INTEGRATED ANALYSIS OF LOW PROFILE UNSATURATED POLYESTER AND VINYLESTER RESINS CURED AT LOW TEMPERATURES

DISSERTATION

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By

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Unsaturated polyester and vinylester resins are used in a wide variety of applications. These materials provide high structural stability, increased resistance to solvent and temperature, and improved mechanical stability. Low profile additives have been found highly effective in eliminating the polymerization shrinkage of unsaturated polyester resins in high temperature molding processes such as compression molding of SMC and injection molding of BMC. In recent years, the improvement focuses on the development of low temperature and low-pressure fabrication techniques, such as low temperature/low pressure SMC, RTM, SCRIMP, to significantly reduce the tooling cost. However, poor performance of low profile additives and high residual reactivity in low temperature molding processes unavoidably undermine further applications of unsaturated polyester and vinylester resins. Therefore, there is considerable potential for improving the process through greater technical understanding of reaction and volume shrinkage control mechanism in low temperature cure of unsaturated polyester and vinylester resins.

An integrated analysis is carried out in this study to investigate the reaction kinetics and shrinkage control of unsaturated polyester or vinylester resins with low profile additives cured at low temperatures. A differential scanning calorimeter (DSC), a
Fourier transform infrared spectrometer (FTIR), and a rheometrics dynamic analyzer (RDA) are used to study the reaction kinetics and rheological behaviors. A dilatometer is applied to study the volume change. A scanning electron microscopy (SEM) and an optical microscopy are employed to investigate the structure and morphology evolution during curing. The effects of curing agents including initiator, promoter, and comonomer on the low temperature polymerization are investigated. These experiments are designed to provide information regarding the polymerization mechanism and microstructure evolution throughout the free radical polymerization. In addition, this information along with the relation between morphology and properties of crosslinked polymeric materials will be used to optimize polymerization conditions of unsaturated polyester and vinylester resins with desired properties for applications in composite matrix.
This dissertation is dedicated

to

my parents
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vi


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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract………………………………………………………………………………...ii</td>
</tr>
<tr>
<td>Dedication………………………………………………………………………………...iv</td>
</tr>
<tr>
<td>Acknowledgement………………………………………………………………………..v</td>
</tr>
<tr>
<td>Vita…………………………………………………………………………………….…vi</td>
</tr>
<tr>
<td>List of Tables…………………………………………………………………………xiii</td>
</tr>
<tr>
<td>List of Figures……………………………………………………………………………xv</td>
</tr>
</tbody>
</table>

## Chapters

1. Introduction…………………………………………………………………………1

   1.1 Polymeric composites……………………………………………………………1

   1.2 Molding problems and solutions………………………………………………5

   1.2.1 Volume shrinkage……………………………………………………………5

   1.2.2 Final conversion and residual monomer…………………………………11

   1.3 Scope of study……………………………………………………………………16

2. Literature review……………………………………………………………………22

   2.1 Styrenic resins……………………………………………………………………22

   2.1.1 Unsaturated polyester resins…………………………………………………22

   2.1.2 Vinylester resins………………………………………………………………28

   2.1.3 Curing of styrenic resin………………………………………………………33
5. Shrinkage control and final conversion of vinylester resin in low temperature molding processes

5.1 Introduction

5.2 Experimental

5.3 Results and discussion

5.3.1 Volume shrinkage and final conversion of vinylester resin with LSA

5.3.1.1 Effect of LSA content

5.3.1.2 Effect of curing temperature

5.3.2 SCRIMP molding

5.4 Conclusions

6. Conclusions and recommendations

6.1 Overview

6.2 Effect of Co-promoter and Comonomer on Volume Shrinkage of low profile unsaturated polyester resins cured at low temperatures

6.3 Shrinkage control and residual styrene of unsaturated polyester resins

6.4 Shrinkage control and residual styrene of vinylester resins

References
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Monomers used in unsaturated polyester systems [Trivedi, et al., 1982]</td>
<td>25</td>
</tr>
<tr>
<td>2.2</td>
<td>Unsaturated polyester building blocks [Trivedi, et al., 1982]</td>
<td>27</td>
</tr>
<tr>
<td>2.3</td>
<td>Ingredients of a vinylester/polyester resin formulation [Juska et al., 1996]</td>
<td>35</td>
</tr>
<tr>
<td>2.4</td>
<td>Mechanisms of phase separation [Sperling, 1992]</td>
<td>63</td>
</tr>
<tr>
<td>3.1</td>
<td>Gel time and gel conversion of UP/St/LPA system cured at 35°C (0.5% cobalt, 1.5% MEKP, 300ppm)</td>
<td>90</td>
</tr>
<tr>
<td>3.2</td>
<td>Gel time and gel conversion of UP/St/LPA system cured at 35°C (0.1% cobalt, 1.0% MEKP)</td>
<td>97</td>
</tr>
<tr>
<td>4.1</td>
<td>Final individual and overall conversions and residual contents in UP/St/LPA systems at different cure temperatures and using different initiators (3.5% LPA, 0.5% CoOct, 300ppm BQ)</td>
<td>132</td>
</tr>
<tr>
<td>4.2</td>
<td>Final individual and overall conversion and residual content in UP/St/LPA systems with different MMA contents cured at 35°C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ)</td>
<td>144</td>
</tr>
<tr>
<td>4.3</td>
<td>Monomer reactivity ratios [Greenley, 1999]</td>
<td>146</td>
</tr>
<tr>
<td>4.4</td>
<td>SCRIMP Molding of UP/St/LPA systems with different MMA contents at 35°C (0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ)</td>
<td>168</td>
</tr>
</tbody>
</table>
5.1 Comparison of final volume change for VER-E with various LSA concentrations cured at 35°C using density and dilatometry measurements (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP)………………………………………………………192

5.2 Volume Shrinkage of VER-E with LSA at various temperature profiles (10% LSA, 0.2% DMA, 0.3% CoOct, 1.0% MEKP)………………………………………………196

5.3 Effect of VER-780 on final conversion and surface quality of molded panels in SCRIMP molding of VER-E resins (0.1% 2,4-P, 0.3% CoOct, 2.0% MEKP)……………………………………………………………………………………………………………………………………………..210
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Surface profile of a standard molded SMC [Barkus, et al., 1970]</td>
<td>8</td>
</tr>
<tr>
<td>1.2</td>
<td>Surface profiles of (a) a molded SMC with low profile additive (b) automotive-grade steel [Atkins, 1993]</td>
<td>10</td>
</tr>
<tr>
<td>2.1</td>
<td>Example of polyesterification reaction [Atkins, 1993]</td>
<td>24</td>
</tr>
<tr>
<td>2.2</td>
<td>Molecular structures of vinyl esters [Young, 1976]</td>
<td>30</td>
</tr>
<tr>
<td>2.3</td>
<td>Basic components of vinylesters</td>
<td>32</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematic diagram of macrogelation of unsaturated polyester resin</td>
<td>40</td>
</tr>
<tr>
<td>2.5</td>
<td>Volume change profile of (a) conventional resin and (b) Low Profile Resin [Barkus et al., 1970]</td>
<td>42</td>
</tr>
<tr>
<td>2.6</td>
<td>Schematic of low temperature mechanism: (1) induction stage, (2) spinodal decomposition, (3) coarsening to (i) the LPA-rich phase dominated structure, or (ii) the UP-rich phase dominate structure, (4) coalescence and growth, (a) coarse co-continuous structure, or (b) LPA-rich phase dominated structure, (5) gelation, and (6) microvoid formation (Li, et al., 2000)</td>
<td>56</td>
</tr>
<tr>
<td>2.7</td>
<td>Composition dependence of $\Delta G_m$ at a temperature within the miscibility gap (note: $\mu_i = \partial \Delta G_m / \partial \phi_i$) [Macknight, 1989]</td>
<td>58</td>
</tr>
</tbody>
</table>
2.8 Development of morphology in polymer blends following spinodal decomposition [Reich, 1986]. .................................................................60

2.9 Schematics of concentration profiles during phase separation for nucleation and growth and spinodal decomposition in miscible blends [Macknight, 1989]......62

2.10 Schematic phase diagram for polymer-polymer blends; — binodal line, --spinodal line (a) UCST; (b) LCST; (c) both UCST and LCST; (d) an “hourglass” phase diagram; and (e) UCST above LCST [Macknight, 1989].................................66

2.11 Phase separation due to (a) temperature jump, (b) unsaturated polyester/styrene copolymerization. [Hsu, 1992] .................................................................68

2.12 Ternary phase diagram of the reacting PVAc-containing system; (a) complete diagram, (b) 8% PVAc, (c) 16% PVAc [Bucknall et al., 1985]...............69

3.1 Schematic of dilatometer [Kinkelaar, 1994b]................................................79

3.2 Reaction kinetics of UP/St/LPA system with different concentrations of 2,4-P cured at 35°C (300 ppm BQ, 0.1% cobalt octoate and 1.0% MEKP): (a) reaction rate; (b) conversion.................................................................83

3.3 Volume change profiles of UP/St/LPA system with different concentrations of 2,4-P content cured at 35°C (300 ppm BQ, 0.1% cobalt octoate and 1.0% MEKP)...........................................................................84

3.4 The volume change profile and reaction conversion of UP/St/LPA system with different 2,4-P or initiator/promoter contents cured at 35°C (300 ppm BQ): (a) conversion; (b) volume change. (■ 0.05% 2,4-P, 0.1% CoB, 1.0% MEKP; ○ 0% 2,4-P, 0.5% CoB, 1.5% MEKP; ▲ 0.05% 2,4-P, 0.5% CoB, 1.5% MEKP)...........................................................................................................86

3.5 Effect of 2,4-P on reaction kinetics of the LPA-rich and UP-rich phase of UP/St/LPA system cured at 35°C (300 ppm BQ, 0.5% cobalt octoate and 1.5% MEKP): (a) reaction rate; (b) conversion.........................................................89

3.6 Reaction kinetics of UP/St/LPA system with 6% comonomer cured at 35°C (0.1% cobalt octoate and 1.0% MEKP): (a) reaction rate; (b) conversion..............93
3.7 Volume change profiles of UP/St/LPA system with 6% comonomer cured at 35°C (0.1% cobalt octoate and 1.0% MEKP). ................................................................. 94

3.8 Effect of TMPTMA on reaction kinetics of LPA-rich and UP-rich phase of UP/St/LPA system cured at 35°C (0.1% cobalt octoate and 1.0% MEKP) (a) reaction rate; (b) conversion ................................................................. 96

3.9 Volume change profile of samples with different 2,4-P content in UP/St/LPA system with 6% TMPTMA cured at 35°C (100 ppm BQ, 0.1% cobalt octoate and 1.0% MEKP). ................................................................. 99

3.10 Reaction kinetics of samples with different 2,4-P content in UP/St/LPA system with 6% TMPTMA cured at 35°C (100 ppm BQ, 0.1% cobalt octoate and 1.0% MEKP): (a) reaction rate; (b) conversion ................................................................. 101

3.11 Volume change vs. conversion of samples with different 2,4-P content in UP/St/LPA systems with 6% TMPTMA cured at 35°C (100 ppm BQ, 0.1% cobalt octoate and 1.0% MEKP) ................................................................. 102

3.12 Optical micrographs following the cure of UP/LPA/St at 27°C (3.5% Neulon T-plus as LPA) a) No 2,4-P and TMPTMA, (b) 6% TMPTMA, (c) 0.03% 2,4-P, (d) 0.03% 2,4-P and 6% TMPTMA ................................................................. 103

3.13 SEM micrographs of cured UP/LPA/St with different amounts of 2,4-P and 6% TMPTMA cure at 35°C (x2000). ................................................................. 106

3.14 Surface quality of SCRIMP samples (by using 28” of vacuum at room temperature). ................................................................. 107

4.1 Spectra of an unsaturated polyester resin during curing (St/UP C=C bond ratio=2/1, 0.5% CoOct, 1.5% MEKP, 60°C, 300ppm BQ) ................................................................. 116

4.2 FTIR calibration curves for peaks of styrene vinyl (912cm⁻¹ and 992cm⁻¹) and UP vinylene groups (982cm⁻¹) at 35°C ................................................................. 117

4.3 Calibration curve of polyester vinylene and styrene vinyl groups in FTIR ……… 120
4.4 Calibration of absorption at 912 cm\(^{-1}\) and 992 cm\(^{-1}\) of styrene vinyl groups in FTIR .................................................................121

4.5 Determination of \(\mathbf{T}_g\) of (a) 35°C cured sample from DSC scanning and (b) completely cured sample from RSA scanning (St/UP=2, 3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).........................................................124

4.6 DSC scanning profiles of UP/St/LPA system initiated by MEKP and TBPB (3.5% LPA, no BQ, scan at 2 °C/min).................................................................128

4.7 FTIR (a) conversion and (b) reaction rate profiles of UP/St/LPA systems initiated by MEKP and TBPB (3.5% LPA, 0.5% CoOct, 300ppm BQ).........................131

4.8 DSC and FTIR resin conversion profiles of unsaturated polyester with different initiators cured at 100°C isothermally (3.5% LPA, 0.5% CoOct, 300ppm BQ)........................................................................................................134

4.9 DSC (a) reaction rate and (b) resin conversion profiles of UP/St/LPA at various temperatures and initiator combinations (3.5% LPA, 0.5% CoOct, 300ppm BQ)........................................................................................................135

4.10 Relative conversion of styrene vs. unsaturated polyester C=C bonds at various temperatures and initiator combinations (3.5% LPA, 0.5% CoOct, 300ppm BQ)........................................................................................................136

4.11 Effect of comonomer (MMA) content on (a) reaction rate and (b) resin conversion of UP/St/LPA cured at 35°C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ)........................................................................................................140

4.12 Reaction rate profiles of UP/St/LPA resin systems with different comonomer (MMA) content cured at 35°C as inhibitor is removed from all reactants (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 100 ppm BQ).........................................................141

4.13 Relative conversion of (a) St vs. UP and (b) St vs. MMA C=C bond of UP/St/LPA resin systems with different MMA contents cured at 35°C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ)........................................143

xviii
4.14 Relative conversion of St vs. UP C=C bond of UP/St/LPA resin systems with different St/UP C=C bond ratios cured at 35°C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ)…………………………………………………………147

4.15 Glass transition temperature ($T_g$) as a function of MMA content in UP/LPA/St resin systems (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ)……………………………………………………………………149

4.16 MMA molar fraction based on St and MMA only vs. UP C=C bond conversion in the UP/St/LPA resin systems with different MMA contents cured at 35°C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ)……………………………………………………………………150

4.17 Volume shrinkage of UP/St/LPA systems cured at different temperatures (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ)……………………………………………………………………153

4.18 Morphology of St/UP/LPA samples cured at different temperatures (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ)……………………………………………………………………154

4.19 DSC conversion profiles of LPA-rich and UP-rich phase of UP/St/LPA system cured at various temperatures (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ). ………………………………………………………………………157

4.20 Final shrinkage vs. MMA content in UP/LPA/St resin systems cured at 35 °C (0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ)……………………………………………………………………160

4.21 Morphology of samples at different MMA/St double bond ratios cured at 35°C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ)……………………………………………………………………162

4.22 Schematic of experimental set-up for SCRIMP……………………………………………………………………164

4.23 Temperature and LVDT profiles during SCRIMP molding (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ)……………………………………………………………………166

4.24 Photographs of SCRIMP molded composite under different conditions (0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ)……………………………………………………………………170

xix
4.25 Comparison of flexural stress of SCRIMP molded composites under different conditions (3.5% LPA). Dash lines are the results of the composite without any LPA and MMA. .................................................................171

5.1 Conversion profiles of VER-E with various LSA concentrations cured at 35°C (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP)..........................................................184

5.2 Volume change profiles of VER-E with various LSA concentrations cured at 35°C (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).................................185

5.3 Final volume change vs. LSA concentrations of VER-E cured at 35°C (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP)..............................186

5.4 SEM micrograph of VER-E with 10% LSA cured at 35°C (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP)......................................................187

5.5 Conversion profiles of VER-E with 10% LSA cured at different temperatures (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).........................189

5.6 Volume change profiles of VER-E with 10% LSA cured at different temperatures (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).......................191

5.7 Volume change profiles of VER-E with 10% LSA cured non-isothermally in dilatometer (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP)..............194

5.8 SEM micrographs of VER-E with 10% LSA cured at 80°C at a heating rate of (a) 1.7°C/min; (b) 4.5°C/min; (c) 6.4°C/min; and (d) 12°C/min (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).........................................................197

5.9 SEM micrographs of VER-E with 10% LSA cured at 60°C at a heating rate of (a) 4.7°C/min; (b) 8.5°C/min; and (c) 14.0°C/min (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).................................................................198

5.10 SEM micrographs of VER-E with 10% LSA cured at 40°C at a heating rate of (a) 0.3°C/min; (b) 0.9°C/min; and (c) 2.54°C/min (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP)............................................................199
5.11 DSC isothermal reaction rate profiles of VER-E with different 2,4-P concentrations cured at 35°C (0.3% CoOct, 2.0% MEKP)..........................203

5.12 Rheological change of VER-E with different 2,4-P concentrations cured at 35°C (0.3% CoOct, 2.0% MEKP).................................................................204

5.13 Effect of external acid on DSC isothermal reaction rate profiles of VER-E with 0.1% 2,4-P cured at 35°C (0.3% CoOct, 2.0% MEKP)...............................205

5.14 Schematic of experimental set-up for SCRIMP..........................................207

5.15 Effect of VER-780 on the temperature profiles in SCRIMP mold curing of VER-E resins (0.1% 2,4-P, 0.3% CoOct, 2.0% MEKP).................................209
CHAPTER 1

INTRODUCTION

1.1 Polymeric Composites

Fiber reinforced polymeric composites have become an important class of engineering materials because of the demand of lightweight, structural sound, and cost effective replacement of conventional materials. They offer outstanding mechanical properties, corrosion resistance, durability, excellent fatigue strength, unique design flexibility, ease of fabrication, and low tooling cost, etc.

Generally, a fiber reinforced polymeric composite is composed of a fiber reinforcement, a matrix resin, and an interface between them. The fiber reinforcement provides sufficient strength and stiffness; the matrix resin protects the reinforcement from adverse environmental effects and binds the fibers together, while the interface serves to transfer stress from the matrix to the fibers. Fiber reinforcements commonly used include glass fiber, carbon fiber and Kevlar fiber of which the majority used in polymer composites is glass fiber.
Traditional fiber reinforced polymeric composite fabrication techniques include compression molding of sheeting molding compound (SMC), injection molding of bulk molding compound (BMC), resin transfer molding (RTM), continuous pultrusion, continuous lamination and casting [Pen, 1966; Mark, et al., 1988]. The processing temperature of these techniques varies from room temperature for casting to around 200 °C for pultrusion, and the pressure ranges from 1 atmosphere for resin casting up to 7 MPa for BMC molding.

In recent years, the improvement focuses on the development of low temperature and low pressure fabrication techniques, which can significantly reduce the tooling cost. The techniques for low cost composite manufacturing processes such as low temperature, low pressure compression molding of sheet molding compound (SMC) [Gaspari, 1996; Atkins, et al., 1996], resin transfer molding (RTM), and vacuum infusion liquid composite molding (e.g. Seemann Composites Resin Infusion Molding Process (SCRIMP) [Seemann, 1990; Lazarus, 1996]) have grown considerably in industry. The molding temperature of these processes ranges from ambient temperature (e.g. SCRIMP), 60°C (e.g. RTM), to about 100°C (e.g. low temperature SMC). This range of temperature is much lower than that of high temperature processes such as SMC compression molding (150°C) or BMC injection molding (≥ 150 °C).

Matrix resins for fabric composites are almost exclusively thermosets i.e. cross-linked polymeric solids. They control processability, upper use temperature, flammability characteristics, and corrosion resistance of the composite. The low viscosity of thermoset
resin prior to cure facilitates fiber wet-out and fabrication of the structure, and the high modulus and solvent insensitivity of the cross-linked network after cure provide the composite with good strength and durability. An ideal resin system is one that can retain long pot life but cure fast, which allows the resin inject at low pressure, improves fiber wet-out, and reduces cycle time. The more advanced requirement for matrix resins is that the cured resin can provide low volume shrinkage to ensure better structural and surface properties. They should also be able to achieve high final resin conversion and less volatile organic compounds (VOC) emission especially in low temperature processes (e.g. RTM and SCRIMP) for more environmental friendly applications and better mechanical properties (e.g. flexural modulus, tensile strength, etc.).

The commonly used thermoset resin systems include phenolics, polyurethanes, unsaturated polyesters, epoxies, and vinyl ester resins. Among these, unsaturated polyester (UP) resins represent about 80% of the total resins used in the thermoset composite market [Mark, et al., 1988]. UP resins are widely used throughout the world because of they can produce components with excellent mechanical and chemical properties, good chemical and weather resistance with relatively low cost. Another advantage of unsaturated polyester resin over other thermosetting resin is that they are easy to handle, can be pigmented, filled and fiber reinforced in the liquid form. They are one of the most successful materials used in polymeric composites with annual consumption worldwide in excess of 2 billion pounds [Juska, et al., 1996]. The annual consumption of unsaturated polyester resin in United States in 1999 exceeds 1.2 billion
pounds, and more than 70% of the consumption is consumed in composite industry [CFA annual statistics report, 1999]. Fiber reinforced UP resins are extensively used in building and construction, transportation, electrics, and electronic industries, and in sanitary and domestic applications. The possibility of curing these resins at room temperature and atmospheric conditions (i.e. ambient conditions) makes them suitable for structural applications such as underground pipes, tanks, boat hulls, automobile bodies, aircraft radomes, and the like [Updegraff, 1982].

Commercial unsaturated polyester resins, neglecting other additives, consist mainly of a linear polyester with different amount of unsaturated unit, a crosslinking monomer (usually 35-45 wt% depending on the resin viscosity and processing conditions) and inhibitors that are used to prevent any cross-linking reaction before the resin being processed. The most frequently used cross-linking monomer is styrene. Other monomers, such as methyl methacrylate, diallyl phtthalate, vinyl toluene, divinylbenzene, and chloostyrene were also studied but scarcely used [Anon, 1949; Smith, et al., 1953, Smith, 1966; Wahl, et al., 1957]. Among these monomers, styrene has the advantage of low cost, high reactivity, good heat distortion temperature, and high flexural. The free radical copolymerization between the vinyl groups allows one polymer molecule connecting with another polymer molecule, and produces a three dimensional network, which converts the viscous resin liquid into a hard, thermoset solid.

Although UP resins provide products with good weather and chemical resistance at low cost and short cycle time, they tend to generate smoke upon combustion and are
sensitive to hydrolysis. Epoxy resins are mainly used for fabricating high performance composites with superior mechanical and electrical properties, resistance to corrosive environment, and good performance at elevated temperatures. Vinyl ester resins, representing a successful combination of epoxies and polyesters, exhibit both of these characteristics, providing a product bridge between the polyester of low cost, rapid cure and easily processing, and epoxies of high performance. Their low viscosity at room temperature coupled with the rapid curing rate and relatively low cost makes them suitable for various molding processes. Since vinyl ester resins cost more than polyesters, they are mainly used in chemically corrosive environments and structural laminates, e.g. boat manufacture, where a high degree of moisture resistance is desired.

1.2 Molding Problems and Solutions

1.2.1 Volume Shrinkage

The major problem of unsaturated polyester resins is their high polymerization shrinkage with the cross-linking monomer, i.e., styrene. For the typical unsaturated polyester, approximately 7-10% shrinkage of total volume occurs during cure [Bartkus, et al., 1970]. Because of the volume shrinkage, the compound tends to pull away from the mold surface and shrink away from the fibrous reinforcement, which reduces the accuracy of mold surface reproduction and leaves the fiber pattern at the surface [Melby, et al., 1989; Kia, 1988]. The high degree shrinkage creates other processing problems as well
which sets limit to the growth of many high-volume applications:

- poor surface appearance, including surface waviness and fiber pattern readout,
- warpage and poor dimension accuracy of molded parts,
- internal cracks and voids in thick sections,
- sink mark on the appearance surface opposite to reinforced ribs or bosses.

The fiber readout together with other molding problems such as porosity and micro-cracking are the causes for surface roughness. Long-term waviness, on the other hand, is due to the fiber distribution through the thickness and polymerization shrinkage. Internal cracks, warpage, and poor dimension accuracy are caused by stresses resulting from the nonuniform shrinkage. Different curing history at different mold positions may lead to part warpage [Osswald, et al., 1990; Atkins, 1993; Mohan, et al., 1993]. Sink mark is a surface defect appearing on the cosmetic surface of the part, opposite to a substructure (e.g. a rib or a boss). Fibers are oriented as the resin flows into a substructure [Melby, et al., 1989]. They tend to cave into the rib and create a resin rich area near the cosmetic side. A high polymerization shrinkage of the resin rich area during cure will result in the formation of a sink mark, and a larger thermal expansion coefficient of the resin rich area will enlarge the sink further during cooling and demolding [Kia, 1989].

The molded part surface appearance measured by a Bendix profilometer is rough and wavy as shown in Figure 1.1 [Bartkus, et al., 1970]. This is undesirable when Class
A appearance is needed. Adding fillers and fibrous reinforcement would reduce the shrinkage, but cannot thoroughly eliminate it [Melby, et al., 1989]. To achieve a better surface appearance, pre-paint preparation is applied. Finishing operations such as dry sanding [Kroekel, et al., 1967] and even putty are used to fix the damage areas. These operations are helpful in correcting the surface and structural defect; however, they are costly and cannot prevent the occurrence of the surface defects completely.

One technique to improve surface quality and to reduce shrinkage related problems is in-mold coating (IMC) [Bartkus, et al., 1970; Kia, 1989, 1990], which is frequently used in SMC molding. In the final stage of curing, the mold is partly opened, and IMC resins, which usually are vinyl ester resins or a polyether urethane/polyester resin blend, are injected into the mold. The IMC resin fills the cavities caused by the polymerization shrinkage, and forms a resin-rich layer that covers all the surface flaws, including fiber readout, microcracks, and sink marks. Another choice to improve surface quality is to modify the molding process using staged pressure in compression molding. A high pressure is applied in mold filling to prevent incomplete filling in compression molding. Then a lower pressure at a certain time during molding would highly reduce sink mark severity and improve the surface quality [Dzietwatkoski, 1992]. However, both in-molding coating and staged molding are costly and labor intensive. There are also many approaches in material modification, including structural modification of the resin and cross-linking monomer, and partial cure of resin before molding; however, none of these methods actually works well [Atkins, 1993].
Figure 1.1 Surface profile of a standard molded SMC [Barkus, et al., 1970].
It was finally found that adding low profile additives (LPA) in resin formulations would efficiently improve the shrinkage control during molding [Atkins, 1978, 1993; Melby, et al., 1989]. Low profile additives are thermoplastics that are generally served as non-reactive additives in unsaturated polyester resins. They are initially soluble or form stable dispersion in the resin mixture before cure, but become incompatible with the cured resin during the curing process and form a characteristic structural morphology. Low profile additives have been found highly effective in eliminating the polymerization shrinkage of unsaturated polyester resins in high temperature molding processes such as compression molding of SMC and injecting molding of BMC. Figure 1.2 shows the surface profiles of (a) a molded SMC with low profile additive (b) an automotive-grade steel [Atkins, 1993]. Obviously, the low profile, low shrinkage technology has allowed molding compounds to compete successfully with steel in exterior automotive applications.

Figure 1.2 Surface profile of (a) a molded SMC with low profile additive (b) automotive-grade steel [Atkins, 1993].
1991; Kinkelaar, et al., 1994a; Kiaee, et al., 1988; Bucknall, 1991a]. Most of them involve thermal expansion of the resin and LPA during heating, phase separation and inversion between the LPA-rich and resin-rich phase during curing, and the formation of microvoids either at the interface or inside the LPA-rich phase to compensate the resin shrinkage during curing and cooling.

Low profile additives of unsaturated polyester resins, however, often do not work effectively in room temperature processes like SCRIMP. Recent studies on the UP/St/LPA system cured at low temperatures [Li, et al., 1998, 2000a-c] found that LPA type and concentration and resin structure affected the shrinkage compensation. The microstructure formation is one of the key steps affecting low profile behavior. The improvement, however, is modest.

1.2.2 Final Conversion and Residual Monomer

Unsaturated polyester and vinylester resins are amenable to most high temperature processes such as compression molding of SMC and pultrusion, etc. At a high curing temperature, high conversion can be reached and residual styrene content can be as low as 20 ppm of composites [Kurashiki, 1982]. Complete curing of resins provides the composite with high strength and is environmentally friendly as well, since residual styrene and polyester unsaturation affect the physical properties of final products and styrene is the source of odor of composites because of its volatile nature. Residual
styrene monomer may also cause blister and voids on the surface of molded products at elevated temperatures. While residual polyester unsaturation is an indication of low cross-linking density of cured polyester resins, which significantly influences the mechanical strength of composites.

