was an insignificant change in the tensile modulus for ABS between these two temperatures. Combined with the results of DMA test, the variation of tensile moduli of polymers helped the explanation of the recovery behaviors of TPU laminates with different substrates and surrounding temperatures in the next chapter.

4.7 Rheological Measurement

The adhesive samples were initially tested for their linear viscoelastic region by running a dynamic strain sweep test for each. The results are reported as storage and loss moduli curves as a function of strain ranging from 0% to 100% at 22^{o}C as shown in Figure 4.7.



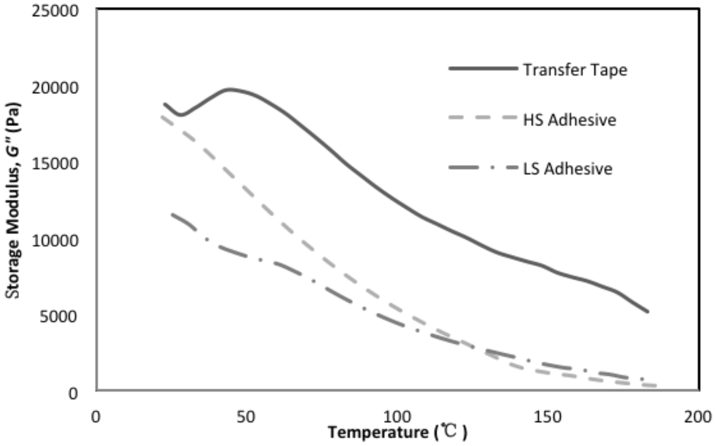
(a) (b)



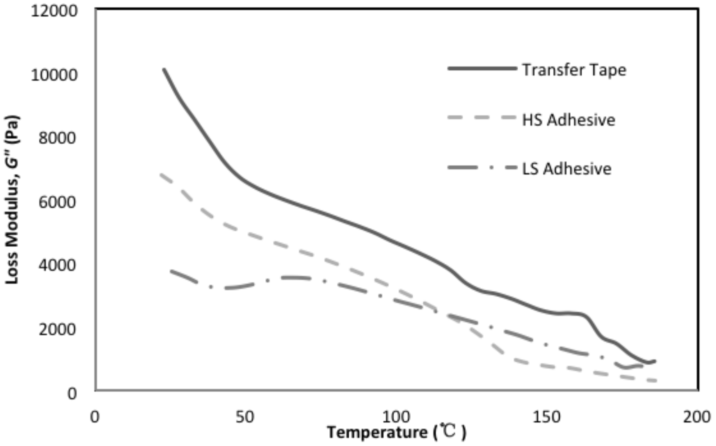
(c)

Figure 4.7: Storage and Loss Moduli *G'* and *G"* with varying strains at 25°C and 1Hz frequency for a) Transfer Tape, b) HS Adhesive and c) LS Adhesive

From observation of the moduli, the region covering strain from 15% to 45% was considered as linear for all the three adhesives. As a result, 30% strain was selected for the following temperature step tests, a value that translated to a 1 Hz frequency. The results of the dynamic temperature step tests for varying temperature (25°C to 185°C) are shown in Figure 4.8 for all the three adhesives.



(a)



(b)

Figure 4.8: Dynamic temperature step tests at 30% strain and 1Hz frequency (a) Storage Modulus G' (b) Loss Modulus G"

Within the tested temperature range, the transfer tape exhibited both higher storage and loss moduli than the HS or LS adhesives. Figure 4.8(a) indicated that the HS adhesive gave a higher shear modulus than LS adhesive when the temperature was below 120^{o}C, and the LS adhesive was stiffer at higher temperature (120^{o}C). This is consistent with the conclusion that LS adhesive is less sensitive to temperature than HS adhesive. In terms of loss modulus (G"), the results were consistent with the storage modulus where the transfer tape had the highest loss modulus, followed by HS adhesive and LS adhesive before 115^{o}C.

During the recovery of formed laminate, the recovery deformation is driven by forces generated by the TPU film. Thus the stress transfer within the multilayer structure will likely have a strong affect on the degree of recovery. The mechanical properties of the adhesive layer under the shear deformation were proven to be different among these three adhesives, and the ramifications of these results will be further discussed in the next chapter.

CHAPTER 5 RESULTS AND DISCUSSION

5.1 Parameters Defined in Stretched-Bend Forming

The simulated thermoforming process as introduced in Chapter 3 allowed the laminate sample to achieve a desired strain under sketched-bend deformation with the defined draw ratio. The schematic diagram in Figure 5.1 indicates the parameters during the forming process with the given diameters of the molds.

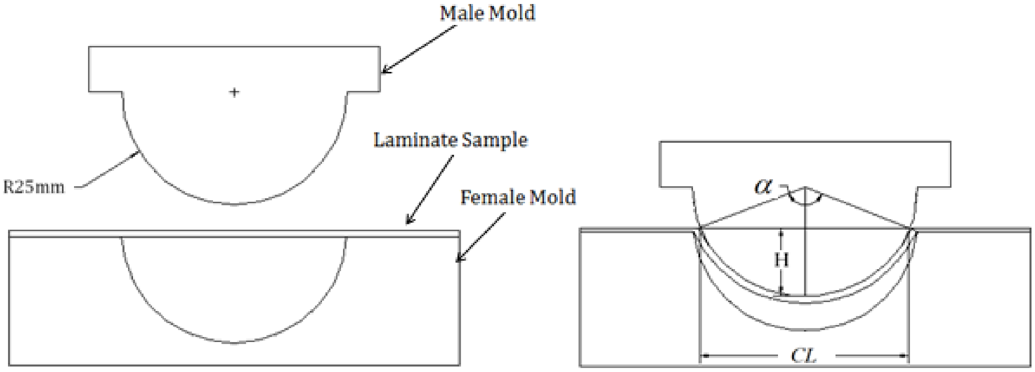


Figure 5.1: Schematic diagram of stretched-bend forming process

Regarding the geometric relationship, with the selected draw depth (H) of process, the central angle of the formed sample as noted in the diagram, α is defined as

$$\alpha = 2 \cdot \arccos(\frac{R-H}{R}) \tag{8}$$

where R is the radius of male mold, thus the arc length of laminate after forming is calculated as

$$S = \alpha \cdot R \tag{9}$$

and the chord length of the formed sample is calculated as

$$CL = 2R \cdot \sin(\frac{\alpha}{2}) \tag{10}$$

which is equivalent to the initial gauge length of the sample before the process. Therefore, the finial strain of the deformed sample is determined as:

$$\varepsilon = \frac{S - CL}{CL} \cdot 100\% \tag{11}$$

According to the derived equations above, the corresponding strains with the selected draw depths of 6mm, 10mm and 12mm in this study are 8.86%, 15.90% and 19.88%.

5.2 Recovery Mechanism

Based on the method of recovery measurement outlined in Chapter 3, the shape memory effect of the TPU in the prepared polymer laminates for different conditions are briefly summarized in Table 5.1 to give some details as the mechanism is discussed. After thermoforming, cooling and trimming, a curved shape of laminate was obtained. The formed sample was stored at a temperature below the glass transition temperature of the TPU, thus its shape was fixed (ex. 15^{o}C condition in table). Once the sample was heated above its T_g (ex. 45^{o}C or 65^{o}C condition in table), the soft segments of the TPU experienced higher mobility and the internal recovery stress stored in the hard segments due to the forming strain becoming dominate. Depending on the strain distribution in the

TPU film after the forming process, the magnitude of the recovery force varied which was applied to the substrate tangentially along the curvature of the bent sample. Although the stiffness of the substrates (PP and ABS) is higher than the TPU film at any level of temperature, the generated recovery force from TPU film was able to provide a bending moment to deform the shape of the laminate to some degree.

The effects of surrounding temperature, draw ratio, polymer substrate properties and adhesive properties on the shape memory behaviour are discussed in detail in the subsequent sections of this chapter.

