# Effect of Low Profile Additives on Thermo-Mechanical Properties of Fibre/UP Composites

By

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Engineering

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# Abstract

Low profile additives (LPA) are thermoplastics that are incorporated to unsaturated polyester (UP) resins in order to improve the surface finish of UP/fibreglass composites, widely used in automotive applications. The effect of using LPA on the thermo-mechanical properties of resin transfer moulded UP/fibreglass composites is investigated. The flexural and shear properties are measured by three-point bending tests. The trend of these mechanical properties is identified for 0% to 40% LPA content. All the mechanical properties like flexural strength, flexural modulus and short beam strength reduce upon addition of LPA. The specimens fail by tension in the flexural test and show a mixed shear/tension failure mode in case of short beam tests. From scanning electron microscopy, morphological change of the fractured surface is observed with an LPA-rich phase. Glass transition temperature (Tg) measured by thermal mechanical analysis (TMA) and dynamic mechanical analysis (DMA) show reproducible data and compare well with each other.  $T_g$  is improved by LPA addition due to the development of a more compatible system compared to neat resin. Differential scanning calorimetry (DSC) is also performed to detect Tg, which gives unreliable results.

# Résumé

Les agents thermoplastiques (LPA) sont des particules incorporées dans les résines polyester insaturées (UP) de façon à améliorer le fini de surface de composites UP/fibres de verre, largement utilisés dans les applications automobiles. L'effet de l'utilisation de LPA sur les propriétés thermomécaniques de composites UP/fibres de verre fabriqués par le procédé d'injection sur renfort (RTM) est étudié. Les propriétés en flexion ainsi qu'en cisaillement sont mesurées par des tests de flexion trois points. La tendance de ces propriétés mécaniques est déterminée pour différentes teneurs en LPA. La résistance en flexion (test en flexion standard et en flexion à courte distance) ainsi que le module en flexion diminuent avec l'addition de LPA. Les échantillons rompent en tension pour les tests de flexion et présentent une rupture mixte cisaillement/tension dans le cas des tests de flexion à courte distance. Les changements morphologiques de la surface au niveau de la rupture ont été observés par microscopie à balayage électronique pour la phase riche en LPA. La température de transition vitreuse (T<sub>g</sub>), mesurée par analyse thermomécanique (TMA) et analyse mécanique dynamique (DMA), est reproductible et présente une bonne corrélation. La T<sub>g</sub> augmente avec l'addition de LPA dû au développement d'un système UP/LPA plus compatible avec les fibres de verre que la résine UP pure. Une analyse calorimétrique différentielle (DSC) a aussi été effectuée pour déterminer la Tg, mais donne des résultats peu consistants.

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# **Table of Contents**

	Abstract	ii
	Résumé	iii
	Acknowledgements	iv
	List of Tables	vii
	List of Figures	viii
	List of Symbols	xi
	List of Greek Symbols	xii
	List of Abbreviations	xiii
1.	Introduction	1
2.	Literature review	4
	2.1 Bending Test Methods	4
	2.2 Methods of Glass Transition Temperature Measurements	8
	2.3 Cure Shrinkage Compensation Mechanism	10
	2.4 Effect of LPA on Mechanical Properties	12
	2.4.1 Relationship between Morphology and Mechanical Properties	13
	2.4.2 Tensile Properties	14
	2.4.2.1 Tensile Strength	14
	2.4.2.2 Strain to Failure	16
	2.4.2.3 Young's Modulus	16
	2.4.3 Impact Strength	18
	2.4.4 Flexural and Shear properties	20
	2.4.5 Fracture and Fatigue Properties	21
	2.5 Effect of LPA on Thermal Properties	22
	2.6 Summary of Literature Review	25
	2.7 Research Motivation & Objectives	26
3.	Sample manufacturing	37
	3.1 Materials	37
	3.2 Resin Transfer Molding Process	38
	3.3 Degree of Cure Measurement	41

v

	3.4 Fibre Volume Fraction Measurement	43
4.	Experiments and results	56
	4.1 Three-point Bending Tests	56
	4.1.1 Specimen Fabrication	56
	4.1.2 Flexural Test	57
	4.1.2.1 Test Setup	58
	4.1.2.2 Test Parameters	58
	4.1.2.3 Test Procedure	60
	4.1.2.4 Verification of Experimental Data	60
	4.1.2.5 Results & Calculations	61
	4.1.2.6 Discussion	63
	4.1.3 Short Beam Test	67
	4.1.3.1 Test Parameters & Procedure	67
	4.1.3.2 Results, Calculations & Failure Mode Observation	68
	4.1.3.3 Discussion	69
	4.2 Thermal Properties Measurement	72
	4.2.1 Thermal Mechanical analysis	72
	4.2.1.1 Glass Transition Temperature (Tg)	73
	4.2.1.2 Coefficient of Thermal Expansion	74
	4.2.2 Dynamic Mechanical analysis	74
	4.2.3 Differential Scanning Calorimetry	75
	4.2.4 Comparative $T_g$	80
5.	Conclusion	95
6.	Future recommendations	97
	List of References	98
	Appendix A	106
	Appendix B	112

vi

# List of Tables

Table 2.1: Common LPA used with UP resins and their thermo-mechanical	
properties	30
Table 2.2: Summary of literature review	31
Table 3.1: Typical properties of Crystic 790 with 30% Calcium carbonate filler by	у. У.
weight	51
Table 3.2: Typical properties of Crystic 790 with 30% Calcium carbonate filler by	y i i
weight and combined with 1 layer Rovicore 600 D3 60051	51
Table 3.3: Resin formulation by weight fraction	52
Table 3.4: Sample dimensions of thermo-mechanical tests	52
Table 3.5: Total heat of reaction of the resin mixture measured by DSC	53
Table 3.6: Degree of cure of the composite plates measured by DSC	53
Table 3.7: Density of composite and matrix samples	54
Table 3.8: Volume fraction calculation	54
Table 4.1: Experimental data of flexural tests	81
Table 4.2: Experimental data of short beam tests	82
Table A.1: Mass calculation of samples	106
Table A.2: Experimental data of flexural tests	107
Table A.3: Experimental data of short beam tests	108
Table A.4: Allowable span and displacement for flexural test	109
Table A.5: Experimental results of long beam tests	110
Table A 6. Experimental data of short beam tests	111

vii

# List of Figures

Figure 1.1: Composite component of a car by Aston Martin	3
Figure 2.1: Three-point and four-point bending setup	30
Figure 2.2: Glass transition temperature and coefficient of thermal expansion by	,
TMA, DMA and DSC	34
Figure 2.3: Curing reaction of UP resin	32
Figure 2.4: Cure shrinkage compensation mechanism by LPA	33
Figure 2.5: The effects of LPA type and concentration on tensile strength	
resins at MR 2/1	34
Figure 2.6: The effects of LPA type and concentration on ultimate strain of cured	I UP
resins at MR 2/1	34
Figure 2.7: The effects of LPA type and concentration on Young's modulus of cu	ıred
UP resins at MR 2/1	35
Figure 2.8: The effects of LPA type and concentration on impact strength of cure	d UP
resins at MR 2/1	35
Figure 2.9: The effects of LPA type and concentration on Fracture toughness of	
cured UP resins at MR 2/1	36
Figure 2.10: The effects of LPA type and concentration on $T_g$ of cured UP resins	at
MR 2/1	36
Figure 3.1: Structure of F3P glass fibre preform	51
Figure 3.2: Schematic diagram of resin transfer molding process	51
Figure 3.3: Steel moulds used for resin transfer molding	52
Figure 3.4: Location of pressure sensors, vent port and injection port with the pic	ture
frame	52
Figure 3.5: Location of thermocouples with the picture frame	53
Figure 3.6: Typical RTM process data of a 10% LPA plate	53
Figure 3.7: Sample locations on a composite plate	54
Figure 3.8: Total heat of reaction by differential scanning calorimetry	55
Figure 3.9: Residual heat of reaction by differential scanning calorimetry	55

viii

Figure 4.1: Bending test sample dimensions	78
Figure 4.2: Flexural test setup	78
Figure 4.3: Schematic diagram of flexural test set-up	78
Figure 4.4: Load-Displacement diagram of Al 6061bar	79
Figure 4.5: Load-Displacement diagram of a long beam sample with no LPA	79
Figure 4.6: Flexural strength and strain to failure Vs LPA content in samples	80
Figure 4.7: Flexural and shear modulus Vs LPA content in samples	80
Figure 4.8: Tensile crack on long beams	81
Figure 4.7: SEM photographs long beam samples showing the fibre pull-out	82
Figure 4.10: Schematic diagram of short beam test set-up	83
Figure 4.11: Load-Displacement diagram of a short beam with 10% LPA	83
Figure 4.12: Apparent short beam strength Vs LPA content in samples	84
Figure 4.13: Effect of span-to depth ratio on failure mode	84
Figure 4.20: Typical failure modes of short beam test	85
Figure 4.15: Failure crack on a short beam sample of 0% LPA containing plate	86
Figure 4.16: Mixed shear-tension failure on a 10% LPA short beam sample	87
Figure 4.17: Failure crack on a 40% LPA short beam sample	88
Figure 4.18 : SEM photographs of shear fracture surface of short beams	89
Figure 4.19: Material morphology of the shear fracture surface of short beams	90
Figure 4.20: Test setup of thermal mechanical analysis	91
Figure 4.21: Experimental curve for TMA of a sample containing 10% LPA	91
Figure 4.22: Linear curve fitting curve on TMA curve to determine $T_g$	92
Figure 4.23: $T_g$ Vs LPA content determined by TMA and DMA	92
Figure 4.24: CTE Vs LPA content determined by TMA	93
Figure 4.25: Storage modulus (G'), loss modulus (G'') and loss factor (tan $\delta$ )	
determined by DMA	93
Figure 4.26: Heat flow Vs Temperature curve determined by DSC	94
Figure B.1: Load-displacement diagrams for long beams with 0% LPA content	112
Figure B.2: Load-displacement diagrams for long beams with 10% LPA content	112
Figure B.3: Load-displacement diagrams for long beams with 40% LPA content	113
Figure B.4: Load-displacement diagrams for short beams with 0% LPA content	113

ix

Figure B.5: Load-displacement diagrams for short beams with 10% LPA content 114 Figure B.6: Load-displacement diagrams for long beams with 40% LPA content 114

# List of Symbols

b	Specimen width
D	Deflection
E	Modulus of elasticity
Ef	Flexural modulus
G'	Storage modulus
<b>G</b> "	Loss modulus
h	Specimen depth
$\Delta$ h	Change in thickness
I	Moment of inertia
L	Support span
m	Slope
n	Number of observations
Р	Load
R	Crosshead speed
S	Standard deviation
r	Strain
S	Standard deviation
$T_g$	Glass transition temperature
Х	Value of single observation
$\overline{X}$	Arithmetic mean of the set of observations
Z	Strain rate

xi

# List of Greek Symbols

- δ Displacement
- $\tau_s$  Short beam strength
- $\sigma$  Normal stress
- τ Shear stress
- $\epsilon_t$  Thermal strain
- $\sigma_f$  Flexural strength
- $\epsilon_{f}$  Flexural strain (mm/mm)

# List of Abbreviations

ASTM	American standard for testing materials
CTE	Coefficient of thermal expansion
DMA	Dynamic mechanical analysis
DOC	Degree of cure
DSC	Differential scanning calorimetry
GRP	Glass reinforced polyester
LPA	Low profile additives
RTM	Resin transfer molding
PCL	Polycaprolactone
PMMA	Poly(methylmethacrylate)
PS	Polystyrene
PU	Polyurethane
PVAc	Poly(vinyl acetate)
RHR	Residual heat of reaction
THR	Total heat of reaction
TMA	Thermal mechanical analysis
UP	Unsaturated polyester

# **Chapter 1**

## Introduction

The introduction of composite materials in automotive industry was driven by the attractive properties of them like low weight, design flexibility, less production and tooling costs. The automotive sector is now looking for lightweight materials as a step towards fuel efficiency. Composites already demonstrated huge potential of weight saving which is one of the main goals in recent automotive research and applications.

Composite materials (mostly based on polyamide or polypropylene) are used in various applications of automobiles like car body panels, structural and semistructural parts and engine parts [1-7]. Thermoplastics are used in under-the-hood components like radiator tanks, heater fan housings and cooling fans; their recent applications are in intake manifolds, rocker covers and engine thermostat parts [8]. Thermosets, specially unsaturated polyesters (UP) are increasingly in demand in the automotive industry due to their versatility, low cost, low weight, high strength and excellent mechanical properties [9]. Combined with glass fibres, they are extensively used in exterior body panels of cars and also in some electrical equipment. *Figure 1.1* shows a car by Aston Marin with one of its components made of composite.

The widely used commercial processes for composite manufacturing are lay-up, compression moulding, injection moulding, reaction injection moulding and pultrusion [10]. However, for fabrication of parts with complex geometry and tight dimensional tolerance, liquid moulding processes are generally applied. Among the moulding processes, resin transfer moulding (RTM) is most extensively used in automotive applications.

One of the most challenging issues in RTM is to obtain the so-called class A surface finish, which is highly desirable in automotive parts. Curing of the UP resin inside the

mould involves copolymerization between UP and styrene (ST) monomer initiated by organic compounds. This chemical reaction results in 6-9% volumetric shrinkage of the final part [11]. As a result, surface finish of the end product deteriorates considerably.

Low profile additives (LPA) are recognized as a viable solution to the volumetric shrinkage encountered in composite moulding processes. LPA are thermoplastics partially compatible with UP resins before the cure [12-13]. Although the shrinkage control mechanism played by the LPA during the cure process has been diversely analyzed, the use of LPA has been reported to produce less and even zero-shrinkage matrix [11, 14].

However, LPA not only enhance the surface aspects of the parts, but eventually also affect other thermo-mechanical properties of the material. From the previous research work on LPA, it has been found that thermo-mechanical properties of UP generally declined upon addition of LPA. Therefore, the extent to which LPA must be incorporated to the UP resin in order to gain the best compromise between the surface quality and desirable properties of the finished product is the main focus of this study.

There are six chapters of this thesis including this introductory chapter. Chapter 2 presents an in-depth analysis of how the low profile additives affect the thermomechanical properties of UP/fibre composites. The conventional methods of bending tests and glass transition temperature measurement are also discussed in this chapter. Chapter 3 describes the manufacturing process of the UP/fibre composites plates used in the experiments by resin transfer moulding, and also other preliminary measurements. Chapter 4 provides the details of the experimental part of bending tests and glass transition temperature measurements followed by their results. Chapter 5 draws conclusions from the results of this experimental study. Chapter 6 indicates fields of possible future investigations which are beyond the scope of this study.