Currently, low temperature and low pressure molding processes like RTM and VARTM are getting more and more attention because of their low cost and convenience to operate. An accelerator or promoter such as cobalt octoate or naphthenate has to be added in the peroxide to induce the chemical decomposition in low temperature processes. In addition, other curing agents, i.e. inhibitor, retarder, or co-promoter, are also needed to adjust the resin pot life, gel time, and cycle time [Dow Chemical, 1994]. When polyester and vinylester resins are cured at low temperatures by a redox (reduction-oxidation) initiation system in hand lay-up, spray-up and VARTM molding processes, they cannot be fully cured under ambient conditions because of the low mobility of polymer chain at low temperature. The reaction exotherm of at ambient temperatures may lead to a raise of the resin temperature, which accelerates the curing reaction [Dow Chemical, 1989]. However, the room temperature processes without any external heating source still cannot provide high chain mobility when the reaction kinetics becomes diffusion control after gelation and vitrification. This impedes the resins cured at low temperature to reach complete reaction and have a high final conversion and low styrene residue.
The incomplete reaction leaves a high residual styrene level and confines the application of UP at low temperature molding processes, especially when the physical properties and health consideration of products are essential [Cassoni, et al., 1977]. The low residual styrene content can be obtained either after long storage at room temperature or thermal post treatment in the case of room temperature curing. However, the first way does not facilitate the cure reaction and the residual styrene level decreases only by natural evaporation. The cross-linking density of cured resin is still undesired and the evaporation of St brings problems to environment and health. Post-curing is the most common way to achieve less styrene residue when high corrosion resistance or heat distortion temperature or low styrene emission is required [Roskott, et al., 1978; Guangzburg, 1980]. In the post cure stage, the temperature is increased to a level higher than the glass transition temperature of the cross-linked unsaturated polyester, the polymer chains then become flexible and release the trapped free radical so the reaction moves on. As the level of styrene is decreased, both the toughness and the glass transition temperatures of the network increase. However, it is not easy to implement the post-cure cycle with very large size products, e.g. boats, tanks, and underground pipes.

Low residual styrene can also be attained by decreasing the glass transition temperature of the crosslinked materials through increasing flexibility of unsaturated polyester chain. Unsaturated polyesters are step-growth products formed by unsaturated and saturated diacid or anhydrides with different difunctional alcohols [Bruins, 1976; Burns, 1982; Penn, 1966; Trivedi, et al., 1982; Mark, et al., 1988; Melby, et al., 1989].
The glass transition temperature (chain flexibility) of unsaturated polyester resin can be decreased by choosing more flexible diacids and glycols and adjusting the double bond unit to a low level with low crosslinking density. Both methods can improve the chain flexibility of the polymer network, but they sacrifice the strength of final products.

Residual unsaturation has been studied by many researchers using different methods, including chemical degradation [Funke, et al., 1961; Hayes, et al., 1957], refractive indices [Learmonth, et al., 1969], resistivity [Learmonth, et al., 1969], gas chromatography [Yang, 1993], infrared spectroscopy [Birley, et al., 1981; Yang, et al., 1987] and the nuclear magnetic resonance (NMR) spectroscopy [Newman, et al., 1996]. Of these methods, NMR method seems to be more reliable, its spectrum shows fewer peaks, and the baseline is more clearly defined across the wide range of styrene contents [Newman, et al., 1996]. Infrared spectroscopy has been the most commonly used method but it cannot detect the minute quality of the component as MNR and gas chromatography. However, FTIR has the advantages of faster experiment and easy to operate and it is accurate enough to determine the residual styrene content at low temperature cure. Another advantage of FTIR is its accurate monitoring of a complex reaction, in this case, the reaction of styrene and UP double bond.

The materials, including the resin type and initiation system used in the reaction, influence the residual unsaturation and residual St level. These effects are more pronounced for resins cure at low temperatures. It was found that the type of initiator
used in the curing of unsaturated polyester resin influences the residual unsaturation and unreacted St monomer level [Rodriguez, 1988]. The lower residual styrene contents are obtained with a higher level of peroxide, and higher exotherm reduces the residual styrene content considerably. Increasing the level of accelerator is far less effective. [Roskott, et al., 1978].

An efficient cure system is to prevent a long cure time and hence a long cycle time and to skip the post cure step. Fujii, S. [1997] studied the polyester resin initiated with Trigonox 40 (acetylacetone peroxide, AAP) and tert-butyl peroxo-3,5,5-trimethyl hexanoate (TBTMH) and cobalt napthenate. The resin mixture was laminated with glass mats at 20°C for 7 days and residual styrene content of the formed composite was less than 0.03% and no odor of elution in H2O. However, no kinetics data were provided. It was still not clear whether the low residual styrene content is the results of nearly completed reaction or the evaporation of styrene due to the long storage time. Nagai [2001] studied the residual styrene content of room temperature cured unsaturated polyester resin at different time periods. The resin was initiated by ketone peroxide and peroxybenzoate at various ratios and cobalt napthenate as promoter. An unsaturated polyester (41.8% styrene content) containing this dual initiator showed 2.3% for 1 week cure, 1.2% for two weeks cure and no residual styrene after two hours post-cure at 80 °C. The residual styrene content is still high if without post cure and needs to be further improved. Although a lot of research has reported that the using different initiator combinations could reduce the styrene residue in the unsaturated polyester and vinyl ester
resin system cured at low temperatures, few reaction kinetics study was carried out to understand the mechanism and this needs to be further studied.

1.3 Scope of Study

Low profile additives play an important role in shrinkage control of unsaturated polyester processing. A thorough understanding of the LPA mechanism not only saves the moldings from trial-and-error, but also may serve as the instruction power of material design. However, the detailed LPA mechanism, especially at low temperature cure, is still not well understood.

Tremendous work has been done on LPAs in unsaturated polyester resins. Most of them focused on the low profile effect at high temperature cure, since LPAs are widely applied to the high-temperature and high-pressure processes. Although the detailed high temperature LPA mechanism is still a subject of controversy, it is now generally agreed that the most important features for LPA in high temperature processes are thermal expansion, phase separation and inversion between LPA and cured UP resin, and microvoid formation along the interface or inside the LPA phase.

Recently, because of the growing interest in new manufacturing processes, further understanding of the low profile mechanism at low-temperature and low-pressure cure is necessary. Since the resin thermal history in the high temperature processes such as SMC
compression molding and in the low temperature processes such as SCRIMP is totally
different, the performance of LPA may vary from process to process. To achieve the
maximum shrinkage control in SMC processing, a large thermal expansion of LPA
during heating and reaction and microvoids formation during cooling are essential.
Therefore, a desirable LPA for high temperature applications should have a large thermal
expansion coefficient and a low glass transition temperature. In contrast, SCRIMP is
conducted at room temperature and there is little temperature change during curing.
Obviously, thermal expansion of LPA can no longer be counted for in the low
temperature cure process.

The low profile additive performance cured at low temperature has been studied
[Li, et al., 1998, 2000a-c] and the low shrinkage control was believed to be governed by
two critical steps: the phase separation and the microvoid formation. Phase separation,
which occurs at the very early stage of reaction when the reaction conversion is lower
than 5%, is critical to the shrinkage control because it determines the sample morphology
that is essential for microvoids formation. The length of the period between the onset of
phase separation and the gel point, and the volume fraction of the LPA-rich phase, which
are determined by the structure of both UP resin and LPAs as well as the concentration of
LPAs, decide the level that the microstructure formation may progress. The microvoid
formation, signalized by the volume expansion, on the other hand, takes place in a fairly
late stage of cure when conversion approaches the final value at the curing temperature.
A hypothesis was also proposed to explain the late stage volume expansion of UP/St/LPA
systems cured at low temperature [Li, et al., 2000c]. It states that the slower reaction in the LPA-rich phase is the main reason why the microvoid formation occurs at the late stage of polymerization. The low reaction rate in the LPA-rich phase is a direct result of two factors: a low promoter concentration and a high St/UP ratio. The low promoter level in the LPA-rich phase is caused by the partition of the promoter into two phases, due to the complex formation between the cobalt ion and the carboxyl groups of UP and LPA molecules. A kinetic study of the samples with acid modified LPA confirmed that the LPA containing more and stronger acid groups tends to attract more cobalt promoter to the LPA-rich phase, resulting in a higher reaction rate. Consequently, the samples with acid-modified LPA show an earlier volume expansion and better shrinkage control [Li, et al., 2000c]. The improvement, however, is modest.

Microvoids start at the interface or in the LPA-rich phase since the UP resin tends to form tightly crosslinked microgels. Microvoids or microcracking would occur when the stress generated by the polymerization shrinkage is greater than the “strength” possessed by the material at the interface or in the LPA-rich phase. The former depends on the copolymerization between UP and styrene, whereas the later should be a function of the modulus of the materials at the interface or in the LPA-rich phase, the stress relaxation behavior of the materials, and the phase structure.

In the low temperature process, the polymerization shrinkage is the main driving force for microcracking because of no significant temperature variation as in high
temperature processes. The lowest volume shrinkage of unsaturated polyester resin with LPA cured at low temperature is 4.5%, however, the volume shrinkage of the same resin system can reach even a negative value (expansion) at high temperature cure. The performance of LPA at low temperature cure is still worse than that at high temperature cure. How to achieve a larger volume compensation in the low temperature process is a major challenge and requires better understanding of the low temperature LPA mechanism. To achieve this goal, an integrated study, which includes the study of reaction kinetics, rheology, morphology, volumetric change, and structure formation, is carried out. The specific goal of this study includes:

- improve the LPA performance by new material design;
- study the relationship between microvoid formation and material characteristics;
- better understand the mechanism of the low temperature LPA behavior;
- study the LPA performance in a real molding process, i.e. non–isothermal conditions.

In addition to shrinkage control of unsaturated polyester resins at low temperature cure, the residual styrene content or final conversion is recognized as being an important issue. Low residual styrene contents are important from both the health considerations and the physical properties of cured composite. Many researchers used different methods to reduce styrene content of cured polyesters, such as changing the initiator content and
initiator combination, varying the rigidity of the resin, postcuring the molded part, which consequently reduced the final styrene content at low temperature cure.

Most studies emphasized the resin flexibility and initiator type. Only a fewer works were carried out to improve the reaction at later stage by increasing the reactivity of crosslinking monomer, such as introducing more reactive comonomer, methyl methacrylate and divinylbenze, into the resin system. A better understanding of the characteristics of reactive materials and reaction kinetics at different curing conditions is an important factor for the design of the curing system as well as the physical properties of the finished product. In this study, an in-depth kinetic analysis is carried out and a better understanding of the reaction kinetics is sought for unsaturated polyester resins at the presence of LPA with different crosslinking monomers and various curing agents cured at low temperatures. The volume shrinkage of the resin system is also investigated in order to provide a molding material having reduced styrene odor without deteriorating the original mechanical strength, molding shrinkage, appearance, gloss, etc.

Chapter 3 covers a low temperature shrinkage control study of UP/St/LPA systems. Performance improvement of LPA at low temperature cure is presented by investigating the effects of comonomers and co-promoter on the shrinkage control. A better understanding of low profile mechanism is also achieved. Chapter 4 focuses on the study of residual styrene content at low temperature curing and its relationship with the reaction temperature and characteristics of the resin system and the initiators system. An
experimental study is carried out for an unsaturated polyester resin system with low profile additive to understand the reaction mechanism and shrinkage compensation during the low temperature cure. In Chapter 5, volume shrinkage and residual styrene of a vinylester resin with low shrinkage additive was investigated. Based on experiment results, an improved room temperature vacuum-assisted resin transfer molding process was designed to achieve good surface quality and less residual styrene. Some conclusions and recommendations are given in Chapter 6 for further study.
CHAPTER 2

LITERATURE REVIEW

2.1 Styrenic Resins

2.1.1 Unsaturated Polyester Resins

Unsaturated polyester resins are one of the most successful materials used in fabricated composites. The annual consumption of unsaturated polyester resin in United States in 1999 exceeds 1.2 billion pounds, and more than 70% of the consumption is in the composite industry [CFA annual statistics report, 1999]. Polyester resins are used in high volume because they are low cost and have good mechanical properties and environmental durability. Their applications can in general be divided into three classes: (1) resins reinforced with continuous glass fiber that cure at room temperature; (2) resins reinforced with short glass fiber that cure at room temperature; (3) resins reinforced with short glass fiber that cure at elevated temperatures. The room temperature cured continuous glass reinforced materials is used for structural applications such as pipes, tanks, and boats, and accounts for about half of the United States polyester consumption.
Unsaturated polyesters are step-growth products of three chemical species: unsaturated acids or anhydrides, saturated aromatic acids and alcohols (glycols) [Penn, 1966; Bruins, 1976; Burns, 1982; Trivedi, et al., 1982; Mark, et al., 1988; Melby, et al., 1989]. A typical unsaturated acid for polyester production is maleic anhydride (MA) and alcohol is propylene glycol. The unsaturated acids provide the backbone of the oligomer with unsaturated carbon-carbon double bonds. The cross-link through the C=\(\text{C}\) double bond produces a three-dimensional network structure. The saturated acid is the major composition variable, in both type and content in unsaturated polyester resin structure. They are employed to adjust the degree of unsaturation, and thereby the reactivity of the resulting polyester. The forming of the general purpose unsaturated polyester resin can be represented by the equation in Figure 2.1 [Atkins, 1993].

Commercial unsaturated polyester resin formulations, neglecting other additives, consist mainly of a linear polyester, a cross-linking monomer (usually 35-45 wt. %), and inhibitors that are used to prevent cross-linking reaction before the resin being processed. The most frequently used cross-linking monomer is styrene. Other monomers, such as methyl methacrylate, diallyl phthalate, vinyl toluene, divinylbenzene, and chlorostyrene were also studied but scarcely used [Anon, 1949; Smith, 1953, 1966; Wahl, et al., 1957]. Their features are summarized in Table 2.1. It is obvious that even though styrene serving as cross-linking monomer has the advantage of low cost, high reactivity, good heat distortion temperature, and high flexural strength, the volumetric shrinkage created by the copolymerization is large and undesirable.
Figure 2.1 Example of polyesterification reaction [Atkins, 1993].
<table>
<thead>
<tr>
<th>Monomer</th>
<th>Boiling point (°C)</th>
<th>Volume shrinkage (%)</th>
<th>Characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>145</td>
<td>15</td>
<td>Low cost, high reactivity, fairly good heat distortion temperature, high flex strength</td>
</tr>
<tr>
<td>Vinyl toluene</td>
<td>171</td>
<td>12.5</td>
<td>Reduced volatility and shrinkage, high reactivity, more flexibility</td>
</tr>
<tr>
<td>Ckloostyrene</td>
<td>187</td>
<td>12</td>
<td>Reduced volatility and shrinkage and fast coreaction</td>
</tr>
<tr>
<td>α-Methylstyrene</td>
<td>166</td>
<td></td>
<td>Control of exothermic heat</td>
</tr>
<tr>
<td>p-Tert-butylstyrene</td>
<td>219</td>
<td>7</td>
<td>Very low shrinkage and low volatility</td>
</tr>
<tr>
<td>Divinylbenzene</td>
<td>195</td>
<td></td>
<td>Extra crosslinking</td>
</tr>
<tr>
<td>Diallyl phthalate</td>
<td>290</td>
<td>18</td>
<td>Very low volatility, fast cure, long shelf life high heat resistance</td>
</tr>
<tr>
<td>Trially cyanurate</td>
<td>162</td>
<td></td>
<td>Improved heat resistance, high reactivity, high flex and tensile strength</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>190</td>
<td>20</td>
<td>Improved weathering, good transluency properties, fairly high heat distortion</td>
</tr>
</tbody>
</table>

Table 2.1 Monomers used in unsaturated polyester systems [Trivedi, et al., 1982]
Depending on the structure of the basic building block, unsaturated polyester resins are divided into a variety of classes. Table 2.2 presents a summary of building blocks of polyesters and their contributions [Trivedi, et al., 1982]. The orthophthalic resins are also known as general-purpose resins. They are one of the least expensive polyesters, but have relatively poor corrosion resistance. In these oligomers, the saturated acid appears to be orthophthalic acid, but actually the anhydride form, phthalic anhydride, is used in the composition because it reacts much faster than the acid. The poor corrosion resistance limits the use of orthophthalic resins, partly because of the presence of residual organic compounds in orthophthalic resin and the low molecular weight compared with isophthalic resins [Ghotra, et al., 1975]. They are mostly used in the circumstances when the corrosion resistance is not the main concern, such as shower stalls, and structural applications.

Isophthalic polyesters produced from isophthalic acid as the saturated acid are premium resins. They cost about 20% more than orthophthalic resins based on current pricing, but are characterized by greater strength, heat resistance, toughness, and flexibility. The isophthalic polyesters are made in two steps, by a so-called double cook process, because the isophthalic acid does not react as quickly as the maleic anhydride with the glycol. The polyester produced by double cook process has the advantage of higher molecular weight and results in the superior thermal, mechanical, and chemical resistance compared to the isophthalic polyesters by one step cook process.

Polyesters that use dicyclopentadiene (DCPD) are in common usage in the boat-building industry, usually blended with other polyesters or vinyl esters. DCPD polyesters
<table>
<thead>
<tr>
<th>Building Blocks</th>
<th>Ingredients</th>
<th>Characteristics</th>
</tr>
</thead>
</table>
| Unsaturated anhydrides and dibasic acids | 1. Maleic anhydride  
2. Fumaric acid                                                                 | 1. Lowest cost, moderately high heat deflection temperature (HDT)  
2. Highest reactivity (cross-linking), higher HDT, more rigidity |
| Saturated anhydrides            | 1. Phthalic (orthophthalic) anhydride  
2. Isophthalic  
3. Adipic acid, azelaic acid, and sebacic acid  
4. Chlorendic anhydride HET anhydride  
5. Nadic methyl anhydride  
6. Tetrachlorophthalic anhydride  
7. Tetrabromophthalic anhydride | 1. Lowest cost, moderately high HDT, provides stiffness, high flex, and tensile strength  
2. Higher tensile and flex strength better chemical and water resistance  
3. Flexibility (toughness, resilience, impact strength); adipic acid is lowest in cost of flexibility acids  
4. Flame retardance  
5. Very high HDT  
6. Flame retardance  
7. Flame retardance |
| Glycols                         | 1. Propylene glycol  
2. Dipropylene glycol  
3. Ethylene glycol  
4. Diethylene glycol  
5. 2,2,4-Trimethyl-1,3-pentanediol glycol  
6. Bisphenol-A adduct  
7. Hydrogenated bisphenol-A adduct  
8. Tetrabromobisphenol-A | 1. Lowest cost, good water resistance and flexibility, compatibility with styrene  
2. Flexibility and toughness  
3. High heat resistance, tensile strength, low cost  
4. Greater toughness, impact strength and flexibility  
5. Corrosion resistance with reduced density  
6. Corrosion resistance, high HDT, high flex and tensile strength  
7. Corrosion resistance, high HDT, high flex and tensile strength  
8. Flame resistance |

Table 2.2 Unsaturated polyester building blocks [Trivedi, et al., 1982]
are less expensive, cure rapidly and completely, and have the better cosmetics than orthophthalic resins. The DCPDs are called low-profile resins due to the fact that DCPDs do not shrink as much as other polyesters during cure. In addition to lower cost and reduced shrinkage, DCPDs are in favor because they "air dry," meaning that they are not air inhibited. The major concern with DCPD polyesters is their secondary bond strength [Pfund, 1992]. As a result of the air-drying nature of DCPDs, the secondary bonding window is narrow. Subsequent laminations must not be delayed more than a few hours, as opposed to the several days allowed in other resins. Another concern is that DCPD resins have low failure strain, which can cause cracking problems in the field.

Chlorendics and Bisphenol A fumarates are two specialty polyesters formulated for applications requiring superior corrosion resistance. Chlorendics can be used up to 350°F (fumes) and have better resistance to concentrated acids than most vinylesters, although they do not have good resistance to alkaline environments. Bisphenol A fumarates are resistant to both acids and bases and can be used continuously up to about 250°F.

### 2.1.2 Vinylester Resins

Vinylester resins are the most recent addition to the family of thermosetting polymers. They are considered as a subset of polyester resins because they are also unsaturated oligomers dissolved in vinyl monomers such as styrene and cured with similar curing agents as polyester resins. However, there are some differences in the oligmer
chemistry set one part from each other. Unsaturated polyester resins are step-growth products of unsaturated and saturated diacids or anhydrides with alcohols. They are usually terminated by carboxylate or hydroxyl groups at the end of molecules, along with several internal C=C double bonds in each molecule to react with cross-linking monomer, forming three-dimensional structure. On the other hand, vinylester resins are produced by esterification of a polyfunctional epoxy resin with an unsaturated mono-carboxylic acid, usually methacrylic, and acrylic acid. The typical structure of a vinylester resin is shown in Figure 2.2. The reactive unsaturation is presented as terminal groups in the polymer (structoterminal), and can be cross-linked by vinyl monomers such as styrene in the same way as conventional polyester. The outstanding physical properties are attributed to the higher reactivity of terminal unsaturation and its regular distribution through the network. Unlike conventional polyesters, there are fewer internal polyester linkages in vinylester chain, therefore less susceptible to hydrolysis, and more resistant to corrosion. Most of the applications of vinylester arise from their superior chemical resistance properties and higher physical properties of composites made with them [Bruins, 1976; Blankenship et al., 1988; Dow Chemical, 1994; Encyclopedia of Polymer Science and Engineering, 1988]. Pendant hydroxyl groups on the backbone, in combination with lower average molecular weight and viscosity, also improve wetting and bonding to fillers and reinforcements.

Vinylester resins were first introduced commercially in the early 1960s [May et al., 1965]. Two well-know commercial products are Shell’s “Epocryl” and Dow Chemical’s “Derakane” [Trivedi, et al., 1982]. Some of the commercial variations
Figure 2.2 Molecular structures of vinyl esters [Young, 1976].
include those based on: 1) bisphenol A epoxy resins; 2) novolac epoxy resin; and 3) modified vinylester resins using specialty epoxy resins, urethanes, or acid anhydrides in the resin cook. The basic components of vinylester resins are shown in Figure 2.3. The properties of vinylester resins depend mainly on the choice of the epoxy resin that determines the mechanical, thermal, and corrosion properties of the cured product. Because the methacrylate crosslinking sites are on the end of the molecular chain, cross-link density decreases as molecular weight of oligomer increases. A vinylester made with a low molecular weight epoxy has a high cross-link density, therefore provides high heat distortion temperature (HDT) and good solvent resistance, but tends to be brittle when cured with vinyl monomer. Resins made with higher molecular weight epoxies have lower cross-link density, less solvent resistance, lower HDT, but are more resilient. Chemical resistance of vinylester resins is mainly affected by the type of unsaturated acid. Vinylester resins intended for structural and corrosion resistant composite applications are made using methacrylic acid since steric hindrance by methyl group increases the resistance of the resin to basic hydrolysis. Acrylic acid is commonly used for resins intended for ultraviolet curable photoresists and laminate adhesives.

During cure, the typical volumetric shrinkage of vinyl ester resins is about 7-10%. The value is higher than those of epoxy resins, but less than those of polyester resins. So far low profile additives have been less effective with vinyl esters than with unsaturated polyesters.
Figure 2.3 Basic components of vinylester resins.
2.1.3. Curing of Styrenic Resin

Polyester and vinylester resins are amenable to most high temperature processes such as compression molding of sheet molding compounds (SMC), injection molding of bulk molding compounds (BMC), and pultrusion, etc. SMC is used in applications that require low cost, good cosmetics, high part throughput, and a large number of identical, relatively small parts. For these reasons, SMC is a popular choice in the automotive industry and it is used in very large volume. BMC is processed by injection or compression molding and used in many applications that require a large number of relatively small complex-shape parts. No matter what high temperature processes are used, all the components of the formulation, including filler, fiber, and curing agents are added by the manufacturers. Peroxides such as diacylperoxides, peresters, diaryl, and dialky peroxides, ketone peroxides and hydroperoxides are all suitable curing agents for high temperature curing. They can generate free radicals by thermal decomposition.

\[
R - O - O - R' \xrightarrow{\Delta} RO\cdot + R'O\cdot
\]  \hspace{1cm} (2.1)

Due to the first order decomposition kinetics of heat cure of most peroxides, specific initiators are effective only over a relatively narrow temperature range. When a single initiator is not satisfactory, blends of initiators often can produce the required production cycle. Thermal analysis by differential scanning calorimeter has been useful for characterizing and optimizing resin initiator combinations.

With the use of a redox (reduction-oxidation) initiation system, both polyester and vinylester resins can also be processed at ambient temperature via hand lay-up, spray-up,
and vacuum-assisted resin transfer molding (VARTM) processes. A typical room
temperature curing resin contains most or all of ingredients listed in Table 2.3.

Usually unsaturated polyester-styrene mixture requires a complicated initiator-
promoter/accelerator-inhibitor system to provide a controlled cross-linking reaction. The
most commonly used initiator for polyesters and vinylesters is methyl ethyl ketone
peroxide (MEKP). Polyester-grade MEKP contains monomer and hydrogen peroxide in
addition to the dimer and causes foaming if used with vinylesters. Vinylester grades of
MEKP are predominantly the dimer with structure as shown in below.

\[
\begin{align*}
\text{MONOMER:} & & \text{DIMMER:} \\
\text{OOH} & & \text{R}^1 \quad \text{R}^1 \\
\text{R}^1 \quad \text{C} & & \text{HOO} - \text{C} - \text{OO} - \text{C} - \text{OOH} \\
\text{OOH} & & \text{R}^2 \quad \text{R}^2
\end{align*}
\]

Although grades of MEKP suitable for vinylester resins containing reduced
quantities of hydrogen peroxide may be used to cure vinylester resins, it cannot be used in
certain conditions in which gas bubble cannot escape. Other nonfoaming initiators, such
as t-butyl peroctoate, t-butyl perbenzoate, and cumene hydroperoxide (CHP), are used for
vinylester resins. MEKP and other initiators cannot cure polyester or vinylester resins
without promoters at ambient temperature because they decompose into free radicals too
slowly. A small amount of promoter/accelerator, usually multivalent metal salts or
tertiary aromatic amines can decompose a large amount of peroxide initiators at lower
temperatures and generate free radicals. Ketone peroxide and cumene
Table 2.3 Ingredients of a vinylester/polyester resin formulation [Juska et al., 1996].

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt %</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligomer</td>
<td>45~65</td>
<td>Determines thermal, mechanical, and chemical properties of resin</td>
</tr>
<tr>
<td>Solvent</td>
<td>35~55</td>
<td>Coreactive monomer; reduces resin viscosity</td>
</tr>
<tr>
<td>Promoter</td>
<td>0.3</td>
<td>Decomposes the initiator</td>
</tr>
<tr>
<td>Co-promoter</td>
<td>0.1</td>
<td>Helps decompose the initiator</td>
</tr>
<tr>
<td>Initiator</td>
<td>1.25</td>
<td>Initiates chemical reactions that cure resin</td>
</tr>
<tr>
<td>Retarder</td>
<td>0.2</td>
<td>Reduces resin exotherm and extends gel time</td>
</tr>
<tr>
<td>Inhibitor</td>
<td></td>
<td>Delays the onset of curing reactions</td>
</tr>
<tr>
<td>Thixotrope</td>
<td>1~3</td>
<td>Prevents drainage prior to gel</td>
</tr>
<tr>
<td>Wax</td>
<td>0.4</td>
<td>Prevents air inhibition; reduces VOC emission</td>
</tr>
<tr>
<td>Air release</td>
<td>0.1</td>
<td>Reduces the void content</td>
</tr>
</tbody>
</table>

Table 2.3 Ingredients of a vinylester/polyester resin formulation [Juska et al., 1996].
hydroperoxide are normally promoted by heavy metal salts such as cobalt, vanadium, and iron, while benzoyl peroxide can be used at ambient temperature in the presence of tertiary aromatic amine promoters. The initiation mechanism is as follows:

\[
\begin{align*}
\text{Co}^{3+} + \text{ROOH} & \rightarrow \text{ROO}^+ + \text{H}^+ + \text{Co}^{2+} \\
\text{Co}^{2+} + \text{ROOH} & \rightarrow \text{RO}^- + \text{OH}^- + \text{Co}^{3+}
\end{align*}
\]

\[\text{BPO} + \text{DMA} \rightarrow \text{∅-N} + (\text{CH}_3)_2 + \text{O-CO∅} + \text{O-CO∅} \]

The combination of methyl ethyl ketone peroxide and cobalt octoate or benzoyl peroxide and dimethylaniline (DMA) is particularly effective for unsaturated polyesters, while the cumene hydroperoxide and cobalt naphthenate pair is commonly employed for vinylester resins.