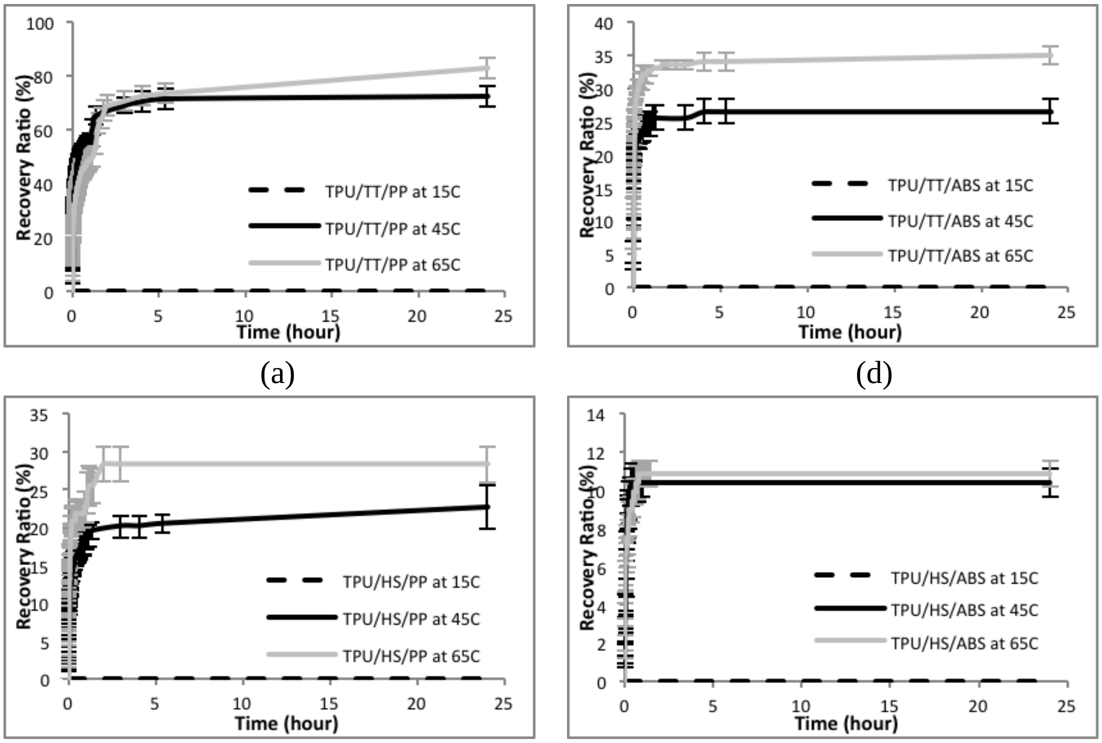
Table 5.1: Summary of recovery measurements on different laminated structure with 15.90% strain at 15°C, 45°C and 65°C

	15 °C		45 °C		65 °C	
Laminate Structure*	Final Recovery Ratio (%)	Recovery Rate (%/min)	Final Recovery Ratio (%)	Recovery Rate (%/min)	Final Recovery Ratio (%)	Recovery Rate (%/min)
TT/PP	**0**	**n/a**	**72 ± 4**	**426**	**83 ± 4**	**355**
HS/PP	**0**	**n/a**	**23 ± 4**	**76**	**28 ± 3**	**204**
LS/PP	**0**	**n/a**	**17 ± 2**	**62**	**30 ± 2**	**181**
TT/ABS	**0**	**n/a**	**26 ± 2**	**245**	**35 ± 2**	**311**
HS/ABS	**0**	**n/a**	**10 ± 4**	**68**	**11 ± 2**	**79**
LS/ABS	**0**	**n/a**	**8 ± 2**	**45**	**10 ± 2**	**62**

* TT = transfer tape, HS = high shear adhesive, LS = low shear adhesive.

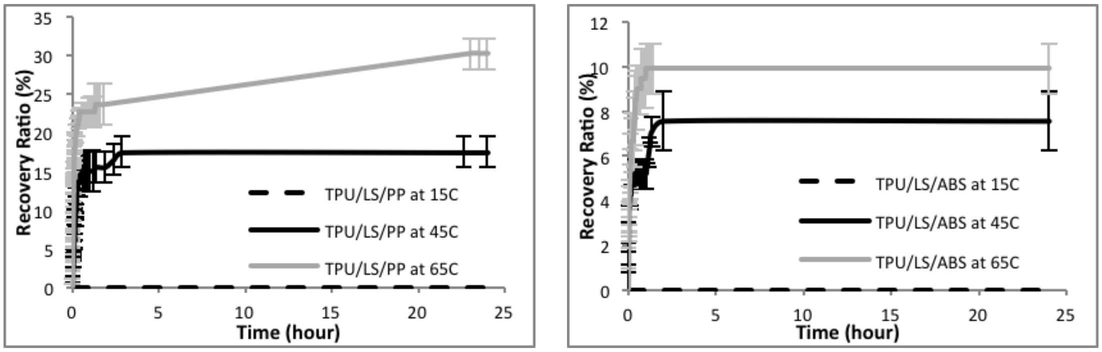
5.3 Effect of Environmental Temperature

The polymer materials used in this project were sensitive to temperature. From the testing results (DMA tests, Tensile Test and Stress Relaxation Test) in the characterization chapter, the mechanical properties of the shape memory film (thermoplastic polyurethane) and the substrates (PP and ABS) are significantly varying related to the environmental temperature (as reported in Chapter 4). Thus, different recovery performances of the laminates were observed at different temperatures. Recovery measurements were conducted under 15^{o}C, 45^{o}C and 65^{o}C, controlled by the water bath. The results were recorded and presented as a recovery ratio versus time, as shown in Figure 5.2.



(a) (d)

(b) (e)



(c) (f)

Figure 5.2: Recovery curves of (a)-(c) laminates with PP substrate and (d)-(f) laminates with ABS substrate for different environmental temperatures: 15°C, 45°C and 65°C

The formed laminates showed good shape fixity below the film T_g since there was no observation of recovery behaviour of any sample at 15°C. The recovery stresses generated by the TPU film were negligible against the resistance from the substrate at this temperature. According to the results from the DSC test, the glass transition temperature of the film was found at 23°C, meaning that the soft segment of the TPU were considered in a glassy state and fixed in its existing shape below room temperature. Thus, the majority of recovery stress of TPU film was balanced and the laminate was able to remain in its formed shape. However, significant recovery deformation was observed for all laminates at both 45°C and 65°C, now above the film T_g. As the soft segments now exhibited higher mobility, the hard segments became the dominant influence on the mechanical behaviour of the TPU film. Thus, the recovery stress generated was in response to the elastic state of the strained hard segment.

In terms of final recovery ratio, as indicated in the graphs corresponded to the laminates with PP substrate, all three samples with different adhesives showed a higher value at 65^{o}C than that at 45^{o}C. From the mechanical characterization obtained from the tensile tests back in Figure 4.6, the stiffness of polypropylene decreased from 345 MPa to 178 MPa and that of TPU film decreased 5.7 MPa to 4.9 MPa as the temperature increased from 45^{o}C to 65^{o}C. Although the elastic modulus of PP was still higher than TPU film at 65^{o}C, the modulus ratio between TPU film and PP substrate rose from $E_f/E_{PP} = 0.0166$ to 0.0273 with the temperature increase. Thus, relatively less resistance was generated against to the recovery forces from the TPU film and hence the final recovery ratio after 24 hours increased. The recovery measurements obtained for laminates with ABS substrate showed the same trend. However, the Young's modulus of ABS did not drop significantly in the tensile test and DMA results within the temperature range of 45^{o}C to 65^{o}C. The calculated modulus ratio, E_f/E_{ABS} at 65^{o}C was 0.00639, which was nearly identical to its value at 45^{o}C (i.e. $E_f/E_{ABS} = 0.00637$). Since both top layer and substrates are polymer materials, the stress relaxation behaviour was taken into consideration at this case. Stress relaxation testing was performed along with the tensile tests on the TPU film and substrates in Chapter 4. The stress relaxation curves were fitted by the Standard Linear Viscoelastic (SLV) model,

$$\dot{\sigma} + \frac{E_{1b}}{\eta_1}\sigma - \frac{E_{1a}E_{1b}}{\eta_1}\varepsilon = (E_{1a}+E_{1b})\dot{\varepsilon} \tag{12}$$

In the stress relaxation test, $\dot{\varepsilon} = 0$ and the equation can be integrated as

$$\dot{\sigma} = \varepsilon E_{1a} + C \exp(-t/\tau) \tag{13}$$

where $\tau = \eta_1/E_{1b}$ is the relaxation time of the samples, the generalized parameters were summarized in Table 5.2

Table 5.2: **Summary of stress relaxation of the TPU, PP and ABS at 21°C, 45°C and 65°C**