Figure 1.1: Composite component of a car [Courtesy: Aston Martin]

# **Chapter 2**

## **Literature Review**

In this chapter, a detailed literature review relevant to the research topic is presented. *Sections 2.1* and 2.2 discuss the different testing methods used to measure thermomechanical properties of composites. The purpose of using LPA and the cure shrinkage compensation behaviour of LPA are discussed in *Section 2.3*. The effects of using LPA on the different mechanical properties of UP/fibre composites are covered in *Section 2.4*. The effects of using LPA on glass transition temperature and coefficient of thermal expansion are discussed in *Section 2.5*. A summary of the literature is presented in *Section 2.6*. Finally, the research motivation and objectives are presented in *Section 2.7*.

### 2.1 Bending Test Methods

Composite structures are often subjected to bending rather than pure axial loading during their service life. Flexural properties are, therefore, as important to determine as tensile or compressive properties. Shear properties are important to know for composites that experience compression loading and the interfacial bonding or matrix failure is critical. Both flexural and shear properties are important parameters depending on specific design problems. With increasing industrial use of composites, these mechanical properties of composites have experienced extensive research in recent years.

Flexural and shear properties of composites are generally measured by bending tests according to the relevant ASTM standards. Both flexural and shear tests can be run on similar setups, widely known as three-point bending setup (*Figure 2.1(a)*). The

specimen is supported by a cylinder at each end and load is applied at a constant speed by a cylindrical loading nose at the mid-span of the specimen until it fails. Material properties such as interlaminar shear strength, flexural modulus and flexural strength can be calculated from the value of maximum load carried by the specimen before failure. The test fixture is simple to fabricate and incorporate to the loading apparatus. The test procedure is also very straight forward.

Shear properties can be measured by the short beam shear strength test, designated as ASTM D2344 [15]. The procedure recommends load application to a short beam having a length four times its thickness. The idea is to induce pure shear stress at the failure load by minimizing the flexural stresses. Ideally a test method should produce pure shear and yield reproducible results [16]. It is very difficult to obtain a state of pure shear under bending mode. Other non-conventional shear test methods like losipescu shear, torsional shear of a thin-walled tube or the ten-degree off-axis tensile test are expensive and involve practical difficulties [17]. The most widely used method is the three-point bending test of ASTM standard.

For flexural properties measurement, standard procedure of three-point bending test is recognized by ASTM D790 [18]. Here a longer specimen is subjected to load until failure point. The span-to-depth ratio, L/h (*Figure 2.1*) is chosen to be at least sixteen, which is believed to be enough to shift the stress condition from shear to flexural.

Materials that do not fail by the maximum strain limit specified at the standard for 3point bending tests are recommended to be tested by 4-point bending method. According to this method, load is applied at two points rather than only one point like in the case of three-point bending. In that case, two loading noses are used rather than just one (*Figure 2.1(b)*). The main difference between 3-point and 4-point bending is in the location of the maximum bending moment and maximum axial fibre stresses. The maximum axial fibre stresses are located on a line under the only loading nose in 3-point bending and over the area between the two loading noses in case of 4-point bending [18].

Both three and four point bending processes have been criticized for their drawbacks. Both suffer from stress concentration problem under the loading noses. In case of a three-point bending test, the rotation of cross-sections during the deformation changes the contact zone between the specimen and the cylindrical supports. Moreover, in a four-point bending test, the contact zone between the specimen and the cylindrical loading noses also changes. These changes affect the value of flexural modulus calculated from the equations and the values obtained by the two types of bending methods differ from each other. A modulus correction method has been proposed which reduced the modulus difference between the two different bending tests from 5 to 1% [19]. However, the four-point bending test method is generally applicable to flexural tests. In case of short beams, four-point bending revealed no particular advantage rather complications [16].

As an attempt to eliminate the problem of stress concentration under point loads, twopoint bending tests have also been carried. Half-ring specimens of unidirectional aramid SVM/epoxy composites were subjected to bending by applying same amount of load on each of the two free ends [20]. Five-point bending has also been performed by Kim and Dharan [21]. Comparing with three-point bending, it was claimed that five-point bending provides high shear stresses and minimal bending stresses.

Despite the specifications mentioned in ASTM documentations, the test parameters and specimen dimensions of bending tests have been the area of interests for many researchers. The mostly varied dimension is the span-to-depth ratio. It has been recommended that the span-to-depth ratio should be increased from the standard, mentioned as four for short beam test, to avoid the high local stress concentrations due to the applied point load, and to better distribute the shear stress. This will reduce the possibility of failure under point force. The primary intention to limit the failure condition by shear can be well achieved by span-to-depth ratio as high as nine, as indicated by experimental results. However, lower ratios produce results closer to those obtained from a general shear test method like Iosipescu Shear. An intermediate value like seven was suggested to balance all concerns [16]. In case of flexural tests, the idea of increasing the span-to-depth ratio to avoid stress concentration is also logical. However, increasing the span will result in failure at large deflections and the assumption of beam theory that the deflection is small compared to the span does not hold any more [22]. So there should be a judicial compromise in choosing the span-to-depth ratio other than the standard. An analytical solution was proposed that considered the deflection in the calculation of the flexural strength. The theory has been validated by experiments at L/h up to 80 [22].

For the same reason of better load distribution, the standard loading nose diameter has also been recommended to increase from 6.35 mm (0.25 inch) to 25.4 mm (1 inch). The increase of loading nose diameter was also found to produce better results in case of flexural tests [16].

Short beam shear test and flexural tests have been carried on unidirectional fibre/epoxy laminates with different fibre orientations. It has been found that both normal and shear stresses is strongly L/h dependant. The transition from shear to flexural failure with change in L/h was analytically determined to compare with the experimental results. A significant discrepancy was found between them [23].

Another important parameter in bending tests is the crosshead speed or loading rate. Although specific crosshead speed value has been recommended at ASTM, the variation in loading rates had produced interesting effects on the failure mechanisms. In a study of three-point bending tests of pultruded half-round rods of fibre/epoxy and fibre/polyester, both span-to-depth ratios and loading rates were varied over a wide range [24]. Experiments were carried with span-to-depth ratios (L/r) varied between 4.5 and 17.6, whereas the crosshead speed was in the range of 1 to 20000 mm/min. With increasing loading rates, the failure mechanism shifted from pure tension to mixed mode of tension/shear and finally to pure shear. This behaviour was related to the interaction between the loading rates, the brittleness and the defect sensitivity. The shear strength and flexural strength increased with increasing loading rate but at 5000 mm/min, it started to decrease due to the sensitivity to processing defects. The

loading rate effect was found to be more pronounced in glass/polyester as this was more ductile compared to fibre/epoxy. With increasing L/r, the failure mode gradually shifted from shear to tension. At intermediate L/r the failure mode shifted from tension to shear with increasing loading rate. This was also attributed to the increase in brittleness and defect sensitivity leading to a shear fracture. The defects are mostly inherent from the pultrusion process.

### **2.2 Methods of Glass Transition Temperature Measurements**

Glass transition temperature ( $T_g$ ) is an important property of composites to determine the maximum temperature at which the part can be exposed during its service life. The cured  $T_g$  of a polymer is the temperature at which it changes from a rigid glassy solid into a softer, semi-flexible material. As a result, chemical structure of the polymer remains the same but the cross-links may move from their position. Above  $T_g$ , the material loses its mechanical properties significantly. It is advisable to restrict the maximum service temperature of a composite to about 10<sup>o</sup>C lower than the  $T_g$ [10].

There are several techniques to determine  $T_g$  of composite materials. However, the following three methods are most commonly applied.

- Thermal mechanical analysis (TMA)
- Dynamic mechanical analysis (DMA)
- Differential scanning calorimetry (DSC)

These methods are briefly discussed next.

#### Thermal Mechanical Analysis (TMA)

In TMA,  $T_g$  is detected by measuring the thermal expansion of a sample as it is heated. The slope of the thermal expansion vs. temperature curve changes at the  $T_g$  as coefficient of thermal expansion (CTE) of the material changes at  $T_g$  (*Figure 2.2(a)*). Above  $T_g$ , CTE is much higher compared to CTE before  $T_g$ . As a consequence, the sample expands linearly below its  $T_g$  at a lower rate than above its  $T_g$ . [10]. CTE of the material can also be determined from the slope of the TMA curve.

#### **Dynamic Mechanical Analysis (DMA)**

In DMA,  $T_g$  is detected by measuring the modulus of a sample as it is heated. DMA is a mechanical measure of the  $T_g$  in which a small bar of cured sample is subjected to bending, torsion or tension while it is being heated.  $T_g$  is the point at which the storage modulus (G' or E') or stiffness drops by several orders of magnitude (*Figure* 2.2(b)). The loss modulus (G" or E") is related to the viscosity or toughness of the material. The loss tangent (Tan  $\delta$ ) is considered as a measure of the energy stored in the polymer's structure due to its viscoelastic behaviour. This stored energy rises to a sharp peak (considered as  $T_g$ ) and then drops rapidly. This may give unrealistic high values for  $T_g$ . A more realistic  $T_g$  may be detected from the interception of two tangent lines on the storage modulus curve, since at this point the material shows a significant loss in mechanical stiffness. The loss tangent is given by *Equation 2.1*.

$$Tan \,\delta = G''/G' \tag{2.1}$$

#### **Differential Scanning Calorimetry (DSC)**

In DSC,  $T_g$  is detected by measuring the heat flow of a sample as it is heated.  $T_g$  is the point at which the heat capacity of the material changes as it changes from glassy to rubbery state (*Figure 2.2(c)*). DSC is sometimes difficult to apply for  $T_g$ 

determination, especially for high cross-linked resin systems. DSC offers the advantage of using a small sample size (25 mg) [10].

## 2.3 Cure Shrinkage Compensation Mechanism

During the cure of UP resins, copolymerization between UP and styrene monomer takes place in the presence of organic initiators. The initiator produces free radicals that bond to one of the carbon atoms in the double bond of the UP and produces a new free radical at the other carbon atom [25]. The curing reaction is shown in *Figure 2.3*.

As curing continues, the temperature and degree of polymerization increases and as a result, the resin shrinks. The shrinkage of the resin results in volumetric shrinkage of the final structure. The amount of this volumetric shrinkage has been reported to be 6-9% of the final shape [11]. This shrinkage creates a gap between the mould and the material during the composite manufacturing process and deteriorates surface finish of the final product. The most common manufacturing defects resulting from the cure shrinkage are fabric print though, ripple or long range waviness and dimensional inaccuracy [26].

Low profile additives are incorporated to UP resins to act as shrinkage compensator during the curing process. Addition of LPA was found to reduce and even eliminate the volumetric shrinkage [11, 14]. *Table 2.1* lists common LPA used with UP resins and their thermo-mechanical properties, among which PVAc is most widely used. The compatibility of these LPA with UP depends on the difference in polarity (solubility parameter) between the LPA and unreacted UP. For example, PVAc and PU are usually compatible with UP while PMMA and PS are not [30]. The factors to consider in the choice of an LPA depends on compatibility, molecular weight, di-polar moment and glass transition properties [31]. The mechanism of cure shrinkage compensation with LPA has been evaluated by different theoretical and experimental approaches [32-44]. However, the predominant mechanisms playing in LPA action were identified as phase separation, void formation, thermal expansion and microstress cracking. These ideas are discussed briefly as follows.

#### **Phase Separation**

Phase separation phenomenon is the most widely accepted explanation of low profile action and recognized as precondition for the shrinkage compensation to take place. An LPA is initially compatible to the UP resin prior to cure and gives a homogeneous mixture upon addition to the resin (*Figure 2.4(a)*). However, as soon as cure starts, the LPA loses its compatibility, as LPA phase starts to develop besides the homogeneous resin phase (*Figure 2.4(b*)) and the polarity of the LPA phase changes significantly. UP starts to form microgel (by intra-particle reaction) and these microgels agglomerate to form macrogel (by inter-particle reaction) as shown in *Figure 2.4(c)*. As temperature increases, the volume of the LPA phase increases, compensating shrinkage. According to some researchers, phase separation occurs at the very beginning of the cure reaction [43-44]. From the morphological study of the material, two distinct phases are identified. One is the UP homogeneous phase and the other is the LPA dispersed phase. The change of morphology of the material due to phase separation phenomenon is discussed in details in *Section 2.4.1* of this chapter.

#### **Microvoid Formation**

Microvoid formation is regarded as the consequence of the phase separation. As the LPA dispersed phase grows up, it triggers a competition of spaces between the two phases and results in microvoid formation (*Figure 2.4(d)*). The  $T_g$  of LPA is lower than that of the UP resin. As a result, below  $T_g$ , LPA contracts more and increases the microvoid content [42]. This increase of microvoid contributes to the shrinkage

compensation. Microvoid formation is also intimately related to the LPA and styrene content. Other parameters influencing this phenomenon are processing temperature, type and quantity of initiator, filler content and external pressure [41].

#### **Thermal Expansion**

After the  $T_g$  of the LPA has been reached during the cure, coefficient of thermal expansion of LPA increases significantly and compensates shrinkage by this increased thermal expansion. It was found that an LPA with low  $T_g$  acted more favourably for shrinkage compensation [27]. The coefficient of linear thermal expansion of a polymeric material above  $T_g$  is much greater than below  $T_g$  and as a result, the volumetric shrinkage is better compensated. The elevated temperature during cure also makes the unreacted styrene of the resin mixture expand and eventually contributes to shrinkage compensation [42].

#### **Microstress Cracking**

After phase separation has taken place, stresses build up between the two phases due to the difference in elastic moduli and coefficient of thermal expansion of them. Microstress cracking was observed when this stress exceeded the 'resistance' force possessed by the interface or LPA-rich phase [39] as shown in. This contributes to microvoid formation and ultimately facilitates shrinkage compensation.

### **2.4 Effect of LPA on Mechanical Properties**

This section is divided into several parts to discuss the effect of LPA on different mechanical properties like tensile, impact, fracture, flexural, and fatigue properties of the cured UP/styrene structures. Before that, *Section 2.4.1* explains the relationship between cured sample morphology and mechanical properties.

### **2.4.1 Relationship between Morphology and Mechanical Properties**

Addition of LPA to an UP resin changes the morphology of the material. The change of the mechanical properties due to the LPA addition has been found to be closely related to this morphology change. Depending on the compatibility of the LPA with the UP resin, typically two morphological structures have been identified. In case of more compatible LPA/UP systems, a co-continuous morphology of homogeneous resin phase and globule LPA phase develops. On the other hand, upon addition of less compatible LPA to the UP resin, morphological studies reveal an LPA-dispersed phase with resin inclusions besides the homogeneous resin phase. With increasing content of LPA, the LPA phase inevitably becomes more prominent and contributes to the shrinkage compensation mechanism. However, mechanical properties are generally reduced by the LPA phase.

From the morphological study of PVAc modified UP, it was found that at a low concentration of LPA in the matrix, only discrete particles of LPA dispersed phases formed whereas at higher concentration, a co-continuous two-phase structure formed [47]. A physical change of the finished product was observed with this morphology change which is the transition of the product from translucent to opaque.