The metal ions can also destroy the radicals by converting them into ions, losing the initiating capability [Elf Atochem, 1995]:

\[\text{Co}^{2+} + \text{RO}^- \rightarrow \text{RO}^- + \text{Co}^{3+}\]

Therefore, overpromotion should be avoided. In case faster cure is needed, it is better to increase the peroxide concentration than the promoter level.

Inhibitors, at the level of ppm, are extremely important component of unsaturated polyester resins. They will provide good shelf life and inhibit premature gelation. During cure, the free radicals generated by initiator are initially consumed by the inhibitors, and
the reaction will not proceed until the inhibitors are completed neutralized, providing a stage called induction period. Examples of inhibitors are hydroquinone, p-benzoquinone, t-butyl catechol, and oxygen.

Chemicals called retarders are sometimes included in resin formulations. The function of retarders is to reduce the cure rate, resulting in a reduction in peak exotherm temperature. Resins cured in thick sections can experience an unacceptable temperature increase because the heat of reaction is generated over a short time period. The rise in temperature further increases the reaction rate, and the process can easily go out of control. This can lead to resin degradation to the point that it may turn yellow or brown or will even ignite. A commonly used retarder for vinylesters is 2,4-pentanedione (2,4-P). 2,4-P extends the gel time like an inhibitor but does not always reduce the peak exotherm temperature. The difference between the function of inhibitors and retarders is that inhibitors destroy the free radical after initiation (formation of the radical), and retarders either slow the rate of radical generation or destroy the propagating radical. Inhibitors delay the onset of curing reactions, and retarders slow the rate of curing reactions.

Low volatile organic content (VOC) resins are becoming increasingly important in the FRP industry due to restrictions on styrene emission. The approach is to add paraffin wax to the formulation in order to form a barrier layer that limits the evaporative loss of styrene when the wax blooms to the surface during molding process. The other approach is to formulate the resin with lower styrene content. Conventional resins contain 40-50%
styrene by weight, but recent formulations only contain styrene less than 34%. Reduction in the styrene content increases the viscosity, so other changes must be made to keep the viscosity acceptable (about 400cps). The low viscosity can be obtained by blending some of the oligomer with DCPC polyesters, which has low viscosity. The other method is to reduce the molecular weight of the oligomer.

2.1.4 Cross-linking Mechanism and Structure

The cross-linking reaction of polyester and vinylester resins is a free radical chain growth polymerization. The polyester/vinylester oligomer provides crosslinking points for network formation, while the styrene monomer provides linear chain extension. The vinylene groups in the polyester/vinylester monomers copolymerize with styrene to form a cross-linked network via bulk free radical chain growth copolymerization. The development of the network significantly affects the physical, chemical, and mechanical properties of the polymer, and thus affects the behavior of the composite. A better understanding of network formation is desired for better design and control of the properties of the thermosetting matrix.

Several researchers have studied the polymeric network formation in polyester resins [Lee, 1981; Huang, et al., 1985; Okasha, et al., 1985a, 1985b; Stevenson, 1986; Yang, 1987, 1988; Han, et al., 1987; Batch, et al., 1987]. It was found that the actual cross-linking behavior of unsaturated polyester deviates from the classical Flory gelation theory, which assumes no intra-molecular reaction. The explanations of this deviation include: cyclization due to intra-molecular reaction, reduced activity of pendent vinyl
groups, and shielding effect of microgel formation on the reaction of the pendant vinyl
groups [Hsu, et al., 1993].

A mechanism was proposed to describe the cross-linking behavior of polyester
resin in five steps [Hsu, 1992], including induction, microgel formation, transition with or
without phase separation, macrogelation, and post-gelation. The first four stages are
schematically described in Figure 2.4.

During the induction period, initiators decompose and generate free radicals. No
propagation occurs because free radicals have been consumed by inhibitor rapidly. In the
next stage after most of the inhibitor is depleted, primary polymers are formed by linking
unsaturated polyester molecules and styrene. In the free radical polymerization reaction
system with dual or multiple carbon double bonds, intra-molecular reactions may exist
besides inter-molecular reactions. Once a double bond of a polymer chain is attacked by
a free radical, other vinyl groups of the polymer chain become so-called pendant vinyl
groups. They may further cross-link with the double bond of other polymer chains (inter-
molecular reaction), or form cyclization with the vinyl groups of the same chain (intra-
molecular reaction). The intra-molecular reaction provides the long chain molecules with
the tendency to form spherical type structure with high cyclization and cross-linking
density, which is described as “microgel” [Dusek, 1982].

In the transition stage, further reaction results in either the growth of microgel
particle or the linkage of the microgel. Since the pendent C=C bonds on the primary
polymer molecules are either buried inside the microgels or located near the surface of the
microgels. The ones that are inside engage in the intra-molecular reaction, thereby
Figure 2.4 Schematic diagram of macrogelation of unsaturated polyester resin.
increasing the crosslinking density of the microgels. The ones near the surface of the microgels may react with the surrounding comonomers and microgels through newly formed free radicals. The viscosity starts to increase slowly because of the formation of larger particles. Phase separation may occur because of the change of resin composition and phase boundary.

In the macrogelation stage, the three-dimensional network is formed through the inter-molecular reaction between microgels and clusters. A sharp viscosity increase can be observed in this stage. The phase separation process stops after the macrogelation, and the domain size of the separated phase remains the same throughout the rest of the reaction period.

2.2 Low Profile Additive

2.2.1 Development of Low Profile Additives

The crosslinking reaction of unsaturated polyester resins is accompanied by a high degree of polymerization shrinkage. The volumetric profile of the unsaturated polyester/styrene reacting system in high temperature molding process measured by dilatometer as shown in Figure 2.5 (a) exhibits three stages of volume change [Bartkus, et al. 1970]. The mixture first goes through a thermal expansion during the initial heating, and then shrinks due to polymerization and thermal contraction. During cooling and demolding, the material shrinks further to final volume shrinkage of 7.1%.
Figure 2.5 Volume change profile of (a) conventional resin and (b) low profile resin [Barkus et al., 1970].
Many approaches were tried to solve this problem, including addition of fillers and fibrous reinforcements, changes in resin and comonomer structure, partially polymerization of the resin before molding, and even in mold coating, but none was completely successful. The best solution is the addition of 7 to 20 wt.% of certain types of thermoplastics, the so-called low profile/shrinkage additives. Figure 2.5 (b) presents a volumetric profile of the resin with acrylic thermoplastic as LPA [Barkus et al., 1970]. Volume expansion together with excellent surface smoothness and dimensional stability was achieved in this resin system.

The development of LPA can be summarized into four generations [Atkins, 1993]. Non-polar materials such as polystyrene (PS) and polyethylene (PE) were used as the first generation. They show improvement on shrinkage control by reducing shrinkage from 0.4-0.5% to about 0.2%. Volume shrinkage can be further reduced by introducing the second generation LPAs, acrylic-based polymer. When used with propylene glycol-maleic anhydride (PG-MA) type of unsaturated polyesters, shrinkage can be down to 0.05% and the systems are suitable for the production of some automotive parts. The next generation is marked by the successful development of poly (vinyl acetate) polymer as shrinkage control additive. Poly (vinyl acetate) (PVAc) polymers are acceptable to a wide range of unsaturated polyester structures, and almost eliminate the polymerization shrinkage to provide true “zero-shrinkage”. The forth and also the current generation are the materials developed in 1980s and currently being improved. Examples are modified PVAc for specific unsaturated polyester resin, polymers based on saturated polyesters, urethanes, or complex mixture of shrinkage control polymers, and polymers based on
dual thickening systems containing isocyanate prepolymers. Currently, effort is also being made on the development of LPAs effective for low temperature processes; there is no claim on success yet.

Besides PS and copolymers [Kopper Corp., 1971; Dow Chemical, 1972; Atkins et al., 1973], poly (methyl methacrylate) (PMMA) and copolymers [Rohm and Haas, 1972a, 1973; Tokoyo Spinning, 1973a, 1973b], and PVAc [Atkins, et al., 1976; Union Carbide, 1973, 1974, 1981a and 1981b] mentioned above, there are many thermoplastics that can also be applied as the low profile additives. Examples are polyurethanes (PU) [B. P. Chemicals, 1974; SCM, 1977; Olin Corp., 1983, 1984; Bayer AG, 1984], polycaprolactones [Union Carbide, 1970, 1972; Atkins et al., 1973], saturated polyesters [Rohm and Haas, 1972b, Union Carbide, 1981c], and some styrene-butadiene copolymers and elastomers [Dupont, 1979; Exxon, 1979, Willis, et al., 1984; Kirkpatrick, et al., 1990]. The range of molecular weight is between 25,000 and 500,000, and the fraction of thermoplastic is 5-20 parts by weight. These polymers demonstrate different degrees of shrinkage control under curing conditions of 140-170°C and 6-8 MPa.

2.2.2 Type and Structure of Low Profile Additive

The LPAs can be divided into two groups if considering the initial miscibility with the unsaturated polyester resin. The first group of LPAs, leading by PVAc and linear polyurethane, are completely miscible with the unsaturated polyester/styrene, and usually provide good shrinkage control. The other group of LPAs, such as polymethyl
methacrylate and polystyrene, is not miscible with the unsaturated polyester/styrene, but some may form relative stable dispersion after thorough mixing [Melby, et al., 1989]. PVAc provides the best shrinkage compensation followed by PMMA and PS [Atkins, 1978; Huang et al., 1996]. The effectiveness of shrinkage control is ranked as PU>PVAc>PMMA>PS, though deviations may occur for some specific cases depending on other cure factors. Other LPAs, such as polyethylene, poly (styrene-co-butadiene), polycaprolactone, and some less common thermoplastics were also investigated by some researchers [Lee, et al, 1987; Atkins et al, 1982; Melby et al., 1989; Atkins, 1993]. Generally, either PVAc or PMMA can represent their performances.

Extensive studies have been done on poly (vinyl acetate) systems [Pattison, et al., 1975; Atkins, 1978; Bucknall, et al., 1985] at high temperature cure. Phase separation between the unsaturated polyester and PVAc occurs during cure was observed under scanning electron microscopy (SEM) [Kinkelaar et al., 1994a]. In this study, resin cure was stopped at different times, and a sample was quenched at each time for SEM observation. The sample morphology was a two-phase structure and did not change significantly once established. One phase, so-call UP-rich phase was observed to be surrounded by the second phase, believed to be LPA-rich, to form spherical particle structure. Depending on the LPA concentration, the globule structure was found either as a disperse phase embedded in the continuous resin matrix, or as a continuous phase with resin presented as dispersed particles. The morphology of the resin with PU as LPA is quite similar to that with PVAc [Huang et al., 1996; Suspene et al., 1991] except a more uniform morphology for PU-containing sample after cure than that for PVAc-containing
sample. The particle size is also smaller. The increase of PU molecular weight enhances the inhomogeneity and increases the particle size.

The resin system with PMMA was also studied [Pattison et al., 1974; Hsu et al., 1991; Kiaee, 1987& 1988]. Microscopy pictures demonstrate that the system is an initially stable, two-phase dispersion consisting of liquid globules (50-100 µm in diameter) in a continuous phase. The liquid globules are composed of PMMA, styrene, and some unsaturated polyesters. During heating and curing, the continuous phase, which consists of unsaturated polyester and styrene, crosslinks and forms the continuous matrix. Inside the globules, reaction between styrene and unsaturated polyester also takes place, and very fine particles (1 µm) are formed, which precipitate from LPA. The morphology of resin systems containing PS as LPA is similar to that containing PMMA [Hsu, et al., 1991]. However, phase separation between the resin and PS occurs much earlier. Most of polystyrene has phased out of the resin-styrene solution before the reaction starts. Therefore, LPA (PS) affects only a small area and the size of fine particles inside the dispersed globules is much smaller than that of PMMA [Huang, et al, 1996].

2.2.3 Factors to Influence Low Profile Additive Performance

2.2.3.1 Material Properties

To achieve maximum shrinkage compensation, the LPA must possess certain physical and chemical properties. Factors such as molecular weight, thermal expansion
coefficients, glass transition temperature ($T_g$), polarity, and acid contents are generally considered important [Atkins, et al., 1976, 1993].

Molecular weight of low profile polymer is tightly related with the compatibility of LPA/resin blend and the phase diagram of the curing system. The optimum molecular weight varies from LPA to LPA. For poly (vinyl acetate), the useful range is 10,000 to 250,000, and preferably between 25,000 and 175,000 [Atkins, 1993]. Polymers with molecular weight higher than this value can lead to reduced shrinkage control at high temperature process. The same trend was observed in the system with PU as LPA [Suspense et al., 1991]. It was explained by a decrease of the miscibility with an increase of polyurethane molecular weight. The better storage miscibility (lower molecular weight) usually leads to a more homogeneous morphology and a better shrinkage control.

Thermal expansion coefficient is considered as a major controlling factor in shrinkage control. Atkins and co-workers [1976] founded that PVAc provides the best shrinkage control, followed by PMMA. PS was found the worst shrinkage controller. The difference was explained by the difference in thermal expansion coefficient of the thermoplastics. During cure, the thermal expansion of thermoplastics and the unreacted monomer creates the force to reduce the polymerization shrinkage. Therefore, the thermoplastic with a higher thermal expansion coefficient (i.e. PVAc) will control the shrinkage better than that with a lower one (i.e. PMMA).

However, the above explanation cannot be applied to PS, since PS has the highest thermal expansion coefficient among the three. The authors used the polarity to explain this contradiction. Both PVAc and PMMA (dipole moment of 1.6 and 1.3, respectively)
are much more polar than PS (dipole moment of 0.3). The quite polar unreacted
unsaturated polyester resin (dipole moment of 2.0-2.5) becomes much non-polar (dipole
moment less than 1.0) during curing. Polar polymers such as PVAc and PMMA tend to
phase out and thermally expand during cure. PS has a lower tendency to become
incompatible, thus less thermally curb the shrinkage.

Glass transition temperature is another important property because thermoplastics
show quite different thermal expansion behaviors before and after glass transition.
Polymers expand more in the rubbery state; therefore T_g below the cure temperature is
with PVAc (T_g=26°C), PU (T_g=-45°C), PS (T_g=100°C), PMMA (T_g=106°C), and
polycaprolactone (T_g=-20°C). Except for PS and PMMA, which have T_g relatively
close to the matrix T_g, two transition temperatures were found. PVAc, PU, and
polycaprolactone have less polymerization shrinkage.

The acid content of thermoplastics also affects the performance of LPA [Melby, et
al., 1989; Atkins, 1993] in SMC/BMC molding when the UP resin is thickened by the
reaction of residual carboxyl groups with alkaline earth oxides or hydroxides such as
magnesium oxide, magnesium hydroxide, calcium oxide, and calcium hydroxide. The
addition of thickener decreases the compatibility between the resin and the LPA, causing
exudation of the LPA. Introducing carboxyl groups onto the LPA stabilizes the LPA
during the thickening reaction and avoids exudation [Rohm and Haas, 1970; Diamond
at an acid content of 0.08 mequiv g⁻¹ shows the minimum shrinkage.
2.2.3.2 LPA Concentration

The effect of LPA concentration was studied at different temperatures [Bucknall, et al., 1985, 1991a & 1991b; Kiaee et al., 1988; Ruffier et al., 1993; Kinkelaar et al., 1992 &1994, Li, 1998b]. In the resins with PVAc as LPA cured at a high temperature (135°C), the optimum concentration was found to be 6% [Ruffier et al., 1993]. The results also suggested that the low profile effect could be enhanced if the thermoplastic phase is well distributed. The more co-continuous the phase structure, the lower the shrinkage.

However, the shrinkage results of Huang et al. [1996] provided a quite different view. In their experiments of resins with various amounts of PVAc, PMMA, PU, and PS at 110°C, the rising LPA concentration decreased the fractional volume shrinkage. Their data exhibit a linear relationship between the LPA concentration and the decrease of shrinkage.

Kinkelaar et al. [1992, 1994] developed a dilatometer and used it as a major tool to study the low profile performance of PVAc. An optimum value of LPA concentration was found at about 2.5% LPA (80°C). They stated that the good low profile performance usually associates with a plateau region in volumetric profile and a loosely packed, irregular particulate microstructure.

The study of concentration effect on LPA performance at low temperature (35°C) was carried out in UP resin with PVAc at different molecular weights, saturated polyester and PU as LPA [Li, et al., 1998a]. LPAs were found effectively only in the concentration range depending on the LPA type and its molecular weight. In this study, the LPA concentration in the UP resin systems was also found to cause changes of the surface
morphology from homogeneous (i.e. flake-like) to heterogeneous (i.e. flake-like and particulate) and then back to homogeneous (i.e. particulate) structure. The sudden exhibition of the low profile effect occurs at the first transition when the particulate structure turns from a dispersed phase to a co-continuous phase. A continuous (or co-continuous) particulate structure allows the formed micro-voids to effectively reduce the sample shrinkage. The loss of the low profile effect takes place at the second transition when the fusion of particles at high LPA concentrations occurs. A severe fusion of particles reduces the micro-void formation at the particle interface.

2.2.3.3 Cure Conditions

Curing conditions, such as temperature, temperature gradient, and pressure could influence the low profile performance and the effect was reported by several researchers [Kinkelaar, et al., 1992, 1994; Li, 1998b; Ruffier, et al., 1993].

The temperature dependence of shrinkage for various PVAc proportions was investigated using a molding simulator (Plastoreactomat-PRM) at 1.6 Mpa [Ruffier et al., 1993]. Their results show that the shrinkage increases with an increase of temperature at all composition. Under SEM, the spherical particle at higher temperatures is smaller and more tightly packed. They suggested that the final morphology and the shrinkage are determined by the competition between the phase separation and the reaction rate. At higher temperatures, phase separation is stopped earlier by macrogelation and results in smaller particles. At lower temperatures, a more homogeneous co-continuous structure is
obtained, which enhances the shrinkage compensation. Kinelaar et al. (1992) investigated temperature dependence of shrinkage in both isothermal and non-isothermal cases, since no molding process is absolutely isothermal. “U” shape shrinkage-concentration relationship was obtained in all cases. However, the optimum LPA concentration shifted from 2.5% for the isothermal cure at 80°C to 6% for the non-isothermal cure with a 8°C/min ramping rate and 7.5% for a 16°C ramping rate. The optimum shrinkage control correlates with loosely packed, irregular-shape particles, which is similar to Ruffier’s work.

Curing pressure on shrinkage control was also investigated [Kinkelaar et al. 1994, Ruffier et al., 1993]. It was found that a lower pressure markedly decreased the final shrinkage. The decrease in pressure has two favorable effects on the shrinkage compensation. One effect is that the drop in pressure reduces the reaction rate by a “thermodynamic effect” (i.e. the reaction increases with pressure because polymerization results in a decrease in volume) [Kubota, 1975]. The other effect is that low pressure actually enhances the phase separation, since the crossing over from a one-phase to a two-phase system is accompanied by a volume increase [Guo, et al., 1990].

2.2.3.4 Other Factors

The pairing of the structures and molecular weight of the unsaturated polyester resin and the thermoplastic additive is very important [Atkins, 1993]. Mitani et al. [1989] tested the volume shrinkage of various pairs of polyester resins and LPAs. They
concluded that volume shrinkage is related to the reactivity of the polyester. PU shows the best shrinkage control for highly reactive polyesters, while the polyesters with low reactivity prefer PS as LPA. It was reported [Lin, 1990] that the shrinkage control thermoplastics (LPA) having very good shrinkage control in the unsaturated polyester resin did not provide good shrinkage control in the vinylester resin.

The effects of thickener and filler on the shrinkage control were also investigated [Kinkelaar et al., 1994; Bucknall, 1991a]. Thickeners tend to have a negative effect on the shrinkage control by hindering the particle formation. Fillers, on the other hand, do not show significant effect on shrinkage compensation.

2.2.4 Low Profile Mechanism

A number of different mechanisms for the shrinkage control in the complex thermoset-thermoplastic system have been proposed. Some of these have been very specific as to the polyester resin structure and may be controversial to each other. The most important mechanisms are reviewed in this section.

The “optical heterogeneity” mechanism [Bartkus, et al., 1970; Rohm and Haas, 1972a, 1973] indicated that distinct thermoplastic domains are dispersed in a cured thermoset matrix. During cure, the styrene monomer inside the dispersed domain boils because of the reaction exotherm and creates internal pressure, which may compensate for the polymerization shrinkage. The unreacted styrene monomer may also migrate from
the less reactive LPA phase to the more reactive resin phase and leaves voids inside the thermoplastic phase. It suggested that after well mixing, the resin system must show optically heterogeneous two-phase structure. This theory is limited to the polyesters with molecular weight-to-double bond ratio of 150 to 186 and a PMMA/PS type LPA. This mechanism failed to explain the systems with PVAc as LPA since the resin with PVAc shows an optically homogeneous appearance under the microscope.

“Thermoplastic expansion” was proposed to explain the difference shrinkage control behavior of different thermoplastic additives [Atkins et al., 1976]. During heating and reaction, the thermal expansion of thermoplastic creates the force to counteract the overall shrinkage. The different performances of PVAc and PMMA were used to prove the theory. The larger specific volume and the lower glass transition temperature of PVAc allow PVAc expanding more than PMMA. PS as LPA is a disproof to this theory since the thermal expansion coefficient of PS is much larger than those of PVAc and PMMA. This inconsistency was attributed to the polarity of PS. In comparison with PVAc and PMMA, PS is much non-polar. Therefore, there is less driving force for PS to phase separate from the resin. As a result, smaller amount of PS is available for thermal expansion.

Other studies on shrinkage control of UP resins with LPA have resulted in modification of the proposed theory. Pattison et al. [1974] proposed the “strain relief through stress cracking” theory to explain PMMA performance as LPA in propylene glycol-fumaric acid polyester (two-phase system). In their theory, the unreacted styrene
monomer thermally expands at the beginning of polymerization to prevent polymerization shrinkage. As styrene is consumed, the thermal expansion is no longer sufficient for shrinkage compensation. Strain develops within the system, particularly concentrates on the interface between the thermoplastic domain and the continuous matrix. The continuous polymerization increases the strain to the point where the stress cracking is initiated. As a result, strain is relieved, voids are formed, and the shrinkage is compensated. A similar mechanism was proposed except it suggests that a large amount of styrene inside the thermoplastic region may homopolymerize, and compensate some shrinkage [Rabenold, 1972; Walker, 1971]. In another paper of Pattison et al. [1975], a similar theory was extended to a one-phase system (PVAc as LPA).

Bucknall et al. [1991a] agreed that crack and void formation is the key response for the low profile effect, especially when the PVAc concentration is high enough to produce a co-continuous morphology. In their statement, LPA itself has no direct influence on shrinkage except provides a weak co-continuous region that may crack in response to tensile stress. They believed that the driving force of the tensile strain comes from the thermal- and cure-contraction in the presence of mechanical constraints instead of polymerization shrinkage. The constraint can be imposed internally by mineral fillers and glass fibers, or externally by forces acting on the surface of the resin.

Li, et al. [1998] proposed a mechanism for UP resin systems containing different types of LPA cured at low temperature. The shrinkage control in the low profile UP resins can be divided into six steps, as illustrated in Figure 2.6. In Step 1, the system
starts as a homogeneous mixture without propagation caused by the presence of the inhibitor, which consumes the free radicals generated by the initiator (the induction period) [Hsu, 1992]. In Step 2, the UP molecules are linked by either inter- or intra-molecular reaction to form microgels. The compatibility of the reacting UP with surrounding LPA and styrene decreases due to the increase of UP molecular weight and the change of polarity. This instability results in the occurrence of the macro scale phase separation (primary phase separation), following the spinodal decomposition mechanism. One phase is the LPA-rich phase and the other is the UP-rich phase. Coarsening and breaking down of the interconnected spinodal structure occurs and two distinguished droplet-matrix structures can be formed in Step 3. The volume fraction is decided by the characteristics of LPA and its concentration, the resin and the ongoing reaction. In Step 4, with the continuous reaction and secondary phase separation in both UP-rich and LPA-rich phases, the sample morphology will change to the UP-rich/LPA-rich phase dominated disperse structure or co-continuous structure. In Step 5, the macro-gelation takes place and the structure formed through the primary phase separation is locked at this stage. In Steps 3, 4 and 5, the reaction mixture turns cloudy and translucent. Resin viscosity starts to increase, and the resin volume keeps shrinking. Stresses may build up internally because of the polymerization shrinkage. At a certain point, i.e. Step 6, local crack may occur and propagate along the interface or inside the weaker phase (the LPA-rich phase). Microvoids are formed and stresses are released, consequently, the polymerization shrinkage is compensated. At this point, the reaction mixture turns opaque, and volume expansion starts.
Table 2.6 Schematic of low temperature mechanism: (1) induction stage, (2) spinodal decomposition, (3) coarsening to (i) the LPA-rich phase dominated structure, or (ii) the UP-rich phase dominate structure, (4) coalescence and growth, (a) coarse co-continuous structure, or (b) LPA-rich phase dominated structure, (5) gelation, and (6) microvoid formation (Li, et al., 2000).
2.3  Phase Separation

2.3.1  Thermodynamics

The thermodynamic criterion of miscibility of two-component polymer mixture (polymers A and B) is strongly related to Gibbs free energy of mixing ($\Delta G_m$). Depending on the Gibbs free energy of mixing, a polymer blend can be either miscible when $\Delta G_m < 0$, or immiscible when $\Delta G_m > 0$. A single-phase mixture will be formed if

$$\left( \frac{\partial^2 \Delta G_m}{\partial \phi_B^2} \right)_{P,T} > 0$$

(2.6)

where $\phi_B$ is the volume fraction of component B. At the binodal point, the chemical potential $\mu_i$ ($\mu_i = \frac{\partial \Delta G_m}{\partial \phi_i}$) of each specimen has the same value in both phases:

$$\mu_i' = \mu_i''$$

(2.7)

where the superscripts prime and double prime stands for the two phases at equilibrium.

At a given temperature, the mixing free energy of an undercomposed mixture varies with composition as depicted by Figure 2.7 [Macknight, 1989]. The spinodal boundary is defined by the condition of

$$\left( \frac{\partial^2 \Delta G_m}{\partial \phi_A^2} \right)_{P,T} = \left( \frac{\partial^2 \Delta G_m}{\partial \phi_B^2} \right)_{P,T} = 0$$

(2.8)

The spinodal and the binodal curves meet at the critical point, where the third derivative of $\Delta G_m$ equals to zero as shown in Equation 2.9:

$$\left( \frac{\partial^3 \Delta G_m}{\partial \phi_A^3} \right)_{P,T} = \left( \frac{\partial^3 \Delta G_m}{\partial \phi_B^3} \right)_{P,T} = 0$$

(2.9)
Figure 2.7 Composition dependence of $\Delta G_m$ at a temperature within the miscibility gap (note: $\mu_i = \partial \Delta G_m / \partial \phi_i$) [Macknight, 1989].
Within the composition range bonded by the spinodal boundary, the curvature of $\Delta G_m$ or $\frac{\partial^2 \Delta G_m}{\partial \phi_B^2}$ is negative, and any small fluctuation in composition will cause a decrease in $\Delta G_m$ and therefore tends towards phase separation. In the region between the spinodal and bimodal, $\frac{\partial^2 \Delta G_m}{\partial \phi_B^2}$ is positive. The small fluctuation in this region results in unfavorable free energy changes, phase separation will occur only when relative large composition fluctuations are present. Therefore, there are three regions of miscibility existing in a binary system: (1) the single-phase miscible region outside the binodal curve, (2) metastable region which locates between the binodal and spinodal curves and (3) phase separated (or spinodal) region enclosed by the spinodal curve.

Phase separation is a dynamic process. There are two phase separation kinetic mechanisms. One is spinodal decomposition (SD), the other is nucleation and growth decomposition (NG). SD occurs when the composition is within the spinodal gap. At this composition range, the mixture is unstable to infinitesimal fluctuations, therefore no thermodynamic barrier exits to phase growth. Phase separation should occur by a continuous and spontaneous process. When phase separation takes place by the SD mechanism, interconnected cylinder-like structure (branch structure), important feature morphology of SD, tends to form. As shown in Figure 2.8 [Reich, 1986], the domains are of about the same size during the early stage of phase separation (micrographs 2 to 3 in Figure 2.8), but tend to grow, coalesce, and eventually form larger spheroidal structure (micrographs 6 to 8 in Figure 2.8). The late stage growth and coalescence is also called 'coasening' or 'ripening' process of the SD structure.
Figure 2.8 Development of morphology in polymer blends following spinodal decomposition [Reich, 1986].
NG is associated with metastability since any small composition fluctuation in this region results in unfavorable free energy change. It can proceed only by overcoming an energy barrier with a large composition fluctuation in composition. The fluctuation is called a nucleus, and once a nucleus is formed, it grows by a normal diffusion process. The NG mechanism results in domain size increasing with time, and the morphology of the domains is normally spheroidal minor component with a sharp boundary between the matrixes. If the amount of the two phases is similar, lamellae morphology may result. The differences between SD and NG are compared in Figure 2.9 and Table 2.4.