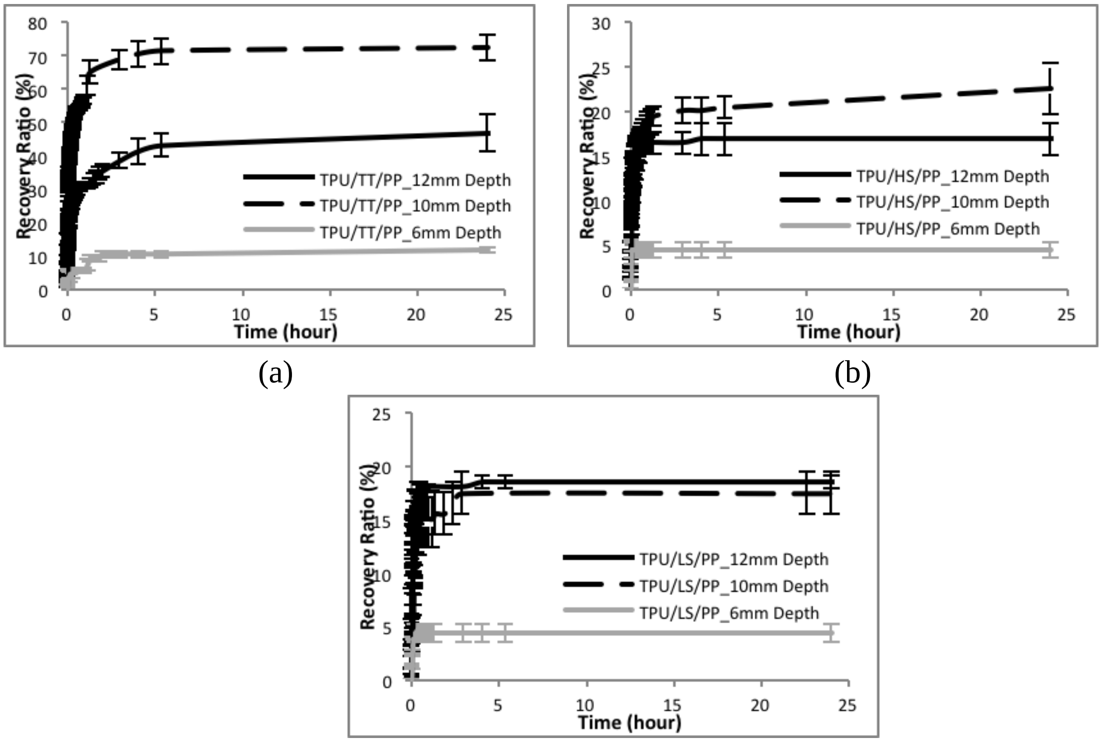
Samples	Averaged Relaxation Time (s)	SD (s)	Averaged E_{1a} (MPa)	SD (MPa)
TPU at 21°C	**36**	**2**	**11.5**	**0.5**
TPU at 45°C	**378**	**13**	**4.0**	**0.2**
TPU at 65°C	**322**	**29**	**3.6**	**0.1**
PP at 21°C	**292**	**5**	**144.3**	**1.9**
PP at 45°C	**309**	**5**	**80.9**	**1.1**
PP at 65°C	**302**	**3**	**53.2**	**0.9**
ABS at 21°C	**294**	**1**	**967.4**	**10.0**
ABS at 45°C	**428**	**13**	**541.5**	**15.9**
ABS at 65°C	**470**	**4**	**282.4**	**1.2**

According to results from the stress relaxation test at 45°C and 65°C, the storage elastic moduli of TPU and ABS after a given time period (30 min) will be reduced from 4.0 MPa to 3.6 MPa and 541.5 MPa to 282.4 MPa, respectively. The elastic storage modulus ratio, E_{1a_TPU}/E_{1a_ABS} increased from 0.0074 to 0.0129, which leads to the higher final recovery ratio seen at 65°C. Consistent conclusions were made from the stress relaxation results for the TPU film and PP, where the modulus ratio, E_{1a_TPU}/E_{1a_PP} was higher at 65°C (0.0686) than at 45°C (0.0498). Nevertheless, there were no significant differences in the cases with the HS and LS adhesives with increasing temperature as shown in Figure 5.2(e), (f), leading to the conclusion that the properties of the adhesive layer were also important to the recovery behaviour of these TPU based laminates.

With respect to recovery rate, the value was obtained from the first 5 minutes observation as shown in Table 5.1. At higher environmental temperature, the recovery rate significantly increased in most cases. As shown in Figure 5.2(b), (c), the formed samples based on PP with HS or LS adhesive showed recovery rates that increased approximately 300% from 76.44%/min and 62.30%/min, respectively at 45^{o}C to 203.77%/min and 181.13%/min, respectively at 65^{o}C. For the formed samples with ABS, an increase in recovery rate was observed as well. According to the recovery mechanism postulated for the SMP polyurethane film, soft segment retard the recovery stresses of the hard segments and lose mechanical strength above the glass transition temperature. With higher surrounding temperature and a higher initial heat flux, the phase transition can be reasonably assumed to accelerate. Therefore, although the stiffness of TPU film decreased at higher temperature, the recovery rate increased.

5.4 Effect of Draw Ratio

With the designed matched molds, the forming system had the capacity to draw sample to a maximum 15 mm draw depth with a curvature radius of 25 mm. However, failure on the gauge section of TPU surface occurred before such a large draw ratio could be achieved. The maximum forming depth of the laminate in this forming system was found to be approximately 12 mm. Since the shape memory behaviour was considered as a natural elastic response of the TPU film, deformational strain of the TPU film determined the internal recovery forces it generated, thus affecting the overall recovery deformation of laminated structure. A series of forming processes with draw depths of 6 mm, 10 mm and 12 mm were performed on the laminates with different adhesives for PP substrate, and the recovery behaviour was recorded and shown in Figure 5.3 at 45^{o}C



(a) (b)

(c)

Figure 5.3: Recovery curves of lamiantes with (a) Transfer tape, (b) HS adhesive and (c) LS adhesive under different pre-deformation draw depths of 6mm, 10mm and 12mm at 45^{o}C

There was a consistent result among these three testing results that laminates drawn to a depth of 6mm demonstrated the lowest recovery ratio (11.80% for TT, 4.40% for HS and LS samples). This trend is predictable as there was lower recovery stress contributing to flatten the deformed laminate due to the relatively low strain of TPU film (8.86%). Compared to the low strained sample, laminate experiencing deeper draw recovered more and recovered faster at 45^{o}C as highlighted in Table 5.3.

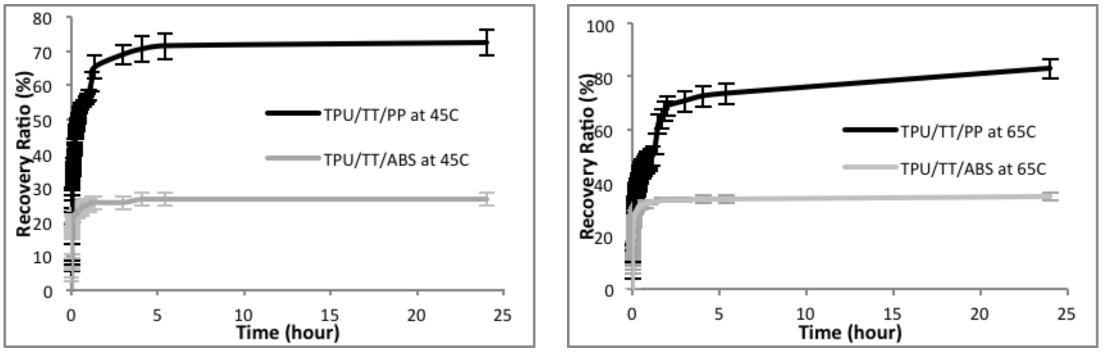
Table 5.3: Summary of recovery measurements on different laminated structure at 45^{o}C

	Draw Depth 6mm		Draw Depth 10mm		Draw Depth 12mm	
Laminate Structure	Final Recovery Ratio (%)	Recovery Rate (%/min)	Final Recovery Ratio (%)	Recovery Rate (%/min)	Final Recovery Ratio (%)	Recovery Rate (%/min)
TT/PP	**12 ±1**	**45**	**72 ±4**	**426**	**47 ±6**	**214**
HS/PP	**4 ±1**	**41**	**23 ±4**	**76**	**17 ±2**	**131**
LS/PP	**4 ±1**	**31**	**17 ±2**	**62**	**19 ±1**	**167**