The different mechanical properties of these different LPA containing resins were measured and correlated with their morphologies by the same group of researchers. The results are discussed in the following respective sections. It was found that molar ratio of styrene to polyester C=C bonds affected the mechanical properties of the material and the optimum molar ratio at which the properties reached a maximum was 2/1. The comparative studies of mechanical properties were preformed at this ratio for all the materials [12,30,45-46,48-49]. The mechanical properties of LPA modified UP systems were found to be dominated by the homogeneous resin phase in the morphological structure.

### **2.4.2 Tensile Properties**

LPA have been found to affect the tensile properties of UP/fibre composites significantly. Among tensile properties, tensile strength, ultimate strain and Young's modulus have been investigated. These are discussed in separate sections as follows.

## 2.4.2.1 Tensile Strength

In comparative studies of the mechanical properties of different LPA systems [12,30], tensile strength showed a decreasing trend with LPA content in all cases (Figure 2.5). Although the crosslinking density in the homogeneous resin phase increased in favour of tensile strength, the volume fraction of the same phase reduced resulting in reduction of tensile strength. According to the compatibility of LPA with UP resin which correlates their comparative tensile properties, the LPA were ranked as PU>PVAc>PMMA>PS. This ranking also follows the relative volume fraction of the resin phase where the co-continuous model representing PVAc and PU possesses comparatively higher volume fraction than the two-phase model representing PMMA and PS, due to less phase separation phenomenon. Besides, for a less compatible system, the molar ratio (MR) of styrene to polyester C=C bonds in the resin phase would be much smaller than the optimum MR 2/1 and the system also suffers from worse interfacial adhesion. However, the microvoid formation phenomenon could not justify the experimental results. For example, the relative volume fraction of microvoids would be generally higher for PVAc system than for PMMA and PS systems based on morphology. Consequently, PMMA and PS systems should possess higher tensile properties than PVAc. Experimental results showed the opposite trend.

In a comparative study of different PU-based LPA [49], higher tensile strength was achieved with the more compatible LPA type due to higher crosslinking density and interfacial adhesion. However the trend of tensile strength with respect to LPA

content was not the same for all samples. For the more compatible PDEA-PU system, adding more LPA results in less tensile strength. On the other hand, adding a higher molecular weight of PU increased the tensile strength of the less compatible PCL-PU systems. This was explained by the phase separation and crosslinking density. Less phase separation and higher crosslinking density favour tensile strength.

Similar results were obtained in case of PVAc based LPA. [45] However, after the initial increase of tensile strength with increasing LPA, the strength followed the reverse trend with further increase of LPA. The crosslinking density and inter facial adhesion still continued to deteriorate. This phenomenon was justified by the microvoid formation mechanism. For the PVAc system with a co-continuous microstructure, the generally dispersed microvoids, generated during the cure at the interface between the LPA-rich and crosslinked UP phases, as well as inside the LPArich phase, were found to be more effective than the microvoids localized in the LPAdispersed phase for the VC-VAc systems with a two-phase microstructure. These dispersed microvoids in the PVAc system can lead to a crack tip blunting effect by releasing the stress concentration at the crack tip and delaying crack propagation. As a result, tensile strength for the PVAc3S system showed considerable improvement. The relative volume fractions of microvoids for the PVAc1S, PVAc2S, and PVAc3S systems were 3.6, 13.9, and 49.0%, respectively. The effect of molecular weight of LPA for the less compatible VC-VAc systems also showed the same trend, although the logic behind was stated as only change in interfacial adhesion between the crosslinked polyester phase and the LPA-rich phase.

The effect of reactive PMMA and PVAc-*b*-PMMA on the tensile properties of UP resin were also investigated. For the same reason of higher crosslinking density and better interfacial adhesion as discussed before, more compatible systems demonstrated higher tensile strength. [46]

An investigation of the effect of five LPA namely PVAC, PMMA, PU, PS and PCL on the tensile strength of polyester matrices [27] revealed that all LPA reduced the

tensile strength of the samples by about 40 to 80 percent. There was also comparatively less reduction in the tensile strength of the PVAc and PU containing samples. This phenomenon was justified by the cured morphology i,e, microvoids in the dispersed phase and/or polyester phase as well as worse interfacial adhesion. The dispersed phase was found to be comparatively small in the samples with PVAc and PU. On the other hand, samples containing PS and PCL showed less tensile strength and breaking strain in which dispersed phase were comparatively large. As a result, large inclusions behaved as the stress raisers in the polyester matrices and induced fracture in those samples.

### 2.4.2.2 Strain to Failure

In a comparative study of the four LPA (PU, PVAc, PMMA and PS), strain to failure followed the same decreasing trend as tensile strength discussed in *Section 2.2.2.1* except for the PU system (*Figure 2.6*) [30]. The result was attributed to the fact that since PU is in the rubbery state at room temperature, increasing PU content increased the ultimate tensile strain. Similar results were obtained in a comparative study of PVAC, PMMA, PU, PS and PCL[27]. However, samples containing PVAc and PU retained their strain, while the other additives reduced the strain by about 30 to 55 percent.

## 2.4.2.3 Young's Modulus

In case comparative studies of the different LPA [12,30], Young's modulus showed the same decreasing trend as tensile strength (*Figure 2.7*) discussed in *Section 2.4.2.1* but the explanation behind was different [30]. Adding LPA reduce the modulus by increasing MR of styrene consumed to polyester C=C bonds reacted in the resin phase. Comparing the Young's modulus at a fixed LPA content, it was observed that

PS and PMMA systems have higher modulus than PU and PVAC systems. This higher value was contributed by the lower average crosslink length of styrene and a more compact network in the resin phase. The PS and PMMA also have comparatively higher tensile modulus than PU and PVAC leading to higher Young's modulus in the UP/LPA systems.

An investigation of the effects of three series of PU-based LPA on different UP revealed that the trend for Young's modulus followed the reversed order of that of the tensile strength in terms of system compatibility [49]. Since Young's modulus represents the extent of resistance to deformation for a sample in the initial stage of a tensile test, during which the sample would be unbroken, it is dependant upon degree of tightness of the network rather than degree of crosslinking of the sample. Moreover in a less compatible ST/UP/LPA system, a higher degree of phase separation during the cure would lead to lower styrene content in the resin phase. The combined effect of a lower average crosslink length of styrene and a more compact network in the resin phase would result in a higher Young's modulus for the whole sample. The effect of adding a higher molecular weight of PU also showed reverse trend in case of Young's modulus when tensile strength was compared. For more compatible PDEA systems, Young's modulus increased with increasing molecular weight while for the less compatible PCL systems, it showed the opposite trend. This was explained by the negative effect of the less negative deviation from MR of 2:1 in the resin phase on Young's modulus, which was found to be favorable in case of tensile strength.

Similar results were obtained from the study of three PVAc and PMMA based LPA. In the comparative study PVAc based LPA namely PVAc, VC-VAc and VC-VAc-MA, the best result was obtained with PVAc3S system. In the other study of PMMA based LPA namely PMMA and PVAc-*b*-PMMA, the highest Young's modulus was found to be of PMMA57K[45,48].

The study of five LPA namely PVAc, PMMA, PU, PS and PCL on the tensile properties of polyester matrices revealed that all samples containing LPA had lower Young's moduli than neat resin. PU and PCL containing samples exhibited comparatively lower Young's moduli which was attributed to their low  $T_g$  [27].

Another study of PVAc containing UP resins showed that with styrene/polyester ratio of 40/60, Young's modulus was independent of PVAc content over the range 0-10% with a value of 3.5 GPa despite the morphology change [50].

### 2.4.3 Impact Strength

The effect of four LPA namely PVAc, PMMA, PU and PS was investigated on the impact strength of the cured samples [12,30]. The impact strength was comparatively higher for the PVAc and PU systems, which was attributed to the higher system compatibilities of these two systems resulting in better interfacial adhesion (*Figure* 2.8). Also from the glass transition temperatures, it was concluded that PVAc (T<sub>g</sub> ~27<sup>0</sup>C) and PU (T<sub>g</sub> ~ -45<sup>0</sup>C) were close to or at rubbery state during test condition at  $25^{0}$ C, while PMMA (T<sub>g</sub> ~105<sup>0</sup>C) and PS (T<sub>g</sub> ~ -100<sup>0</sup>C) were in the glassy state. This was another rationale for PVAc and PU having higher impact strength. [30]

While for the less compatible PMMA and PS systems, impact strength gradually decreased with increasing LPA concentration, the trend was not the same for the PVAc and PU systems. In case of the latter two systems, impact strength increased until 5% (for PVAc) and 10% (for PU) concentration of LPA. This phenomenon was explained by the microvoid formation mechanism. For the PVAc and PU systems with a co-continuous microstructure, the generally dispersed microvoids were found to be more effective than the localized microvoids for the PMMA and PS systems. These microvoids led to a crack tip blunting effect releasing the stress concentration at the crack tip and delaying crack propagation. However, the crack would eventually propagate through the voided plane and excessively high volume fraction of microvoids led to decrease the impact strength. At a fixed LPA content, the volume fraction of the microvoids was found to be higher for the PVAc system than the PU

system. Consequently, the maximum impact strength was at lower LPA content for the PVAc system (5%) than the PU system (10%). At the maximum LPA content under study (15%), the impact strength of the PU system was higher than that of the neat resin system, while the opposite was true for the PVAc system. [30]

In the study of PU-based LPA, it was found that for a more compatible PDEA system, with a flake-like microstructure, adding a higher content of PU increased the impact strength. This could be due to the role of PU as a better energy absorber. On the other hand, in the case of a less compatible PCL system with globule morphology, adding a higher molecular weight of PU reduced the impact strength. The reason behind was the higher degree of reaction-induced phase separation during the cure resulting in worse interfacial adhesion for the system [49].

In case of PVAc based LPA, it was concluded that adding LPA can affect the interfacial adhesion along with the dynamic phase characteristics of St/UP/LPA systems by two ways [45]. It can increase the phase separation time by increasing the solution viscosity. As a result, interfacial adhesion would increase. On the other hand, it can also increase the degree of phase separation by decreasing the entropy change in the solution process. This would lead to less interfacial adhesion. The better the interfacial adhesion of the system, the higher is the impact strength of the resulting sample. Depending on the combined effect of the above mentioned phenomena, impact strength can either increase or decrease with higher LPA content. Besides, the author also suggested that the relations between the molecular weight of the modifier, the temperature, the mixture viscosity, the interfacial energy, the conversion, and the phase separation degree would also affect the interfacial adhesion as investigated by other researchers. Another study about PVAc revealed that addition of 13.2% of the LPA to the UP resin reduced the impact energy of the material by 33%. [47]

Similarly, in a study of PMMA and PVAc-b-PMMA LPA, impact strength was found to be dependent on the system compatibility and interfacial adhesion between the phases. PMMA26K and VAc-b-MMA31K systems showed the highest impact strength [48].

An investigation of the effect of LPA on pultruded UP resin with unidirectional Eglass fibre samples containing 10, 15 and 20% PVAc revealed that the apparent strengths measured from the impact tests were about 20% higher than in the case of the static tests [51]. This behaviour was explained in terms of vanishing viscoelastic effects under impact conditions. The compression yielding, which is a time dependent behaviour, could not build up under the very high loading rates involved during impact.

### **2.4.4 Flexural and Shear properties**

In an investigation of the effect of LPA on pultruded UP resin with unidirectional Eglass fibre, samples containing 10, 15 and 20% PVAc were tested [51]. Each sample also contained 20% clay powder as filler. The tests were performed at five span (L)to-depth (h) ratios (L/h= 5, 6, 11, 16, and 24). The three-point bend tests at L/h = 5 and 16 comply with ASTM D2344 and ASTM D790 respectively for the determination of the apparent interlaminar shear strength and flexural strength, respectively. As L/h ratio increased, the fracture moved from compressive to shear and then to tension mode. In terms of loading capabilities, L/h = 11 represented the weakest situation At this ratio, although the 10% LPA system did not significantly affect the shear strength, the 20% LPA system decreased the shear strength by about 26%. This behaviour was attributed to the fact that above a critical amount of LPA, the microvoid content would increase and compensate the volume shrinkage at the cost of reduced material properties. This critical LPA content was dictated by morphological changes known as phase inversion [31]. The load carrying capabilities of the material decreased with increase in LPA content for all the tests. Studies of the effect of PVAc on mechanical properties of UP resin revealed that the addition of 13.2 wt% PVAc reduced the flexural modulus and flexural strength of the material [47].

## **2.4.5 Fracture and Fatigue Properties**

In a comparative study of the four LPA (PU, PVAc, PMMA and PS), at a fixed MR 2/1, fracture toughness decreased with increasing LPA concentration for all the samples except PU systems (*Figure 2.9*) [30]. This trend was different than the impact strength results for PU and PVAc systems. This was attributed to the much slower test speed for three-point bending fracture test than the impact test which possibly changed the fracture mechanism regarding crack initiation and crack propagation. Depending on the volume fraction of microvoid, the crack tip blunting effect to delay crack propagation was observed for the PU system which was absent in the PVAc system. This could again be due to the smaller size of microvoids in PU system (<0.1 µm) than in PVAc system (1 µm).

Another study of PVAc on the fracture properties of UP resins showed that with styrene/polyester ratio of 40/60, fracture toughness increased almost linearly with PVAc content up to 4%, then it showed a sharp fall and varied little between 6 and 10% [50]. This was correlated to the cured sample morphology. At 4% PVAc, the structure changed from particulate to nodules, being distinctly inhomogeneous. At 6% PVAc, only the nodular morphology formed and there was little change until 10% PVAc.

An investigation of the effect of five LPA namely PVAC, PMMA, PU, PS and PCL on the fracture properties of polyester matrices revealed that in a mixture of 2:1 resin and LPA, all LPA contributed to the fracture properties of the samples [27]. However, the fracture properties could not be related to the sample morphology. The possible reason for improvement of fracture toughness and energy was presumed to be due to the energy absorption capacity of the LPA and other toughening mechanism like shear yielding, crazing and cavitation of the LPA in the resin.

An investigation of the effect of LPA on pultruded UP resin with unidirectional Eglass fibre samples containing 10, 15 and 20% PVAc revealed that the fatigue resistance give the same trend like the impact strength. The best result was obtained with 15% LPA which correlated the morphological changes related to the so-called phase inversion [51].