SD can be possibly described by a quantitative theory since the entire decomposition process can be treated as a purely diffusion problem and morphology can be described by an approximate solution to the diffusion equation [Kwei, 1978]. Cahn et al. [1958, 1961 and 1968] has derived a diffusion equation (Equation 2.10) describing the kinetics of SD in isotropic binary mixture. Theories of dynamics of phase separation are based on the assumption that the free energy is a function of both concentration and concentration gradients. This theory is not adequate to describe the phase dynamics of small molecule liquids, but quite successful in describing the phase separation in polymer blends.

\[
\frac{\partial \phi}{\partial t} = M \left( \frac{\partial^2 G}{\partial \phi^2} \right) \nabla^2 \phi - 2MK \nabla^4 \phi \tag{2.10}
\]

where \( \phi \) is the concentration, \( M \) is the mobility constant and \( K \) is the energy gradient term. The local concentration of the mixture can be solved:

\[
\phi - \bar{\phi} = \sum \{ \exp[R(\beta) t] \} [A(\beta) \cos(\beta \cdot r) + B(\beta) \sin(\beta \cdot r)] \tag{2.11}
\]
Figure 2.9 Schematics of concentration profiles during phase separation for nucleation and growth and spinodal decomposition in miscible blends [Macknight, 1989].
1. Nucleation and growth

(a) Initial fragment of more stable phase forms.
(b) Two contributions to free energy: (i) work spent in forming the surface and (ii) work gained in forming the interior.
(c) Concentration in immediate vicinity of nucleus is reduced; hence diffusion into this region is downhill (diffusion coefficient is positive).
(d) Droplet size increases by growth initially.
(e) Requires activation energy.

2. Spinodal decomposition

(a) Initial small-amplitude composition fluctuations.
(b) Amplitude of wavelike composition fluctuation increases with time.
(c) Diffusion is uphill from the low concentration region into the domain (diffusion coefficient is negative).
(d) Unstable process: no activation energy required.
(e) Phases tend to be interconnected.

Table 2.4 Mechanisms of phase separation [Sperling, 1992].
where $\bar{\phi}$ is the average concentration, $\beta$ is the wave number of the sinusoidal composition fluctuation, A and B are $\beta$-dependent parameters, and $r$ is the position variable. The $R(\beta)$ is the kinetic amplification factors determined by:

$$R(\beta) = -M\beta^2[(\partial^2 G/\partial \phi^2) + 2K\beta^2]$$

(2.12)

Since the exponential dependence on $R(\beta)$ in Equation 2.11, any compositional excursion from the average will decay or grow rapidly, depending on whether $R(\beta)$ is positive or negative. When $\partial^2 G/\partial \phi^2 > 0$ (outside the spinodal region), $R(\beta)$ is negative for all values of $\beta$, leading to the diminish of any fluctuation and a homogeneous system. Therefore Equation 2.10 does not apply to nucleation expected in the metastable region. Inside the spinodal, $\partial^2 G/\partial \phi^2 < 0$; $R(\beta)$ is a nonmonotonic function of $\beta$. The maximum $R(\beta)$ can found by setting the first derivative of Equation 2.12 to zero:

$$R_m = -MD\beta_m^2/2; \quad \beta_m = (-D/4K)^{1/2}$$

(2.13)

Where D is the second derivative of the free energy of mixing. The product $MD \equiv D^C$, is defined as the Cahn-Hilliard diffusion constant. Since phase separation occurs through a "uphill" diffusion process in the spinodal region, D and $D^C$ must be negative.

Cahn and Hilliard approach provides a qualitatively correct description of SD. However, it is only applicable to the early stage of SD since it over-emphasizes the difference in the mechanism of phase separation at the spinodal boundary [Utracki, 1989]. Some more comprehensive models can be found in the work of Pincus [1981] and Binder [1983].
2.3.2 Phase separation behaviors

There are many variables, such as temperature, reaction, pressure, composition, molecular weight and polydispersity, and stress fields, may change the phase stability and result in phase separation of a system. In polymer blending, temperature change is most commonly employed to create phase separation. Nucleation and growth is a more familiar mechanism for phase separation than spinodal decomposition since it is difficult or impossible to “quench” the mixture sufficiently into the spinodal region for completing effectively spinodal decomposition.

Depending on the thermodynamic properties of mixture, polymer blends demonstrate various phase behaviors as shown in Figure 2.10. In polymer mixtures with an upper critical solution temperature (UCST) behavior, phase separation occurs at some lower temperature. It is popular for polymer solutions and is also quiet common for blends of oligomers [Koningsveld, et al., 1974]. The lower critical solution temperature (LCST) behavior, phase separation occurring at some higher temperatures, also exists in many systems. It is characteristic of exothermic mixing and negative excess entropy [Taylor, et al., 1975]. Because of the low entropy of mixing, high molecular weight polymer blends exhibit LCST behavior, while UCST may be seen when the polymer chains are short [Sperling, 1992]. Phase diagrams may show both LCST and UCST behavior for copolymer blends. UCST may lie below or above the LCST or even merge with LCST, showing a ‘closed loop’ phase diagram [Macknight, 1989].

Reaction induced phase separation is more complicated and the study is less extensive than the temperature induced phase separation. For thermoplastic polymer
Figure 2.10 Schematic phase diagram for polymer-polymer blends; — binodal line, -- spinodal line  (a) UCST; (b) LCST; (c) both UCST and LCST; (d) an “hourglass” phase diagram; and (e) UCST above LCST [Macknight, 1989].
blends, phase separation takes place when system temperature changes from the one-phase region to the two-phase region, following either SD mechanism or NG mechanism. The boundary between the one-phase and two-phase regions does not change. For a reactive system, the reaction results in changes of phase boundary and reactant composition. These changes force the system moving from the one-phase region to the two-phase region, and induce phase separation as shown in Figure 2.11.

In general, the morphology induced by crosslinking reactions is controlled by the rate of the reaction and the phase separation. The former tends to suppress the phase separation by slowing down the polymer chain diffusion, while the latter is activated by the reaction via thermodynamical instabilities. Several researchers observed both NG and SD during the reaction process of rubber modified epoxy systems [Ludwico, et al. 1975; Verchere, et al. 1989; Kim, et al. 1991]. The dynamics of phase separation during the course of a polyurethane-unsaturated polyester interpenetrating network formation were explored by Chou and Lee [1994]. They found that the phase separation follows SD mechanism except at low temperatures. Nucleation and growth process followed by the spinodal decomposition mechanism was proposed in the reactive polymer mixture of poly(styrene-stat-(chloromethyl) styrene) and poly (vinyl methyl ether) [Harada, et al., 1997].

Bucknall et al. [1985] provided a qualitative model to explain the phase behavior during reaction, as shown in Figure 2.12. As the monomer polymerizes, phase separation occurs and two phases are created, whose composition is given by the tie-lines. At PVAc level of 8%, the resin-rich phase is the major component and forms the continuous matrix. Phase diagram for the resin-rich phase is no longer valid after gelation takes
Figure 2.11 Comparison of phase separations due to (a) temperature jump, (b) Polymerization [Hsu, 1992].
Figure 2.12. Ternary phase diagram of the reacting PVAc-containing system; (a) complete diagram, (b) 8% PVAc, (c) 16% PVAc [Bucknall et al., 1985].
places in the resin matrix. Phase separation goes on inside the LPA-rich droplet since it has not reached the gel point yet. The major phase turns to be LPA-rich, and the minor phase is resin-rich, forming particles surrounded by PVAc. In case of 16% PVAc, phase separation follows the same path, except that it occurs earlier and the LPA-rich phase is the major component.

Lee and co-workers [Kiaee, et al., 1988; Kinkelaar, et al., 1990; Hsu, et al., 1991; Kinkelaar, 1994] suggested that the addition of LPAs (thermoplastic) enhanced the phase separation during cure of unsaturated polyester resins. As reaction starts, the linking of the adjacent polyester molecules forms the locally polyester-rich area. Because the increase of molecular weight and the change in polarity, PVAc may phase out from these areas, and form a LPA-rich layer surrounding the polyester-rich region.

2.3.3 Experimental

There are many well-established methods to study phase separation behaviors in polymers, such as optical and electron microscopy, light and X-ray scattering, thermal expansion, heat capacity, and dielectric or mechanical measurements [Kwei, 1987]. Combining phase diagram, laser light scattering (SALLS), SEM and TEM study, the curing process of UP resins can be divided into five stages: storage stage, heating stage, phase separation stage, macrogelation stage, and microvoid formation stage. Interfacial tension was suggested to be the governing factor for the final stage of phase separation.
Nishi, et al. [1975] used light transmission, optical microscope, and pulse NMR method to study the phase separation by both SD and NG mechanism. The diffusion coefficient was found to be negative. Davis, et al. [1980] examined the phase transformation of polystyrene and poly (vinyl methyl ether) blend with optical microscope and glass transition experiments. Among all the methods, time-resolved scattering techniques, with light or neutron sources are the most frequently used experimental methods in studying spinodal decomposition in the polymer mixtures. The kinetics of phase separation and phase dissolution of polymer blends were studied by Hasimoto, et al. [1983 and 1984] using the light scattering method. Small angle neutron scattering and temperature jump light scattering techniques were employed by Han, et al. [1986] in studying both static and kinetic phase behavior of a polymer blend.
CHAPTER 3

EFFECT OF CO-PROMOTER AND COMONOMER ON VOLUME SHRINKAGE OF UNSATURATED POLYESTER/STYRENE/LOW PROFILE ADDITIVES SYSTEMS CURED AT LOW TEMPERATURES

SYNOPSIS

As reviewed in Chapter 1, the volume expansion during low temperature curing occurs at a very late stage of reaction and an increase of the reaction rate in the LPA-rich phase results in an earlier volume expansion and better shrinkage control. In this chapter, two approaches were applied to fasten the reaction rate at the LPA-rich phase. One is introducing comonomer; the other is addition of co-promoter, acetylacetone or 2,4-pentanedione (2,4-P). The effect of 2,4-P and comonomer on reaction kinetics and shrinkage control of the UP/St/LPA system is investigated and their effect on the curing agent partition and viscosity change in each phase is also studied. The experimental methods used include differential scanning calorimetry (DSC), rheometry, dilatometry, and scanning electron microscopy (SEM). Composite samples are also prepared by room temperature SCRIMP in order to measure the surface quality of the cured composites.
3.1 Introduction

Unsaturated polyester (UP) resins are the most widely used thermoset polymers in the composite industry. Severe polymerization shrinkage of this resin, however, induces many deficiencies in the molded products. Many thermoplastic materials can serve as low shrinkage or “low profile” additives (LPAs) to reduce the shrinkage of UP resins. The effects of LPA structure, molecular weight and concentration, thermal expansion coefficient and the glass transition temperature on shrinkage control performance and surface quality of various resin systems cured at high temperatures have been extensively investigated [Bartkus, et al., 1970; Pattison, et al., 1974; Atkins, et al., 1976; Atkins, et al., 1978; Bucknall, et al., 1985; Lam, 1989; Melby, et al., 1989; Hsu, et al., 1991; Suspene, et al., 1991; Atkins, et al., 1993; Kinkelaar, et al., 1994]. Several mechanisms have been proposed for shrinkage control of LPA in high temperature cure [Bartkus, et al., 1970; Pattison, et al., 1974; Atkins, et al., 1976; Hsu, et al., 1991; Suspene, et al., 1991; Kinkelaar, et al., 1994; Rhom and Hass, 1973; Kiaee, et al., 1988; Bucknall, et al., 1991a]. Most of them involve thermal expansion of the resin and LPA during heating, phase separation and inversion between the LPA-rich and resin-rich phase during curing, and the formation of micro-voids either at the interface or inside the LPA-rich phase to compensate the resin shrinkage during curing and cooling.

In recent years, demand for low cost composite manufacturing processes, such as low temperature/low pressure SMC, RTM, and SCRIMP, has grown considerably in industry. Commercial LPAs, however, often do not work effectively in room temperature processes like SCRIMP. Recent studies on the UP/St/LPA system cured at low
temperatures [Li, et al., 1998a, 2000a-c] indicated that the reaction-induced micro void formation, instead of the thermal expansion/shrinkage dominated micro void formation at high temperatures, is the main factor in shrinkage compensation. Micro-void formation is related to the build-up of reaction-induced stresses at the interface of the resin-rich and the LPA-rich phases. This in turn depends on the relative reaction rate and modulus of the two phases, as well as the phase structure of the reacting mixture.

It was found [Li, et al., 2000c] that volume expansion, which can compensate volume shrinkage, during low temperature curing occurs at very late stage of reaction and increasing the reaction rate in the LPA-rich phase results in an earlier volume expansion and better shrinkage control. A hypothesis was also proposed in this paper to explain the late stage volume expansion of UP/St/LPA systems cured at low temperature. It states that the slower reaction in the LPA-rich phase is the main reason why the micro-void formation occurs at the late stage of polymerization. The low reaction rate in the LPA-rich phase is a direct result of two factors: a low promoter concentration and a high St/UP ratio. The low promoter level in the LPA-rich phase is caused by the partition of the promoter into two phases, due to the complex formation between the cobalt ion and the carboxyl groups of UP and LPA molecules. A kinetic study of the samples with acid modified LPA confirmed that the LPA containing more and stronger acid groups tends to attract more cobalt promoter to the LPA-rich phase, resulting in a higher reaction rate. Consequently, the samples with acid-modified LPA show an earlier volume expansion and better shrinkage control [Li, et al., 2000c]. The improvement, however, is modest.
It has been found [Atkins, et al., 1997] that adding a highly reactive olefinically unsaturated chemical species, like divinylbenzene (DVB), to the UP/St/LPA systems is able to reduce shrinkage and increase physical properties such as tensile strength and resistance to crack of cured resin in high temperature molding processes. However, the actual mechanism is unclear. One of the two tasks of this study is to investigate the effect of DVB and trimethylpropane trimethacrylate (TMPTMA), which has three acrylic functional groups and is often used as a cross-linking agent [Datta, et al., 1996; Zlatanic, et al., 1999], as a comonomer, on shrinkage control of UP/St/LPA systems cured at low temperatures.

It is well known that peroxide can be decomposed efficiently at low temperature with the aid of metal ions. The reactivity of metal ions in the redox decomposition of peroxide is appreciably influenced by the type of ligands that form a counter ion [Hiatt, et al., 1968]. Acetylacetone or 2,4-pentanedione (2,4-P) was found synergistic with the reactive metals in the redox polymerization [Chetakan, et al., 1971]. This is because that 2,4-P is an effective chelating agent capable of interacting with metal ions to form new complex. The formed chelate may decrease, enhance, or have no catalytic effect on the decomposition of peroxide, depending on its relative ability to take part in the redox reaction as compared to that without 2,4-P. The effect of 2,4-P on shrinkage control of the UP/St/LPA system is also investigated in this study.

The experimental methods used include differential scanning calorimetry (DSC), rheometry, dilatometry and scanning electron microscopy (SEM). The reaction kinetics and viscosity change in both the LPA-rich and the UP-rich phases are compared to
understand how the relative reaction rate and viscosity change in each phase influence the shrinkage compensation. A dilatometer is used to study the volume change of UP/St/LPA systems cured at low temperature and SEM is used for the morphology observation. Composite samples are also prepared by room temperature SCRIMP in order to measure the surface quality of the cured composites.

3.2 Experimental

3.2.1 Materials

The unsaturated polyester resin used in this study was Q6585 (with 35% styrene content) from Ashland Chemical. Q6585 is a 1:1 mixture of maleic anhydride and propylene glycol with an average of 10.13 vinylene groups per molecule and an average molecular weight of 1580 g/mol. The cross-linking monomer used was styrene (St) from Aldrich. The LPA used in this study was Neulon-T plus, modified polyvinyl acetate (PVAc), from Union Carbide. The two comonomers (SM) from Aldrich used in this study were divinylbenzene (DVB, an 80% isomer mixture of \( m \)-DVB and \( p \)-DVB), and trimethylpropane trimethacrylate (TMPTMA, with three vinylene groups per molecule). One co-promoter used, also from Aldrich, was 2,4-pentanediione (2,4-P).

All the samples being tested were formulated to provide a St double bond to UP double bond ratio of 2.0. The initiator used was 1.0% methyl ethyl ketone peroxide (MEKP, Aldrich Chemical) with 0.1% cobalt octoate (CoOct, 6% cobalt octoate in mineral spirits, Pfaltz & Bauer). Before the experiment, the unsaturated polyester and the
styrene were weighed and well mixed in a vial. Then cobalt octoate was introduced and mixed until the solution was uniform. MEKP was added right before the measurement. In the dilatometry study, about 30 minutes preparation time was need for the assembly of the dilatometer. Therefore, inhibitor benzoquinone was used to control the curing process to make sure no obvious reaction was found in the first 30 minutes at 35°C. All the samples were cured at 35°C.

3.2.2 Instruments and Procedures

3.2.2.1 Differential Scanning Calorimeter (DSC)

A differential scanning calorimeter (DSC2910, TA Instruments) was used to measure the reaction kinetics. The sample was sealed in a hermetic aluminum sample pan, which can withstand 2 atm internal pressure after sealing. Upon finishing mixing the reactant, about 10 mg sample was placed in a DSC pan. Isothermal runs were conducted at 35°C for long enough time until no further reaction exotherm could be detected. The samples were then followed by scanning the samples from 30°C to 300°C to determine the residual heat with a heating rate of 5°C/min.

The exotherm data measured during cure can be converted to reaction rate and conversion as a function of time by using the following equations, based on the assumption that the thermal physical properties of the resins such as density, heat capacity, and heat of reaction do not change during the reaction:
\[
\frac{d \alpha}{dt} = \left( \frac{d \Delta H_t}{dt} \right) \left( \frac{1}{\Delta H_{total}} \right)
\]
\[
\alpha = \frac{\Delta H_t}{\Delta H_{total}} = \frac{\Delta a_t}{\Delta a_{total}}
\]

where \(d\alpha/dt\) and \(\alpha\) are the reaction rate and conversion respectively at a given time; \(\Delta H_t\) is the accumulated exotherm from the beginning of the cure to the given time, \(t\); \(\Delta H_{total}\) is the total reaction exotherm; \(\Delta a_t\) is the accumulated area under the isothermal DSC curve from \(t=0\) to the time \(t\); and \(\Delta a_{total}\) is the total area under the scanning DSC curve.

### 3.2.2.2 Dilatometer

The volume change of the sample materials during the curing was measured by an in-house constructed dilatometer [Kinkelaar, 1994b]. The schematic of the dilatometer is shown in Figure 3.1.

The sample was heat-sealed in a polyethylene (inert to styrene) pouch with 75mm in diameter. The sample weight was about 5 to 6 grams to ensure the sample thinner than 1.5mm and the sample could be cured under pseudo-isothermal condition. Since the existence of air bubble may seriously disturb the shrinkage measurement, it is very important to remove all the air bubbles trapped in the sample. The sealed sample pouch was first degassed under vacuum. Then, a small hole was poked at the edge of the pouch, and air bubbles inside the pouch that had been formed under vacuum were squeezed out. The pouch was heat-sealed again, and placed inside the sample chamber of
Figure 3.1 Schematic of dilatometer [Kinkelaar, 1994b].
the dilatometer. The measurements were taken under a pressure of 0.69 MPa (100 psi) at 35°C. The specifications and limitations of the dilatometer and details regarding the dilatometer design and operation can be found elsewhere [Kinkelaar, 1994b].

The percentage volume change due to the polymerization shrinkage was determined by subtracting the second curve from the cure curve (i.e. the first curve), counting for the sample volume and the dilatometer geometry:

\[
\text{Percent volume change} = \left( \frac{\Delta L \pi R^2}{V} \right) \times 100\%
\]

where \( R \) is the cylinder radius, \( \Delta L \) is the position difference between the cure and baseline, and \( V \) is the sample volume calculated by dividing the sample weight by the sample density.

3.2.2.3 Rheometrics Mechanical Spectrometer (RMS)

The rheological changes during curing were measured by a Rheometrics Mechanical Spectrometer (Rheometric Scientific™ RMS-800). A set of parallel plates with an air oven as a heating chamber was employed. The diameter of the plates was 50 mm, and the gap between them was on the order of 1 mm. Viscosity was measured under isothermal condition (35°C) and at a shear rate of 1.0 s\(^{-1}\). The gel point is defined as the point where the reduced viscosity \( \eta_r = \eta / \eta_0 \) (\( \eta \) is the instantaneous viscosity and \( \eta_0 \) is the initial viscosity) reaches 10\(^3\) Pa.s.
3.2.2.4 Scanning Electron Microscopy (SEM)

For the morphological measurement, a Philip XL-30 scanning electron microscope was used. The effective source or crossover of the field emitter (tungsten fiber) is about 10nm. The advantage of SEM includes large magnification range, high depth of focus, high contrast and resolution, and easy handling [Wischnitzer, 1981; Goldstein, 1981]. The sample cured in the dilatometer without etching by any solvent was gold-coated for morphological measurements. The fracture surfaces were observed under 10 KV power. The magnification in this study varied from 200x to 10,000x depending on the surface structure.

3.2.2.5 SCRIMP

Before molding, three layers of dry glass fiber mats (QM6408 from Brunswick Technologies, Inc.) were laid upon a glass plate. The fiber stack was covered by a polyester film to form a vacuum bag whose outer edges were sealed by tacky tape. A resin inlet and a vacuum outlet on each end of the mold were also formed. During molding, vacuum was applied through the outlet, which forced the bag to press tightly against the fiber stack. The liquid resin was introduced to the inlet through a supply line, then cured in the vacuum bag for 24 hours.

The surface quality of the molded samples was measured by a profilometer, Federal’s Surfanalyzer 4000. The chosen tracing length was 1 inch. An average roughness (Ra), which is the arithmetic average height of surface irregularities measured
from the mean line within the sample length, was used as a quantitative standard to compare the surface quality.

3.3 Results and Discussions

3.3.1 Reaction Kinetics and Volume Shrinkage

3.3.1.1 Effect of 2, 4-Pentanediione

To investigate the influence of acetylacetone or 2,4-pentanediione (2,4-P) on the reaction kinetics and volume change of the UP/St/LPA systems, the resin samples with different amounts of 2,4-P were cured at 35°C in the DSC. The same isothermal runs were carried out under pressure of 0.69 MPa (100 psi) in the dilatometer. The ratio between the styrene double bond and the UP resin double bond was adjusted to 2.0 by adding extra styrene. All samples contained 3.5% LPA. The initiation system included 0.1% cobalt octoate and 1.0% MEKP. 300 ppm BQ was added into the system to allow enough sample preparation time, i.e. 30 minutes.

The results of reaction kinetics are shown in Figures 3.2(a) and (b). The reaction rate increased and the induction time decreased as the content of 2,4-P increased. Therefore, 2,4-P is a co-promoter for UP resins cured by cobalt and MEKP [Dow Chemical, 1994]. The resin conversion shows the same trends, but the final conversion is independent of the 2,4-P content.

Figure 3.3 presents the volume change profiles of samples with various amount of 2,4-P (0, 0.03 and 0.05 wt.%). The volume expansion of the sample with 2,4-P was
Figure 3.2 Reaction kinetics of UP/St/LPA system with different concentrations of 2,4-P cured at 35°C (300 ppm BQ, 0.1% cobalt octoate and 1.0% MEKP): (a) reaction rate; (b) conversion.
Figure 3.3 Volume change profile of UP/St/LPA system with different concentrations of 2,4-P content cured at 35°C (300 ppm BQ, 0.1% cobalt octoate and 1.0% MEKP).
observed occurring earlier than the sample without 2,4-P. The samples with 2,4-P showed much larger volume shrinkage compensation than the sample without 2,4-P. The final volume shrinkage for the sample without 2,4-P under this curing condition was 4.2%. On the other hand, the final volume shrinkage was about 2.9~3.0% for the sample with 0.03% or 0.05% 2,4-P under the same curing condition.

From dilatometry results, it is clear that the addition of 2,4-P leads to an earlier volume expansion, which improves the shrinkage compensation. DSC results showed that the reaction rate increased by adding 2,4-P. In order to study the effect of reaction rate on shrinkage control of UP/LPA/St systems, a series of experiments were carried out by changing the content of initiator/promoter or 2,4-P. The kinetics and dilatometer results are summarized in Figure 3.4. The reaction rate is increased by either increasing the content of initiator/promoter but without adding any 2,4-P, or keeping the 2,4-P content at 0.05 wt.% but increasing the amount of initiator/promoter. Both methods increased the reaction rate significantly, however, for the samples with higher initiator/promoter content, the addition of 2,4-P only slightly accelerated the total reaction rate. The volume change behavior of these samples, however, was quite different. For the two samples with 0.05%2,4-P, increasing the content of cobalt octoate and MEKP in the system resulted in a higher reaction rate and earlier volume expansion, but the final volume shrinkage did not decrease as the curing agent content increased. No volume expansion was observed for the sample with a higher reaction rate but without 2,4-P. It is obvious that higher total reaction rate alone cannot improve the shrinkage control, and it is 2,4-P that improves the volume shrinkage of UP/St/LPA systems.
Figure 3.4 Reaction conversion and volume change profile of UP/St/LPA system with different 2,4-P or initiator/promoter contents cured at 35°C (300 ppm BQ): (a) conversion, (b) volume change. ■ 0.05% 2,4-P, 0.1% CoOct, 1.0% MEKP; ○ 0% 2,4-P, 0.5% CoOct, 1.5% MEKP; ▲ 0.05% 2,4-P, 0.5% CoOct, 1.5% MEKP).
An important feature in the cure of UP/St/LPA is the formation of a two-phase structure (LPA-rich and UP-rich phase). The polymerization shrinkage is compensated by the micro-void formation at the interface of the LPA-rich and UP-rich phase or in the LPA-rich phase. To further understand how the change in total reaction rate or the addition of 2,4-P affects the shrinkage control, the reaction rate and rheology changes of the LPA-rich and UP-rich phases of UP/St/LPA systems with different amounts of 2,4-P during curing were investigated.

A reaction induced phase separation in the actual resin polymerization is a dynamic and evolving process. It is impossible to track this unceasingly changing phase behavior. Here, a temperature forced phase separation method was used as a qualitative assessment of how the partition of chemical species during phase separation affects the resin reaction and the shrinkage control in the UP/St/LPA systems. Since this method takes more than 10 hours, the initiator and the promoter have to be separated during phase separation. Two resin mixtures were prepared for each formulation, one with a double amount of cobalt octoate but without MEKP, and the other with a double amount of MEKP but without cobalt octoate. The mixtures were then forced into phase separation by decreasing the temperature to -2°C to form two layers. The upper layer is an LPA-rich phase, while the lower layer is an UP-rich phase. For the resin mixture with cobalt octoate, it appeared that most cobalt promoter went into the UP-rich phase, since the lower phase (UP-rich) was pink (color of cobalt ion), and the upper phase (LPA-rich) was colorless or very light pink.
The two phases were separated, and their reaction rate and viscosity change were measured at 35°C by mixing an equal amount of resin from the same phase of the two mixtures. Figure 3.5 shows that the reaction rate of each phase increased due to the addition of 2,4-P; however, the influence in the LPA-rich phase is much larger than that in the UP-rich phase. The viscosity change and gel time of the LPA-rich phase and the UP-rich summarized in Table 3.1 shows that the gel time of the UP-rich phase of systems with and without 2,4-P was 10.8 minutes and 20.3 minutes respectively. Due to the very slow reaction rate in the LPA-rich phase, using a conventional rheometer to measure the gel time is difficult because of styrene evaporation. The method used here is to place the LPA-rich phase with initiator in a small glass bottle and record the time when the resin cannot flow in a 35°C water bath. It was found that the gel time of the LPA-rich phase with and without 2,4-P was much longer than that of the UP-rich phase, i.e. 170 minutes and 324 minutes respectively. It was also found that the gel conversion of the UP-rich phase was lower than 5%. Although the gel time of the systems with or without 2,4-P is different, the gel conversion of the same phase (i.e. the LPA-rich or UP-rich phase of both systems, with and without 2,4-P) is the same. The gel conversion of the UP-rich phase is lower than that in the LPA-rich phase (3.8% compared to 8.5%). This suggests that the styrene C=C double bond and UP C=C double bond ratio in the LPA-rich phase is higher. Other researchers [Huang, 1995] found a similar result by measuring the composition in each phase using FTIR and a different phase separation method.