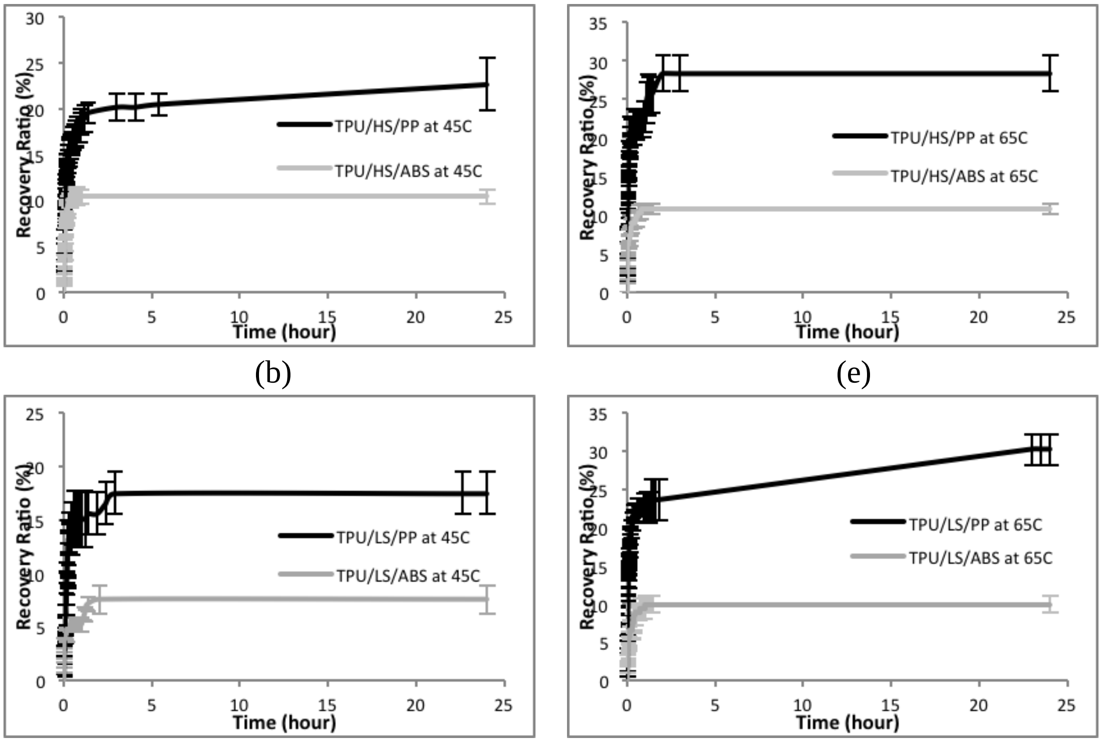
Although there was no significant variation on the recovery behaviour of LS adhesive samples with draw depth of 10 mm and 12 mm, there is a surprising observation on the results shown in Figure 5.4(a), (b). Laminates at the highest forming strain (19.9%) demonstrated a lower recovery ratio than the samples at 15.9% strain, especially in the case of TT bonded laminate. It is true that more recovery force was generated on the TPU film with deeper drawing process. However, the moment required to flatten the bended sample was not solely depending on the magnitude of the driving force. As the draw depth increased, the curvature radius of arched sample decreased. Thus, the overall moment generated on the whole structure may not be proportional to the internal force. Based on the results presented in this section, it is reasonable to assume that there is a maximum recovery ratio at a certain depth of drawing around 10 mm. It was also possible that this extent of strain was too high, exceeding the creep resistance of the polymer and hence some of the strain recovery energy dissipated before shape recovery could occur.

5.5 Effect of Substrate

The simulated thermoforming process was conducted at a processing temperature that was around 20^{o}C~30^{o}C below the melting temperature of the substrate. The PP and ABS were formed and orientated into the new shape, with little residual stresses generated by the quenching process (as evident by the negligible recovery found at 45^{o}C and 65^{o}C in the absence of film). Therefore, the supporting substrate presented a resistance against the recovery stresses of the film during recovery. Thus, the mechanical property of the substrate was thought to be important to the recovery deformation in a laminated structure. Figure 5.4 shows the recovery curves of TPU based laminates with PP and ABS substrates.



(a) (d)



(b) (e)

(c) (f)

Figure 5.4: Recovery curves of lamiante at (a)-(c) 45°C and (d)-(f) 65°C with different substrates PP and ABS

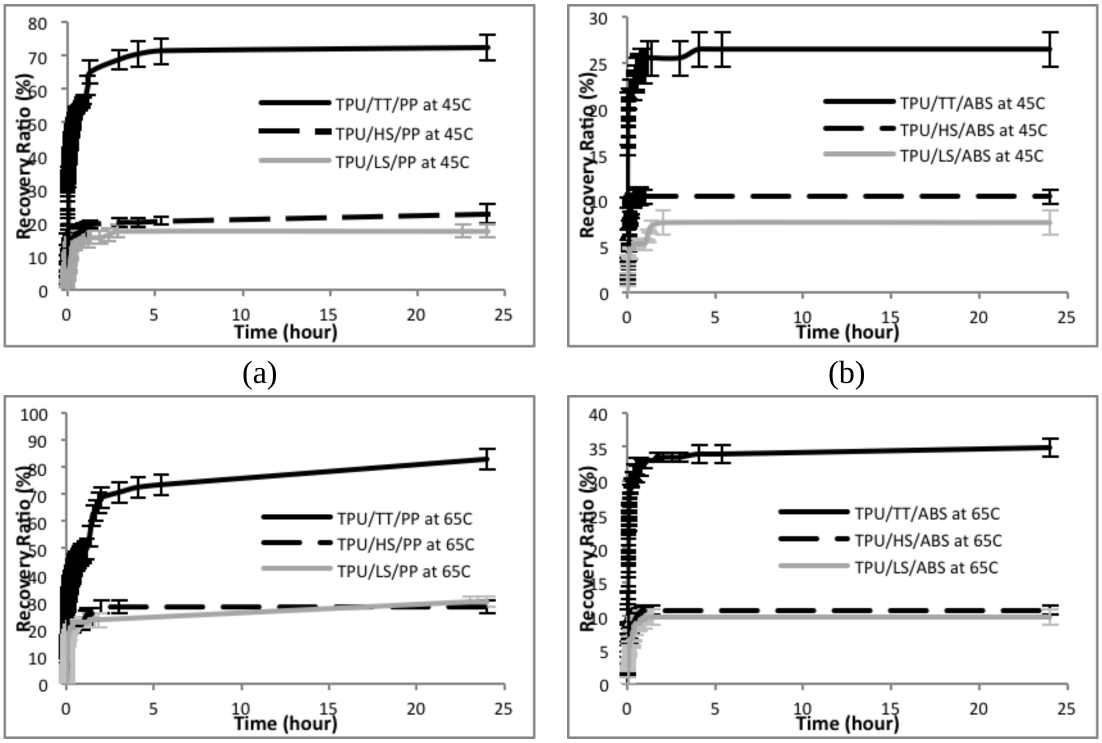
From all the graphs above, it can be seen that the recovery ratios of samples with PP were higher than with ABS substrate at both 45°C and 65°C no matter which adhesives were applied. The distinct differences in the mechanical properties of PP and ABS were considered as the main reason for this phenomenon. From the result of tensile tests in Figure 4.6, the Young's moduli of ABS were calculated as 969 MPa, 897 MPa and 762 MPa at 21°C, 45°C and 65°C, respectively, while the stiffness of polypropylene substrate were less than half of the moduli of ABS at each temperature. Therefore, PP provided less supporting force for shape fixity of laminate. The resistive stresses in the rigid material (ABS in this case) against the recovery stresses were higher, thus the recovery effect was attenuated.

For the effect of substrate on recovery rate, the corresponding magnitudes for the laminates with TT, HS and LS adhesives and PP substrate at 45^{o}C are 426.4%/min, 76.4%/min and 62.3%/min. Compared to that with ABS substrate (245.3%/min, 67.9%/min and 45.3%/min), PP was more compliant to the recovering TPU film for each adhesive. Similar trend was found in the measurements for the surrounding temperature of 65^{o}C. Discussion of the adhesive effect in these data will be given in a following section of this chapter.

5.6 Effect of Adhesive

5.6.1 Experimental Approach

Typically, an adhesive is simply considered the bonding substance in a laminated structure, and more concern is given to its adhesive properties. From the perspective of laminate shape recovery, an adhesion failure would produce delamination and hence change the mechanical behaviour of the overall structure. But, the mechanical properties of the adhesive layer should also be considered as an important factor during the deformation and recovery of thin-film laminates. The recovery behaviour presented in this work was basically driven by the restorative recovery stress in the top TPU film, and that stress was then transferred to the substrate polymer through the adhesive layer. In order to investigate the effect of stiffness property of adhesive on the shape memory behaviour of formed laminate without the possibility of viscous sliding, the free end of each trimmed sample was sealed by epoxy as mentioned in Chapter 3. Figure 5.5 indicates the recovery measurement results of TPU laminates with three adhesives, namely transfer tape, HS and LS supported by two substrates, PP and ABS.