### **2.5 Effect of LPA on Thermal Properties**

In an investigation of four LPA namely PU, PVAc, PMMA and PS, at MR 2/1,  $T_g$ reduced upon LPA addition for all the samples as shown in Figure 2.10 [30]. Also  $T_g$ exhibited the same trend as tensile strength since it depends on the crosslinking density. The only exception was the sample containing PU. This is due to the fact that  $T_g$  of neat PU is as low as -45<sup>o</sup>C resulting in adverse plasticization effect in the resin phase suppressing the favourable MR effect. The effects of LPA on Tg as measured by DMA showed the same trend as found by TMA. Besides, Tg in the co-continuous or LPA dispersed phase (referred as Tg2) was also measured by DMA. Due to the interaction of LPA phase and the resin phase,  $T_{g2}$  was found to be higher than the  $T_g$ of the corresponding neat LPA for all the samples. In contrast to  $T_g$ ,  $T_{g2}$  improved upon LPA addition due to the higher crosslinking density. Also it was found that MR would be less deviated than 2/1 in the co-continuous or LPA dispersed phase at higher LPA content. This was due to the less phase separation prior to gelation, where the higher viscosity of the system led to less global phase separation. Concurrently, MR in phase would also deviate less from 2/1 resulting in higher crosslinking density in that phase. As a result, T<sub>g</sub> decreased as the plasticization effect became dominant than the crosslinking effect in the homogeneous resin phase.
Another investigation of the effects of three series of thermoplastic PU -based LPA on two different UPs (MA-PG and MA-PG-PA) with different chemical structures and molecular weights also showed consistent results [49].  $T_g$  would depend upon the relative importance of the two opposing effects, namely, the plasticization effect of the LPA phase on the homogeneous resin phase and the crosslinking effect of the resin phase. For the less compatible MA-PG-PA systems, the crosslinking effect was dominant and as a result the most compatible PDEA system showed the highest  $T_g$ . On the other hand, in case of the more compatible MA-PG systems, the plasticization effect was dominant and PDEA system showed the lowest  $T_g$ . Adding a lower molecular weight of PU increased  $T_g$  in MA-PG-PA systems while decreased  $T_g$  in MA-PG systems.

The study of PVAc and VC-VAc LPA on MA-PG-PA systems exhibited similar results. For a more compatible PVAc system, the plasticization effect predominated and for a less compatible VC-VAc system, the crosslinking effect predominated [45]. In the investigation of PMMA and VAC-b-MMA LPA, similar results were obtained, where VAC-b-MMA systems were found to be more compatible than PMMA systems [48].

In investigation of three PMMA-based LPA namely PMMA, MMA-BA and MMA-BA –MA produced interesting results. In either a highly compatible (PMMA) or highly incompatible (MMA-BA) system, the crosslinking effect predominated whereas the moderately incompatible MMA-BA –MA system was predominated by the plasticization effect [46].

An investigation of the effect of LPA on pultruded UP resin with unidirectional Eglass fibre samples containing 10, 15 and 20% PVAc revealed that  $T_g$  (measured by DMA) reduced to around 100°C from 114°C (with no LPA) and it did not vary much with LPA content [51]. This result was attributed to the fact that molecular motion occurred at a lower temperature in LPA containing samples. Also the internal damping capacity Tan  $\delta$ , related to the molecular motion increased with increasing

LPA content. Increased molecular motion could be due to presence of microvoids and/or insufficient cure. The result was further investigated by performing post curing to find its effect on cure kinetics. Adequate postcuring (2 hrs at 130°C) helped to regain the original  $T_g$  ( $T_g$  with no LPA). The result indicated that LPA slowed the reaction kinetics and consequently the cure cycle. For maintaining the cure cycle post cure was recommended to recover a higher  $T_g$ .

An investigation of the effect of five LPA namely PVAC, PMMA, PU, PS and PCL on  $T_g$  produced results consistent with the above discussion [27].  $T_g$  decreased as a result of adding LPA and  $T_{g2}$  was found to be higher than the  $T_g$  of the corresponding neat LPA for all the samples. The decrease of  $T_g$  is explained by the following effects. The additives act as plasticizers in the polyester matrices and hence facilitate the transition from glassy to rubbery state. Secondly, the crosslinking density decreases significantly as the LPA are less reactive than neat resin.

It is desirable to use a LPA having low  $T_g$  in moulding processes of polyesters. [52] This is because the coefficient of linear thermal expansion of a polymer above its  $T_g$  is much greater than that below  $T_g$ . As a result, volumetric shrinkage can be better compensated by the greater thermal expansion of the LPA, especially near the gel point [27].

Coefficient of thermal expansion (CTE) of LPA/UP systems has rarely been investigated. CTE of pultruded UP/LPA systems investigated by TMA showed that addition of LPA gives mixed trend of CTE. This behaviour was attributed to the system compatibility and phase separation phenomenon that changes material morphology [51].

## 2.6 Summary of Literature Review

From the present source of information, the following observations revealed about the effects of LPA on thermo-mechanical properties of UP/fibre composites:

- LPA improve surface finish of automotive parts by shrinkage compensation during the cure process. Use of LPA inevitably affects thermo-mechanical properties of the composites. This affect is the result of the LPA action mechanism, which is primarily contributed by phase separation, microvoid formation, thermal expansion and microstress cracking. In general, LPA demonstrated unfavourable affect on the measured properties. However, in some cases, the opposite trend was found that is addition of LPA led to the property improvement. This was related to the compatibility of the overall system and better interfacial adhesion between the phases. Among mechanical properties, tensile, impact, fracture, fatigue, flexural and shear properties are evidently affected by addition of LPA. However, flexural and shear properties are rarely studied and the single investigation was about pultruded composites with unidirectional fibres. Flexural and shear properties of composites are most commonly measured by three-point bending tests.
- Among thermal properties, glass transition temperature has already been the point of interest for researchers. Thermal mechanical analysis and dynamic mechanical analysis are generally applied to measure  $T_g$  of the LPA modified UP resin. Depending on the UP/LPA system compatibility, LPA either contributes or deteriorates the  $T_g$  of neat resin. Coefficient of thermal expansion was studied rarely by TMA and showed a mixed trend with LPA addition.
- If material is considered, almost all the past studies are conducted on UP/LPA/Styrene systems without any fibre. Also, no studies have been found about combination of different LPA in the same mixture.

Table 2.2 presents an overview of the literature presented on the above discussion.

# 2.7 Research Motivation & Objectives

From the above discussion, it was clearly understood that the effects of LPA on thermo-mechanical properties of UP/fibre composites is still incomplete and deserves intensive research. This study is an attempt towards bridging this gap within the scope of its limits.

Resin transfer moulding is an efficient and cost-effective process to manufacture complex automotive parts. Therefore, it is interesting to correlate the effects of LPA, which are used to enhance the surface finish of moulded parts, to the thermo-mechanical properties of the material. The main objectives of this research are to investigate the effect of LPA on the thermo-mechanical properties of fibre reinforced UP composites manufactured by resin transfer moulding. As LPA, a combination of PVAc/PMMA LPA was used in this study.

Among mechanical properties, flexural and shear properties of the UP/Fibre composites are measured by three-point bending. The flexural and shear behaviours of the material with respect to the amount of LPA incorporated in the resin formulation are attempted to be identified. The properties are to be measured according to the relevant ASTM standards. Besides the quantitative analysis of the properties, the failure mode is also to be investigated by microscopic study.

Among thermal properties, the glass transition temperature of the moulded parts and its trend with respect to the amount of LPA content in the resin formulation is the point of interest. There are different available techniques to determine  $T_g$  of composites. Among them, the most common ones are chosen to be applied in this study. Three different techniques are applied in the measurement of  $T_g$ . They are thermal mechanical analysis (TMA), dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Coefficient of thermal expansion (CTE) of the material is also investigated from the TMA test method. CTE is to be found before and after the occurrence of  $T_g$  during the test.

	Th	ermal							
	pro	roperties [28]							
LPA	Tg	СТЕ	Tensile	Elongation	Young's	Flexural	Flexural	Izod	
	[27]	[28]	strength	at break	modulus	strength	modulus	impact	
								strength	
	<sup>0</sup> C	µm/m <sup>0</sup> C	MPa	%	GPa	MPa	GPa	J/cm	
Poly(vinyl acetate): PVAc	26	·····			1.27-2.26*				
Poly(methylmethacrylate): PMMA	106	50-90	48.3-73.3	2-6	2.27-3.28	73-133	2.27-3.21	0.1-0.2	
Polyurethane: PU	-45	62-76	49.6-69.9	60-180	1.33-2.17	71-105	1.64-2.31	0.8-1.3	
Polystyrene: PS	100	50-83	35.9-52.4	1-3	2.31-3.32	70-102	2.65-3.42	0.2	

Table 2.1: Common LPA used with UP resins and their thermo-mechanical properties

\*[29]

Researcher	LPA	Mechanical properties					Thermal prope	erties		
(Year),Reference		Tensile	Ultimate	Young's	Impact	Fracture	Fatigue	Flexural	Tg (Method)	CTE
		strength	strain	modulus				& Shear		
Bucknall(1991), [50]	PVAc			V		$\checkmark$				
Huang(2006), [48]	PVAc								V	
	PMMA	- √ _	···· √ ···	$\checkmark$	√				(DMA & TSC)	
Huang(2004), [46]	РММА								√ (DMA)	
Huang(1998), [30]	PVAc,			-						
	PMMA,	$\checkmark$	<b>√</b>	$\sim$	√	· √ · .			(TMA & DMA)	
	PU, PS	· · · · · · · · · · · · · · · · · · ·								
Huang(2003), [45]	PVAc	V	1		- N				√ (DMA)	
Juan(1993), [47]	PVAc				V			1		
Boukehili (2006), [51]	PVAc				V.		V	V	√ (DMA)	V
Lam (1989), [27]	PVAc,					,				
	PMMA,	$\sim$ $$	√.	$\sqrt{1}$		$\checkmark$			$\checkmark$	
	PU, PCL,								(DMA)	а 
	PS									-

# Table 2.2: Summary of literature review

Researcher	LPA	Mechanical properties							Thermal properties	
(Year),Reference	-	Tensile	Ultimate	Young's	Impact	Fracture	Fatigue	Flexural	Tg (Method)	CTE
		strength	strain	modulus		· · ·		& Shear		
Huang (1998),[12]	PVAc,	V		√	V					
	PMMA,			ж		· •				
	PU,									
Huang(2000), [49]	PU	1		V	1			· · · · · · · · · · · · · · · · · · ·	√ (TSC)	

Table 2.2: Summary of literature review (cont')





Figure 2.1: (a) Three-point bending setup (b) Four-point bending setup



Figure 2.2: Glass transition temperature (Tg)

(a) and coefficient of thermal expansion (CTE) by TMA (b) by DMA and (c) by DSC [10]



Figure 2.3: Curing reaction of UP resin [25]



(d) Microvoid formation

(c) Intra & inter-particle reactions





Figure 2.5: The effects of LPA type and concentration on tensile strength of cured UP resins at MR 2/1 (Tensile test at a constant crosshead speed of 2 mm/min) [30]



Figure 2.6: The effects of LPA type and concentration on ultimate strain of cured UP resins at MR 2/1(Tensile test at a constant crosshead speed of 2 mm/min) [30] Here ultimate strain refers to the strain to failure



Figure 2.7: The effects of LPA type and concentration on Young's modulus of cured UP resins at MR 2/1(Tensile test at a constant crosshead speed of 2 mm/min) [30]



Figure 2.8: The effects of LPA type and concentration on impact strength of cured UP resins at MR 2/1 (Izod impact test) [30]



Figure 2.9: The effects of LPA type and concentration on Fracture toughness of cured UP resins at MR 2/1 (Fracture mechanics test) [30]



Figure 2.10: The effects of LPA type and concentration on  $T_g$  of cured UP resins at MR 2/1 (TMA from -50°C to 200°C at 10°C/min) [30]

# **Chapter 3**

# **Sample Manufacturing**

In this chapter, materials used in the study and the sample manufacturing process are discussed. *Section 3.1* presents material specifications, *Section 3.2* gives the procedure of the manufacturing process of composite plates by resin transfer moulding and *Section 3.3* presents the degree of cure measurement of the plates by differential scanning calorimetry. Finally *Section 3.4* presents the fibre volume fraction measurement of the plates.

## **3.1 Materials**

The resin under study is an unsaturated polyester namely PD9551 supplied by Scott Bader. PD9551 is a modified version of Crystic 790 which is a polyester resin. Typical properties of Crystic 790 as mentioned in the product datasheet are given by *Table 3.1. Table 3.2* presents the mechanical properties of a laminate made with Crystic 790 and one layer of Rovicore 600 D3 600. Rovicore is a glass fibre reinforcement, which consists of a synthetic non-woven core, made from large diameter fibres, sandwiched between chopped glass fibres, and mechanically stitched together [53].

The low profile additive is also supplied by Scott Bader namely PD9419 which is a combination of Poly vinyl-acetate and Poly methyl-methacrylate. The resin was supplied in three compositions by the manufacturer with varying percentages (0, 10 and 40%) of LPA and in solution of Styrene. The constituents of the UP resin and the composition of the resin in terms of its constituents are not declared by the supplier.

However, the LPA is based on Poly vinyl-acetate and the styrene content in the resin mixture is approximately 45 to 50%.

Calcium carbonate supplied by Omya BLR2 was used as filler at 30% of the resin weight. Trigonox 93 (Tert-butyl peroxybenzoate) was used as catalyst at 2.6% of resin weight. Accelerator NL-53 (Cobalt 2-ethylheaxanoate) was used as accelerator at 0.5% of resin weight. Both the catalyst and the accelerator were supplied by Akzo Nobel Chemical. *Table 3.3* presents the resin formulation in terms of weight fraction. The same formulation was used with the 0, 10 and 40% LPA containing resin.

Rectangular F3P (Ford programmable performing process) glass fibre preforms, measuring 26 cm by 24 cm were used as reinforcements. The preform has three layers of glass fibres (*Figure 3.1*). The middle layer, which is the structural mat, is comparatively thick and is made of chopped fibre bundles. Both the surface layers are made of thin continuous fibres of an average diameter of 20  $\mu$ m. These surface layers are called surface veils which are used to improve the surface finish of the part. One of the surface veils has higher binder concentration than the other and this could lead to deteriorated surface quality. The surface veils are only 18.4% by weight of the preform and the remaining 81.6% is the structural mat.

### **3.2 Resin Transfer Moulding Process**

Resin transfer moulding (RTM) is one of the most popular composite moulding processes. RTM is mostly used for manufacturing large and complicated shape parts with high strength-to-weight ratios by a low-cost and efficient procedure.

In a typical RTM process, a low-viscosity thermoset resin is injected under low pressure (usually less than 700 kPa) into a closed mould cavity, inside which a fibre preform, having a shape close to the finished product is pre-placed. Upon injection, the resin fills up the mould cavity and impregnates the preform. The preheated mould

cavity cures the resin at high temperature and the final part is removed from the mould. *Figure 3.2* presents a schematic diagram of the RTM process to show the manufacturing steps [25, 54-56].

Composite plates with different LPA content were manufactured by RTM to measure their thermo-mechanical properties. Details of this manufacturing process are presented in this section as follows.