Another important observation in this experiment is that the conversion of the UP-rich phase at the gel point of the LPA-rich phase gel, is different for the systems with or
Figure 3.5 Effect of 2,4-P on reaction kinetics of the LPA-rich and UP-rich phase of UP/St/LPA system cured at 35°C (300 ppm BQ, 0.5% cobalt octoate and 1.5% MEKP): (a) reaction rate; (b) conversion.
<table>
<thead>
<tr>
<th></th>
<th>UP rich phase</th>
<th>LPA rich phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel time (min)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0% 2,4-P</td>
<td>20.3</td>
<td>324</td>
</tr>
<tr>
<td>0.05% 2,4-P</td>
<td>10.8</td>
<td>170</td>
</tr>
<tr>
<td>Gel conversion (%)</td>
<td>3.9</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>3.8</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Table 3.1 Gel time and gel conversion of UP/St/LPA system cured at 35°C (0.5% cobalt, 1.5% MEKP, 300ppm BQ)
without 2,4-P. For the sample with 0.05% 2,4-P, this conversion was 61.1%, which is lower than its final conversion (72.1%). But for the sample without 2,4-P, the conversion reached 70.6%, which is almost the final conversion of the UP-rich phase. The LPA rich phase has to reach a sufficiently high modulus in order to form micro-voids, because a liquid LPA phase can release stress resulted from polymerization shrinkage. After gelation of the LPA-rich phase, the stress-induced local cracking caused by shrinkage in both phases is the main driving force for micro-void formation. In the UP/St/LPA system with 2,4-P, the UP-rich phase kept reacting after the gelation of the LPA-rich phase. This polymerization shrinkage provided more chance to generate micro-cracking in the system to compensate the volume shrinkage. On the other hand, in the system without any 2,4-P, the UP-rich phase has reached its final conversion when the LPA-rich phase gelled. The driving force for micro-void formation, therefore, is quite weak.

The above results reveal that the addition of 2,4-P can accelerate the reaction in the LPA-rich phase more than that in the UP-rich phase. This difference results in an earlier volume expansion and lower final volume shrinkage. A higher overall reaction rate does not necessarily achieve a better shrinkage control.

3.3.1.2 Effect of Comonomer

To study the effect of a comonomer (SM) on the reaction kinetics of the UP/St/LPA system, isothermal cure was carried out at 35°C. The ratio between the styrene double bond and the UP resin double bond was adjusted to 2.0 by adding extra
styrene. The initiation system included 0.1% cobalt octoate and 1.0% MEKP. The samples contained 3.5% LPA and 6% comonomer (SM) based on the total resin weight. Two SMs were used i.e. divinylbenzene (DVB) and trimethylolpropane trimethacrylate (TMPTMA).

Figure 3.6 presents the effect of SMs on the reaction kinetics of the UP/St/LPA system. The overall reaction rate and final conversion of the sample with DVB are lower than the sample without any SM. The reaction of the sample with TMPTMA does not show much difference compared to the sample without SM, and the final conversion is slightly higher than the sample without any SM.

A series of dilatometry tests were conducted with SMs at 35°C to investigate the shrinkage control behavior of UP/St/LPA with SMs. The formulae were the same as those used in the reaction kinetics study. Figure 3.7 shows the volume change profile vs. time during curing. The volume expansion of the system without SMs occurred at 296.3 minutes, when the volume shrinkage reached 7.28%. For the system with TMPTMA, volume expansion occurred at 236.3 minutes and volume shrinkage at this point was 6.73%. It can be seen that the sample with TMPTMA exhibits an earlier volume expansion and better shrinkage control. The volume expansion of the sample with DVB occurred later than the other two samples and the addition of DVB did not show any improvement in shrinkage control.

To further study this phenomenon, formulated unsaturated polyester resin, LPA, TMPTMA, and cobalt octoate were mixed simultaneously so that a transparent (single-phase) mixture was obtained. The method used for phase separation study is the same as
Figure 3.6 Reaction kinetics of UP/St/LPA system with 6% comonomer cured at 35°C (0.1% cobalt octoate and 1.0% MEKP):
(a) reaction rate; (b) conversion.
Figure 3.7 Volume change profiles of UP/St/LPA system with 6% comonomer cured at 35°C (0.1% cobalt octoate and 1.0% MEKP).
that used before. The two phases were separated, and their reaction rate and viscosity change were measured at 35°C by mixing an equal amount of resin from the same phase of the two mixtures.

The results are shown in Figure 3.8. It is obvious that the reaction in the UP-rich phase is much faster than in the LPA-rich phase, both with and without TMPTMA. The addition of TMPTMA can increase the reaction rate in both UP-rich and LPA-rich phases, but the effect of TMPTMA on the reaction rate in the LPA-rich phase is more profound. Although the reaction in the LPA-rich phase is still much lower than in the UP-rich phase, the increasing reaction rate in the LPA-rich phase due to the addition of TMPTMA results in micro-void formation occurring at an earlier stage. It leads to earlier volume expansion and consequently better shrinkage control.

The viscosity change of each phase was also measured during curing and is summarized in Table 3.2. The gel time of the UP-rich phases in systems with and without TMPTMA is 21.8 minutes and 25.7 minutes respectively. However, the gel time of the LPA-rich phase is much longer than in the UP-rich phase, i.e. 188 minutes and 231 minutes respectively. It was also found that the gel conversion of each phase is lower than 5%. Comparing with Figure 3.7, it can be seen that the volume expansion resulting from micro-void formation occurs after gelation of the LPA-rich phase.
Figure 3.8. Effect of TMPTMA on reaction kinetics of LPA-rich and UP-rich phase of UP/St/LPA system cured at 35°C (0.1% cobalt octoacte and 1.0% MEKP) (a) reaction rate; (b) conversion.
<table>
<thead>
<tr>
<th></th>
<th>UP rich phase</th>
<th>LPA rich phase</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gel time (min)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0% TMPTMA</td>
<td>25.7</td>
<td>231</td>
</tr>
<tr>
<td>6% TMPTMA</td>
<td>21.8</td>
<td>188</td>
</tr>
<tr>
<td><strong>Gel conversion (%)</strong></td>
<td>4.61</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>3.72</td>
<td>3.34</td>
</tr>
</tbody>
</table>

Table 3.2 Gel time and gel conversion of UP/St/LPA system cured at 35°C (0.1% cobalt, 1.0% MEKP)
3.3.1.3 Effect of Combining TMPTMA and 2, 4-Pentanedione

The above results reveal that addition of either TMPTMA or the co-promoter 2,4-P can decrease the final shrinkage of the UP/St/LPA system. TMPTMA and 2,4-P can increase the reaction rate in both LPA-rich and UP-rich phases, but the effect on the LPA-rich phase is more profound, which results in an earlier volume expansion and in turn a better shrinkage control.

To investigate the effect of the combination of 2,4-P and TMPTMA on the volume shrinkage control of UP/St/LPA systems, a series of experiments were carried out on samples with various amounts of 2,4-Pentanedione (0, 0.03%, 0.05%) in UP/St/LPA with 6% TMPTMA. Again the ratio between the styrene double bond and the UP resin double was adjusted to 2.0 by adding extra styrene. All samples contained 3.5% LPA. The initiation system included 0.1% cobalt octoate and 1.0% MEKP. 100 ppm BQ was added into the system to allow 30 minutes sample preparation time.

Figure 3.9 presents the volume change profile of several samples cured at 35°C and 0.69 MPa (100 psi). As the concentration of 2,4-P increased in the presence of 6% TMPTMA, an earlier volume expansion was observed and the final volume shrinkage decreased. The trend is the same as that in the system without TMPTMA as shown in Figure 3.3. In Figure 3.3, the system with 0.05% 2,4-P but without TMPTMA has a 3.0% final shrinkage, while adding 0.6% TMPTMA into the system, resulted in a final shrinkage of 2.8% (Figure 3.9). Thus the final volumetric shrinkage does not show any improvement with the combination of TMPTMA and 2,4-P. The reaction kinetics of
Figure 3.9 Volume change profiles of samples with different 2,4-P content in UP/St/LPA system with 6% TMPTMA cured at 35°C (100 ppm BQ, 0.1% cobalt octoate and 1.0% MEKP).
UP/LPA/St systems with 6% TMPTMA and various contents of 2,4-P shown in Figure 3.10 indicates that reaction occurs earlier for samples with more 2,4-P.

In order to understand the relationship between the resin conversion and the volume change, the volumetric change of samples is plotted vs. resin conversion as shown in Figure 3.11. It was found that the samples, which give better shrinkage control (0.03% and 0.05% 2,4-P), show a volume expansion at a lower conversion.

### 3.3.2 Morphology

In order to understand the effect of 2,4-P and TMPTMA on the shrinkage control of UP/St/LPA, on-line optical microscopy (Nicolet Nic-Plan™ infrared microscope) (×200) was used to analyze the dynamics of phase separation process during curing at room temperature (27°C). This device is capable for monitoring the morphological changes during reaction. A drop of resin mixture was bounded by two circular cover slips for observation at room temperature. Figure 3.12 depicts the phase separation process of UP/St/LPA with different amounts of 2,4-P or TMPTMA. All samples were initially homogeneous. Phase separation occurs between 35 min. to 47 min., but the micro-crack was found at different times. For the sample with 0.03% 2,4-P, micro-crack occurred around 137 min and grew rapidly into a co-continuous structure. For the samples with TMPTMA, micro-crack occurred later than the samples with 2,4-P, but earlier than the samples without 2,4-P and TMPTMA (>10hr at room temperature).
Figure 3.10. Reaction kinetics of samples with different 2,4-P content in UP/St/LPA system with 6% TMPTMA cured at 35°C (100 ppm BQ, 0.1% cobalt octoate and 1.0% MEKP): (a) reaction rate; (b) conversion.
Figure 3.11 Volume change vs. conversion of samples with different 2,4-P content in UP/St/LPA systems with 6% TMPTMA cured at 35°C (100 ppm BQ, 0.1% cobalt octoate and 1.0% MEKP).
Figure 3.12 Optical micrographs following the cure of UP/LPA/St (3.5% Neulon T-plus as LPA) at 27°C. (a) No 2,4-P and TMPTMA, (b) 6% TMPTMA, (c) 0.03% 2,4-P, (d) 0.03% 2,4-P and 6% TMPTMA.
Figure 3.12. (continued)

On-set of micro-void  Final

(c)  5 hr  25 hr

(d)  280 min  10 hr

100 µm
The morphology of cured samples of UP/St/LPA systems with different 2,4-P and TMPTMA content was observed by a scanning electron microscope (SEM). Micrographs of samples cured in dilatometry at 35°C are shown in Figure 3.13. The morphology of samples with TMPTMA is different from that of the samples without TMPTMA. Adding 2,4-P does not make any significant difference on the sample morphology. However, the presence of 0.05% 2,4-P reduced the volume shrinkage of the sample from 4~6% to 3%.

### 3.3.3 Surface Quality

A series of room temperature SCRIMP experiments were carried out to test the effect of adding SM and co-promoter on shrinkage control. The samples were cured at room temperature and 72 cm vacuum. Surface quality of the molded samples was measured by a profilometer, Federal’s Surfanalyzer 4000. Every SCRIMP panel was measured at five different locations and the evaluation length chosen for calculation was 4 mm. An average roughness (Rₐ), which is the arithmetic average height of surface irregularities measured from the mean line within the sample length, was used as a quantitative standard to compare the surface quality. The results are summarized in Figure 3.14. As seen from this figure, the surface quality of molded panels with 6% TMPTMA or 0.05% 2,4-P is better than those without any comonomer and co-
3.13 SEM micrographs of cured UP/LPA/St with different amounts of 2,4-P and 6% TMPTMA cure at 35°C (x2000).

- No 2,4-P or TMPTMA (final shrinkage: 4.9%)
- 6% TMPTMA (final shrinkage: 4.0%)
- 0.03% 2,4-P (final shrinkage: 3.0%)
- 6% TMPTMA + 0.05% 2,4-P (final shrinkage: 2.8%)
Figure 3.14. Surface quality of SCRIMP samples (by using 28” of vacuum at room temperature).
promoter. It is also indicated in Figure 3.14 that the molded panel with 0.05% 2,4-P has a slightly better surface quality than the panel with 6% TMPTMA. This trend is the same as the dilatometry result. The standard deviation of surface roughness shows that samples with better surface smoothness, also have a more uniform distribution. The results of surface quality of the SCRIMP panels further confirm that both TMPTMA and 2,4-P can decrease the volume shrinkage of UP/St/LPA systems and yield improved surface quality of molded products.

3.4. Conclusions

In this study, it was found that the addition of comonomer or co-promoter could improve the shrinkage control of the UP/St/LPA systems. For the samples with co-promoter 2,4-P, the reaction rate of both LPA-rich and UP-rich phase increases as compared to the sample without 2,4-P, and the increase in the LPA-rich phase is more pronounced. It was also found that the gelation of the LPA-rich phase occurs earlier by adding 2,4-P into the resin system. This turns out to be critical for the earlier onset of micro-void formation and volume expansion, which in turn gives better shrinkage control. For the sample containing comonomer TMPTMA, the reaction rate of the LPA-rich phase is faster than that of the sample without TMPTMA. The sample showed an earlier volume expansion and a better shrinkage control than the sample without TMPTMA. It further confirms the hypothesis mentioned above.
The kinetics and volume change study of UP/St/LPA systems with both 2,4-P and TMPTMA also showed that a better shrinkage control can be obtained when the volume expansion occurs at a lower conversion. The final volume shrinkage, however, shows no further improvement with the combination of TMPTMA and 2,4-P.

The morphology of the samples with TMPTMA is quite different from that without TMPTMA. It is obvious that TMPTMA affects both cross-linking and phase separation processes in the UP/St/LPA systems. The samples with 2,4-P show no morphology changes. Both approaches: either adding TMPTMA, or adding 2,4-P can reduce the shrinkage of the resin system. The relationship between sample morphology and shrinkage control is still not well understood and needs to be further investigated.
CHAPTER 4

SHRINKAGE CONTROL AND RESIDUAL STYRENE OF UNSATURATED POLYESTER RESINS CURED AT LOW TEMPERATURES

SYNOPSIS

In low temperature molding processes, shrinkage control and residual styrene are very important concerns. The presence of LPA can reduce the shrinkage of unsaturated polyester/styrene resins cured at low temperatures under proper processing conditions but may increase the residual styrene content. A systematic study was carried out to investigate the effect of reaction temperature, initiator system, and secondary monomer on structure evolution, final resin conversion, and shrinkage control of UP resins with LPA. A series of SCRIMP molding experiments were conducted to study the relationship among materials, processing, and properties of the molded composite in low temperature processes.
4.1 Introduction

Unsaturated polyesters are widely used in the composite industry. They can provide excellent mechanical and chemical properties, good chemical and weather resistance with relatively low cost. Other advantages of unsaturated polyester resins over other thermosetting resins are that they are easy to handle, can be pigmented, and easily filled and fiber reinforced in a liquid form. The cross-linking reaction between unsaturated polyester resins and vinyl monomers, i.e., styrene, allows one polymer chain to connect with other polymer chains, and to produce a three dimensional network, which converts resin from a viscous liquid into a hard, thermoset solid. In the room temperature processes without any external heating source, polymer chains become more difficult to move when reaction kinetics becomes diffusion control after gelation and vitrification. This impedes unsaturated polyester resins to complete reaction for achieving high final conversion and low styrene residue when cured at low temperatures.

Residual styrene may cause problems to environment and also result in blisters and voids on the surface of molded products at elevated temperatures. Therefore, control and detection of styrene content in the fiber reinforced unsaturated polyester resin are very important. Many researchers have studied the effect of resin system, curing agent and reaction condition on residual styrene content of polyesters [Sakaguchi, 1974; Rodriguez, 1988; Fujii, 1997] by using various analytical instruments to measure the residual styrene content and to determine physical properties (e.g. heat distortion temperature, flexural strength, compressive yield strength, and tensile strength) of cured resins. Large difference exists between initiators and initiator combinations with respect
to their influence on the residual styrene content of molding panels. Most studies emphasized on the resin flexibility and initiator type. Few works were carried out to improve the reaction at later stage by increasing the reactivity of monomer, such as introducing more reactive comonomers, e.g. methyl methacrylate and trimethylolpropane trimethacrylate, into the resin system.

During the molding process, LPA is usually added into the resin system to compensate polymerization shrinkage of the UP resin. Although LPAs can provide shrinkage control in unsaturated polyester resin systems, it may reduce the reaction exotherm because it is a non-reactive component in the systems. Therefore, it is very important to design the resin systems, which can reduce styrene residue but without deteriorating molding shrinkage, appearance, gloss, etc when cured at low temperatures. In this study, an in-depth kinetic analysis is carried out and a better understanding of the reaction kinetics is sought for unsaturated polyester resins with different monomers and curing agents cured at low temperatures. The volume shrinkage of the resin system is also investigated.

4.2 Experimental

4.2.1 Materials

An unsaturated polyester resin, Aropol Q6585, provided by Ashland Chemical was used in this study. It is a 1:1 mixture of maleic anhydride and propylene glycol with an average of 10.13 vinylene groups per molecule and an average molecular weight of
1580 g mole\(^{-1}\), containing 35% by weight of styrene. The low profile additive used was
Neulon-T plus, a modified carboxylated poly (vinyl acetate), from Union Carbide (now Dow Chemical). All the samples being tested were formulated to provide a monomer
double bond to unsaturated polyester double bond ratio of 2.0, except in a few cases.

Cobalt octoate (6% cobalt octoate in mineral spirits, Pfaltz & Bauer) was
employed as the promoter to decompose the initiator at low temperatures. Inhibitor, 300
ppm benzoquinone (BQ, Aldrich), was used to control the curing process. The initiators
used included a single component initiator, methyl ethyl ketone peroxide (MEKP, Hi-
point 90, Witco), and a dual initiator system, i.e. MEKP/tert-butyl per oxybenzoate
(TBPB, Trigonox C, Akzo Noble). Trigonox C is a solution of 98% tert-butyl
peroxybenzoate with 8.0% activate oxygen, while Hi-point 90 contains 38% peroxide
with 9.0% activate oxygen. All materials were used as received without further
purification in order to mimic industrial applications.

4.2.2 Instrumentation and Procedure

4.2.2.1 Differential Scanning Calorimeter (DSC)

The overall reaction rate was measured by a DSC. Detailed procedures of DSC
measurement have been given in Section 3.2.2.1.

4.2.2.2 Fourier Transform Infrared (FTIR) Spectroscopy
Because it is difficult to get information by means of DSC measurements to differentiate overlapped multiple reactions, a computer-assisted Fourier Transform Infrared (FTIR) spectroscope (Nicolet, Magna 550II) with a resolution of 4 cm\(^{-1}\) in the transmission mode was used in this study for kinetic measurements of individual reaction of both St and UP C≡C bonds. FTIR has the ability to accurately monitor the complex reactions based on spectra changes of different functional groups. After the reactants were mixed, one drop of mixture was placed between two sodium chloride plates, which were then mounted on a sample holder located in the FTIR instrument. A temperature chamber was designed to maintain the reaction temperature. Four consecutive 10 seconds scans were taken at each sampling time and the sampling interval was 1 second to 5 minutes depending on the reaction rate during the reaction. Measurement was ended at a preset time. All IR spectra in this study are shown in the absorbance mode.

Infrared absorption is based on the fact that each chemical group in a sample absorbs infrared radiation of some characteristic frequencies. The amount of light intensity of transmission relative to the amount of light intensity incident on the sample can be related directly to the concentration of the absorbing species by Beer's law

\[ A_i = \beta_i l C_i \]  

where \( A_i \) is the absorbance of species which can be determined from the peak height or peak area, \( \beta \) is the absorptivity which is characteristic of absorbing species, \( l \) is the pathlength (sample thickness), and \( C_i \) is the concentration of absorbing species \( i \).
The FTIR analysis is based on the relationship between peak change and concentration of functional groups or characteristic linkage during the reaction period according to Beer’s law. Figure 4.1 shows typical FTIR spectra of unsaturated polyester resin during reaction. Consumption of styrene C=C bonds is indicated by changes of peak area at 912 cm⁻¹ and 992 cm⁻¹ (CH₂=CH deformation), while that of unsaturated polyester C=C bonds is indicated by a peak area change at 982 cm⁻¹ (trans CH=CH deformation) [Yang, et al., 1987]. To compensate the changes of thickness and opacity in the sample during curing of UP resin, the C-H peak at 2942 cm⁻¹ was chosen as the internal standard to normalize the interested spectra area.

Before applying Beer's law to the quantitative analysis, the calibration curves for styrene C=C bonds and unsaturated polyester C=C bonds were established by preparing a series of styrene-dibromomethane solution and unsaturated polyester-dibromomethane solution of known concentration. During calibration, the solutions were placed between two sodium chloride plates with a 25µm thick Teflon spacer to keep the sample in the same thickness. The calibration curves based on the change of peak area for styrene-912 cm⁻¹, styrene-992 cm⁻¹, and UP-982 cm⁻¹ are shown in Figure 4.2. A linear relationship between the peak area and monomer concentration was obtained for all three peaks. The absorptivity for each peak can be determined from the slope of the calibration line.

In the reaction system of unsaturated polyester and styrene, the styrene consumption during the reaction can be determined easily from the peak area change at 912 cm⁻¹ based on Beer’s law. Styrene conversion (\(\alpha_s\)) can then be determined according
Figure 4.1 Spectra of an unsaturated polyester resin during curing (St/UP C=C bond ratio=2/1, 0.5% CoOct, 1.5% MEKP, 60°C, 300ppm BQ).
Figure 4.2 FTIR calibration curves for peaks of styrene vinyl (912 cm\(^{-1}\) and 992 cm\(^{-1}\)) and UP vinylenic groups (982 cm\(^{-1}\)) at 35\(^\circ\) C.
to the following equation

$$\alpha_{st} = 1 - \frac{A_t}{A_0}$$ (2)

where $A_0$ and $A_t$ are normalized absorbance of the functional group before the reaction and at reaction time $t$ respectively. However, the consumption of polyester C=C bonds cannot be followed directly from peak 982 cm$^{-1}$ because it overlaps with peak 992 cm$^{-1}$ as shown in Figure 4.1. A subtraction method was used to separate the overlapping peaks [Yang, et al., 1987] and the unsaturated polyester conversion ($\alpha_{up}$) can be calculated according to the following equation:

$$\alpha_{up} = 1 - \frac{1}{BI} \left[ 1 - \left( \frac{A_t}{A_0} \right)_{982+992} \right] \left( 1 + BI \right) - \left( 1 - \alpha_{st} \right)$$ (3)

where $B=\beta_{982}/\beta_{992}$ and $I=(C_{up}/C_{st})_0$ which is the initial concentration ratio of UP ($C_{up}$) and styrene ($C_{st}$) C=C bond. The overall conversion of C=C bonds ($\alpha_T$) can be expressed as

$$\alpha_T = \frac{\alpha_{st} + I\alpha_{up}}{1 + I}$$ (4)

In the resin system with LPA, it is noticed that styrene, UP and LPA all have a weak absorption peak at 1020 cm$^{-1}$ that overlaps somewhat with the absorption peak at 992 cm$^{-1}$, and this make the calculation more complicated. However, the absorptivity at 1020 cm$^{-1}$ seems to be negligible because it is much weaker than the absorptivity at 992 and 982 cm$^{-1}$. In order to confirm this assumption, the absorbance of peak at 992 and 982 cm$^{-1}$ in the resin system at different St/UP ratios was determined by FTIR.
The absorbance of St C=C bond at 992 cm\(^{-1}\) in St/UP or St/UP/LPA mixture can be calculated on the basis of Beer’s law.

\[
A_{992} = \left( \frac{\beta_{992}}{\beta_{912}} \right) A_{912} = CA_{912} \tag{5}
\]

where the absorbance of St at 912 cm\(^{-1}\) can be easily obtained because there is no other absorbance peaks in this region. Constant C was obtained by plotting the absorbance at 912 cm\(^{-1}\) vs. that at 992 cm\(^{-1}\) at different styrene concentrations in dibromomethane. A linear relationship can be clearly seen in Figure 4.3 and C has a value of 0.48. \(A_{982}\) in the resin mixtures can then be determined by subtracting \(A_{992}\) from the overall peak area of overlapped peaks. As shown in Figure 4.4, peak area ratio vs. concentration ratio gives a linear relationship for the two interested peaks, 982 cm\(^{-1}\) and 992 cm\(^{-1}\), and verifies the constant B according to Beer’s law \(A_{982}/A_{992} = B (C_{UP}/C_{St})\). Therefore, the absorbance at 1020 cm\(^{-1}\) due to LPA can be neglected and Equations 2 to 4 can also be used to calculate the individual and overall conversion of resin system with LPA.

### 4.2.2.3 Volume Shrinkage Determination

Density and volume change of the cured sample were also measured in this study. About five grams of a liquid resin with initiators were sealed in a plastic pouch with a surface dimension of 70×60 mm and a thickness of near 1mm. The sealed sample pouch was degassed under vacuum and the air bubbles inside the pouch were squeezed out through a hole made at the edge of the pouch. The pouch was then heat sealed again and
Figure 4.3 Calibration of absorption at 912 cm$^{-1}$ and 992 cm$^{-1}$ of styrene vinyl groups in FTIR.
Figure 4.4 Calibration curve of polyester vinylene and styrene vinyl groups in FTIR.
placed in an oven to cure isothermally. The density of the cured samples was determined by weighing the samples in air and in water respectively at 25°C. The density of the cured sample ($\rho_s$) and the volume shrinkage were calculated according to the following equations:

$$\rho_{s0} = 1/\sum_{i=1}^{n}(W_i / \rho_i)$$  \hspace{1cm} (6)

$$\rho_s = \rho_{_{H_2O}} \times W_i / (W_i - W_w)$$  \hspace{1cm} (7)

Volume Shrinkage ($\%$) = \((1 - \rho_{s0} / \rho_s) \times 100\)  \hspace{1cm} (8)

where $\rho_{s0}$ is the theoretical density of the resin before cure calculated by the summation of the weight content ($W_i$) and density ($\rho_i$) of each component $i$, and $n$ is the total number of components in the resin system before cure. $\rho_{_{H_2O}}$ is the density of water at 25°C. $W_s$ and $W_w$ are the sample weight when weighed in air and in water respectively.

4.2.2.4 Glass Transition Determination

The glass transition temperature, $T_g$, is one of the most important material parameters for glassy polymers. It is not easy to determine the $T_g$ of low temperature cured samples by the conventional method since all of the samples are partially cured. Several researchers reported that the derivative of the heat flow curve during a DSC scan of the partially cured sample at 5°C/min could be used to determine $T_g$. A peak
temperature in the plot of heat flow derivative vs. temperature has been used to represent
the partially cured sample [Lee, et al., 1994; Yang, et al., 2002]. Others have chosen the
temperature when the residual reaction starts to occur during the scanning run of the
partially cured sample [de la Caba, et al., 1996]. $T_g$ of the post-cured UP/St/LPA resins
was measured through dynamic mechanical analysis, which was performed using a
rheometer (Rheometrics Solid Analyzer, RSAII). Samples with the dimensions of 30 mm
x 13 mm x 2 mm were first cured in a 35°C oven with different MMA contents for 600
minutes, and then heated in the RSA chamber through scanning at 5°C/min from room
temperature to 250°C. A sinusoidal deformation is applied to the sample in the three
bending mode at a frequency of 1 Hz. The support span is 20 mm and the strain imposed
is 0.015%. Runs were carried out from room temperature to 250°C at a heating rate of
2°C/min. $T_g$ values were determined from the tanδ peaks [Guo, et al., 1999], which are
shown in Figure 4.5.

4.2.2.5 Scanning Electron Microscopy (SEM)

Sample morphology was observed by a SEM. Detailed procedures of SEM have
been given in Section 3.2.2.4.
Figure 4.5 Determination of $T_g$ of post-cured sample from RSA scanning (St/UP=2, 3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).
4.2.2.6 Properties of SCRIMP Panels

The surface quality of the molded samples was measured by a profilometer, Federal’s Surfanalyzer 4000. During test, a hinged probe rides along the surface of the part, and the stylus tip moves up and down in relation to the probe body. The chosen tracing length was 2.54 cm. Each sample was tested randomly at six different spots, and the average value was calculated as the final result.

The average roughness (Ra) is used to quantify the surface quality. Ra is the arithmetic average deviation of the roughness profile from the roughness centerline. It is computed as the following equation:

$$Ra = \frac{1}{N} \sum_{i=1}^{N} y_i$$

where N is the number of points in the roughness profile and yi is the individual point in the roughness profile. A smaller value of Ra represents a better surface quality.