(a) (b)

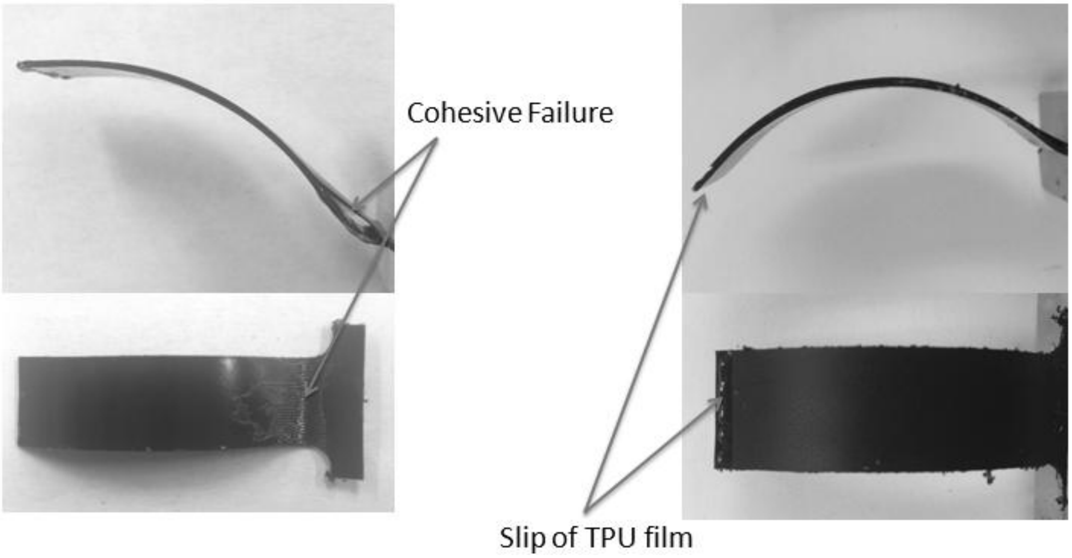
(c) (d)

Figure 5.5: Recovery curves of laminate at (a)-(b) 45°C and (c)-(d) 65°C with different adhesives.

Compared to the sample laminated with the transfer tape, it is obvious that both of final recovery ratio and recovery rate of laminates (Table 5.2) were dramatically decreasing with HS and LS bonding in all the situations. This result was consistently observed for the laminates with either PP or ABS substrate. Comparing results of the HS and LS adhesives, although the HS adhesive had higher lap shear strength and peel strength versus the LS adhesive at room temperature, the physical differences between these two adhesive was narrower as temperature increases. By 65^{o}C, the lap shear strength and peel load of the LS adhesive was 90.8 MPa and 336.9 N, which were even a bit higher than that of HS adhesive. Thus, the recovery behaviour of samples with HS and LS adhesives did not show significant differences at the two investigated elevated temperatures.

With respect to the mechanical properties of these adhesives, the results obtained from lap shear test at 45^{o}C and 65^{o}C indicated that the transfer tape exhibited the highest shear strength compared to the other two adhesives. In terms of stiffness under the shear field, the corresponding shear storage modulus of all the three adhesives were obtained as 18.11 kPa, 13.66 kPa and 9.08 kPa, respectively at 45^{o}C and 16.49 kPa, 10.12 kPa and 7.85 kPa, respectively at 65^{o}C for TT, HS and LS. The internal recovery stress of the top layer TPU film can be considered to apply along the surface of a substrate in the tangential (shear) direction. During stress transfer through the adhesive layer to the bottom layer, a stiffer bond line is able to transfer the stress faster and effectively (Le and Nairn, 2014). Therefore, the laminate with most rigid adhesive (transfer tape) would introduce a higher recovery ratio which is matched with the experimental results.

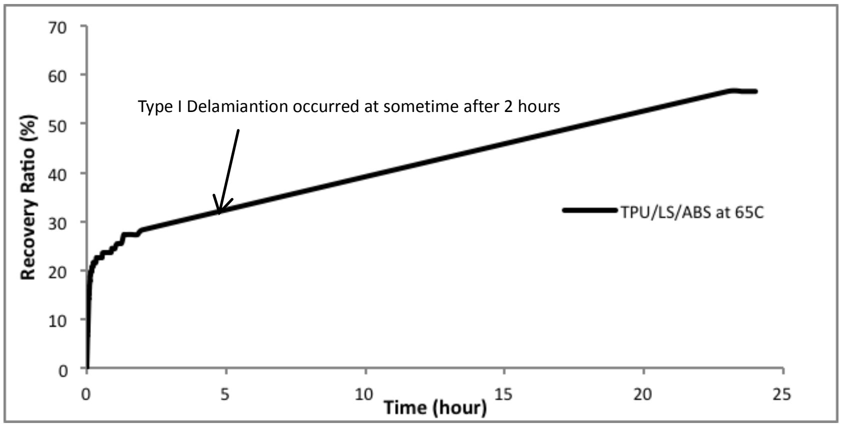
Another interesting observation was when delamination occurred during recovery of a sample. Since the adhesion provided by transfer tape was relatively strong, no delamination was observed during the recovery measurement. However, two types of delamination could occur in a sample with HS and LS adhesives, as classified and visually shown in Figure 5.6.



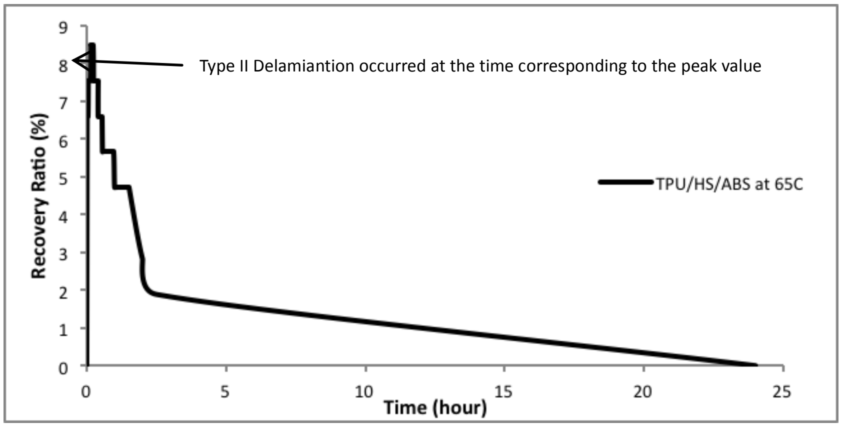
(a) Type-I (b) Type-II

Figure 5.6: Illustration of delamination of TPU based laminate with HS or LS adhesives (a) Type-I, cohesive failure at the bend, (b) Type-II, TPU slip at the edge

Examples of how the recovery curves reflected these two types of delamination are presented in Figure 5.7. As the temperature of sample increased, the adhesion between top layer and substrate became weaker and failed. The first type of delamination frequently occurred when the free end of sample was sealed and only at the higher temperature condition, 65^{o}C. Upon cohesive failure, the TPU film detached from the substrate and a large bending moment was generated over the whole structure, pulling the free end of the substrate in the clockwise direction. The recovery ratio of laminate with LS adhesive and ABS substrate in Figure 5.7(a) showed an unexpected increasing trend after 2 hours' recovering.



(a)



(b)

Figure 5.7: Typical recovery curves of laminate with a) Type I delamination, b) Type II delamination

The resultant recovery ratio was listed in Table 5.4, indicating a relative high recovery ratio due to this type of delamination. The second type of bond failure resulted in slippage of the TPU film freely along the substrate surface when the end of the trimmed sample was free (i.e. no epoxy). Compared to the sample with sealed tip, the consequence of type-II delamination was that the recovery ratio of laminate dramatically reduced depending on the distance that the TPU film could slid. As demonstrated in Figure 5.7(b), the recovery ratio rose up as usual then started to decrease down to zero (example is for a laminate with HS adhesive at 65^{o}C). The TPU film was found to start sliding once the peak recovery ratio shown on the curve arose. Since most of the recovery stresses were relieved by the TPU being allowed to revert back to its original length without need to transfer its recovery stress to the substrate (particularly at 65^{o}C where the adhesives had little shear strength), the laminate experienced little or no recovery.

Table 5.4: Final Recovery Ratio of laminates with different types of delamination at varying temperature

	Recovery Ratio	
	Type-I Delamination Cohesive failure at the bend	Type-II Delamination TPU slip at the edge
LS/PP @ 45^{o}C	**N/A**	**6%**
HS/PP @ 45^{o}C		**8%**
LS/PP @ 65^{o}C	**64 %**	**0%**
HS/PP @ 65^{o}C	**52%**	**1%**
LS/ABS @ 45^{o}C	**N/A**	**4%**
HS/ABS @ 45^{o}C		**1%**
LS/ABS @ 65^{o}C	**57%**	**0%**
HS/ABS @ 65^{o}C	**43%**	**0%**

***N/A states that there was no delamination observed**

5.6.2 Numerical Analysis

In this project, the thickness of pressure-sensitive adhesive (PSA) (0.13mm) could not be ignored as it was relatively significant compared to the TPU film (0.2 mm). To investigate the effect of the adhesive layer on stress transfer within a laminated structure, finite element analysis (FEA) was used with the aid of ANSYS Mechanical APDL software (ANSYS Inc.; Canonsburg, PA). The problem was analyzed as a simplified 2D system. A three-layer structure (40mm × 0.83mm) was conducted with the element PLANE182, and the thickness of each layer was defined as 0.5 mm, 0.13 mm and 0.2 mm for substrate, PSA layer and TPU materials, respectively as shown in Figure 5.8. The contact pairs were created to constrain the deformation between each layer. In order to simplify the contact problem, the interfacial relationship of the contact pairs was selected as Bonded (always). Thus, neither separation in normal direction nor slip in tangential direction would occur during the deformation.