#### Equipment

Resin transfer moulding was performed to manufacture composite plates on a heated steel mould mounted on a hydraulic press. The mould had a mirror like polished finish which is desired for the surface finish of the manufactured plates. The mould was equipped with J type thermocouples and Dynisco PT422 pressure sensors connected to a Vishay's System 6000 data acquisition system for online temperature and pressure measurements. The mould had two parts which are named as the top mould and the bottom mould (Figure 3.3). On the bottom mould, a 3.175 mm thick picture frame was placed inside which the fibre preform was attached. The frame measured 26 cm by 25 cm. The fibre preform was smaller by 1 cm than the frame at one edge (measuring 26 cm by 24 cm) and the plate manufactured was the same size as the frame. So about 1 cm of the plate at that edge was free of fibre as shown in Figure 3.4. The injection and vent ports on the mould were designed to create a uniform linear flow front through the fibre preform [26]. Thermocouples were attached to the top and the bottom mould to record temperature variations in the mould. Pressure sensors were located near the injection and vent ports and one pressure sensor was located on the injection pump to record injection pressure. Figure 3.4 shows the location of the pressure sensors, injection port and vent port on the mould with respect to the position of picture frame. Figure 3.5 shows the location of the thermocouples on the mould. For resin injection into the mould cavity, a Radius Engineering constant pressure pneumatic-controlled injector was used. The mould parts were heated with a Conair circulating water heating system.

## **Process Parameters**

The resin mixture was injected into the mould cavity at room temperature and at a pressure of 621 kPa as measured by the pressure sensor P<sub>4</sub> (*Figure 3.4*). A temperature gradient was created by keeping the top and the bottom mould away from each other and by setting them at a temperature difference of  $15^{\circ}$ C. The bottom mould was set at  $90^{\circ}$ C whereas the top mould was set at  $75^{\circ}$ C by setting the temperature of the water heating system. The temperature and pressure levels were chosen according to the optimum value as obtained from the previous studies on the surface finish measurement of the composite plates manufactured on the same setup and with the same material [26].

#### **Resin Preparation**

The resin mixture was prepared immediately before injection. A total 450 gm of mixture was prepared according to the composition mentioned in *Table 3.3*. At first, resin containing the required amount (0, 10 or 40%) of LPA was measured. Then filler was added to the resin and was mixed thoroughly by a mixer powered by a drill. Next the accelerator followed by the catalyst was added in two separate steps and stirred thoroughly between each step. After injection, a small excess amount of resin was left inside the pump.

#### **Mould Preparation**

The mould surfaces were cleaned using a mould cleaner. On the clean mould, two layers of release agent PMR-90 were applied at ten minutes interval. Similarly, release agent was applied on all surfaces of the picture frame and the shims. The picture frame was sealed using a Gore-Tex joint sealant gasket. The glass fibre preform attached to the picture frame was placed on the bottom mould with the surface having less binder concentration downward. Then the moulds were closed with the press before resin injection.

#### **Resin injection and curing**

*Figure 3.6* shows the typical process data of the RTM for a 10% LPA containing plate. The injection pressure (P4) was increased to 621 kPa by the pump and then the resin was injected through the injection port (*Figure 3.4*). The vent port (*Figure 3.4*) was closed when the resin flowed out of it. All the pressures (P1,P2,P3 & P5) started to drop at this stage as the resin started to gel and shrink and the plate lost contact with the mould surfaces. Next the pressures increased significantly as the plate came back in contact with the mould surfaces due to LPA expansion. The injection pressure was held for 45 min at the required level (621 kPa), which was apparently the resin curing period.

From the manufactured plates, samples were cut according to the required dimensions as shown by *Table 3.4* for different thermo-mechanical tests. *Figure 3.7* shows the sample locations in the plates.

### **3.3 Degree of Cure Measurement**

The thermo-mechanical properties of composites depend strongly on the degree of cure of the resin. For degree of cure measurement, non-isothermal scans were performed on a TA Instruments Q100 differential scanning calorimeter. Both resin mixture as used in RTM and thin samples of the manufactured composite plates were tested by differential scanning calorimetry (DSC).

In order to measure the total heat of reaction of the resin mixture (THR(resin)) injected to make the plates, similar composition was prepared. 20 grams of each of the 10 and 40% LPA containing resin was mixed with filler, accelerator and catalyst in the same proportion as used in the injected mixture. This mixture was sealed in aluminium hermetic pans which are heated from 20 to  $240^{\circ}$ C at the rate of  $20^{\circ}$ C/min. For each of the composition, three samples were tested.

From the experimental data, total heat of reaction was obtained from the area under the exothermic peak as shown in *Figure 3.6. Table 3.5* presents the results of total heat of reaction for all samples. Although the average heat of reaction was found to be 20 J/g less for 40% LPA containing samples compared to the 10% LPA samples, the standard deviation for both cases were as high as 31 J/g and 20 J/g respectively. Therefore, the heat of reaction could be considered independent on the amount of LPA.

For degree of cure measurement, thin circular samples were cut from the surfaces of four composite plates, two of which were made with 10% LPA and the other two with 40% LPA. The samples were sealed in non-hermetic aluminium pans and were heated at a rate of  $20^{\circ}$ C/min from 20 to  $240^{\circ}$ C. The residual heat of reaction for the composite (RHR(composite)) was obtained from the area under the exothermic peak as shown in *Figure 3.9*. The residual heat of reaction for the resin (RHR(resin)) was calculated by dividing the residual heat of reaction for the composite by the resin weight fraction. *Equation 3.1* was used to calculate the residual heat of reaction for resin matrix.

$$RHR(re\sin) = \frac{RHR(composite)}{W_m}$$
(3.1)

Where, matrix weight fraction ( $W_m$ ) for 10% and 40% LPA samples was taken from *Table 3.8.* Degree of cure (DOC) was calculated by *Equation 3.2.* 

$$DOC = \frac{THR(resin) - RHR(resin)}{THR(resin)}$$
(3.2)

where,

THR = Total heat of reaction (J/g) obtained from DSC of resin matrix

Degrees of cure for all the four plates are presented in *Table 3.6*. The degree of cure of the 10% and 40% LPA samples was found as 0.90 (standard deviation=0.01) and 0.92 (standard deviation=0.015) respectively. The thermo-mechanical properties of

the composite plates are not expected to vary significantly due to this 2% variation in the degree of cure.

# **3.4 Fibre Volume Fraction Measurement**

For fibre volume fraction (V<sub>f</sub>) measurement, density data for the sample and the constituents (fibre and matrix) are required. Rectangular samples were cut from the composite plates (one from each LPA containing plates) to measure density. These samples were weighed with a digital balance and their dimensions on each side were measured with a digital micrometer (*Table 3.7*). From this dimensions, volume of the samples were calculated by *Equation 3.3*.

$$Volume = Length * Width * Depth$$
(3.3)

From the weight and the volume, density of the sample was calculated Equation 3.4.

$$Density = \frac{Mass}{Volume}$$
(3.4)

As the dimension of the manufactured composite plate was about 1 cm larger than the dimension of the fibre preform on one edge, that part of the plate was free of fibre. Samples of this particular portion of each of the plates used for thermo-mechanical tests were cut, which we can call the resin samples. The density of these samples was also calculated similarly and is presented in *Table 3.7*.

It was found that upon addition of 10% LPA, density of the resin was reduced from 1355 kg/m<sup>3</sup> to 1183 kg/m<sup>3</sup>. Again for 40% LPA, density of the resin was found to be 1146 kg/m<sup>3</sup>. Similarly, density of the LPA containing samples was lower than that of the sample with no LPA. This was expected as LPA has a density lower than the polyester. The density of the neat UP resin is 1260 kg/m<sup>3</sup> [26] whereas PMMA has a density of 1180 kg/m<sup>3</sup> [29]. Furthermore, density could also reduce upon LPA

addition due to the creation of microvoids, which is a part of the shrinkage compensation mechanism by LPA [51]. The density of the fibre and the neat resin (without any additive) is  $2500 \text{ kg/m}^3$  and  $1260 \text{ kg/m}^3$  respectively as reported by the manufacturer.

Fibre volume fraction was measured according to the standard ASTM procedure designated as D3171-99 [57]. The samples of the composite plates with measured density were placed into pre-weighed crucibles. The crucibles were cleaned by heating to  $600^{\circ}$ C in a muffle furnace and cooling in a desiccator to room temperature. The crucibles with the samples were then placed into a preheated muffle furnace at  $600^{\circ}$ C for six hours. After the matrix burn-off inside the furnace, the crucibles were cooled in a desiccator to room temperature and weighed. The resin burned off and the fibre and filler were left.

Mass of matrix  $(M_m)$  was calculated by subtracting the final mass from the initial mass of the sample. From this  $M_m$  and the initial composition of the injected resin mixture, mass of filler in the burned sample was calculated by *Equation 3.5*.

$$M_{m} = M_{re \sin} + M_{filler} + M_{catalyst} + M_{accalerator}$$
(3.5)  
Or,  $M_{m} = R + 0.3R + .026R + 0.005R = 1.331R$   
So,  $M_{filler} = 0.3R$ 

From the final mass of the specimen, mass of fibre was calculated by subtracting the mass of filler. The calculated masses are given in *Appendix A (Table A.1)*. From these mass values, the following parameters were calculated.

#### **Fibre Weight Fraction**

Fibre weight fraction,  $W_f$  was calculated by *Equation 3.6*.

$$W_f = \frac{M_f}{M_i} \tag{3.6}$$

where,

 $M_f$  = Mass of fibre in final mass ( $M_{final}$ ) of specimen (gm) and

 $M_i$  = Initial mass of specimen (gm)

# **Matrix Weight Fraction**

Matrix weight fraction,  $W_m$  was calculated by Equation 3.7.

$$W_m = \frac{M_i - M_f}{M_i} \tag{3.7}$$

#### **Fibre Volume Fraction**

Fibre volume fraction,  $V_f$  was calculated by *Equation 3.8*.

$$V_f = \frac{W_f * \rho}{\rho_f} \tag{3.8}$$

Where,

 $\rho$ = Density of specimen (kg/m<sup>3</sup>) and  $\rho_f$ = Density of fibre = 2500 kg/m<sup>3</sup>

#### **Matrix Volume Fraction**

Matrix volume fraction,  $V_m$  was calculated by *Equation 3.9*.

$$V_m = \frac{W_m * \rho}{\rho_m} \tag{3.9}$$

where,

 $\rho_{\rm m}$  = Density of resin (kg/m<sup>3</sup>)

#### **Void Volume Fraction**

Void volume fraction,  $V_v$  was calculated by *Equation 3.10*.

$$V_{v} = 1 - (V_{f} + V_{m}) \tag{3.10}$$

All the calculated values from *Equations 3.6* to *3.9* are presented by *Table 3.8*. It was found that the fibre volume fraction,  $V_f$  was in the range of 19 to 21%. For this amount of variation, both flexural strength and flexural modulus of fibre/polyester were found to vary by around 6% [58]. As mechanical properties of composites are strongly dependent on fibre content, it was important to determine the variation of fibre content in different plates.

The void volume fraction,  $V_v$  was found to be only 2.8% in the sample with no LPA. For 10% and 40% LPA samples,  $V_v$  was even smaller, which are 0.4% and 0.2% respectively. Apparently, the void content is expected to reduce with LPA content due to the microvoid formation. However, the void volume contributed by the microvoids has been taken into account in the matrix volume fraction. The calculated  $V_v$  is believed to be due to the manufacturing defects.

Table 3.1: Typical properties of Crystic 790 with 30% Calcium carbonate filler by weight (cured at 20<sup>o</sup>C for 24 hours and at 80<sup>o</sup>C for 3 hours) [59]

Barcol Hardness (Model GYZJ 934-1)	30
Tensile strength	27 MPa
Tensile modulus	3.1 GPa
Elongation at break	0.9%
Deflection temperature under load (1.8 MPa) (post-cured at 120 <sup>0</sup> C for 3 hours)	112 <sup>0</sup> C
Viscosity at 25 <sup>0</sup> C	0.28 Pa-s
Density*	1260 kg/m <sup>3</sup>

\*[26]

Table 3.2: Typical properties of Crystic 790 with 30% Calcium carbonate filler by weight and combined with 1 layer Rovicore 600 D3 600 (cured at 20<sup>0</sup>C for 24 hours and at 80<sup>0</sup>C for 3 hours) [59]

Tensile strength	80 MPa
Tensile modulus	5.39 GPa
Elongation at break	2%
Flexural strength	178 MPa
Flexural modulus	6.5 GPa

Constituent	Specification	Weight fraction
Resin	Unsaturated polyester	65% of
	(PD9551, Scott Bader)	composite panel
Low profile	PVAc & PMMA	0, 10 or 40% of resin
additive	(PD99419, Scott Bader)	
Filler	Calcium carbonate	30% of resin
	(Omya BLR2)	
Catalyst	Tert-butyl peroxybenzoate	2.6% of resin
	(Trigonox 93, Azko Nobel Chemicals)	
Accelerator	Cobalt 2-ethylheaxanoate	0.5% of resin
	(Accelerator NL-53, Azko Nobel Chemicals)	

# Table 3.3: Resin formulation by weight fraction

Table 3.4: Sample dimensions of thermo-mechanical tests

Type of test	Length (mm)	Width (mm)	
Flexural test	70	12	
Short beam test	21	7	
Thermal mechanical analysis	5	5	
Dynamic mechanical analysis	50	12	
Differential scanning calorimetry	Circular thin samples (weight=10 to 20 mg)		

LPA	Sample	Weight	Total heat	Average
			of reaction	Total heat of reaction
%	#	mg	J/gm	J/gm
10	1	12.72	296	
10	2	10.95	255	268 (S=20)
10	3	10.86	252	
40	4	9.86	244	
40	5	12.52	303	288 (S=31)
40	6	12.38	316	

Table 3.5: Total heat of reaction of the resin mixture measured by DSC

Table 3.6: Residual heat of reaction (composite) measured by DSC and calculatedresidual heat of reaction (resin) and degree of cure

LPA	Plate	Weight	RHR	RHR	Degree of	Average Degree of
			(Composite)	(Resin)	Cure	Cure
%	#	mg	J/gm	J/gm		
10	1	13.88	20	30	0.89	0.90 (S=0.010)
10	2	9.16	17	25	0.91	
40	3	14.73	12	18	0.94	0.92
40	4	11.55	16	25	0.91	(S=0.015)

LPA	Mass	Length	Width	Thickness	Volume	Density
	M	L	b	h	2 <b>V</b>	ρ or ρ <sub>m</sub>
%	gm	mm	mm	mm	mm <sup>3</sup>	kg/ m <sup>3</sup>
0 (composite)	1.417	22.379	12.479	3.256	909	1558
10 (composite)	1.355	22.477	11.990	3.479	937	1444
40 (composite)	1.373	22.044	12.281	3.539	958	1432
0 (resin)	0.897	20.371	9.981	3.255	661	1355
10 (resin)	0.723	21.432	8.255	3.454	611	1183
40 (resin)	0.787	24.225	8.054	3.519	686	1146

Table 3.7: Density of composite and resin samples

Table 3.8: Volume fraction calculation

LPA	Fibre	Matrix	Specimen	Resin	Fibre	Matrix	Void
	weight	weight	density	density	volume	volume	volume
	fraction	fraction			fraction	fraction	fraction
	W <sub>f</sub>	W <sub>m</sub>	ρ	ρ <sub>m</sub>	V <sub>f</sub>	Vm	V <sub>v</sub>
(%)			$(kg/m^3)$	(kg/m <sup>3</sup> )			
0	0.34	0.66	1558	1355	0.210	0.761	0.028
10	0.32	0.67	1444	1183	0.187	0.808	0.004
40	0.35	0.65	1432	1146	0.198	0.799	0.002



Figure 3.1: Structure of F3P glass fibre preform



Figure 3.2: Schematic diagram of resin transfer moulding process



Figure 3.3: Steel moulds used for the resin transfer moulding







T9 : room temperature

T8 : temperature at the center of the preform





Figure 3.6: Typical RTM process data of a 10% LPA plate



Figure 3.7: Sample locations on a composite plate



Figure 3.9: Residual heat of reaction of a 10% LPA sample measured by DSC

# **Chapter 4**

# **Experiments and Results**

In this chapter, experimental details of thermo-mechanical properties measurement techniques are presented followed by their results. *Section 4.1* discusses the three-point bending test methods for flexural and shear properties measurement. *Section 4.2* discusses the different techniques applied for the measurement of thermal properties, which are glass transition temperature  $(T_g)$  and coefficient of thermal expansion (CTE).