To characterize the flexural properties of the composite, a three-point bending test according to ASTM D790-96a was selected. For flexural measurements, five rectangular bars of 130 mm long and 13 mm wide were cut from each sample. The rate of cross-head motion was 2.8 mm/min. The load was recorded as a function of displacement for 5 samples of each material. Values of modulus and strength at failure were obtained from the resultant load-displacement curves and the average values were reported.
4.3 Results and Discussion

4.3.1 Reaction Kinetics and Final Conversions of Unsaturated Polyester Resins

4.3.1.1 Effect of Initiators

The type of initiator can influence the residual UP unsaturation and styrene monomer in the curing of unsaturated polyester resins [Rodriguez, 1988; Fujii, 1997]. An earlier study found that a low residual styrene content could be obtained with high levels of peroxide in polyester resins cured at room temperature [Roskott, et al., 1978]. However, a high initiator content may shorten the gel time. A sufficiently long gel time is very important for mold filling and fiber wetting. Recently, more effort has been given to the design of efficient curing agent systems to achieve desired performance at low temperature cure, i.e. high final conversion, long pot life, and short cycle time [Li, et al., in press; Fujii, 2002].

Most high temperature molding processes involving UP resins use a combination of two or three peroxides. They work in a stepwise fashion. The low temperature peroxides start to decompose first, while the higher temperature peroxides are slow to decompose in the beginning, but become highly activated to propel the reaction towards the end due to reaction exotherm. This concept can be used in low temperature molding processes as well by choosing different initiator combinations.

In this study, MEKP/TBPB was chosen as a dual initiator combination since both MEKP and TBPB can be accelerated with metal-based promoters. MEKP alone can be
used as an initiator when the temperature is higher than 60°C. At ambient temperature, it decomposes into free radicals very slowly and cannot cure unsaturated polyester resin without promoters. In the presence of cobalt octoate or naphthenate, it can be decomposed rapidly for fast polymerization and to achieve short curing cycle. On the other hand, TBPB is a typical high temperature initiator with a half-life of one hour at 122°C (Trigonox C). The effect of cobalt on the decomposition of TBPB at low temperature is not as significant as on MEKP.

Figure 4.6 shows the scanning DSC results of the unsaturated polyester resin with 3.5% LPA cured at a heating rate of 2°C/min by different initiator combinations. Under this scanning rate, the reaction in the system initiated by 0.4% TBPB occurs only when the temperature reaches 110°C, which is intrigued by the thermal decomposition of peroxybenzoate. In the presence of promoter (CoOct), the redox initiation takes place so that the reaction may occur at a lower temperature, i.e. 90°C, as compared to the case without any promoters. When the resin system is initiated by 1.3% MEKP, the reaction could occur when the temperature is 75°C at the absence of CoOct, and at 30°C with 0.5% CoOct.

TBPB alone (even with 0.5% CoOct) cannot be considered a low temperature initiator because the reaction temperature needs to reach almost 90°C to ensure the occurrence of reaction. However, TBPB is more active compared to MEKP at high temperatures. For systems initiated by TBPB, when the temperature reaches the decomposition temperature of TBPB the reaction takes place and completes rapidly with
Figure 4.6 DSC scanning profiles of UP/St/LPA system initiated by MEKP and TBPB (3.5% LPA, no BQ, scan at 2 °C/min).
a very narrow reaction peak. Although MEKP decomposes at a lower temperature, the reaction is gradual and has a broad peak. Therefore, TBPB is a good initiator to finish the reaction if the reaction exotherm can reach its decomposition temperature.

The resin systems were also initiated by a dual initiator of MEKP/TBPB. A combination of MEKP and TBPB was found to have a synergistic effect on the reaction of unsaturated polyester resin systems. As shown in Figure 4.6, the reaction of a system initiated by MEKP/TBPB without CoOct occurs at a lower temperature than the system initiated by either MEKP or TBPB. This is probably because the decomposition of TBPB can be induced by free radicals already existing in the system, such as radicals derived from MEKP [Blomquist, et al., 1951; Davies, 1961]. In the presence of 0.5% CoOct, the reaction initiated by MEKP/TBPB has almost the same profile as that by MEKP alone at a temperature lower than 75°C. However, a reaction peak is observed at 88°C by using MEKP/TBPB, which is lower than the decomposition temperature of TBPB with 0.5% CoOct. These results clearly demonstrate that the effective temperature of TBPB in the presence of CoOct can be as low as 75°C when TBPB is combined with MEKP. Therefore, if the reaction exotherm increases the system temperature to 75°C, the presence of TBPB may push the reaction to a higher conversion.

In order to study the efficacy of dual initiator on the final conversion of resin systems, unsaturated polyester resins with LPA cured by different initiator combinations under the same temperature profile were carried out in FTIR. The temperature profile was chosen according to the reaction exotherm profile of a UP/St/LPA system cured at
room temperature. The system temperature was raised from 25°C to 110°C at a rate of nearly 6°C/min, and then decayed to 25°C. As shown in Figure 4.7, the resin reaches nearly complete conversion when initiated by the dual initiator MEKP/TBPB, while the conversion is lower when initiated by MEKP alone even at a higher MEKP content. It is also observed that the reaction initiated by the dual initiator completes earlier than the reaction by MEKP only. The reaction rate profile shows an additional reaction peak in the resin system initiated by the dual initiator after 12 minutes (when the temperature reaches around 90°C) and the reaction completes very quickly. This agrees well with the DSC results shown in Figure 4.6. The final individual conversions of St and UP in Table 4.1 show that St and UP residue can be as low as 0.06 and 0.25 wt% respectively when initiated by the dual initiator, which is much lower compared to 2.44 and 2.69 wt% respectively when initiated by 2.0% MEKP at the same condition. An extra amount of MEKP does not provide the same efficacy as the dual initiator for resin conversion.

4.3.1.2 Effect of Temperatures

Reaction exotherm plays an important role in the curing of polyester resins. The peak temperature depends, among other factors, on the curing system and the thickness of samples. In low or ambient temperature cure, the peak temperature may reach 200°C for very thick pure resin samples, or only 40°C for thin samples with a large amount of fillers and fibers in typical composite molding processes. In order to study the effect of temperature on the reaction kinetics and final conversion of UP/St/LPA systems cured by
Figure 4.7 FTIR (a) reaction rate and (b) conversion profiles of UP/St/LPA systems initiated by MEKP and TBPB (3.5% LPA, 0.5% CoOct, 300ppm BQ).
Table 4.1 Final individual and overall conversions and residual contents in UP/St/LPA systems at different cure temperatures and using different initiators (3.5% LPA, 0.5% CoOct, 300ppm BQ).

<table>
<thead>
<tr>
<th></th>
<th>Temperature</th>
<th>α_{Total} (%)</th>
<th>α_{St} (%)</th>
<th>α_{UP} (%)</th>
<th>Residual (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td></td>
<td></td>
<td></td>
<td>St</td>
</tr>
<tr>
<td><strong>1.3% MEKP 0.4% TBPB</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>78.7</td>
<td>77.8</td>
<td>80.6</td>
<td><strong>12.3</strong></td>
<td>8.0</td>
</tr>
<tr>
<td>60</td>
<td>96.1</td>
<td>98.4</td>
<td>91.5</td>
<td><strong>0.9</strong></td>
<td>3.5</td>
</tr>
<tr>
<td>75</td>
<td>98.0</td>
<td>99.5</td>
<td>94.9</td>
<td><strong>0.3</strong></td>
<td>2.1</td>
</tr>
<tr>
<td>100</td>
<td>99.6</td>
<td>100.0</td>
<td>98.4</td>
<td><strong>0.0</strong></td>
<td>0.7</td>
</tr>
<tr>
<td><strong>1.3% MEKP 0% TBPB</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>72.0</td>
<td>68.2</td>
<td>79.7</td>
<td><strong>17.6</strong></td>
<td>8.4</td>
</tr>
<tr>
<td>60</td>
<td>86.9</td>
<td>86.9</td>
<td>87.0</td>
<td><strong>7.2</strong></td>
<td>5.4</td>
</tr>
<tr>
<td>75</td>
<td>87.4</td>
<td>87.2</td>
<td>87.5</td>
<td><strong>7.1</strong></td>
<td>5.2</td>
</tr>
<tr>
<td>100</td>
<td>98.8</td>
<td>99.2</td>
<td>98.1</td>
<td><strong>0.5</strong></td>
<td>0.8</td>
</tr>
<tr>
<td><strong>1.3% MEKP non-isothermal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90.7</td>
<td>90.2</td>
<td>91.9</td>
<td><strong>5.44</strong></td>
<td>3.35</td>
<td></td>
</tr>
<tr>
<td><strong>2.0% MEKP non-isothermal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>94.9</td>
<td>95.6</td>
<td>93.5</td>
<td><strong>2.44</strong></td>
<td>2.69</td>
<td></td>
</tr>
<tr>
<td><strong>1.3% MEKP 0.4% TBPB non-isothermal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>99.7</td>
<td>99.9</td>
<td>99.4</td>
<td><strong>0.06</strong></td>
<td>0.25</td>
<td></td>
</tr>
</tbody>
</table>
different initiator combinations at different temperatures, a series of isothermal experiments were carried out at 35, 60, 75, 100°C in both DSC and FTIR. In Figure 4.8, the resin conversion profile at 100°C measured by FTIR shows the same trend as the DSC profiles, but is slightly different from DSC results especially at the later stage of the reaction. The difference exists because of instrument variation and the sensitivity limitation of DSC at high conversion. Within experimental error, the results from both methods agree with each other fairly well. Figure 4.9 shows that the reaction rate and final resin conversion of UP/St/LPA increase with the reaction temperature as expected. This occurs because the chains of the polymer network become more mobile and the resin can further react at higher temperatures, resulting in higher final conversion and lower styrene residue. When the resin systems are initiated by MEKP only, the final conversion at each temperature is not as high as the conversion in the dual initiator system. This effect is more obvious at lower temperatures.

The reaction of polyester resin is a copolymerization between styrene and unsaturated polyester C=C bonds. The structure formation depends on the relative reaction rates of styrene vinyl to unsaturated polyester vinlylene groups. Figure 4.10 shows the relative reaction rates of styrene vs. unsaturated polyester C=C bonds measured by FTIR at different temperatures with different initiator combinations. The dashed lines shown in the figure represent two extreme cases: the upper one is under the azeotropic condition and the lower one is for alternating copolymerization. As can be seen from this figure, the actual reaction profiles lie between these two extremes and are concave upward. In the beginning, the curves are nearly linear (with a slope around
Figure 4.8 DSC and FTIR resin conversion profiles of unsaturated polyester with different initiators cured at 100°C isothermally (3.5% LPA, 0.5% CoOct, 300ppm BQ).
Figure 4.9 DSC (a) reaction rate and (b) resin conversion profiles of UP/St/LPA at various temperatures and initiator combinations (3.5% LPA, 0.5% CoOct, 300 ppm BQ).
Figure 4.10 Relative conversion of styrene vs. unsaturated polyester C=C bonds at various temperatures and initiator combinations (3.5% LPA, 0.5% CoOct, 300 ppm BQ).
In the later stage, the reaction of the unsaturated polyester vinylene group slows down after 70% conversion, while the styrene reactivity remains relatively high depending on the reaction temperature and initiator used. The results imply that, at low conversion, both styrene and unsaturated polyester molecules are active, and the copolymerization follows a constant consumption rate of both monomers. At higher conversion, due to the low mobility of unsaturated polyester vinylene groups in the highly crosslinked network, most of the reaction occurs between styrene vinyl groups. The addition of TBPB further increases the reaction of St at the later stage since it can provide free radicals then.

Table 4.1 summarizes the final residual St and UP content of UP/St/LPA systems cured at different temperatures and using different initiator combinations measured by FTIR. As the temperature increases from 35 to 100°C, the residual St content decreases from more than 10% to nearly 0% when initiated by the dual initiator systems. It was also observed that the final conversion of systems initiated by MEKP only was lower compared to that initiated by the dual initiator system. It is clear that St monomers can further react in the presence of TBPB when the UP vinylene double bonds become immobile.

### 4.3.1.3 Effect of Comonomer

During the free radical copolymerization of unsaturated polyester (UP) and styrene (St), crosslinking causes the formation of a three dimensional network, which
results in gelation and microgel formation [Hsu, et al., 1993]. The reaction becomes diffusion controlled near and after gelation since the mobility of free radicals and reactants is impeded by the network structure. Unsaturated polyester is much less mobile than styrene monomer because of the size and the functionality of molecules. Polyester molecules are trapped in the network, which makes further reaction very difficult [Yang, et al., 1987]. Therefore, at high conversion, the styrene reaction is more favorable than the polyester reaction. However, the homopolymerization rate of styrene is very low [Li, et al., 200c], so it is difficult to achieve a high final conversion especially at low temperatures. The reaction at later stage may be enhanced at the presence of comonomers that have a high copolymerization reactivity with styrene, such as acrylonitrile, methyl methacrylate, isoprene, etc.

In order to study the effect of comonomer on reaction rate and final conversion of UP/St/LPA resin systems, a series of experiments were carried out at 35°C isothermally. The comonomer chosen was methyl methacrylate (MMA) because the copolymerization between MMA and styrene is much higher than that of styrene homopolymerization. The monomer reactivity ratios in copolymerization, i.e. the ratios of the rate constant for a given radical adding its own monomer to that for adding the co-monomer, in the styrene (M1)-methyl methacrylate (M2) system are: $r_1=0.28\sim0.59$ and $r_2=0.31\sim0.54$. Both $r_1$ and $r_2$ are less than one, meaning that the radical prefers to add the co-monomer in the St/MMA copolymerization with a selectivity about 2 in this case [Billmeyer, 1984; Greenley, 1999].
The effect of MMA content on the reaction kinetics measured by both DSC and FTIR is shown in Figure 4.11. The monomers, styrene and MMA, to unsaturated polyester vinylene double bond ratio remains at 2/1 for all of the samples. One can see that the reaction of UP/St/LPA systems slows down and the onset of auto-acceleration occurs at a later time as more MMA is added into the resin system. The highest reaction rates for different MMA contents are similar except for the system with a MMA/St molar ratio of 1. This system has a lower peak reaction rate and a longer reaction time at 35°C. However, the final resin conversion is higher as more MMA is added into the UP/St/LPA systems.

MMA monomer contains 10-100 ppm monomethyl ethyl hydroquinone (MEHQ) as inhibitor while St monomer contains 10-15 ppm tert-butylcatechol (TBC) as inhibitor. The amount of MEHQ and TBC changes as more MMA is introduced into the resin system. Since each inhibitor has its own inhibition efficiency [Flory, 1953], this may result in a different reaction onset time. In order to keep a constant inhibitor content in the resin system, the inhibitors in St and MMA were removed. Solid UP resin and LPA were then dissolved in the inhibitor-removed monomers. 100 ppm benzoquinone (BQ) was then added put into the resin mixture during sample preparation in the DSC study to prevent premature reaction. Figure 4.12 shows reaction profiles of the resin systems. The reaction of the UP/St/LPA systems still slows down and the onset of auto-acceleration occurs at a later time as the MMA in the resin system increases. This indicates that the type and amount of inhibitor in the reactants do not significantly
Figure 4.11 Effect of comonomer (MMA) content on (a) reaction rate and (b) resin conversion of UP/St/LPA cured at 35°C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BO).
Figure 4.12 Reaction rate profiles of UP/St/LPA resin systems with different comonomer (MMA) content cured at 35°C as inhibitor is removed from all reactants (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 100 ppm BQ).
influence the reaction trend in the resin system. Another possible factor is the reactivity
difference between MMA and St and it could be the main reason.

The UP/St/LPA system with MMA is a very complicated reaction. There are
three reactive components in the system, and the reactivity among them may affect the
reaction rate and final structure of the cured resin. Figure 4.13 summarizes the relative
conversion profiles for St/UP C=C bond pair and St/MMA C=C bond pair at different
MMA content. Compared to the system without MMA, St C=C bond in the resin system
with MMA shows relatively higher conversion when UP C=C bond reaches the same
conversion, and up-bending of the curve at later stage becomes less obvious. The
conversion of St C=C bonds is higher than that of MMA C=C bonds at early stage since
the conversion of St C=C bonds is higher than the azeotropic polymerization line.

Table 4.2 summarizes the residual St, MMA, and UP content of UP/St/LPA
systems with different MMA contents cured at 35°C. The residual St content decreases
from more than 10% to 0.3% as the MMA content in the system increases. The final UP
residue also decreases, except for the system with a MMA/St molar ratio of 0.1. On the
other hand, more residual MMA is found in the cured sample when the MMA content
increases. However, the total amount of styrene and MMA residue decreases.

Unsaturated polyester used in this study is a step growth product of maleic
anhydride (MA) and propylene glycol (PG). The conventional polyesterification
procedures lead to substantial isomerization of maleate to fumarate. From the literature,
Figure 4.13 Relative conversion of St vs. UP and MMA C=C of UP/St/LPA with different MMA contents cured at 35°C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).

143
### Table 4.2 Final individual and overall conversion and residual content in UP/St/LPA systems with different MMA contents cured at 35°C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ).

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>$\alpha_{Total}$ (%)</th>
<th>$\alpha_{St}$ (%)</th>
<th>$\alpha_{UP}$ (%)</th>
<th>$\alpha_{MMA}$ (%)</th>
<th>Residual (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/1/5.5</td>
<td>80.8</td>
<td>81.1</td>
<td>78.9</td>
<td>88.2</td>
<td>9.6 8.7 0.6</td>
</tr>
<tr>
<td>10/4/7</td>
<td>86.3</td>
<td>86.8</td>
<td>81.2</td>
<td>94.3</td>
<td>5.3 7.8 0.9</td>
</tr>
<tr>
<td>10/8/9</td>
<td>90.9</td>
<td>97.2</td>
<td>86.4</td>
<td>88.2</td>
<td>0.9 5.7 2.8</td>
</tr>
<tr>
<td>10/10/10</td>
<td>93.1</td>
<td>98.8</td>
<td>95.0</td>
<td>85.6</td>
<td>0.3 2.1 3.9</td>
</tr>
</tbody>
</table>
there is 95% fumarate structure in PG-MA type of unsaturated polyester resins [Trivedi, et al., 1982]. Therefore, it is reasonable to assume that the reactivity of UP vinylene is close to that of diethyl fumarate (DEF). The monomer reactivity ratios among St, MMA, and DEF are given in Table 4.3 [Greenley, 1999]. As can been seen from this table, the homopolymerization rate of unsaturated polyester molecules (DEF C=C bonds) is very low and UP C=C bonds can polymerize with St and MMA much easier. In fumarate/MMA C=C bond pair, it was found that the fumarate content in the copolymer of DEF and MMA is much lower than that in the initial feed though $^1$H NMR study [Masahiro, et al., 1992]. Since $r_2$ (M$_2$=MMA) is larger than 1, MMA prefers homopolymerization than copolymerization with the fumarate UP resin. Therefore, UP C=C bonds would react more favorably with St when MMA is introduced into the resin system. This results in a higher St conversion than MMA as shown in Figure 4.13b.

In this study, the monomer (both St and MMA) double bonds to unsaturated polyester double bonds ratio was fixed at 2.0. Adding MMA into the resin system results in a lower St/UP double bond ratio (decreases from 2/1 to 1/1). As shown in Figure 4.14, the St C=C bond conversion at the same UP conversion increases, but the final St C=C bond conversion remains nearly the same as St/UP double bond ratio decreases from 3 to 1. Similar results were also reported in the literature [Huang, et al., 1992, 1993 a and b]. Therefore, a decreased initial St content would not substantially reduce St residue. After reaction becomes diffusion control, the copolymerization between UP and St becomes more difficult since UP C=C bonds or radicals are bonded to the network structure. The
<table>
<thead>
<tr>
<th>Monomer 1</th>
<th>Monomer 2</th>
<th>$r_1$</th>
<th>$r_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEF</td>
<td>St</td>
<td>0.02~0.11</td>
<td>0.29~0.63</td>
</tr>
<tr>
<td>DEF</td>
<td>MMA</td>
<td>0.04~0.05</td>
<td>2.1~40.3</td>
</tr>
<tr>
<td>St</td>
<td>MMA</td>
<td>0.28~0.59</td>
<td>0.31~0.54</td>
</tr>
</tbody>
</table>

Table 4.3 Monomer reactivity ratios [Greenley, 1999].
Figure 4.14 Relative conversion of St vs. UP C=C bond of UP/St/LPA resin systems with different St/UP C=C bond ratios cured at 35°C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).
remaining reaction would mainly be St homopolymerization if there were no MMA in the resin system. Since copolymerization between St and MMA is much easier than St homopolymerization, the presence of MMA would reduce residual St content.

Besides the reason mentioned above, the addition of MMA into the resin system may affect the flexibility of the polymer network. $T_g$ of the post-cured samples with various amount of MMA after cured at 35°C isothermally was compared in Figure 4.15 because resin system can achieve higher final conversion with high MMA content and $T_g$ depends greatly on the resin conversion [Gillham, et al., 1994; Wisanrakkit, et al., 1990]. As shown in Figure 4.15, the $T_g$ of post-cured samples decreases with an increase of MMA content in the resin system, except that $T_g$ of the sample with a MMA/St molar ratio of 0.1 is lower than the sample of a MMA/St ratio of 0.4. It has been reported in the literature that introducing MMA segments into polystyrene would influence $T_g$ of the MMA/St random copolymer [Schneider, et al., 1997]. When the MMA molar fraction in St/MMA monomer mixture is less than 0.6, the $T_g$ of the random copolymer shows a negative deviation and the copolymer chain tends to be more flexible [Schneider, et al., 1997]. With the MMA/St molar ratio ranges from 0 to 1.0 in this study, molar fraction of MMA is from 0 to 0.5 if considering the mixture of St and MMA only. The molar fraction of MMA remains less than 0.6 till UP C=C bond conversion reaches 80% as shown in Figure 4.16, which may lead to a lower $T_g$ of the network compared to the system with only styrene as the crosslinking monomer. This may result in higher chain mobility in the network structure during reaction, consequently, reaction is relatively easy.
Figure 4.15 Glass transition temperature ($T_g$) as a function of MMA content in UP/LPA/St resin systems (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ).
Figure 4.16  MMA molar fraction based on St and MMA only vs. UP C=C bond conversion in the UP/St/LPA resin systems with different MMA contents cured at 35°C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).
to go further after it becomes diffusion control and a higher final conversion can be achieved. The detailed mechanism needs further investigation.

4.3.2. Volume Shrinkage of Unsaturated Polyester Resins

Unsaturated polyester resins have very large volume shrinkage during polymerization. There are several problems associated with the high shrinkage of UP resins, including sink mark formation, surface waviness, warpage, poor dimension accuracy, internal crack, etc. These problems can be solved by adding LPAs. The shrinkage control mechanism of LPAs has been investigated extensively. Although not fully understood, it is generally accepted that the shrinkage compensation is due to the stress-related micro-void formation in the LPA phase and interfacial regions between the LPA and UP resin [Li, et al., 1998a; Hsu, et al., 1991; Suspene, et al., 1991; Huang, et al., 1995]. A phase separation between the LPA and UP resin during curing is necessary for stress cracking because it provides an LPA-rich phase and an interface between the UP-rich and LPA-rich phases. The phase separation is related not only to the chemical structure, molecular weight, and dipole moment of LPAs [Li, et al., 1998a; Atkins, 1978; Huang, et al., 1996], but also to the structure and composition of UP resin and monomer [Li, et al., 1998a]. UP resin structure may affect the miscibility between the UP resin and LPAs and change the reactivity of the system as well. Consequently, it may affect the reaction kinetics and the phase separation simultaneously. This, in turn, may influence the microstructure formation and the overall LPA performance. The micro-void and
micro-crack formation for volume shrinkage compensation is influenced by the relative reaction rate in the LPA-rich and the UP-rich phases, which also depends on the resin and LPA structure and the reaction temperature and curing agent [Li, et al. 2000c; Cao, et al., 2001]. The results in the previous sections show that both the curing agent and reaction temperature, and comonomer have strong influence on the reaction kinetics and final conversion of UP/St/LPA resins systems. In this section, the effect of reaction temperature on volume shrinkage control of UP/St/LPA resins initiated by dual initiator is studied.

Figure 4.17 summarizes the volume shrinkage of UP/St/LPA initiated by the dual initiator MEKP/TBPB at different temperatures. Samples were cured in an oven at preset temperatures. In order to achieve a nearly isothermal condition, five grams of sample were cured in a plastic pouch with a large surface area and the sample thickness was about 1 mm. This figure shows that LPA performance in samples with the same formulation varies as curing temperature changes. The volume shrinkage of the sample becomes larger as the temperature increases from 35°C to 75°C, but is smaller when the curing temperature reaches 100°C. Li and Lee [1998] explained the shrinkage control behavior of UP/St/LPA systems cured at different temperatures by two competing factors: shrinkage caused by polymerization and expansion induced by micro-void formation. A difference in curing temperature may also cause a remarkable change on sample morphology. It can affect the size and the amount of micro-voids formed in the materials, which in turn has an effect on the volume shrinkage of the systems [Zhang, et al., 2000]. As shown in Figure 4.18, the sample morphology reveals a two-phase
Figure 4.17 Volume shrinkage of UP/St/LPA systems cured at different temperatures (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm)
Figure 4.18 Morphology of St/UP/LPA samples cured at different temperatures (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ).
co-continuous structure at 35°C. One is a particulate phase (LPA-rich) in which spherical particles with diameters ranging from 1 to 5 µm are loosely packed. The other phase is a flake-like region (UP-rich) with domain sizes ranging from 10 to 20 µm. When the curing temperature reaches 60°C, a similar two-phase structure is again observed but it is no longer co-continuous. The particulate region is smaller and becomes the dispersed phase with a domain size less than 20 µm, while the flake-like region forms the continuous phase. By further increasing the curing temperature to 75 and 100°C, the structures of the samples become similar to that cured at 60°C except that the size of the particulate region is even smaller. The various morphological structures result in different interface areas, strongly affecting the shrinkage control.

The curing temperature may also influence the relative reaction rate in the LPA-rich and UP-rich phases, which is an important factor for micro-void formation. Therefore, it is important to investigate the effect of temperature on reaction in each phase. Since reaction-induced phase separation in resin polymerization is a dynamic and evolving process, it is impossible to track this continuously changing phase behavior. In this study, a temperature-forced phase separation method was used as a qualitative assessment on how the partition of chemical species during phase separation affects resin reaction and shrinkage control in the UP/St/LPA systems. The formulated UP, St, LPA, and BQ were mixed with either CoOct or MEKP/TBPB simultaneously so that a transparent (single-phase) mixture was obtained. The formulation was the same as that used in the kinetic and volume shrinkage study, except that the content of promoter or
initiators was doubled. The detailed procedures of temperature induced phase separation can be found in a previous paper [Cao, et al., 2001]. After two phases were separated, their reaction conversion and gel time were measured at different temperatures by mixing an equal amount of resin from the same phase of the two mixtures. The results are shown in Figure 4.19. It is obvious that the reaction in the UP-rich phase is much faster than in the LPA-rich phase at all temperatures. The dashed lines in the figure indicate the time when the LPA-rich phase gels. At this time, the UP-rich phase has a slightly lower conversion when cured at a higher temperature. Since the final conversion of the resin system cured at the higher temperature is higher, a larger extent of polymerization has occurred in the UP-rich phase after gelation of the LPA-rich phase. The large polymerization shrinkage in the UP-rich phase may have induced substantial micro-void formation that compensates the overall resin shrinkage [Cao, et al., 2001].

As the reaction temperature increases, the LPA may change from the glassy state to the rubbery state. This may provide a large thermal expansion to compensate polymerization shrinkage of the UP resins in the non-isothermal curing cases, and weaken the LPA-rich phase to facilitate micro-void formation in the isothermal curing cases. The $T_g$ of the LPA used in this study was measured by DSC to be 43-45°C. In the cured system, the $T_g$ of the LPA-rich phase should be higher than 43-45°C, but lower than 100°C ($T_g$ of polystyrene). Therefore, the thermal effect on LPA performance cannot be neglected in the temperature range used in this study.
Figure 4.19 DSC conversion profiles of LPA-rich and UP-rich phase of 
UP/St/LPA system cured at various temperatures (3.5% LPA, 0.5% 
CoOct, 1.3% MEKP, 0.4% TBPB, 300ppm BQ).
From the above discussion, many factors such as phase separation, relative reaction rates in the LPA-rich and UP-rich phases, and the T_g of the LPA will affect the final volume shrinkage of the cured resin. The resin systems with the same formulation but cured at different temperatures show different volume shrinkage because of the competition from all these factors. At 35°C, the LPA is in the glassy state. The system shows fairly good shrinkage control since it has a clear phase separation and a large interface area for micro-void formation. When the system is cured at 100°C, the thermal effect dominates and the resin system can again provide good shrinkage control. When the resin system is cured at the intermediate temperatures, the phase separation is not very clear and the thermal effect is not very strong; consequently, the shrinkage control turns out to be poor.