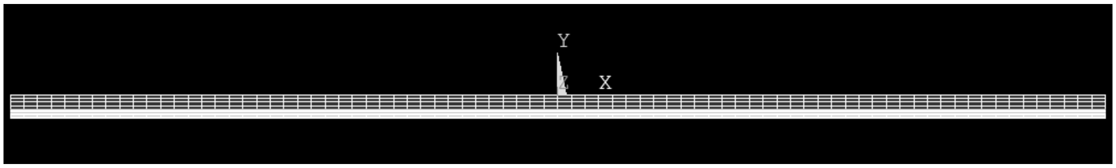


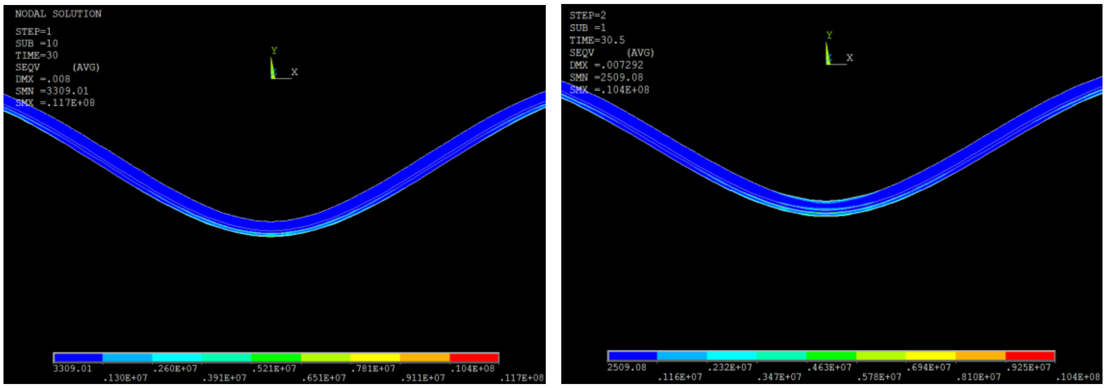
Figure 5.8: Schematic diagram of finite element model with three layers: Substrate, adhesive and film. (From top to bottom)

The stress-strain curve of the TPU layer could have been fitted to the Mooney-Rivilin model for system temperatures above Tg to give a hyper-elastic property of material, but to reduce nonlinearity in the simulation model for satisfactory convergence the TPU was instead treated as a simple isotropic elastic material (E_x=500 MPa, Poisson Ratio$_{xy}$=0.3). A viscoelastic property was assigned to the PSA layer based on a 3-element generalized Maxwell model (mentioned in Chapter 2) with relative modulus of 0.8 and relaxation time of 1.72 s, and a stiffness varying from 5 MPa, 10 MPa or 15 MPa. In the generalized Maxwell model in ANSYS, the relaxation modulus was defined as:

$$\mathrm{E(t)} = \mathrm{E_0}[\alpha_i + \sum_{i=1}^{n} \alpha_i \exp\left(-\frac{t}{\tau_i}\right)] \tag{14}$$

Where α_i is the relative modulus representing the percentage of stiffness that is lost with relaxation time τ_i, and E_0 is the stiffness at t = 0 s. During the thermoforming process, the substrate (E_x=800 MPa, Poisson Ratio_{xy}=0.4) was heated to a softened state. Thus, the substrate was assumed to experience exclusive plastic deformation with a relatively low yield stress ($\sigma_y = 10000Pa$) in the simulation of forming at high temperature.

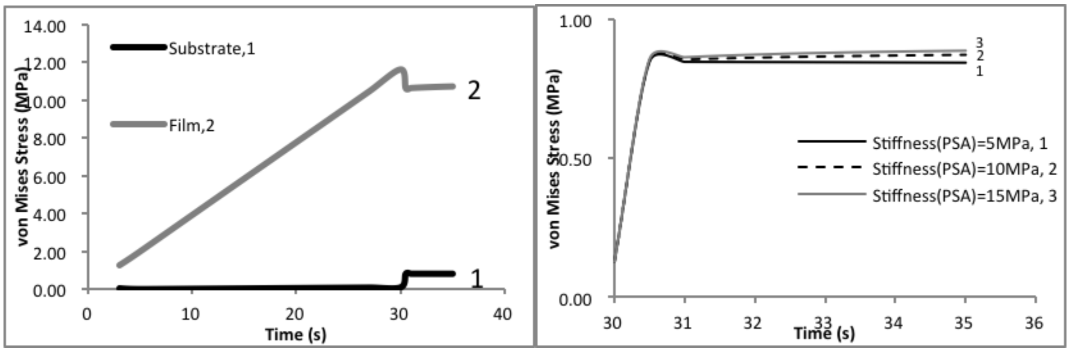
In the first 30 s, a displacement of 10 mm was applied on the centre position on the top of substrate, and two end of laminate was fixed for all degrees of freedom. Thus, the laminate would be stretched and bent at high temperature. In the second load step, the load at the centre of laminate was removed and the response of structure was investigated for 5 seconds with the same applied boundary conditions as load step 1. As shown in Figure 5.9 (a), (b), the laminate recoiled to a small degree once the load was removed.



(a) (b)

Figure 5.9: Stress distribution of laminate right after (a) Loading (b) Unloading

Individual simulations were conducted with the three different adhesives for varying stiffness (case 1: E_{PSA}=5 MPa; case 2: E_{PSA}=10 MPa; case 3: E_{PSA}=15 MPa), and the equivalent stress (von Mises stress) at the centre of substrate along the load direction was recorded during the loading and unloading process. Since the substrate yielded at an early stage with loading at high temperature, any elastic stresses stored in the substrate were negligible, thus the calculated stresses recorded in the substrate were a result of strain release by the film when unloaded.



(a) (b)

Figure 5.10: Stress-time curves of (a) Substrate and film in case 1 (E_{PAS}=5MPa), (b) Substrate in three cases with different adhesives

As indicated in Figure 5.10(a), stresses generated in the substrate did not arise until

30.5 s into the process when a corresponding drop in stress was noted for the film. The effect of adhesive stiffness was demonstrated in the Figure 5.10(b), although there was no major difference in the resulting stresses in the substrate based on the three different PSAs. It was found that the stresses in the substrate increased as the adhesive stiffness increased and perhaps more importantly showed gradually increasing substrate stresses after 30 s (10 MPa and 15 MPa cases) rather than the plateau noted with 5 MPa. This trend could explain the results found in Figure 5.5 that the stiffer transfer tape adhesive transferred the stress from the TPU to the substrate more effectively and caused higher recovery ratio. This may be too simple of an answer since the model is neglecting other behaviours in the adhesive such as shear deformation or adhesion failures as well as creep in the substrate, but the fact that the trends seen in Figure 5.5 could be predicted by only considering the modulus of the adhesive was remarkable as it shows how influential this otherwise overlooked layer can be on mechanical response.

Because of the simplifications made in the model to neglect nonlinearity in these materials, the simulation of the recovery behaviour as well as the delamination and damping effect of adhesion were not completed at this time; more efforts in the FEA on this shape memory material is needed.

CHAPTER 6 CONCLUSIONS

Because of its shape memory effect, multiphasic thermoplastic polyurethane (TPU) has drawn a great deal of attention from academia and industry. With unique anti-scratch properties and a high level of mechanical strength and flexibility, film-grade TPU is considered to be an alternative material for paint replacement in the automotive industry. The possibility for in-mold forming of the TPU film is considered important to broaden its application. However, the shape fixity of a formed part with TPU film is influenced by its shape memory effect, and hence introduces a new factor for consideration in normal forming processes.

In this study, the shape memory TPU film was laminated to one of two common plastic substrates (PP or ABS) with one of three different pressure sensitive adhesives (designated as Transfer tape, HS and LS adhesives). The rigid substrates provided resistance against the recovery forces and reinforced shape fixity of the laminate after thermoforming, whereas the adhesive served to bond the TPU film to the substrate. A stretching-bending process like thermoforming was simulated in this project using a pair of matched molds, and the shape memory behaviour of the resulting formed laminate sample was investigated by a specialized measurement method.

In terms of temperature effect, the formed laminate showed good shape fixity at

15^{o}C, which was below the TPU's glass transition temperature (23^{o}C). The recovery behaviour was only observed in cases when the ambient temperature was above T_g, namely 45^{o}C and 65^{o}C. Although there was no significant difference in Young's modulus for the TPU between these two temperatures, the drop in modulus of the substrate from 45^{o}C to 65^{o}C led to a higher recovery ratio of laminate at the higher temperature. The recovery rate was found to be higher at 65^{o}C as well, which was the result of higher molecular motion in the soft segments.

The laminate samples were formed with differing degrees of curvature to study the effect of draw ratio on their shape memory behaviour. The results indicated that the recovery rate of laminate increased with a deeper molding as a result of larger recovery stresses beings generated in TPU. Samples with 10 mm draw depth showed the highest recovery ratio at 45^{o}C, while the lowest recovery ratio was found in the sample with 6 mm draw depth. Beyond 10 mm draw depth the recovery ratio again decreased. No explanation could be determined for this maxima.