## **4.1 Three-point Bending Tests**

For flexural and shear properties measurement of the composite plates, three-point bending tests were performed with an Instron machine according to the relevant ASTM procedures. The details of the experiment and results are discussed in this section. The properties measured are the flexural strength, flexural strain, flexural modulus and short beam strength. A binocular was used to take magnified pictures of the specimens, from which failure mode was identified for each sample. The fractured surface was also observed by scanning electron microscopy (SEM).

#### **4.1.1 Specimen Fabrication**

From the composite plates manufactured by RTM, rectangular samples were cut according to the required dimensions of the relevant ASTM standards [15,18]. The nominal thickness of the plates was 3.5 mm. After fabrication, sample dimensions were measured with a digital micrometer having an accuracy of 0.001 mm. The width

and depth of each specimen were measured at the mid-span and were reported to the nearest 0.03 mm, as required by ASTM D790 [18]. *Figure 4.1* presents a schematic diagram of the bending test sample to show its dimensions.

For flexural tests, 70 mm by 12 mm rectangular samples were cut, which are called the long beams. The length of the specimen allows 7.25 mm overhanging at each support with a support span of 55.5 mm (*Figure 4.1*). The minimum allowable overhanging is 10% of the support span [18] that is 5.55 mm at each support for a 55.5 mm span. The maximum allowable width of a sample is one-fourth of the support span, which is 13.875 mm for the specified span. *Table A..2 (Appendix A)* presents the dimensions of all long beam samples. Six samples of each of the 0, 10 and 40% LPA containing plates were tested to check reproducibility of results.

In case of short beam tests, the required specimen length is six times the specimen depth and the required specimen width is twice the specimen depth [15]. As the nominal depth of the specimen is 3.5 mm, 21 mm by 7 mm rectangular samples were cut following the requirement. The support span is 14 mm, which allows 3.5 mm overhanging at each support end. These specimens are called the short beams. Five samples of each of the different LPA containing plates were cut having dimensions as presented in *Table A..3 (Appendix A)*.

# 4.1.2 Flexural Test

For flexural properties measurement, three-point bending tests were performed by an Instron 1123R according to the procedure of ASTM D790. Details of test setup, parameters, procedure and results are discussed in the following sections.

# **4.1.2.1** Test Setup

A 217-17 (serial no. 0165) model load cell was used which has a range of 10-500 kg load. The instrument was operated at a constant crosshead speed as required by the standard test procedure. The test setup with a long beam sample is shown in *Figure 4.2*. A cylindrical loading nose having a diameter of 6.35 mm was used to apply load at the specified crosshead speed. According to the ASTM specifications, a pair of radial supports having diameter of 6.35 mm were fabricated to use at each end of the span. The supports were screwed to a pair of fixtures, which could be moved on a glider to adjust the support span according to test specifications. This setup could be easily mounted on the Instron. A data acquisition system (model 4500) was connected to the Instron to record load and displacement data during the test.

## **4.1.2.2 Test Parameters**

The test parameters were chosen according to ASTM D790. The support span, crosshead speed and maximum allowable displacement are discussed in this section. The specified support span is 16 times (with tolerance +/-1) the specimen depth. From this information, the allowable range of support span, L was calculated from the depth of the specimen by the following expressions. Here h is the specimen depth.

Maximum support span,  $L_{max} = 17$ \*h Minimum support span,  $L_{min} = 15$ \*h

The allowable span range for each of the samples was calculated as presented by *Table A.4 (Appendix A)*. For convenience, the same span (55.5 mm) was used for all the samples. This span was within the allowable range for each of the samples. The crosshead speed or loading rate was calculated by *Equation 4.1*, as specified by the standard, to allow 1% strain rate.
$$R = \frac{ZL^2}{6h} \tag{4.1}$$

Where,

R = Crosshead speed (mm/min)

Z = Strain rate of the outer fibre (mm/mm/min) = 0.01

L = Support span (mm) and

h =Specimen depth (mm)

The crosshead speed for each of the test is given by *Table A.2 (Appendix A)*. The speed was varied from 1.4 to 1.5 mm/min due to the variation in specimen thickness of *Equation 4.1*.

The maximum allowable displacement at the mid-span was calculated by *Equation 4.2*.

$$D = \frac{rL^2}{6h} \tag{4.2}$$

Where,

D = Mid-span deflection (mm)

r = Strain (mm/mm) = 0.05

L = Support span (mm) and

h =Specimen depth (mm)

The test was to be terminated when the loading nose passed this displacement, if the specimen did not fail. This is the displacement for the maximum allowable strain which is 0.05 mm/mm. The maximum allowable displacement for all of the samples is shown in *Table A.4 (Appendix A)*.

# 4.1.2.3 Test Procedure

In flexural test, support span is the most important parameter and therefore, span must be measured accurately for use in the calculation of material properties afterwards. For accurate measurement, the supports were marked at the peak of the radius (*Figure* 4.2). Then each support was screwed to each of the fixtures and the fixtures were bolted on the glider at the approximate span. In order to fix a span of 55.5 mm, the distance between the supports must be 49.15 mm which is obtained by subtracting the support diameter (6.35 mm) from the desired span (55.5 mm) as shown in Figure 4.3. The distance between the supports was measured with a digital slide caliper (of accuracy 0.01 mm) and was adjusted to 49.15 mm. The specimen was also marked to its span and was placed on the supports so that these marks aligned to the marks on the peaks of the radial supports. Before starting the experiment, the loading nose was moved close to the specimen by a manual switch until it touched the upper surface of the specimen. The crosshead speed and maximum allowable displacement were specified by the software. The specimen was then loaded until the point of rupture which was detected by the online data. At the point of rupture, the load started decreasing and the test was terminated.

### **4.1.2.4 Verification of Experimental Data**

In order to verify the accuracy of the experimental data, an Aluminum (Al 6061) bar of known property was tested on the Instron at a span of 200 mm and at a crosshead speed of 1.5 mm/min. The load-displacement curve was plotted from the experimental data. Also, the theoretical load was calculated from the displacement equation (*Equation 4.3*) for a simply-supported beam [60].

$$\delta = \frac{PL^3}{48EI} \tag{4.3}$$

60

Where,

δ = Displacement (mm)
P = Load (N)
L = Support span (mm)
E = Modulus of elasticity = 6

E = Modulus of elasticity = 68.9 GPa for Al 6061T6 [61] and

I = Moment of inertia  $(mm^4) = bh^3/12$ 

Where,

b = Specimen width (mm) and

h =Specimen depth (mm)

This theoretical load was also plotted and compared with the experimental data. The comparative curves are shown in *Figure* 4.4. The two curves compared well with each other only with 0.3% difference in the slope. The experimental endeavour of this study is focused on the comparative properties of the different LPA containing samples. Therefore, this minor error in the experimental output was considered acceptable.

### 4.1.2.5 Results & Calculations

From the experimental data, load-displacement curve was plotted for each of the long beam samples. From this curve, maximum load, P and the displacement at maximum load, D were determined as shown in *Figure 4.5*. Also, slope m of the initial straight portion of the curve was determined to calculate flexural modulus. Load-displacement curve for each of the samples is presented in *Appendix B*.

Flexural strength, strain and modulus were calculated by *Equations 4.4, 4.5* and *4.6* respectively. In case the displacement at maximum load, D exceeded 10% of the support span that is if D was greater than 5.55 mm, flexural strength was calculated by *Equation 4.7*, which gives a more reliable value of strength calculated at large deflections.

$$\sigma_f = \frac{3PL}{2bh^2} \tag{4.4}$$

$$\varepsilon_f = \frac{6Dh}{L^2} \tag{4.5}$$

$$E_f = \frac{mL^3}{4bh^3} \tag{4.6}$$

$$\sigma_f = \frac{3PL}{2bh^2} [1 + 6(D/L)^2 - 4(d/L)(D/L)]$$
(4.7)

Where  $\sigma_f$  = Flexural strength (MPa)

 $\varepsilon_f$  = Flexural strain (mm/mm)

 $E_f = Flexural modulus (MPa)$ 

P = Maximum load (N)

L =Support span (mm)

b = Beam width (mm)

h = Beam thickness (mm)

D = Displacement at maximum load (mm) and

m = Slope of the tangent to the initial linear portion of the load-displacement curve (*Figure* 4.5)

The calculated material properties for all the samples are presented in Appendix A (*Table A.5*) with the average flexural strength and flexural modulus for each of the 0, 10 & 40% LPA containing samples. The standard deviation was calculated by Equation 4.8 [18].

$$S = \sqrt{(\sum X^2 - n\overline{X}^2)/(n-1)}$$
(4.8)

Where,

S = Estimated standard deviation

X = Value of single observation

n = Number of observations and

 $\overline{X}$  = Arithmetic mean of the set of observations

## 4.1.2.6 Discussion

The different mechanical properties obtained from the above experimental results and the observed failure modes for the long beams are discussed in this section.

#### **Flexural Strength**

The average flexural strength for the samples is plotted against LPA content in *Figure 4.6*. With no LPA, the average flexural strength was 131.78 MPa. The measured volume fraction of the samples with no LPA was 21% as shown in *Table 3.8*. For a similar combination of chopped strand mat fibre and unsaturated polyester resin, flexural strength of composite plaques was found to be around 135 MPa with a fibre volume fraction of 20% [58]. In the ASTM standard [18], the average flexural strength of glass reinforced polyester (GRP) is stated as 134.45 MPa.

It was found that flexural strength reduced as LPA was added to the resin. The amount of reduction was around 11% with addition of 10% LPA and around 20% with addition of 40% LPA to the resin. This behaviour complies with past studies where it was found that tensile strength of polyester generally decline with addition of LPA [12,30,45-46,47-48]. However, it was claimed in a study of pultruded unidirectional FRP that LPA did not affect the flexural strength at a high span-to-depth ratio like 24 when pure tensile failure occurred. When a standard span-to-depth ratio of 16 was chosen, flexural strength reduced with LPA content and a mixed shear/tension failure was observed [51]. The calculated standard deviation in flexural strength was found to be higher in case of the samples containing 40% LPA. This was believed to be due to the more inhomogeneous structure of the material resulting from the development of LPA rich phase.

#### **Flexural Modulus**

The average flexural modulus for the samples is plotted similarly against LPA content in *Figure 4.7*. Flexural modulus showed the same diminishing behaviour as LPA was added to the resin. The same trend was found in past studies of Young's modulus for LPA modified polyesters [12,30,45-46,48-49]. The average value of modulus with no LPA was found to be 6.59 GPa. From the study of a similar UP/fibre system with no filler, flexural modulus was found to be around 4.9 GPa [58]. One of the advantages of using filler in composite manufacturing is that filler improves the matrix modulus. In this study, addition of 30% filler improved the flexural modulus of the material. For this reason, the flexural strength was found to be close to the value obtained in a similar system whereas flexural modulus was found to be comparatively high [58]. The average flexural modulus of GRP is stated as 5.63 MPa in the ASTM standard [18].

The amount of reduction in flexural modulus with the addition of LPA was found to be around 18% for 10% LPA and around 40% for 40% LPA. The reduction of flexural modulus was expected as thermoplastics like PVAc and PMMA, which replaced the polyester in the resin mixture have lower modulus values compared to UP resin.

The flexural moduli of the plates were determined by using traditional micromechanics (Mori-Tanaka method [62]) for perfectly random fibres. The material properties shown in *Table 4.5* were given as input for three cases with 0, 10 and 40% LPA. As flexural modulus data was not available, tensile modulus of the materials were used in this method. For the first case with no LPA, modulus of matrix ( $E_{matrix}$ ) was taken as the tensile modulus of Crystic 790 with 30% Calcium carbonate (*Table 3.1*). For 10 & 40% LPA,  $E_{matrix}$  was calculated by applying rule of mixture to the LPA/resin mixture, where modulus of LPA (for PVAc) was taken from *Table 2.2*. Fibre volume fraction was taken as 0.2 (*Table 3.3*) which was considered constant for

all three cases due to the comparison purposes. The aspect ratio of the fibre was measured with a digital micrometer.

The theoretical modulus is plotted beside the experimental modulus in *Figure 4.7.* The modulus value is quiet high in the theoretical curve compared to the experimental results. With no LPA, theoretical modulus is 9% higher than the experimental modulus. In case of 10% and 40% LPA, this variation is 24% and 42% respectively. This was expected as the material properties for the LPA are not known and the values taken are approximated from similar materials. Also, the variation in the theoretical modulus with LPA content is 6% with 40% LPA, whereas experimental results show much higher variation (40% with 40% LPA). This is attributed to the fact that with addition of LPA, morphology of the material changes and this change results in the deterioration of the mechanical properties as found in previous studies. The reduction of flexural strength could also be attributed to this morphology change.

Similar to flexural strength, standard deviation of flexural modulus was found to be higher in case of 40% LPA containing samples. This was again attributed to the more inhomogeneous morphology of the material resulting from phase separation. However, the variation in case of both strength and modulus could also be attributed to the inhomogeneity of the material, as a chopped fibre mat was used as reinforcement.