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The effect of the MMA content on volume shrinkage in UP/St/LPA systems is shown in Figure 4.20. In the absence of LPA, the volume shrinkage of the resin system depends on the polymerization shrinkage of monomer. The volume shrinkage of the resin system increases with more MMA added into the resin system. This may result from the addition of MMA into the polyester network structure, which increases the compactness of the St/MMA crosslinked UP network because MMA has closer polarity to the polyester molecule than St. Since styrene has a polymerization shrinkage of 15% and MMA has a shrinkage of 20% [Trivedi, et al., 1982], larger polymerization of MMA than St may also contribute to the higher volume shrinkage. In the presence of LPA, the volume shrinkage of the resin system with the MMA/St molar ratio of 0.1 is nearly the same as the system without any MMA. The LPA is more effective on shrinkage control since the intrinsic volume shrinkage of the resin system (the volume shrinkage of the resin system without LPA) is higher when compared with the system without any MMA (as shown in Figure 4.20). The performance of LPA becomes less effective when the MMA/St molar ratio is higher than 0.1 and LPA eventually functions like a filler when the MMA/St molar ratio reaches 0.8. This can be explained by the phase behavior of the UP resin system with LPA. The LPA used in this study is poly (vinyl acetate) that has a dipole moment of 1.6. When there is no MMA in the UP/LPA/St resin system, the highly polar UP resin (dipole moment of 2.0-2.5) becomes less polar (dipole moment less than 1.0) during curing due to polymerization and the introduction of the non-polar polystyrene segment (dipole moment of 0.3) into the network. LPA with a dipole moment of 1.6 tends to phase out during curing [Atkins, et al., 1976]. However, in the
Figure 4.20 Final shrinkage vs. MMA content in UP/LPA/St resin systems cured at 35 °C (0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).
presence of MMA, the polarity of the cured unsaturated polyester resin may not decrease as much as in the system without MMA, since MMA is more polar than styrene and PMMA has a dipole moment of 1.3. Consequently, LPA may be more compatible with the resin system and phase separation is less likely to take place. As more MMA is added, the cured sample changes from opaque to translucent or even transparent, and the volume shrinkage increases substantially.

The morphology of samples cured at 35 °C with different MMA content is shown in Figure 4.21. The morphology of the sample without any MMA is a two-phase co-continuous structure. One is a particulate phase (LPA-rich) in which spherical particles with diameters ranging from 1 to 5 µm are loosely packed. The other phase is a flake-like region (UP-rich). A similar two-phase structure is observed when the MMA/St molar ratio is 0.1 in the resin system. The particle diameter is still in the range of 1 to 5µm and is loosely packed. The domain size in the sample with the MMA/St molar ratio of 0.4 is much smaller than the sample with the MMA/St molar ratio of 0.1. Further increase of the MMA content results in a very uniform and flat-like morphology. It clearly demonstrates that the system becomes more compatible when more MMA is added. Since a strong phase separation between the LPA-rich and the UP-rich phases during curing is necessary for stress cracking and micro-void formation [Li, et al., 2000], the effect of volume shrinkage control of the resin system turns to be less effective when more MMA is added into the resin system.
Figure 4.21 Morphology of samples at different MMA/St double bond ratios cured at 35°C (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).
4.3.3 SCRIMP Molding

In order to understand the performance of the resin system with a comonomer MMA in the real molding process, a series of low temperature Seemann Composite Resin Infusion Molding Process (SCRIMP) experiments were carried out using a glass mold at 35°C as shown in Figure 4.22. Three layers of dry stitched E-glass fiber mats (QM6408 from Brunswich Technologies, Inc.) were laid upon a glass plate mold. Q6408 is a non-bindered and quadraxial mat, which is composed of five layers, i.e. 0°, 90°, +45°, -45° continuous E-glass fiber and one layer of 50 mm chopped E-glass fiber. Each layer was 150 mm long and 125 mm wide except for the bottom layer fiber mat, which was 25 mm longer to control the minimum mold filling time. The fiber stack was covered by a transparent polyester film to form a vacuum bag whose outer edges were sealed by tacky tape. A resin inlet and a vacuum outlet on opposite ends of the mold were also formed.

Before mold filling, vacuum was applied through the outlet, forcing the bag to press tightly against the fiber stack. The liquid resin with the curing agent was degassed to remove trapped air and then introduced into the fiber stack under vacuum through a supply line. The gel time of each resin system was determined when there was no liquid resin dropping off from the outlet. During molding, reaction exotherm was recorded by a Diana Chart recorder through a thermocouple placed in the center of the fiber stack. A Linear Variable Differential Transformer (LVDT) was placed on the top of the fiber stack to monitor the dimension change of the molded panel. The residual reactivity of the molded composite parts was examined 24 hours after molding by DSC in the scanning
Figure 4.22 Schematic of experimental set-up for SCRIMP.
mode of 5°C/min from room temperature to 300°C, based on a total reaction exotherm of the corresponding resin system according to a DSC kinetics study (the summation of reaction exotherm from the both isothermal run and residual scanning). Three samples were taken at the surface of each part and the average value was calculated. It was found that the calculated conversion (i.e., residual heat) varied with ±3%.

Figure 4.23 shows the molding results of the resin system without any MMA. At time zero the mold filling started and the time to complete mold filling was about 5 minutes. The resin started as a clear solution, then turned cloudy indicating phase separation. The resin gelled after phase separation at 90 minutes, which then led to an increase of temperature due to reaction exotherm. In the meantime, the LVDT position increased, indicating a thinner molding panel because of polymerization shrinkage. At 140 minutes, the temperature reached the maximum value (i.e., 38.2°C), then started to decline because of heat loss to the surroundings. The LVDT position kept increasing until 163 minutes. At about 175 minutes, a white spot could be seen in the molded panel and it eventually expanded to the whole panel area. The LVDT position then started to decrease suggesting expansion. The whitening of the molded panel is believed to be a result of micro-void formation in the resin phase. Similar temperature and LVDT profiles were observed in other experiments, except that the panel did not turn white in some cases.

The effect of the comonomer MMA on the SCRRIMP molding of UP resins, i.e. the phase separation time ($t_p$), gel time ($t_g$), and final conversion ($\alpha_f$), is summarized in
Figure 4.23 Temperature and LVDT profiles during SCRIMP molding (3.5% LPA, 0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).
Table 4.4. As seen in this table, the final resin conversion increases when more MMA is added into the resin system, which is consistent with the kinetics study.

The onset of phase separation was noted by the onset of turbidity (i.e., cloudy point), while the gel point was determined when the resin stopped to flow. It is interesting to note that an increase in the amount of MMA leads to a later phase separation and a delayed gelation. Moreover, the length of the phase separation period of resin systems with MMA is longer than that of resin systems without MMA, except when the MMA to St molar ratio is 0.1. The time difference \((t_g - t_p)\) of resin systems without any MMA was about 55 minutes, while for resin systems with the MMA to St molar ratio of 0.6 the time difference was 69 minutes. A larger \((t_g - t_p)\) generally provides more time for phase separation and a better shrinkage control of resins with LPA [Li, et al., 2000b]. However, the shrinkage of the resin system with a longer phase separation period is worse under this curing condition, which is indicated by a large volume shrinkage. A possible explanation is that the phase separation is influenced by the both thermodynamics of the resin system and phase separation kinetics. For the curing condition used in this study, the phase separation period \((t_g - t_p)\) is at least 55 minutes, which may be sufficiently long for phase separation. Thermodynamics (compatibility of the resin system) then becomes a determining factor. An increase of the MMA content results in a more uniform and flat-like morphology, which suggests poor phase separation and consequently, a poor shrinkage control of the resin system.
Table 4.4 SCRIMP Molding of UP/St/LPA systems with different MMA contents at 35°C (0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ).

<table>
<thead>
<tr>
<th>LPA (%)</th>
<th>MMA /St</th>
<th>$t_p$ (min)</th>
<th>$t_g$ (min)</th>
<th>$\Delta t$ (min)</th>
<th>$\alpha_f$ (%)</th>
<th>$S_f$ (%)</th>
<th>Ra (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>-</td>
<td>83</td>
<td>-</td>
<td>81.2</td>
<td>10.2</td>
<td>0.74</td>
</tr>
<tr>
<td>3.5</td>
<td>0</td>
<td>35</td>
<td>90</td>
<td>55</td>
<td>78.5</td>
<td>-1.2</td>
<td>0.34</td>
</tr>
<tr>
<td>3.5</td>
<td>0.1</td>
<td>38</td>
<td>84</td>
<td>46</td>
<td>80.8</td>
<td>-1.3</td>
<td>0.13</td>
</tr>
<tr>
<td>3.5</td>
<td>0.4</td>
<td>79</td>
<td>142</td>
<td>63</td>
<td>82.1</td>
<td>6.6</td>
<td>0.67</td>
</tr>
<tr>
<td>3.5</td>
<td>0.6</td>
<td>87</td>
<td>156</td>
<td>69</td>
<td>86.8</td>
<td>8.3</td>
<td>0.94</td>
</tr>
</tbody>
</table>

$t_p$: phase separation time; $t_g$: gel time; $\Delta t$: time period between $t_p$ and $t_g$; $\alpha_f$: final conversion; $S_f$: volume shrinkage of resin system.
4.3.4 Properties of SCRIMP Molded Composites

4.3.4.1 Surface Quality

Several photographs of the surface appearance are shown in Figure 4.24. It can be seen that the cosmetic appearance of resin systems with LPA and a MMA to St molar ratio less than 0.1 is much better than that of other samples. These panels have fewer fiber read-outs and a shiny surface indicated by a clear reflection image of fluorescent light bulbs off the surface. The other samples have a rougher surface and the fiber filament can be seen clearly on the composite surface. The composite panel with a MMA/St molar ratio of 0.6 appears transparent. The surface roughness $R_a$ is used to quantify the effect of MMA on the surface quality. The results are given in Table 4.4. As the MMA content increases, the surface roughness of UP composites with LPA exhibits a decrease first, followed by an increase and reaching a minimum value at the MMA/St molar ratio of 0.1. The surface of the composite panel with a MMA to St molar ratio of 0.6 is even rougher than the system without LPA. These results correlate quite well with the volume shrinkage results of resin systems without any fiber reinforcement.

4.3.4.2 Flexural Property

To characterize the flexural properties of the composites, a three-point bending test was carried out. The species size, span length and cross-head were determined according to the sample thickness. Figure 4.25 shows the flexural strength of composites
Figure 4.24 Photographs of SCRIMP molded composites under different conditions (0.5% CoOct, 1.3% MEKP, 0.4% TBPB, 300 ppm BQ)
Figure 4.25  Comparison of flexural strength of SCRIMP molded composites under different conditions (3.5% LPA). Dash lines are the results of composites without any LPA and MMA.  

- Original composite  
- 12 hr in 5 wt.% KOH  
- 24 hr in 5 wt.% KOH
under different conditions. As shown in this figure, the flexural strength rises as the MMA content in the resin system increases, except when the MMA/St ratio equals 0.1. This could be attributed to the fact that increasing the MMA content could elevate the final conversion of the cured resin system, leading to a favorable effect on the flexural strength. The slightly lower flexural strength of the composite with a MMA/St ratio of 0.1 is the result of final conversion and morphology from Table 4.2 and Figure 4.21. Compared to the resin system without any MMA, the system at this MMA content has a similar morphology of two-phase co-continuous structure (Figure 4.21). Since the volume shrinkage is lower, this sample has a higher volume fraction of micro-void. Since the crack would eventually propagate through the voided plane during the flexural testing of specimens, this higher volume fraction of micro-void could cause an adverse effect on flexural strength. For the composite without any MMA, a decrease in flexural strength was observed when compared with the neat resin system without any LPA. The flexural strength decreases from 458 MPa to 409 Mpa. The presence of LPA and the micro-void formation inside the composite panel could explain the decrease of strength. However, the composites with 3.5% LPA and a MMA/St molar ratio higher than 0.4 are stronger than the neat resin composite.

In order to characterize the corrosion resistance of composite, SCRIMP panels with different MMA content were soaked in the boiled KOH solution for a certain time and flexural strength was then measured afterward. The flexural strength decreases for all of the samples after 12 hours and 24 hours in a boiling 5% KOH solution. The strength of
the system with the MMA/St ratio larger than 0.4 is still higher than the composites with or without LPA in the absence of MMA. Therefore, the addition of MMA can improve the mechanical properties and corrosion resistance of unsaturated polyester composites. However, the volume shrinkage control and surface quality of composites suffer.

4.4. Conclusions

The residual styrene, volume shrinkage, and mechanical properties of unsaturated polyester resin with a low profile additive cured with low temperature curing agents under different reaction temperatures, initiator combinations, and comonomer contents were investigated. In the study of reaction kinetics, both DSC and FTIR were employed to obtain the overall and individual reaction rate and conversion profiles. It was found that the final conversion and residual styrene could be improved greatly by introducing a dual initiator system and the comonomer MMA into the resin system. The relative reaction profiles of styrene vs. UP C=C bonds indicate that the reaction of the unsaturated polyester vinylene group slows down in the later stage, while the styrene reactivity remains relatively high depending on the reaction temperature and initiator used. The results imply that the addition of TBPB further increases the reaction of St at the later stage. The relative reaction profiles of styrene, MMA and UP C=C bonds suggests that a higher consumption rate of St occurs compared to the system without MMA, indicating a favorite copolymerization of St and MMA.
The study on shrinkage control shows that LPA performs worse in the intermediate temperature range (e.g. 60 and 75°C). The effect of temperature on morphology, the relative reaction rate in the LPA-rich and UP-rich phases and micro-void formation all influence the final shrinkage. MMA has a negative effect on shrinkage control of UP/ST/LPA system because the system becomes more compatible with the addition of MMA, indicated by a uniform and flat-like morphology. Consequently, phase separation becomes more difficult, leading to poor shrinkage control. The surface quality and the flexural property of unsaturated polyester resin depend strongly on the volume shrinkage and final conversion of the resin system.
CHAPTER 5

SHRINKAGE CONTROL AND FINAL CONVERSION OF VINYLESTER RESIN
IN LOW TEMPERATURE MOLDING PROCESSES

SYNOPSIS

Vinylester resin is a major thermoset polymer used in low temperature composite manufacturing processes such as the Seemann Composite Resin Infusion Molding Process (SCRIMP). Volume shrinkage and residual styrene are important concerns for composites produced in such processes. A low shrinkage additive (LSA) is a typical agent added to control the volume shrinkage of vinylester resins during molding. In this chapter, effects of LSA content and temperature profile (temperature gradient and peak temperature) on volume shrinkage control of a vinyl ester resin were investigated. The reaction kinetics of the resin system was also studied. Based on experimental results an improved SCRIMP molding process was designed to increase resin conversion, reduce resin shrinkage, and provide composites with better properties.
5.1 Introduction

Unsaturated polyester (UP) resins and vinylester (VE) resins are two of the most successful materials used in the fabricated composite industry. Vinylester resins have excellent chemical and corrosion resistance coupled with outstanding heat performance, making them a good choice for fiber reinforced polymer (FRP) applications. The reactive unsaturation of vinylester resins is presented as terminal groups in the polymer, which can be cross-linked with vinyl monomers (such as styrene) in the same way as. However, unlike conventional polyesters, unsaturated polyesters unsaturated polyesters have no internal polyester linkages. Therefore, vinylester resins provide better corrosion resistance compared to unsaturated polyesters [Bruins, 1976; Juska, et al., 1996; Encyclopedia of Chemical Technology, 1996]. Vinylester resins are amenable to most high temperature processes such as compression molding of sheet molding compounds (SMC), injection molding of bulk molding compounds (BMC), pultrusion, etc. By using a redox (reduction-oxidation) initiation system, vinylester resins can also be processed at ambient temperature via hand lay-up, spray-up, and vacuum-assisted resin transfer molding (VARTM) processes.

In recent years, many researchers have focused on the development of low temperature and low pressure fabrication techniques that can significantly reduce the tooling cost. Techniques for low cost composite manufacturing processes such as low temperature, low pressure compression molding of SMC [Gaspari, 1996; Atkins, et al., 1996], resin transfer molding (RTM), and vacuum infusion liquid composite molding (e.g. Seemann Composites Resin Infusion Molding Process (SCRIMP) [Seemann, 1990;
Lazarus, 1996) have grown considerably in the industry. The molding temperature of these processes ranges from ambient temperature (e.g., SCRIMP) to 60°C (e.g., RTM), and up to about 100°C (e.g., low temperature SMC). This range of temperatures is much lower than that of high temperature processes, such as SMC compression molding (150°C) and BMC injection molding (≥ 150 °C).

During curing, the typical volume shrinkage of vinylester resins is about 7-10%. The volume shrinkage resulting from polymerization reduces the dimension accuracy of the molded products and may expose the fiber pattern on the composite surface. The fiber readout, together with other molding problems such as porosity, internal cracks, warpage, and poor dimension accuracy, limits usage of vinylester resin in many high-volume applications. The addition of low profile additives (LPAs), i.e. certain thermoplastics, can partially compensate or essentially eliminate polymerization shrinkage of UP resins [Arakawa, et al., 1992]. However, LPAs have been less effective with vinylester resins [Lin, 1990], especially when cured at low temperatures. Although thermoplastics used in vinylester resin systems do not show the same shrinkage control efficiency as low profile additives in unsaturated polyester resin systems, they can effectively reduce the surface defects and internal stresses resulting from polymerization shrinkage, and improve the properties of molded products. Therefore, they are usually called low shrinkage additives (LSAs). Attempts have been made to improve the surface properties (reduced volumetric shrinkage) by incorporating special thermoplastics into the vinylester resin [Chang, et al., 1992]. A saturated polyester formed from dibasic acid and an ethylene oxide/propylene oxide (EO/PO) block copolymer was developed for
shrinkage control of unsaturated polyester and vinylester resins [Chang, et al., 1992]. The block copolymer has an EO/PO molar ratio ranging from about 0.1 to 0.9 and the polyester has an acid value of greater than about 10 in order to thicken the SMC paste well. The authors concluded that for good physical properties and shrinkage control, the EO/PO block copolymer-based polyester is equally effective in the formulation of all vinylester resins, unsaturated polyester resins, or any combination of the two in high temperature SMC processes. In the presence of filler, the volume shrinkage could be lower than 1% at 150°C. Other authors [Chiyou, et al., 2000] found that volume shrinkage of the vinylester resin with filler and styrene-2-hydroxyethyl methacrylate copolymer (Mw=220,000, a low shrinkage additive with a specified functional group of hydroxyl, carboxyl or amino) could be reduced to 1.0% and the cured sample showed no warpage. Although these studies demonstrated good shrinkage control of vinylester resins in high temperature molding processes, there is little work on low temperature curing of vinylester resin systems.

In addition to shrinkage control, the residual styrene content or final conversion is recognized as an important issue in low temperature cure of vinylester resins. A low residual styrene content is important for both health considerations and physical properties of the cured composite. When vinylester resins are cured at low temperature by a redox (reduction-oxidation) initiation system, they cannot be fully cured under ambient conditions because of the low mobility of the crosslinked polymer chains. The reaction exotherm due to polymerization at ambient temperatures may lead to a rise in the resin temperature, which accelerates the curing reaction [Dow Chemical, 1989]. It was
found that a higher final conversion could be obtained with high levels of peroxide in polyester resins cured at room temperature [Roskott, et al., 1978]. However, a high initiator content may sacrifice molecular weight and mechanical properties of the cured resin and shorten the gel time. A substantially long gel time is very important for mold filling and fiber wetting. Recently, more effort has been given to the design of efficient curing systems to achieve desired performance (i.e. high final conversion, long pot life, and short cycle time) in low temperature molding processes [Li, et al, in press; Fujii, 2002].

Generally, curing agents like inhibitors or retarders are needed to prevent premature gelation and provide a sufficiently long time for mold filling. However, in room temperature processes where no external heat is applied, the addition of inhibitors or retarders results in a low curing rate and a long cycle time. The low curing rate prevents the accumulation of reaction exotherm, which in turn may lead to low resin conversion. Such a conflict (i.e. a long gel time in mold filling vs. a high curing rate in mold curing) is a very critical issue in composite fabrication, especially for manufacturing large parts.

In the study of redox initiation of t-butyl hydroperoxide in chlorobenzene [Hiatt, et al., 1968], it was found that the decomposition of initiators was retarded by the addition of a millimolar amount of substances providing strongly complex metal ions. For example, 2,4-pentanedione (acetylacetone, 2,4-P), an enolizable β–diketone, has been incorporated into the redox initiation system at a level of 0.05% to 0.3% to retard the gelation of vinylester resins at low temperatures [Brinkman, et al., 1968; Chetakian, et al.,
1971; Heck, et al., 1984]. The gel time can be extended by as much as tenfold, without adversely affecting the final cure and corrosion resistance of the finished composites [Brinkman, et al., 1968].

It was also found that the function of 2,4-pentandione (2,4-P) in unsaturated polyester and vinylester resins is dependent on resin acidity [Li, et al, in press; Heck, et al., 1984]. For less acidic VE and UP resins, 2,4-P functions as a retarder in the redox initiation. The non-acidic resin and 2,4-P may interact with the transition metal cations (such as cobalt ions) to form a six-membered chelate. This chelate ring is more stable than cobalt naphthenate. Consequently, the redox reaction between peroxide and cobalt ion becomes more difficult [Li, et al, in press]. On the other hand, 2,4-P is a co-promoter for acidic VE and UP resins due to the acid-liability of cobalt acetylacetonate compounds. As a good retarder for non-acidic resins, 2,4-P is capable of extending the gel time for mold filling. When externally adding acid to non-acidic resins, 2,4-P functions as a co-promoter. A resin design based on this concept was proposed [Li, et al, in press], in which 2,4-P was added to the resin system at a high content (i.e. 0.15%) to achieve a long resin gelation time. An acid such as maleic anhydride was sprayed on the fiber mat. After mold filling, the acidity of the impregnated resins was changed, thereby altering the function of 2,4-P from a retarder to an accelerator. A shorter cure time and a higher final resin conversion were achieved through this method for both VE and UP resins.

In this study, the effect of low shrinkage additives and curing conditions on shrinkage control of vinylester resin systems cured at low temperature was investigated. To achieve this goal, an integrated analysis was carried out including the study of reaction
kinetics, morphology, and volume change. A low temperature SCRIMP resin system was designed to achieve good shrinkage control and a high final conversion.

5.2 Experimental

The vinylester resin used in this study is VER-E (Dow Chemical) with a high polarity backbone. It is a methacrylated bisphenol-A resin that contains 50 wt. % of styrene, offering a styrene to vinylester C=C bond ratio of about 4.2. The low shrinkage additive (LSA) used is a low molecular weight, polyurethane-based polymer. Methyl ethyl ketone peroxide (MEKP, Witco® HiPoint 90) and cobalt naphthenate (CoN, OMG Americas Inc.) were used as the low temperature initiator and the promoter, respectively. N, N-dimethylaniline (DMA) was used as the accelerator, and 2,4-pentanedione (2,4-P) was added in order to provide adequate sample preparation time. The external acid applied during the SCRIMP molding process was an acidic vinylester resin VER-780 (DOW Chemical). The pH values of VER-E and VE-780, as measured in 10 wt.% methanol solutions, are 6.6 and 2.9, respectively.

The volume shrinkage of the samples was measured by an in-house constructed dilatometer. The sample, weighing from 5 to 6 grams, was sealed in a polyethylene pouch, and then degassed under vacuum. A small hole was made at the edge of the pouch, and air bubbles inside the pouch that had been formed under vacuum were squeezed out. The pouch was heat-sealed again, and then placed inside the sample chamber of the dilatometer. The measurement was taken under a pressure of 0.69 MPa.
(100 psi) and a pre-specified temperature. More details regarding the construction and operation procedures of the dilatometer can be found elsewhere [Kinkelaar, et al., 1992; Li, et al., 1998a].

A differential scanning calorimeter (DSC2910, TA Instruments) was used to measure the reaction kinetics. Detailed procedures of DSC measurement have been given in Section 3.2.2.1.

Sample morphology was observed by a SEM. Detailed procedures of SEM have been given in section 3.2.2.4.

Surface quality of the molded samples was measured by a profilometer, Federal’s Surfalyzer 4000. The chosen tracing length was 25.4 mm. The average roughness ($R_a$), which is the arithmetic average height of surface irregularities measured from the mean line within the sample length, was used as a quantitative standard to compare the surface quality.

5.3 Results and Discussion

5.3.1 Volume Shrinkage and Final Conversion of Vinyl Ester Resin with LSA

5.3.1.1 Effect of LSA Content

In order to study the effect of LSA concentration on shrinkage control and final conversion of the vinyl ester resin VER-E cured at low temperatures, a series of reactions was carried out at 35°C isothermally. All of the samples were cured with 0.045% 2,4-P,
0.2% DMA, 0.1% CoN, and 0.5% MEKP to ensure the desired reaction rate, as well as a long induction time for sample preparation in the dilatometry experiment. Figure 5.1 shows the resin conversion profiles vs. time at various LSA concentrations. The reaction rate of the resin systems with more LSA is lower, but the final conversions at different LSA concentrations are about the same at around 80%. The dilatometry profiles in Figure 5.2 show that the volumetric shrinkage decreases as the LSA concentration increases. All of the samples (with varying amounts of LSA) exhibit different degrees of shrinkage but follow the same shrinkage pattern.

The sample without LSA has a final shrinkage of 9.07%. If LSA is considered as a filler only, its effect on the volumetric change of VER-E resin is shown as the dashed line in Figure 5.3. The effect of LSA on the final shrinkage of samples cured isothermally at 35°C is only slightly better than that of the filler. In other words, the LSA acts almost like a filler. All of the samples with different LSA concentrations cured in the dilatometer at 35°C were translucent implying few micro-voids inside the sample and, consequently, poor shrinkage control [Li, et al., 2000]. Figure 5.4 shows the SEM micrograph of the VER-E resin with 10% LSA cured isothermally at 35°C. The sample has a two-phase structure, where the continuous phase is a flake-like region and the dispersed phase consists of small droplets with diameters ranging from 1 to 2 µm. Inside the droplets, tiny particles with diameters of less than 1 µm were found tightly packed and coagulated. The droplets are LSA-rich, while the flake-like region is VER-rich. From the micrograph, one can see that the region where the LSA is effective is very small
Figure 5.1 Conversion profiles of VER-E with various LSA concentrations cured at 35°C (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).
Figure 5.2 Volume change profiles of VER-E with various LSA concentrations cured at 35°C (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).
Figure 5.3 Final volume change vs. LSA concentrations of VER-E cured at 35°C (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).
Figure 5.4 SEM micrographs of VER-E with 10% LSA cured at 35°C (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).
at this concentration level. This may be why volume shrinkage control is poor at these
cure conditions.

The structure of unsaturated polyester and vinylester resins is important for
shrinkage control [Atkins, 1993]. Generally, the propylene glycol-maleic anhydride (PG-
MA) type of unsaturated polyester resin responds well to the low shrinkage additive. However, for UP resins containing orthophthalic acid or isophthalic acid units, low shrinkage additive is less effective. The vinylester resins, produced by the reaction of epoxy resin based bisphenol A with unsaturated carboxylate, are considered the most difficult resins to interact with the low shrinkage additive. The VER-E resin used in this study belongs to this group, and the experimental results confirm that the LSA is ineffective when the resin is cured isothermally at low temperatures. It is therefore a challenge to design proper curing conditions to improve the efficacy of LSA in the VE/LSA system.