The recovery measurement of laminate samples with different substrates showed that the stiffer ABS compared to PP provided more resistance to the recovery force of the TPU, thus reducing the recovery ratio and recovery rate of formed laminates at both test temperatures (45^{o}C and 65^{o}C).

The influence of adhesion on the shape memory behaviour of the TPU laminate was a central focus to this study, varying the shear strength of the adhesive layer. The recovery results of all laminates bonded with the high shear strength transfer tape showed a significantly higher recovery ratio and recovery rate than found with the laminates with HS and LS adhesives. A finite element analysis was performed by considering the stiffness of adhesives as a variable in the forming and recovery of a three-layer structure. The numerical simulation indicated that the stress transferred more efficient within the laminate with stiffer bond line, which could explain why the stiffer transfer tape produced a higher recovery ratio and recovery rate in its laminates. A desire might be to use HS and LS with their relatively low adhesion strength in order to minimize stress transfer and reduce recovery in formed parts compared to transfer tape; however, delamination or sliding was found during recovery. The TPU film was found to slide at with these two lower strength adhesives when the edges of specimens were not sealed, which released the stored recovery stress of the film with less transfer to the substrate over 24 hours investigations. When the edges of specimens were sealed and the film could not slide, a cohesive failure was observed but only at the highest test temperature (65^{o}C). In the latter case, a higher bending moment actually occurred thus increasing the apparent recovery ratio.

In conclusion, the shape memory behavior of TPU based laminate with varying adhesives and substrates was studied. The effects of temperature, draw ratio, substrate and adhesive were investigated. In particular, the adhesive layer showed its importance to the deformation behavior of the laminate.

REFERENCES

3M_AUTOMOTIVE_AFTERMARKET&MARINE. 2015. *Scothgard Paint Protection Film Pro Series* [Online]. [Accessed 05/02 2015].

ABRAHAMSON, E. R., LAKE, M. S., MUNSHI, N. A. & GALL, K. 2003. Shape memory mechanics of an elastic memory composite resin. *Journal of Intelligent Material Systems and Structures,* 14**,** 623-632.

AMARO, A., REIS, P. & DE MOURA, M. 2011. Delamination effect on bending behaviour in carbon–epoxy composites. *Strain,* 47**,** 203-208.

ASLOUN, E. M., NARDIN, M. & SCHULTZ, J. 1989. Stress transfer in single-fibre composites: effect of adhesion, elastic modulus of fibre and matrix, and polymer chain mobility. *Journal of materials science,* 24**,** 1835-1844.

BAI, J. & SUN, C. 1995. The Effect of Viscoelastic Adhesive Layers on Structural Damping of Sandwich Beams*. *Journal of Structural Mechanics,* 23**,** 1-16.

BALAMURUGAN, G. P., PUKADYIL, R. N., NIELSEN, K. E., BRANDYS, F. A. & THOMPSON, M. R. 2013. Role of a micro-patterned adhesive interface on the performance of thermoformable multi-layered decorative polymeric film laminates. *International Journal of Adhesion and Adhesives,* 44**,** 78-90.

BALDEN, A. 2004. Review: adhesively bonded joints and repairs in metallic alloy, polymers and composite materials: adhesives, adhesion theories and surface pretreatment. *J Mater Sci,* 39.

FUCHS, I. L. 2014. *PAINT REPLACEMENT FILM WITH POLYMER LAYER CONTAINING POLYURETHANE*. PCT/US2014/043755.

FUJII, T. 1993. Dynamic response of sandwich beams with an adhesive damping layer (generalized Maxwell model for a viscoelastic adhesive layer). *International journal of adhesion and adhesives,* 13**,** 201-209.

GHINET, S. & ATALLA, N. 2007. Modeling of general laminate composite structures with viscoelastic layer. *Canadian acoustics,* 35**,** 202-203.

HANSEN, S. W. & SPIES, R. D. 1997. Structural damping in laminated beams due to interfacial slip. *Journal of sound and vibration,* 204**,** 183-202.

HU, J. L., JI, F. L. & WONG, Y. W. 2005. Dependency of the shape memory properties of a polyurethane upon thermomechanical cyclic conditions. *Polymer international,* 54**,** 600-605.

JEONG, H. M., LEE, S. Y. & KIM, B. K. 2000. Shape memory polyurethane containing amorphous reversible phase. *Journal of materials science,* 35**,** 1579-1583.

JOHNSON, C. D. & KIENHOLZ, D. A. 1982. Finite element prediction of damping in structures with constrained viscoelastic layers. *AIAA Journal,* 20**,** 1284-1290.

LAPIQUE, F. & REDFORD, K. 2002. Curing effects on viscosity and mechanical properties of a commercial epoxy resin adhesive. *International journal of adhesion and adhesives,* 22**,** 337-346.

LAWCOCK, G., YE, L., MAI, Y.-W. & SUN, C.-T. 1997. The effect of adhesive bonding between aluminum and composite prepreg on the mechanical properties of carbon-fiber-reinforced metal laminates. *Composites Science and Technology,* 57**,** 35-45.

LE, E. A. & NAIRN, J. A. 2014. Measuring interfacial stiffness of adhesively bonded wood. *Wood Science and Technology,* 48**,** 1109-1121.

LEE, B. S., CHUN, B. C., CHUNG, Y.-C., SUL, K. I. & CHO, J. W. 2001. Structure and thermomechanical properties of polyurethane block copolymers with shape memory effect. *Macromolecules,* 34**,** 6431-6437.

LENDLEIN, A. & KELCH, S. 2002. Shape-memory polymers. *Angewandte Chemie International Edition,* 41**,** 2034-2057.

LENG, J., LAN, X., LIU, Y. & DU, S. 2011. Shape-memory polymers and their composites: stimulus methods and applications. *Progress in Materials*

Science, 56**,** 1077-1135.

LIANG, C., ROGERS, C. & MALAFEEW, E. 1997. Investigation of shape memory polymers and their hybrid composites. *Journal of Intelligent Material Systems and Structures,* 8**,** 380-386.

LIN, J. & CHEN, L. 1998a. Study on shape-memory behavior of polyether-based polyurethanes. I. Influence of the hard-segment content. *Journal of applied polymer science,* 69**,** 1563-1574.

LIN, J. & CHEN, L. 1998b. Study on shape-memory behavior of polyether-based polyurethanes. II. Influence of soft-segment molecular weight. *Journal of applied polymer science,* 69**,** 1575-1586.

LIN, J. & CHEN, L. 1999a. The mechanical-viscoelastic model and WLF relationship in shape memorized linear ether-type polyurethanes. *Journal of Polymer Research,* 6**,** 35-40.

LIN, J. & CHEN, L. 1999b. Shape-memorized crosslinked ester-type polyurethane and its mechanical viscoelastic model. *Journal of applied polymer science,* 73**,** 1305-1319.

MILES, R. N. & REINHALL, P. 1986. An analytical model for the vibration of laminated beams including the effects of both shear and thickness deformation in the adhesive layer. *Journal of Vibration and Acoustics,* 108**,** 56-64.

NGUYEN, T. D., QI, H. J., CASTRO, F. & LONG, K. N. 2008. A thermoviscoelastic model for amorphous shape memory polymers: incorporating structural and stress relaxation. *Journal of the Mechanics and Physics of Solids,* 56**,** 2792-2814.

NISSHA PRINTING CO., L. 2015. *Construction Methods of IMD* [Online]. [Accessed 05/02 2015].

OHKI, T., NI, Q.-Q., OHSAKO, N. & IWAMOTO, M. 2004. Mechanical and shape memory behavior of composites with shape memory polymer. *Composites Part A: applied science and manufacturing*, 35**,** 1065-1073.

ROBERTS, T. 1989. Shear and normal stresses in adhesive joints. *Journal of Engineering Mechanics*, 115**,** 2460-2479.

ROTHEISER, J. 2000. In-Mold Decorating - What are the Options? *Plastics Decorating.*

SENTHIL, L. 2012. Pros and Cons of Thermoforming. *EzineArticles.*

SHERMAN, L. M. 2004. Where the Action Is: Decorating with Formable Films. *Plastics Technology*

TAKAHASHI, T., HAYASHI, N. & HAYASHI, S. 1996. Structure and properties of shape-memory polyurethane block copolymers. *Journal of Applied Polymer Science*, 60**,** 1061-1069.

TIWARI, R. 2014. Growth of Thermoplastic Polyurethane Industry *RnR Market Research.*

TOBUSHI, H., HASHIMOTO, T., HAYASHI, S. & YAMADA, E. 1997. Thermomechanical constitutive modeling in shape memory polymer of polyurethane series. *Journal of Intelligent Material Systems and Structures,* 8**,** 711-718.