#### **Flexural Strain to Failure**

The calculated flexural strain was found to vary between 2.7 to 4.4%. The average flexural strain with 0, 10 and 40% LPA was found to be 3.7, 3.3 and 3.9% respectively (*Figure 4.6*). The strain was expected to reduce with LPA content as the flexural strength reduced. On the other hand, LPA acted as plasticizer leading to more deformation of the material under load. As a combined effect, the strain did not show any particular trend like other properties upon LPA addition. However, in previous studies, ultimate strain reduced when PVAc, PMMA or PS was added to polyester

whereas PU led to increase in strain [30]. Another study revealed that samples containing PVAc and PU retained their ultimate strain while PMMA, PS and PCL reduced the ultimate strain by about 30 to 55 percent [27].

#### Mode of Failure

When a beam is subjected to three-point bending, its bottom surface experiences tensile load whereas its top surface is subjected to compressive load. The mid-plane is the neutral plane where shear stress is maximum. *Figure 4.8* shows the magnified photographs of the failure cracks on the long beam samples. For all the samples, the crack initiated at the bottom surface of the specimen, which was subjected to tensile load by three-point bending. Therefore, it was clear that the specimen failed by tension. The crack developed until around the mid-plane where flexural stress is zero and shear stress is the maximum. At this point the crack propagated along the mid-plane either in one direction as shown in *Figure 4.8 (b)* or in both directions as shown in *Figure 4.8(a)*. In some cases of 40% LPA containing plates, the crack did not propagate along the mid-plane as shown in *Figure 4.8(c)*.

The propagation of the crack along the mid-plane is attributed to the low shear strength of the material. Since the material is weak in shear, failure was induced to the maximum shear plane following the tensile crack. In case of 40% LPA samples, the tensile crack was found not to follow a straight line (*Figure 4.8(c)*) as compared to 0 and 10% samples. This could be due to the higher proportion of the LPA phase where the crack followed the interface of the two phases. The SEM photographs (*Figure 4.9*) clearly show the fibre pull-out at the tensile crack for each LPA containing samples.

## 4.1.3 Short Beam Test

Three-point bending test as specified by ASTM D2344 is the most widely applied method for shear properties measurement of composites. Short beam tests were performed at the same Instron machine and similar setup with a few changes in the test parameters. The radial supports used in these tests were different than those used in the flexural tests. According to the standard requirement, a pair of radial supports having diameter of 3.175 mm were fabricated. The same loading nose was used as in the flexural test.

### 4.1.3.1 Test Parameters & Procedure

The test parameters were chosen according to the relevant ASTM standard designated as D2344. The required support span is 4 times the specimen depth. The nominal specimen depth is 3.5 mm. Therefore the support span was calculated as 14 mm. The crosshead speed is specified in the standard as 1 mm/min.

Before testing, each sample was measured by a digital micrometer and marked to its span as before. In a similar manner as explained in *Section 4.1.2.3*, the distance between the supports was measured with a slide caliper. The span was adjusted to 14 mm by fixing the distance between the supports to 10.825 mm (*Figure 4.10*), as the support diameter is 3.175 mm. The test was performed similarly as discussed in *Section 4.1.2.3*.

According to the standard, the test must be terminated when either of the following occurred:

- A load drop-off of 30%

- Two-piece specimen failure or
- The head travel exceeded the specimen nominal thickness.

The maximum crosshead displacement was specified by the software as 3.5 mm which is the nominal thickness of the specimen. The last two phenomena did not occur in any case and the test was terminated when a significant load drop (minimum 30%) occurred.

## 4.1.3.2 Results, Calculations & Failure Mode Observation

Similar to flexural tests, load-displacement curve was plotted for each of the short beam samples. From this curve, maximum shear load was determined as shown in the *Figure 4.11*. The peak on the curve prior to the maximum shear load, P is attributed to the tensile failure which is discussed in the *Section 4.1.3.1*. Load-displacement curve for each of the short beam samples is presented in *Appendix B*.

From this load, short beam strength was calculated by Equation 4.9.

$$\tau_s = \frac{0.75P}{bh} \tag{4.9}$$

Where

 $\tau_s$  = Short beam strength (MPa)

P = Maximum shear load (N)

b = Beam width (mm)

h = Beam thickness (mm)

The calculated short beam strength for all the samples are presented in Appendix A (*Table A.6*) with the average value and standard deviation for each of the 0, 10 & 40% LPA containing samples.

## 4.1.3.3 Discussion

The experimental results and observed failure modes of the short beam tests are discussed in this section.

#### Short Beam Strength

The average short beam strength is plotted against LPA content in *Figure 4.12*. With no LPA, the average short beam strength was found to be 15.19 MPa. In a previous study of UP/fibre composites, the interlaminar shear strength was found to be around 14.25 MPa [63]. However, the fibre used was a plain-woven E-glass cloth. Since the shear strength depends more on matrix properties rather than fibre properties, this value is comparable to the material used in this study and it shows good agreement.

With addition of LPA, the short beam strength declined as presented in *Figure 4.12*. The amount of reduction was around 18% with addition of 10% LPA and around 21% for 40% LPA. This implies that there is only a little reduction in the shear properties for a higher amount of LPA addition. This phenomenon agrees with the previous study of interlaminar shear strength of pultruded unidirectional fibre/UP composites [51]. However, the amount of strength reduction became significant (around 26%) with the addition of 20% LPA. Similar to the flexural properties, standard deviation of short beam strength was found comparatively higher in case of 40% LPA containing samples.

#### **Transition of Failure Mode**

Before discussing the observed failure mode for the short beam samples, it is desirable to understand the effect of span-to-depth ratio on the failure mode of a material subjected to three-point bending. In bending mode, a beam is subjected to both normal and shear stresses [64]. However, a high span-to-depth ratio favours normal stress and a low span-to-depth ratio favours shear stress [51]. As a result,

higher span induces tensile failure and lower span initiates shear failure. Normal and shear stresses may be presented by *Equations 4.10* and *4.11* respectively.

$$\sigma = \frac{3PL}{2bh^2} \tag{4.10}$$

$$\tau = \frac{0.75P}{bh} \tag{4.11}$$

Where,

 $\sigma$  = Normal stress and

 $\tau$  = Shear stress

The material is expected to fail by bending rather than shear when the maximum normal stress (given by *Equation 4.10*) is greater than the maximum shear stress (given by *Equation 4.11*). From the above two expressions, the critical span-to-depth ratio for the transition of the failure mode from shear to tension can be obtained by equating the P/bh term (for the same load) as follows.

$$\frac{\sigma}{\tau} = \frac{2L}{h}$$
Or,  $\left(\frac{L}{h}\right)_{critical} = \frac{\sigma}{2\tau}$ 
(4.12)

Figure 4.13 shows the effect of span-to-depth ratio on the shear stress of the material. As can be seen, with higher ratio, shear stress diminishes and as a result flexural stress increases. From the experimental result, the critical ratio for the transition of the failure mode from shear to tension was calculated by replacing normal and shear stress in *Equation 4.12* with the average flexural strength (131.78 MPa) and apparent short beam strength (15.19 MPa) respectively found for the specimens with no LPA. This ratio was found to be around 4. As the short beam test was performed at a ratio of 4, a mixed failure mode of shear and tension is expected instead of a pure shear failure.

#### **Failure Mode Observations**

Figure 4.14 shows the common failure modes encountered in short beam test as shown in the ASTM standard. If the failure pictures of the short beam samples presented in Figure 4.15-4.17 are compared with these typical failure modes, it can be easily concluded that a mixed failure mode of shear and tension was encountered in all the different LPA containing samples. The shear crack was not exactly at the midplane as (Figure 4.15-4.17) could be expected for an isotropic material. This is not unusual as composites are anisotropic in nature; especially when a randomly oriented fibre mat is used, the anisotropic behaviour of the material is even more pronounced. In case of 40% LPA samples, the crack length was less (Figure 4.17) compared to the other samples.

*Figure 4.18* shows the SEM photographs taken at 100X, with the chopped fibre bundle at the fractured surface, which clearly indicates shear failure. At a higher magnification (15000X), as shown in *Figure 4.19* the morphology of the material revealed. With no LPA, a homogeneous resin structure was observed. Upon LPA addition, an inhomogeneous co-continuous resin/LPA structure developed. This observations agree with previous morphology studies of UP/PVAc systems [27,47,50]. The co-continuous structure was more prominent at 40% LPA.

The phenomenon of mixed failure mode was also revealed in the load-displacement diagram (*Figure 4.11*), where prior to the main load drop, more peaks are observed. This could be due to the tensile failure prior to the occurrence of the shear crack. There must be a significant load drop (at least 30% as mentioned in the standard) corresponding to shear failure and so the last peak prior to the main load drop on the curve (load P) is considered as the maximum shear load and has been used in the calculation of the short beam strength. However, since failure occurred in a mixed mode, this calculated strength cannot be considered as the true short beam strength. The

71

flat plateau of the curve can be attributed to the low shear strength of the material [65].

## **4.2 Thermal Properties Measurement**

Thermal properties like glass transition temperature and coefficient of thermal expansion of the manufactured composite plates were measured by three different techniques namely thermal mechanical analysis (TMA), dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Experimental details of each of them are discussed next in separate sections as follows.

### **4.2.1 Thermal Mechanical analysis**

Thermal mechanical analysis was performed by a Du Pont 943 TMA equipped with a 1090 thermal analysis system. *Figure 4.20* shows the test setup. A small 5 mm by 5 mm rectangular sample was cut for the TMA. The thickness of the specimen was first measured by a dimension probe. Then the specimen was placed in touch with a temperature probe. The sample was heated from 60 to  $180^{\circ}$ C at  $3^{\circ}$ C/min and again was cooled back to  $60^{\circ}$ C at the same rate of  $3^{\circ}$ C/min. This thermal cycle was repeated twice to ensure the repeatability of the data. From the experimental data, thermal strain was calculated by *Equation 4.13*.

$$\varepsilon_{t} = \frac{\Delta h}{h} \tag{4.13}$$

Where,

 $\varepsilon_t$  = Thermal strain

 $\Delta$  h = Change in thickness and

h = Original thickness

The calculated thermal strain was plotted against temperature as shown in *Figure 4.21*. From this curve,  $T_g$  and CTE was determined as discussed in the following sections.

# **4.2.1.1 Glass Transition Temperature** (T<sub>g</sub>)

 $T_g$  is detected at the point where the TMA curve changes its slope. In order to determine the point of slope change, linear curve fitting was performed on the curve. Two lines were drawn which are tangent to the initial and final portions of the curve as shown in *Figure 4.22*.  $T_g$  was determined as the temperature at the intersection point of these two lines. However,  $T_g$  was taken on the cooling curves of the last two ramps as these produced more consistent data. During the first heating cycle, the sample experienced some postcuring since it was subjected to a much higher temperature (180<sup>o</sup>C) than the previous curing temperature (90<sup>o</sup>C) during the manufacturing process. For this reason, the first heating curve shows a different trend (*Figure 4.21*) than the other ramps. This behaviour also showed in the DSC test which is discussed in *Section 4.2.3*.

 $T_g$  was plotted against LPA content of the samples in *Figure 4.23*. It was found that  $T_g$  increased from around 139<sup>o</sup>C to 150<sup>o</sup>C as 10% LPA was added. Although the general trend of  $T_g$  with addition of LPA is decreasing as discussed in *Section 2.5.1*, the reverse phenomenon as found in this study also complies with previous studies, where addition of 10% PVAc and PMMA to the UP led to 8<sup>o</sup>C increase in  $T_g$  [46, 48]. In this study, a combination of PVAc and PMMA was used for which no previous report has been found. The reason behind this improvement in  $T_g$  was explained by the better compatibility of the UP/Styrene/LPA system. LPA played a positive role in the chemistry of the curing process by improving the crosslinking density of Styrene and UP. Also, it was explained by the globule microstructure of the material induced by the addition of LPA which enhanced the conversion of C=C bond in UP leading to increased crosslinking density [46]. For samples with 40% LPA,  $T_g$ 

was found to be around  $147^{0}$ C, which is higher than neat resin samples and a bit lower than 10% LPA samples. This complies with the findings from the study of LPAs in general where increasing LPA content led to T<sub>g</sub> reduction. However, in this study T<sub>g</sub> decreased only by 3<sup>0</sup>C as LPA content increased from 10 to 40%.

# **4.2.1.2 Coefficient of Thermal Expansion**

CTE was determined from the cooling curve of the TMA, which is simply the slope of the curve. CTE was determined below and above  $T_g$  from the slope of the tangents drawn to the initial and final portions of the TMA curve (*Figure 4.22*). The average CTE was plotted against LPA content of the sample in *Figure 4.24*. Similar to  $T_g$ , CTE also dropped with LPA content. For samples with no LPA, average CTE was found to be 12 X 10<sup>-5 0</sup>C<sup>-1</sup> which dropped to 7.5X10<sup>-5 0</sup>C<sup>-1</sup> for 10% LPA and 4.5 X 10<sup>-5 0</sup>C<sup>-1</sup> for 10% LPA.

CTE was found to be much higher above  $T_g$  compared to CTE below  $T_g$ . For example, in case of samples with no LPA, CTE below  $T_g$  was found to be 11.9 X 10<sup>-5</sup>  $^{0}C^{-1}$  whereas CTE above  $T_g$  was found to be 19 X 10<sup>-5 0</sup>C<sup>-1</sup>. This was also expected as CTE of a polymeric material above  $T_g$  is much greater than that below  $T_g$  [27].

#### **4.2.2 Dynamic Mechanical analysis**

Dynamic mechanical analysis was performed by a rheometer at the same temperature range as TMA which is 60 to  $180^{\circ}$ C at  $3^{\circ}$ /C min. Rectangular specimens were cut from the composite plates measuring 50 mm by 12 mm. The sample was subjected to torsion during the test. From experimental data, storage modulus (G'), loss modulus

(G") and loss factor (Tan  $\delta$ ) was plotted against temperature as shown in *Figure 4.25*. T<sub>g</sub> is detected as the temperature where Tan  $\delta$  is maximum.

 $T_g$  as found by DMA was plotted against LPA content in sample in *Figure 4.23*. At 10% LPA content,  $T_g$  increased to 159<sup>o</sup>C compared to neat resin which showed  $T_g$  as 150<sup>o</sup>C. At 40% LPA content  $T_g$  was found to be 157<sup>o</sup>C. The reason behind this behaviour is the higher crosslinking density of the system, as discussed in the previous section due to the development of a more compatible system as LPA was added to the UP/Styrene mixture.

From *Figure 4.23*, it is clear that TMA and DMA curve compare well with each other in the trend. However, DMA results are around  $10^{\circ}$ C higher than the TMA results. This was also expected as two different techniques are applied to measure T<sub>g</sub> as a function of two different material properties. In case of TMA, thermal strain was taken as a measure of T<sub>g</sub> whereas in case of DMA, loss of torsional modulus was considered to determine T<sub>g</sub>. Both TMA and DMA gave reproducible data.