5.3.1.2 Effect of Curing Temperature

The effect of temperature on shrinkage of the VER-E resin system with 10% LSA
was investigated by dilatometry at various temperatures, i.e. 35, 45 and 60°C
isothermally. Figure 5.5 shows the conversion profiles of the resin system at different
temperatures. As the reaction temperature increases, the final conversion reaches a higher
value, from 79.8% to 87.2%. The reaction also takes place earlier and the time required
to reach the final conversion is reduced. However, the early occurrence of
Figure 5.5 Conversion profiles of VER-E with 10% LSA cured at different temperatures (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).
reaction is undesirable for mold filling and fiber wetting during the molding process. As seen in Figure 5.6, the volumetric shrinkage of the sample decreases slightly when the temperature is increased from 35 to 60°C. The volume change of the cured sample at 35°C is −7.83%, while that at 60°C is −7.21%. However, when the resin system was cast in a 35°C oven, it showed a significant appearance change (turning white) compared to the sample cured at 35°C isothermally in the dilatometer (remaining translucent). In order to determine the volume shrinkage of the sample cured in the oven, a density measurement method was applied in this study. The density of the cured sample ($\rho_s$) and the volume change are calculated according to the following equations:

$$\rho_s = \rho_{H_2O} \times W_s /(W_s - W_w)$$

Volume change ($\%$) = ($\rho_{n0} / \rho_s - 1$)$\times$100

where $\rho_{n0}$ is the theoretical density of the resin system before cure and $\rho_s$ is the density of the resin system after cure. $\rho_{H_2O}$ is the density of water at 25°C. $W_s$ and $W_w$ are the sample weight when weighed in air and in water respectively. Table 5.1 summarizes the volume change of the VER-E resin with different LSA contents cured at 35°C, determined by both the dilatometer and the density measurement methods. The final volume change measured by the density method is slightly less than the dilatometry result, but the trend is similar. Therefore, the density measurement method could be used as a characterization method to quantify the final volume change of the cured samples.
Figure 5.6 Volume change profiles of VER-E with 10% LSA cured at different temperatures (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).
Table 5.1 Comparison of final volume change for VER-E with various LSA concentrations cured at 35°C using density and dilatometry measurements (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).

<table>
<thead>
<tr>
<th></th>
<th>Density measurement volume change(%)</th>
<th>Dilatometry measurement volume change(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% LSA</td>
<td>-8.4</td>
<td>-9.07</td>
</tr>
<tr>
<td>4% LSA</td>
<td>-7.6</td>
<td>-8.51</td>
</tr>
<tr>
<td>10% LSA</td>
<td>-6.8</td>
<td>-7.96</td>
</tr>
<tr>
<td>16% LSA</td>
<td>-5.4</td>
<td>-7.43</td>
</tr>
</tbody>
</table>
The volume change of the sample cured at 35°C in the oven was only –2.4%, while it was –6.8% when the sample with the same formulation was cured in the dilatometer at the same temperature (both were measured by the density measurement). The major difference between the two cases is the temperature profile. For samples cured in the dilatometer, the temperature was kept at 35°C constantly. While in casting, the sample temperature was not controlled and could reach as high as 110°C in the center. The difference in thermal history may explain why the samples exhibited very different volume shrinkage control.

In order to investigate the effect of temperature profile on curing, an isothermal mode and a ramp mode were combined in a dilatometer experiment, resulting in a temperature profile similar to that in the casting process. The results are shown in Figure 5.7. The volume of the sample decreased first due to polymerization shrinkage. When the temperature reached the maximum value (i.e. at 40 minutes), a volume expansion was observed. This expansion compensated for most of the polymerization shrinkage and the vinylester resin with LSA ended with only 3.20% final shrinkage (instead of 8~9% in the isothermal cases). The final shrinkage determined by density measurement was 2.60%, which agrees fairly well with the dilatometry result. Therefore, the efficiency of LSA depends greatly on the thermal history of the resin system.

In order to further understand the effect of thermal history during sample curing on shrinkage control of the resin system, the volume change of samples with the same formulation but cured at different ramping rates and peak temperatures was measured. All samples were sealed in thin plastic pouches (0.05 mm thick) and heated from room
Figure 5.7 Volume change profile of VER-E with 10% LSA cured non-isothermally in the dilatometer (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).
temperature to a pre-specified temperature (40, 60 or 80°C) in a water bath at different heating rates, i.e., from 0.34 to 14°C/min. The temperature was then maintained at the pre-specified value and the resin was allowed to react for 5 hours. As shown in Table 5.2, the samples cured at a low heating rate could turn cloudy (i.e. phase separation) before the temperature reached the peak temperature and these samples showed good shrinkage control (i.e. low volume shrinkage). The larger the temperature difference between the cloudy point and the peak temperature, the better the shrinkage control.

The SEM micrographs of all samples are shown in Figures 5.8-5.10. At a pre-specified curing temperature of 80°C, the samples have a particulate structure independent of the heating rate. However, when the heating rate is 12°C/min, the particles tend to coagulate tightly in many cases. Some samples show loose packed particulate structure (Figure 5.8). When the samples are cured at 60°C with different heating rates, the sample morphology is also particulate-like except that the particle size and packed patterns are different (Figure 5.9). At a high heating rate the particles become smaller and are packed together more tightly, while at low heating rate the particles are larger and loosely packed.

The morphology of samples cured at 40°C is different from samples cured at 60 and 80°C. The particles are less identifiable (Figure 5.10). However, the samples cured at a low heating rate can still provide good shrinkage control. From the above results, more uniform and loosely packed particulate structure can be developed at a low heating rate. At high heating rates, the reaction rate may be too high to achieve well-developed particulate structure. The LSA used in this study is a low molecular weight
Table 5.2 Volume change of VER-E with LSA under various temperature profiles
(10% LSA, 0.2% DMA, 0.3% CoOct, 1.0% MEKP).

<table>
<thead>
<tr>
<th>Peak temperature (°C)</th>
<th>Heating rate (°C/min)</th>
<th>Cloudy temperature (°C)</th>
<th>ΔT (°C)</th>
<th>Volume change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>1.7</td>
<td>50</td>
<td>60</td>
<td>3.00±0.0</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>55</td>
<td>25</td>
<td>3.00±0.0</td>
</tr>
<tr>
<td></td>
<td>6.4</td>
<td>70</td>
<td>10</td>
<td>3.00±0.0</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>80</td>
<td>0</td>
<td>-4.19±0.42</td>
</tr>
<tr>
<td>60</td>
<td>4.7</td>
<td>55</td>
<td>5</td>
<td>1.9±0.29</td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>60</td>
<td>0</td>
<td>0.39±0.05</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>60</td>
<td>0</td>
<td>-2.99±0.01</td>
</tr>
<tr>
<td>40</td>
<td>0.34</td>
<td>33</td>
<td>7</td>
<td>3.00±0.0</td>
</tr>
<tr>
<td></td>
<td>0.92</td>
<td>38</td>
<td>2</td>
<td>1.75±0.02</td>
</tr>
<tr>
<td></td>
<td>2.54</td>
<td>40</td>
<td>0</td>
<td>-0.94±0.21</td>
</tr>
</tbody>
</table>

ΔT: Temperature difference between peak temperature and the temperature when sample turns cloudy.
Figure 5.8 SEM micrographs of VER-E with 10% LSA cured at 80°C at a heating rate of (a) 1.7°C/min; (b) 4.5°C/min; (c) 6.4°C/min; and (d) 12°C/min (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).
Figure 5.9 SEM micrographs of VER-E with 10% LSA cured at 60ºC at a heating rate of (a) 4.7ºC/min; (b) 8.5ºC/min; and (c) 14.0ºC/min (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).
Figure 5.10 SEM micrographs of VER-E with 10% LSA cured at 40°C at a heating rate of (a) 0.3°C/min; (b) 0.9°C/min; and (c) 2.54°C/min (0.045% 2,4-P, 0.2% DMA, 0.1% CoN, 0.5% MEKP).
polyurethane-based polymer, which has a glass transition temperature lower than room
temperature. Therefore, the thermal expansion of LSA during polymerization may play a
very important role. At low heating rates, the temperature gap between the onset of phase
separation and the peak temperature is large, which allows LSA’s large thermal
expansion within large and loosely packed particulate structure in the LSA-rich phase to
initiate and propagate micro-crack during polymerization [Kinkelaar, et al., 1992]. This
provides a good volume shrinkage control. The temperature ramping also provides a
higher level of polymerization-induced internal stresses than in isothermal cases owing to
the fast reaction facilitating micro-crack formation. The detailed mechanism of volume
shrinkage control needs to be further investigated.

5.3.2 SCRIMP Molding

The above experimental results show that good volume shrinkage control could be
achieved if the temperature is raised slowly to allow phase separation and reaches a high
value after phase separation to allow micro-void formation. However, in actual low
temperature molding processes like SCRIMP, it is not easy to achieve such a temperature
profile because there is no external heating source. The temperature profile depends
mostly on the resin reaction kinetics. It would be desirable if the reaction exotherm could
be accumulated in the composite. In this way, a higher temperature could be reached
during curing, accelerating the curing rate of the composite. This would then produce
more heat and a high peak temperature, which not only benefits shrinkage control of the
resin system but can also drive the reaction to completion. On the other hand, the
SCRIMP process is typically used for making large composite parts. Therefore, the resin gel time needs to be long for complete mold filling and good fiber wetting. In order to prevent premature gelling, a certain amount of inhibitor/retarders is often added to the resin system in order to prolong the resin gel time. This would result in a low curing rate, preventing the accumulation of reaction exotherm because of heat dissipation to the surroundings. Consequently, poor shrinkage control, low resin conversion, and high residual styrene would result. It would be desirable if the resin system can be designed in such a way that the gel time is long during mold filling, while the curing rate is low initially but becomes high later and can reach a high temperature.

It was found that in the non-acidic vinylester or unsaturated polyester resin systems, 2,4-P functions as a retarder that provides a longer gel time but a lower reaction rate [Li, et al., in press; Heck, et al., 1984]. On the other hand, 2,4-P works as a co-promoter in acidic resin systems, resulting in a shorter gel time but higher reaction rate. Adding external acids into the non-acidic resins to change the acidity of the resin system may also turn 2,4-P from a retarder to a co-promoter. This concept has been applied to the design of a better low temperature resin system by spraying an external acid on the fiber mats instead of premixing the acid with the matrix resins [Li, et al., in press]. The gel time can be extended by adding 2,4-P as a retarder in a non-acidic resin. Once the resin flows through the fiber reinforcement, it dissolves the pre-sprayed acid. The dissolved acid can then increase the acidity of the resin system, changing the function of 2,4-P from a retarder to a co-promoter. We adopted this idea here to develop a low temperature SCRIMP resin system, allowing good surface quality (shrinkage control) and low residual styrene of molded vinylester composites.
VER-E is a non-acidic resin (pH=6.6 measured in a 10% methanol solution). The effect of the 2,4-P content on the reaction rate was studied by DSC at 35°C isothermal cure. As shown in Figure 5.11, the initial reaction rate decreases as the content of 2,4-P increases. Although the maximum reaction rate tends to be slightly higher when 2,4-P is added, the gel time becomes longer as more 2,4-P is added. As shown in Figure 5.12, the gel time of the resin system can be extended from 19 to 32 min when 0.15% 2,4-P is added into the resin system. It is clear that 2,4-P can be used as a retarder to adjust the gel time and initial reaction rate of the VER-E resin.

Figure 5.13 shows the resin system cured at 35°C with 0.1% 2,4-P, but with different external acids: maleic anhydride (MA, Aldrich Chemical) and VER-780 (Dow Chemical). These two acids were chosen because they can be dissolved in the VER-E resin easily. Maleic anhydride is a small-molecule acid, while VER-780 (solid) is an epoxy-based dimethacrylate vinylester prepolymer with a grafted acid functional group. The results show that the initial reaction rate increases if either of these two acids is added into the resin system. As more MA is added into the resin system with 2,4-P, the reaction rate becomes higher. It was also noted that the addition of VER-780 is not as effective as adding MA. This is because VER-780 is a prepolymer with a lower acid number per unit mass than MA. From the results presented in the previous section, a slow reaction before phase separation and a high temperature after phase separation are essential for good volume shrinkage control of vinylester VER-E resin. Based on these
Figure 5.11 DSC isothermal reaction rate profiles of VER-E with different 2,4-P concentrations cured at 35°C (0.3% CoOct, 2.0% MEKP).
Figure 5.12 Viscosity change of VER-E with different 2,4-P concentrations cured at 35°C (0.3% CoOct, 2.0% MEKP).
Figure 5.13 Effect of external acid on DSC isothermal reaction rate profiles of VER-E with 0.1% 2,4-P cured at 35°C (0.3% CoOct, 2.0% MEKP).
observations, a new SCRIMP design is proposed, in which 2,4-P is added to the non-acidic vinylester resin (with a low shrinkage additive) to serve as a retarder. This design provides a long gel time for mold filling and a low initial reaction rate for phase separation. An external acid, VER-780, is distributed on the fiber mats uniformly during preform preparation to serve as a binder. As the resin is infused into the mold and the VER-780 binder is slowly dissolved into the VER-E resin, the resin acidity increases. 2,4-P then becomes a co-promoter during curing to fasten the curing rate. This may lead to a higher peak temperature that is critical for good shrinkage control. The resin conversion may also increase (i.e., less styrene residue) because of the higher reaction exotherm.

To verify this design, a series of SCRIMP experiments were carried out. Two molding temperatures were chosen: one was a room temperature of 26°C, and the other was 42°C to simulate the molding temperature in the summer. The experimental set-up is shown in Figure 5.14. Ten layers of dry glass fiber mats (QM6408 from Brunswick Technologies, Inc.) were laid upon a glass plate. The fiber stack was covered by a polyester film to form a vacuum bag whose outer edges were sealed by tacky tape. A resin inlet and a vacuum outlet on opposite ends of the mold were also formed. The resin was first stored in a tank. The initiator was added to the resin system immediately before mold filling. During molding, vacuum was applied through the outlet, forcing the bag to press tightly against the fiber stack. The liquid resin was introduced into the inlet through a supply line and cured in the vacuum bag for 24 hours. The gel time of each resin system was measured at molding temperatures in a vial (25 mm in diameter) containing
Figure 5.14 Schematic of experimental set-up for SCRIMP.
10 grams of sample. The residual activity of the molded composite parts was examined two days after molding by DSC in the scanning mode at 5°C/min from room temperature to 300°C, based on a total reaction exotherm of about 360 J/g. Three samples were taken at the surface of each part and the average value was calculated. In the cases where an external acid was introduced into the molding system, 5 wt.% of VER-780 based on the resin weight of the molded panel was distributed uniformly on the fiber mat. First the prepolymer VER-780 was dissolved in acetone and the fiber mats were soaked in the solution for 24 hours. The mats were then dried in a vacuum oven at 40°C for 24 hours to remove the acetone.

Figure 5.15 shows the temperature profiles during SCRIMP molding of the VER-E resin with and without VER-780. The temperature profiles show little difference due to the presence of VER-780 on the fiber mats in the first 10 minutes at 42°C cure and the first 50 minutes at 26°C cure. This is because VER-780 needs time to dissolve into the matrix resin to change its acidity. The dissolved VER-780 then leads to a rapid temperature rise due to the co-promoter nature of 2,4-P in the acidic resin system. The maximum temperature is increased from 52 to 73°C during SCRIMP molding at 26°C initial temperature, and from 80 to 109°C at 42°C initial temperature. Since VER-780 was distributed on the fiber mats before mold filling, the gel time was not affected. As shown in Table 5.3, the gel time for systems with and without VER-780 is the same, i.e. 36 minutes at 26°C and 15 minutes at 42°C. In both SCRIMP molding cases, a higher final conversion is achieved with VER-780 introduced into the molding system. The increase of the final conversion is the result of a higher cure temperature inside the mold.
Figure 5.15 Effect of VER-780 on temperature profiles in SCRIMP molding of VER-E resins (0.1% 2,4-P, 0.3% CoOct, 2.0% MEKP).
Table 5.3 Effect of VER-780 on final conversion and surface quality of molded panels in SCRIMP molding of VER-E resins (0.1% 2,4-P, 0.3% CoOct, 2.0% MEKP).

<table>
<thead>
<tr>
<th></th>
<th>26 °C No acid</th>
<th>26 °C 5% VE-780</th>
<th>42 °C No acid</th>
<th>42 °C 5% VE-780</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel Time (min)</td>
<td>36</td>
<td>36</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Peak Temp (°C)</td>
<td>51.1</td>
<td>73.3</td>
<td>80.3</td>
<td>108.9</td>
</tr>
<tr>
<td>Peak Time (min)</td>
<td>123.3</td>
<td>98.3</td>
<td>43.8</td>
<td>31.7</td>
</tr>
<tr>
<td>Residual heat (J/g)</td>
<td>60.5</td>
<td>38.1</td>
<td>36.7</td>
<td>23.3</td>
</tr>
<tr>
<td>Final Conversion (%)</td>
<td>83.2</td>
<td>89.4</td>
<td>89.8</td>
<td>93.5</td>
</tr>
<tr>
<td>Rₐ (μm)</td>
<td>0.70</td>
<td>0.22</td>
<td>0.30</td>
<td>0.36</td>
</tr>
<tr>
<td>SD (μm)</td>
<td>0.19</td>
<td>0.11</td>
<td>0.19</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Rₐ: Average surface roughness  SD: Standard deviation of Rₐ
The surface quality of the molded panel is also improved by adding VER-780 at low temperature molding; however, no improvement is observed for 42°C molding. The higher cure temperature may result in too high initial reaction rate that affects the phase separation and microstructure formation as discussed earlier. Although a higher peak temperature is reached at a higher initial molding temperature, the micro-void formation for shrinkage compensation may suffer if there is not a good enough phase separation in the early stage of curing. Among the four SCRIMP molding cases, the one with VER-780 cured at low initial temperature provides the best surface quality, while the one with VER-780 cured at 42°C provides the highest resin conversion.

5.4 Conclusions

In this chapter, the shrinkage control of a vinylester resin with low shrinkage additive cured at low temperatures was investigated. It was found that volume expansion did not occur for samples cured isothermally with different LSA concentrations. However, a large volume expansion was observed for samples cured non-isothermally. These results suggest that the temperature profile has a strong effect on shrinkage control. The temperature gradient affects the rate and degree of phase separation, which is critical for micro-void formation and volume shrinkage compensation during curing. A low initial heating rate and a high peak temperature during curing are the most desirable for shrinkage control. This observation is applied
to the design of a better SCRIMP resin system for vinylester resins. 2,4-P is added into the resin to achieve a long resin gelation time. An acidic resin such as VER-780 is distributed on the fiber mat. After mold filling, the acidity of the impregnated resins is changed, altering the function of 2,4-P from a retarder to an accelerator. This results in a high reaction exotherm that leads to a higher final resin conversion and better shrinkage control.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Overview

Unsaturated polyester and vinylester resins are premium materials in composite industry. With an increasing interest in demand for low cost composites, low temperature manufacturing processes such as low temperature/low pressure sheet molding compound (SMC), resin transfer molding (RTM), and Seemann Composite Resin Infusion Molding Process (SCRIMP) have grown considerably in industry. As compared to the high temperature curing processes, a variety of curing agents are needed in order to induce the low temperature free radical polymerization, as well as better tailor the curing and gelation rate. This difference would certainly change the reaction mechanism and kinetics, and consequently affect the curing behavior of resins (e.g., final conversion, chemorheological changes, microstructure formation, shrinkage control, cycle time, etc.), and the properties of the finished parts. An integrated analysis has been carried out to study the reaction kinetics and shrinkage control of unsaturated polyester or vinylester resins with low profile additives cured at low temperatures. Different experimental techniques, including differential scanning calorimetry (DSC) and Fourier
Transform Infrared (FTIR) spectroscopy for reaction kinetics, rheometry using Rheometrics Dynamic Analyzer (RDA) for viscosity change, dilatometry for volume change, scanning electron microscopy (SEM) and optical microscopy (OM) for morphology are employed for this purpose.

### 6.2. Effect of Co-Promoter and Comonomer on Volume Shrinkage of Low Profile Unsaturated Polyester Resins Cured at Low Temperatures

The large volume shrinkage of unsaturated polyester resins is a major drawback to impede their applications. The addition of thermoplastics, i.e. low profile additives (LPAs) could greatly reduce polymerization shrinkage in the high temperature curing processes. In low temperature cure, the performance of LPA is not as good as in high temperature cure. It is believed that less thermal expansion of LPA at low temperature is the main reason. The major driving force for volume shrinkage compensation at low temperatures is the reaction-induced phase separation and micro-void formation through stress cracking resulting from strain relief. It has been reported that the volume expansion during low temperature curing occurred at a very late stage of reaction and an earlier volume expansion resulted in better shrinkage control.

In this study, two approaches were applied to shift the volume expansion to an earlier time. One is introducing comonomers, i.e. divinylbenzene (DVB) and trimethylpropane trimethacrylate (TMPTMA), and the other is the addition of a co-promoter, acetylacetone or 2,4-pentanediol (2,4-P). The effect of 2,4-P and comonomer
on reaction kinetics and shrinkage control of the UP/St/LPA system was investigated and their effect on the curing agent partition and viscosity change in the LPA-rich and UP-rich phases was also studied. The kinetic results demonstrated that the addition of co-promoter and comonomer could change the relative reaction rate and gelation in the LPA-rich and UP-rich phases. For the samples with co-promoter 2,4-P, the reaction rate of both the LPA-rich and UP-rich phases increased as compared to the sample without 2,4-P, but the increase in the LPA-rich phase was more pronounced. It is also found that gelation of the LPA-rich phase occurred earlier by adding 2,4-P into the resin system. Both faster reaction and earlier gelation of the LPA-rich phase are critical for the earlier onset of stress cracking. For the sample containing the comonomer TMPTMA, the reaction rate of the LPA-rich phase is higher than that of the sample without any TMPTMA because of its high mobility and faster copolymerization with styrene than styrene homopolymerization, in particulate in the LPA-rich phase. The dilatometry results demonstrated that samples with comonomer or co-promoter show earlier volume expansion, as a result of higher reaction rate in the LPA-rich phase and earlier occurrence of micro-void formation.

The kinetics and volume change study of UP/St/LPA systems with both 2,4-P and TMPTMA also shows that a better shrinkage control can be obtained when the volume expansion occurs at a lower conversion. The final volume shrinkage, however, shows no further improvement with combination of co-promoter 2,4-P and comonomer TMPTMA.

The morphology of samples with TMPTMA is quite different from that without TMPTMA. It is obvious that TMPTMA affects both crosslinking and phase separation
process in the UP/St/LPA systems. The samples with 2,4-P showed no morphology changes. By using optical microscopy, the micro-crack was found at different times. The results clearly demonstrated that not only the final morphology but also the structure evolution combined with multiphase chemorheology are critical to final volume shrinkage compensation.

However, the study of structure evolution using the optical microscope is not very successful at very early stage of reaction because the detailed structure formed is in a much smaller scale. Further investigation of the micro-gel formation and the local phase separation in this stage may provide valuable information regarding the influence of resin structure and reaction kinetics on the phase separation and sample morphology, and consequently, the shrinkage control. Dynamic light scattering (DLS) technique can be employed for this purpose. DLS has the capability of measuring molecule size to the nanometer level. In the work of Hsu [1992], DLS was used to characterize the formation of microgels before macro-gelation during the reaction of UP/St. By employing the similar experimental technique, the difference on the detailed structure formation among various resin systems may be revealed. Atomic force microscopy (AFM) technique has been successfully used to characterize topography at the nanometric scale and it may define the particle boundary more clearly than SEM [Serre, et al., 2001]. It does not require any specific preparation if the observation is performed on the flattest possible surface and could be used to monitor more detailed morphology development.
6.3. Shrinkage Control and Residual Styrene of Unsaturated Polyester Resins

In low temperature molding processes of unsaturated polyester resins, shrinkage control and residual styrene are very important concerns. A systematic study was carried out to investigate the effect of reaction temperature, initiator system, and comonomer on structure evolution, final resin conversion, and shrinkage control of UP resins with LPA. In the study of reaction kinetics, DSC and FTIR were employed to obtain both the overall and individual reaction rates and conversion profiles. The mechanical properties of unsaturated polyester composites containing different amounts of MMA were studied based on the ASTM methods. Experimental results indicated that both the reaction temperature and the resin composition along with the cure agents affect the curing behaviors of unsaturated polyester resins. A higher cure temperature increases the reaction rate and the final conversion, but affect the volume shrinkage of resin system. The effect of temperature on morphology, relative reaction rate in the LPA-rich and UP-rich phase, as well as micro-void formation may influence the final shrinkage. A higher MMA content results in a higher final conversion that consequently influences the mechanical properties of the cured resin. However, MMA has a negative effect on shrinkage control of UP/ST/LPA system because phase separation becomes more difficult with MMA in the resin system.

Although qualitative explanation is provided in this study to explain the final conversion and volume shrinkage of resin system with LPA, the quantitative information is more useful for designing resin systems with low volume shrinkage and residual St
content. However, detailed study on reaction kinetics, phase separation and micro-void formation is difficult because of the lack of information about the composition in each phase, and there is no direct way to quantify the "driving" force as well as the "resistance" force for the micro-void formation in the local scale. However, the temperature-induced phase separation used in this study cannot exactly reflect the dynamic phase separation and composition change occurred in each phase. Theoretically calculation through thermodynamical theory with information on copolymerization will more closely estimate the real process. Huang et al. [1998, 2000] calculated UCST of a ternary St/UP/LPA system by using the generalized Gibbs free energy equation of mixing to predict the miscibility of the resin system in the presence of different LPAs without reaction. The prediction had good correlation with experimental results. In the future study, the similar concept can be used to predict the miscibility of the UP/St/LPA system with comonomer during reaction. With an integrated reaction kinetics study of copolymerization through FTIR for relative reaction rate between the reactive components and nuclear magnetic resonance (NMR) spectroscopy for copolymer sequence, clear information of copolymerization kinetics and copolymer sequence can be obtained. Such information can be used to predict the instantaneous composition of copolymer during polymerization. It is very important to know the instantaneous composition of copolymer in order to use generalized Gibbs free energy equation of mixing to predict the miscibility of the resin system and the composition in separated phases during reaction. Once the composition is known, ‘model’ systems can be set up to study the chemical and physical
changes in each phase separately, which may provide detailed information of reaction 
kinetics volume shrinkage ("driving" force for micro-void formation) and modulus 
("resistance" force for micro-void formation) in each phase. Further exploration on the 
reaction kinetics, structure changes, and shrinkage control can be carried out. The low 
profile mechanism can be further elucidated. This would also serves as a good criterion 
for comonomer screening.

Mechanical property and corrosion resistance of unsaturated polyester composites 
increased with higher final conversion. The combination of infrared spectroscopy, gas 
chromatography, thermal analysis (DSC, DMA, TGA) and mechanical characterization 
may help to elucidate more detailed relationship between the degree of cure and the 
performance of the cured composite.

The corrosion resistance of unsaturated polyester composites is very poor even 
with improved final conversion. This is indicated by the large drop of flexural strength of 
composites at the presence of strong base solution. Introducing nanoparticles such as 
nanoclay into the resin system may provide better barrier properties and consequently 
better corrosion resistance.

6.4 Shrinkage Control and Residual Styrene of Vinylester Resins

Vinylester resins are one of the most widely used thermoset resins in the 
composite industry. They usually have less volume shrinkage during polymerization than
unsaturated polyester resins; however, low profile additives are less effective in vinylester resin systems. In this study, the shrinkage control of vinylester resins with a low shrinkage additive (LSA) at low temperature cure was investigated. Volume expansion did not occur for samples cured isothermally with different LSA concentrations, but it was observed for samples cured non-isothermally. The temperature profile had a strong effect on shrinkage control, and a low heating rate and a high peak temperature during curing were the most desirable conditions for shrinkage control. The temperature gradient may affect the rate and degree of phase separation, which is believed to be critical for micro-void formation and volume shrinkage compensation during curing. It is still not well understood how reaction temperature profile affects the phase separation and micro-void formation. In order to better understand this phenomenon, further study on reaction kinetics, rheology behavior, and morphology evolution under non-isothermal condition needs to be carried out.

The relationship between shrinkage control and thermal history of the sample during cure was applied to design a better SCRIMP resin system of vinylester resins. In order to provide long gel time and good phase separation at the early stage, a good retarder for the vinylester resin is needed, while a promoter is essential for good shrinkage compensation and high final conversion at late stage of cure. This was achieved through the addition of 2,4-P into the resin system by taking the advantage of its unique property in resin systems with different acidity. The function of 2,4-P changes from a retarder to a promoter when an acidic resin VER-780 was distributed
on fiber mats and dissolved into the non-acidic resin system during the molding process. Molding experiments were conducted to verify the concept of this resin design. The system showed lower volume shrinkage (better surface quality) and higher final conversion (low styrene residue), yet maintained a long gel time.

The SCRIMP curing of this novel resin system is quite complicated due to the occurrence of acid dissolution (mass transfer), co-polymerization of the reactive resin system (reaction kinetics), the phase separation of resins with LSA (thermodynamics), as well as heat transfer. All these factors have interaction among one another and may affect the final conversion as well as volume shrinkage of the resin system. In the future study, the phase separation and reaction kinetics, in the presence of different amount of acid component, should be carried out to better understand the effect of acid distribution and acid dissolution rate on the final conversion and volume shrinkage control of vinylester resin systems. Micro-void formation or volume shrinkage compensation under well-defined thermal history should also be carried out quantitatively through kinetics modeling and heat transfer simulation. These studies can provide a better understanding of the manufacturing process and better control of the quality of the molded composite.
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