TOBUSHI, H., HASHIMOTO, T., ITO, N., HAYASHI, S. & YAMADA, E. 1998. Shape fixity and shape recovery in a film of shape memory polymer of polyurethane series. *Journal of Intelligent Material Systems and Structures,* 9**,** 127-136.

TSAI, M. & MORTON, J. 1995. The effect of a spew fillet on adhesive stress distributions in laminated composite single-lap joints. *Composite structures,* 32**,** 123-131.

YANG, J. H., CHUN, B. C., CHUNG, Y.-C. & CHO, J. H. 2003. Comparison of thermal/mechanical properties and shape memory effect of polyurethane block-copolymers with planar or bent shape of hard segment. *Polymer,* 44**,** 3251-3258.

YUAN, H., WU, Z. & YOSHIZAWA, H. 2001. Theoretical solutions on interfacial stress transfer of externally bonded steel/composite laminates. *Journal* *of the Japan Society of Civil Engineers*, 27-39.

ZHANG, C.-S. & NI, Q.-Q. 2007. Bending behavior of shape memory polymer based laminates. *Composite Structures,* 78**,** 153-161.

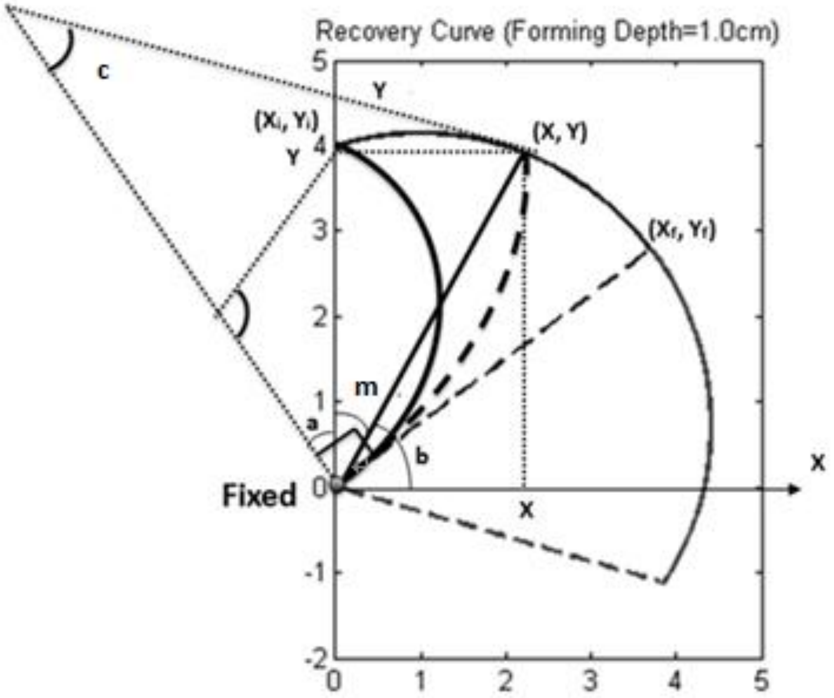
ZIA, K. M., BHATTI, H. N. & BHATTI, I. A. 2007. Methods for polyurethane and polyurethane composites, recycling and recovery: A review. *Reactive and functional polymers,* 67**,** 675-692.

APPENDICES

Appendix A. MatLab Code for Recovery Curves

To check the position of formed sample's free end during the recovery, a recovery curve was simulated in MatLab. The arc length of specimen was assumed to be a constant number, S. The free end of sample was initially located at position (X_i, Y_i) as shown in the diagram. After a time of recovering, the position of free end was found at (X, Y). Assuming that the curved laminate was fully recovered to the flat shape, the position of free end was defined as (X_f, Y_f). The simulated recovery curve (X, Y) was calculated based on two assumptions: the arc length of specimen was assumed to be a constant number (S); the curved sample with one end fixed changed shape of circular arc with a varying central angle (c).

Diagram of Recovery Curve



MatLab Code:

```
global R h a S xf yf

%For an example of laminate with 1.0cm forming depth by a 2.5cm radius mold.

R=2.5;

h=1.0;

a=asin((R-h)/R); % angle a as shown in the diagram was calculated based on simple triangular geometry

S= R*(pi-2*a); % arc length of specimen equals to radius multiplied by initial central angle
```

```
%Define the free end position when fully recovery to flat shape
xf=S*cos(a);
yf=tan(a)*xf;
%Define a function describing the X and Y relationship of the free end position
function f= recovery(x,y)
    global R a b c cl
    b= atan(y./x) % the angle b as shown in the diagram
    c=2*(b-a) %based on the geometry c=pi-2*(a+m), m+b=pi/2,
    cl=(x.^2+y.^2).^(0.5)%chord length of specimen after a time of recovering
    f=R*(pi-2*a)-c*cl/(2*sin(c/2)); %function f defined by the difference between initial arc length and the arc length at a time.
end
rc= ezplot(@recovery,[0 xf yf 6]); %Plot the x, y curve
```

Appendix B. ANSYS code of Deformation of Polymer Laminate

```
! An example of laminate with 5MPa stiffness adhesive layer

/FILENAME, LAMIANTE

/TITLE, DEFORMATION OF LAMINATE
/PREP7                                  !Entre preprocessor

ET,1,PLANE182                              !Define element type
MP,EX,1,5E8                             !Define material properties
MP,PRXY,1,0.3
MP,EX,2,5E6
MP,PRXY,2,0.3
TB,PRONY,2,1,1,SHEAR
TBDATA,,0.8,1.75,,,,
MP,EX,3,8E8
MP,PRXY,3,0.4
TB,BISO,3,2,2,
TBTEMP,65
TBDATA,,3E7,2.1E7,,,,
TBTEMP,160
TBDATA,,10000,2.1E6,,,,.
RECTNG,-0.02,0.02,0,-0.0005,            !Modeling
RECTNG,-0.02,0.02,-0.0005,-0.00063,
RECTNG,-0.02,0.02,-0.00063,-0.00083,
LSEL,S,,,1,11,2                            !divided the horizontal lines into 50
LESIZE,ALL,,,50
LSEL,S,,,2,12,2                            !divided the horizontal lines into 5
LESIZE,ALL,,,5
MAT,3                                   !Attribute the materials and Meshing
AMESH,1
MAT,2
AMESH,2
MAT,1
```

```
AMESH,3
LSEL,S,,,1
NSLL,S,1
CM,SUB_BOT,NODE
LSEL,S,,,7
NSLL,S,1
CM,ADHESIVE_TOP,NODE
LSEL,S,,,5
NSLL,S,1
CM,ADHESIVE_BOT,NODE
LSEL,S,,,11
NSLL,S,1
CM,FILM_TOP,NODE
ET,2,169                                  ! Create contact pair elements
ET,3,172
R,3,,,0.5,0.1,0,
RMORE,,,1.0E20,0.0,1.0,-1E8
KEYOPT,3,12,5
NSEL,S,,,ADHESIVE_TOP                       ! Generate the target surface on adhesive
CM,_TARGET,NODE
TYPE,2
ESLN,S,0
ESURF
NSEL,S,,,SUB_BOT                                ! Generate the target surface on substrate
CM,_CONTACT,NODE
TYPE,3
ESLN,S,0
ESURF
ALLSEL
ET,4,169                                  ! Create contact pair elements
ET,5,172
R,5,,,0.5,0.1,0,
RMORE,,,1.0E20,0.0,1.0,-1E8
KEYOPT,5,12,5
NSEL,S,,,FILM_TOP                          ! Generate the target surface on film
CM,_TARGET,NODE
TYPE,4
```

```
ESLN,S,0
ESURF
NSEL,S,,,ADHESIVE_BOT                        ! Generate the target surface on adhesive
CM,_CONTACT,NODE
TYPE,5
ESLN,S,0
ESURF
ALLSEL
FINISH

/SOLU                                    ! Solution
ANTYPE,4                                 ! Transient analysis
TRANOPT,FULL
NSUBST,50,50,50
TIME,30
LSEL,S,,,2,12,2                           ! Fix the two ends of lamiante
DL,ALL,,ALL,0

D,P51X, ,-0.008, , , ,UY                 ! Apply a displacement of -0.008 at the centre
                                          of substrate surface through GUI
LSWRITE,1,                               ! Define load step 1
NSUBST,20,20,20
TIME,35
DDELE,P51X,ALL                            ! Remove the displacement at the centre of
                                          substrate surface through GUI
LSWRITE,2                                ! Define load step 2
ALLSEL
SOLVE
FINISH

/POST1                                   ! Postprocessor
SET,30                                   ! Select the last set of load step 1
PLNSOL,S,EQV                             ! Plot von Mises stress
SET,31                                   ! Select the first set of load step 2
PLNSOL,S,EQV                             ! Plot von Mises stress
FINISH
```