As the specimen was subjected to torsion during the DMA, the torsional or shear modulus was also determined from the experimental data. The initial storage modulus given by the test is considered as the shear modulus. The average shear modulus is plotted against the LPA content in *Figure 4.7*, which also showed the same decreasing trend as flexural modulus.

## 4.2.3 Differential Scanning Calorimetry

The last procedure to determine  $T_g$  is the differential scanning calorimetry (DSC). Circular thin samples weighing 10 to 20 mg were cut from the composite plate surface. DSC is a technique which is difficult to apply for determination of  $T_g$  for inhomogeneous resin samples as used in this study. Therefore, a wider temperature range was chosen for the DSC test. The sample was heated from -10<sup>o</sup>C to 200<sup>o</sup>C at  $2^{0}$ C/min and again it was cooled back to  $-10^{0}$ C to at the same cooling rate. Even after that, T<sub>g</sub> could not be detected reliably from the test. There was hardly any slope change in the cooling curve (*Figure 4.26*) from which T<sub>g</sub> could be determined. On the heating ramp, the curve shows clearly the exothermic reaction due to the curing of the sample.

	Nominal	Nominal		Support	No. of
Type of test	width	depth	Length	span	test
	mm	mm	mm	mm	samples
Flexural		· · · · · · · ·			
(ASTM D790)	12	3.5	70	55.5	6
Short beam					
(ASTM D2344)	7	3.5	21	14	5

Table 4.1: Bending test sample specifications

Table 4.2: Theoretical flexural modulus

LPA	% E <sub>matrix</sub> (GPa)	E <sub>fibre</sub> (GPa)	V <sub>f</sub>	Aspect ratio of fibre	Ecomposite (GPa)
0	3.10				7.25
10	3.00	72.4*	0.2	53	7.12
40	2.76				6.80

\*[61]

77



Figure 4.1: Bending test sample dimensions



Figure 4.2: Flexural test setup



Figure 4.3: Schematic diagram of flexural test set-up



Figure 4.4: Load-Displacement diagram of Al 6061bar



Figure 4.5: Load-Displacement diagram of a long beam sample with no LPA



Figure 4.6: Flexural strength and strain to failure Vs LPA content in samples



Figure 4.7: Flexural modulus (From Mori-Tanaka method & bending tests) and shear modulus (From DMA at 60<sup>0</sup>C) Vs LPA content in samples



Figure 4.8: Tensile crack on a long beam of (a) 0% LPA (b) 10% LPA and (c) 40% LPA containing plate



Figure 4.9: SEM photographs of (a) 0% LPA (b) 10% LPA and (c) 40% LPA containing long beam samples showing the fibre pull-out

Diameter = 6.35 mm



Diameter = 3.175 mm

Figure 4.10: Schematic diagram of short beam test set-up







Figure 4.12: Apparent short beam strength Vs LPA content in samples



Figure 4.13: Effect of span-to depth ratio on bending failure mode



Figure 4.14: Typical failure modes of short beam test (a) & (b) Shear failure (c) Tensile failure





(b) Shear failure (c) Tensile crack



(a)



(b)

Figure 4.16(a) & (b) : Mixed shear-tension failure on a short beam sample of 10% LPA containing plate observed by a binocular



Figure 4.17: Failure crack on a short beam sample of 40% LPA containing plate observed by a binocular (a) Mixed shear-tension failure(b) Shear failure (c) Tensile crack











Figure 4.20: Test setup of thermal mechanical analysis



Figure 4.21: Experimental curve for TMA of a sample containing 10% LPA



Figure 4.22: Linear curve fitting curve on TMA curve to determine  $T_g$ 



Figure 4.23:  $T_g \mbox{ Vs LPA}$  content determined by TMA and DMA



Figure 4.24: CTE Vs LPA content determined by TMA



Figure 4.25: Storage modulus (G'), loss modulus (G'') and loss factor (tan  $\delta$ ) for a 10% LPA sample determined by DMA



Figure 4.26: Heat flow Vs Temperature curve determined by DSC for a 10% LPA sample
## **Chapter 5**

#### Conclusion

Low profile additives are thermoplastics, which are incorporated to unsaturated polyester resins as a solution to the volumetric shrinkage problem during the curing reaction of the resin. The experimental endeavour of this thesis was focused to understand the effect of using low profile additives on the thermo-mechanical properties of fibre reinforced unsaturated polyester composite plates, manufactured by resin transfer moulding process. Three composition of resin with 0, 10 and 40% LPA were used in the manufacturing process. From the experimental results and observations, the following conclusions can be drawn.

- All the mechanical properties (flexural strength, flexural modulus and short beam strength) measured by the three-point bending tests reduced upon addition of LPA to the resin. The amount of reduction was more for 10% LPA containing resin. At 40% LPA, although the properties reduced compared to 10% LPA, the amount of reduction was less.
- The failed samples were observed to identify the failure mode encountered. All the samples of the flexural tests failed by tension, whereas those of the short beam tests failed by a mixed tension/shear mode. This was attributed to the low ratio of flexural to shear strength of the material. From the SEM photographs, an LPA phase was identified on the shear fracture surface of the short beams.
- In order to measure the glass transition temperature of the material, three common techniques were applied namely thermal mechanical analysis, dynamic mechanical analysis and differential scanning calorimetry. It was found that T<sub>g</sub> improved by 11<sup>o</sup>C as 10% LPA was added to the resin. Upon addition of 40% LPA, T<sub>g</sub> reduced at a less amount although higher compared to the neat resin.

This was attributed to the compatibility of the UP/LPA/Styrene system as addition of LPA led to a more compatible system than the neat resin.

- Both TMA and DMA gave reproducible data and compared well with each other. However, T<sub>g</sub> given by DMA was higher than that given by DMA, as two different material properties were considered to measure T<sub>g</sub> in these two methods. T<sub>g</sub> could not be identified by DSC successfully.
- Coefficient of thermal expansion of the material was also determined from the TMA curve. CTE also showed the same decreasing trend like the mechanical properties upon addition of LPA. CTE was determined both before and after the occurrence of  $T_g$ . CTE after  $T_g$  was found to be higher compared to CTE before  $T_g$ , as the material expands more when it reaches its rubbery state at  $T_g$ .

It can be concluded that although LPA improves the surface finish of the composite parts by compensating the volumetric shrinkage during the curing process of the resin, it affects the thermo-mechanical properties of the material significantly, which is not favourable in many cases. There must be a judicial compromise between the surface quality and material properties in the choice of using LPA in composite manufacturing depending on the design and service requirement of the parts manufactured.

## **Chapter 6**

#### **Future Recommendations**

From previous studies and the results of this research project, the effect of LPA on thermo-mechanical properties of UP/fibre composites were found to be unfavourable. Therefore, the effect of LPA on other mechanical properties like tensile, impact, fatigue and fracture properties needs to be investigated in case of different combination of LPA. The focus would be to optimize the LPA content in order to avail the best compromise between surface quality and design properties.

As styrene affects the crosslinking density and eventually the material morphology, the styrene content is another parameter that can be adjusted to obtain better mechanical properties from the optimized chemical composition.

The thermo-mechanical properties of composites are strongly dependant on the degree of cure. Postcuring is another field of interest to gain lost properties due to the morphological changes.

Finally, the material has low shear strength and showed a mixed shear/tension failure mode at a span-to-depth ratio of four, which was chosen according to the ASTM standard. Short beam tests can be attempted to perform at a lower span-to-depth ratio to favour shear stress. This can be achieved by reducing sample thickness. Non-conventional shear tests like the Iosipescu shear method can also be performed.

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# Appendix A

LPA	Initial	Mass of	Final mass of	Final	Initial	Mass	Final
	mass of	crucible	specimen+crucible	mass of	mass	of	mass
	specimen			specimen	of	filler	of
					matrix		fibre
%	Mi	M <sub>c</sub>	$M_{c}+M_{final}$	$\mathbf{M}_{\mathbf{final}}$	M <sub>m</sub>	M <sub>filler</sub>	M <sub>f</sub>
L	(g)	(g)	(g)	(g)	(g)	(g)	(g)
0	1.417	30.840	31.491	0.651	0.766	0.173	0.479
10	1.355	30.932	31.540	0.608	0.746	0.168	0.440
40	1.373	29.940	30.581	0.641	0.731	0.165	0.476

Sample ID		] ]	Experin	ent Pa	Output		
LPA	Sample	Width	Depth	Span	Crosshead	Max	Displacement
					Speed	Load	at Max Load
-		b	h		R	P	D
%	#	mm	mm	mm	mm/min	N	mm
	1	12.69	3.39		1.5	241.95	5.75
	2	12.48	3.36		1.5	214.48	5.39
0	3	12.00	3.27		1.4	207.03	5.49
	4	12.87	3.33		1.4	223.68	5.45
	5	11.16	3.27		1.5	174.34	6.57
	6	12.06	3.27		1.5	196.21	6.10
	1	11.82	3.48		1.5	213.70	5.22
	2	12.33	3.45		1.5	213.05	4.47
10	3	12.00	3.54		1.5	220.29	5.70
	4	12.24	3.54		1.4	215.76	4.58
	5	12.27	3.48	55.5	1.4	204.16	5.03
	6	12.51	3.48		1.4	208.62	3.99
	1	12.09	3.42		1.5	185.12	5.05
-	2	11.55	3.42		1.5	161.69	5.14
40	3	11.97	3.45	· · · .	1.5	189.57	6.48
1. 1. 1. 1.	4	12.30	3.36		1.4	184.09	4.70
	5	12.27	3.42	<i>n</i>	1.4	192.80	6.63
	6	12.24	3.48		1.4	175.10	6.43

Table A.2: Experimental data of flexural tests

Sample ID		F	Experim	ent Pa	Output		
LPA	Sample	Width	Depth	Span	Crosshead	Max	Displacement
	-				Speed	Shear	at Max
	2 and 1	b	h	L	R	Load	Shear Load
			-			Р	D
%	#	mm	mm	mm	mm/min	N	mm
	1	7.74	3.42			545.03	1.08
	2	7.50	3.42			503.05	1.35
*.	3	6.93	3.27			460.53	1.15
	4	6.84	3.24			459.96	1.15
0	5	6.96	3.27			456.39	1.15
	1	6.90	3.42			423.38	1.92
	2	6.96	3.39			443.50	1.34
	3	6.96	3.36	14	1	415.38	1.21
	4	6.99	3.33			436.11	0.83
10	5	7.14	3.54			488.89	1.45
	1	6.69	3.48			365.15	1.54
	2	6.93	3.45			398.95	1.16
	3	6.90	3.42			355.66	1.50
	4	6.87	3.48			380.31	1.37
40	5	6.84	3.48			400.52	1.57

Table A.3: Experimental data of short beam tests

LPA	Specimen	Minimum	Maximum	Chosen	Maximum
	depth	Span	Span	Span	displacement
	h	L <sub>max</sub>	$\mathbf{L}_{\min}$	L	D
%	mm	mm	mm	mm	mm
0	3.39	50.85	57.63		7.57
	3.36	50.4	57.12		7.64
	3.27	49.05	55.59		7.85
-	3.33	49.95	56.61		7.71
	3.27	49.05	55.59		7.85
	3.27	49.05	55.59		7.85
10	3.48	52.2	59.16		7.38
	3.45	51.75	58.65	· .	7.44
	3.54	53.1	60.18		7.25
	3.54	53.1	60.18		7.25
	3.48	52.2	59.16	55.5	7.38
	3.48	52.2	59.16		7.38
40	3.42	51.3	58.14		7.51
	3.42	51.3	58.14		7.51
	3.45	51.75	58.65		7.44
	3.36	50.4	57.12		7.64
	3.42	51.3	58.14		7.51
	3.48	52.2	59.16		7.38

 Table A.4: Allowable span and displacement for flexural test

	Sample	Flexural	Average	Flexural	Average	Slope	Flexural	Average	Mode
		strength	Flexural	Strain	Flexural		Modulus	Flexural	of
			strength		Strain		-	Modulus	Failure
LPA		$\sigma_{\mathrm{f}}$	σ <sub>ave</sub>	ε <sub>f</sub>	Eave	m	$\mathbf{E_{f}}$	$\mathbf{E}_{\mathbf{ave}}$	
%	#	MPa	MPa	mm/mm	mm/mm		GPa		
·	1	138.12		0.038		75.24	6.50		
	2	126.73		0.035		73.48	6.63		
	3	139.39	131 78	0.034		60.98	6.57	6.59	
0	4	130.48	121.10	0.035	0.037	75.16	6.76		
	5	133.37		0.041		57.01	6.60		
	6	135.06	(S=3.77)	0.038	(S=0.002)	62.03	6.46	(S=0.2)	
	1	124.28		0.035	- <u>-</u>	62.28	5.34		
	2	120.86		0.030		68.33	5.77		
· · · ·	3	121.95		0.039		66.37	5.33		
10	4	117.10	118.87	0.032	0.033	68.69	5.41	5.41	
	5	114.38		0.034		64.61	5.34		Tension
	6							(S=0.2)	
		114.64	(S=3.74)	0.027	(S=0.004)	65.01	5.27		
	1	108.98		0.034		46.37	4.10		
	2	99.64		0.034		43.67	4.04		
40	3	110.77	106.65	0.044	0.039	39.26	3.41		
	4	110.37		0.031		51.45	4.71	3.93	
	5	111.85		0.044		44.08	3.84		
	6	98.322	(S= 5.5)	0.044	(S=0.006)	42.24	3.50	(S=0.4)	

## Table A.5: Experimental results of long beam tests

LPA	Sample	Apparent	Average	Mode of
		Short beam	apparent	Failure
		strength	Short beam	
			strength	
	•	$ au_{ m s}$	$(\tau_s)_{ave}$	
(%)	#	MPa	MPa	
	1	15.00		
	2	15.26		
0	3	14.77	15.19	
	4	15.50		
	5	15.42	(S=0.27)	
	1	13.48		
	2	14.10		
10	3	13.40	13.90	Shear + Tension
	4	14.00	(S=0.42)	
	5	14.55		
	1	11.80		
	2	12.60		
40	3	11.32	12.03	
	4	11.88	(S=0.49)	·
· .	5	12.57		

Table A.6: Experimental data of short beam tests





Figure B.1: Load-displacement diagrams for long beams with 0% LPA content



Figure B.2: Load-displacement diagrams for long beams with 10% LPA content



Figure B.3: Load-displacement diagrams for long beams with 40% LPA content



Figure B.4: Load-displacement diagrams for short beams with 0% LPA content



Figure B.5: Load-displacement diagrams for Long beams with 10% LPA content



Figure B.6: Load-displacement diagrams for Long beams with 40% LPA content