### POLYMER BLENDS AND THEIR APPLICATIONS IN ULTRA-LOW VOLATILE ORGANIC COMPOUND EMISSION THERMOSET FILMS

by

Spencer L. Giles A Dissertation Submitted to the Graduate Faculty of George Mason University in Partial Fulfillment of The Requirements for the Degree of Doctor of Philosophy Chemistry and Biochemistry

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### Polymer Blends and Their Applications in Ultra-Low Volatile Organic Compound Emission Thermoset Films

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## Dedication

To my loving wife, Carlise and our beautiful daughters, Sydney and Addison.

### Acknowledgements

I would like to extend my greatest appreciation and never ending thanks to my parents, Douglas and Katherine Giles, for without whom this journey would have been impossible to undertake. I would also like to thank my wife, Carlise, and daughter Sydney, for traveling with me across the nation in order to reach the goal of earning a doctorate degree.

The research conducted herein would not have been possible without the guidance and support from my dissertation committee members, research advisors, lab group members and collaborators. This project was funded under a Strategic Environmental Research and Development Program (SERDP) effort. Thanks to Dr. Brian Rasley from the University of Alaska Fairbanks for participating as my dissertation Co-Director and for the encouragement to finish my graduate career and showing me that earning a doctorate degree would be worth the effort; Dr. Gerald Weatherspoon from George Mason University for participating as my dissertation Director and for the guidance throughout the doctoral program at George Mason University, including editing and providing valuable feedback through the proposal and dissertation writing process; committee members Dr. Robert Cozzens and Dr. Robert Honeychuck for providing valuable input for my research project; Dr. Jeffrey Lundin for his never ending faith in polyoxometalate catalysis in the absence of hydrogen peroxide, as well as his generous, unsolicited and countless words of wisdom in the dissertation writing process; Dr. Peter Coneski for his polymer chemistry expertise and advice; Mr. Nick Heller and Dr. Clive Clayton of Stony Brook University for their collaborative efforts and feedback throughout the entirety of the project; as well as Mr. Mark Wytiaz and Mr. Mark Walker of Sherwin-Williams for their coatings expertise and guidance. Lastly, I would like to thank Dr. James Wynne for finding the time and effort to bring the project to life and allow me the opportunity to experience being a research chemist.

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## List of Abbreviations

AFM	Atomic force microscopy
ALPH	Aliphatic diisocyanate
ATR	Attenuated total reflectance
AVG	Average
CPVC	Critical pigment to volume concentration
CYCLOALPH	Cycloaliphatic diisocyanate
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
Е'	Storage modulus (elastic response)
E"	Loss modulus (viscous response)
FTIR	Fourier transform infrared spectroscopy
LSCM	Laser scanning confocal microscopy
MPa	Mega Pascal
PTFE	Polytetrafluoroethylene
PVC	Pigment to volume concentration
RMS	Root mean square
SEM	Scanning electron microscopy
Sq	Surface roughness value
STDEV	Standard deviation
Tan $\delta$	Ratio of Loss Modulus (E"): Storage Modulus (E')
TEM	Transmission electron microscopy
Tg	Glass transition temperature
TGA	Thermal gravimetric analysis
VOC	Volatile organic compound

#### Abstract

# POLYMER BLENDS AND THEIR APPLICATIONS IN ULTRA-LOW VOLATILE ORGANIC COMPOUND EMISSION THERMOSET FILMS

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George Mason University, 2015

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Due to current and future emissions regulations, the development of powder coating technologies is at the forefront of organic coatings research. The control of surface morphology and the enhancement of physical-chemical characteristics exhibited by polymeric materials in the absence of solvent is extremely important for the future of low volatile organic compound (VOC) emission coatings. Several unique acrylic polymeric resins with different polar and hydrogen bonding characteristics have been developed and blended together with commercially available fillers and pigments to generate solvent free coatings with unique physical-chemical properties. Characterization of the physicalchemical properties exhibited by the thermoset films of polymer blends has been performed. Analysis of both pigmented and control clear coatings was executed using various microscopy, thermal, mechanical and spectroscopic techniques. The in-depth analysis of thermoset polymer blended films has provided valuable insight into modulation of the physical-chemical properties of resin blended powder coatings through small adjustments to the reaction conditions and processing parameters. Thermoset powder coatings pose a significant challenge with respect to analysis of reaction progress *in situ* because of moderate temperature conditions. Therefore, through adjusting reaction conditions and processing parameters, an understanding of thermoset resin blended coating modulation was performed.

### **Chapter 1 : Background**

### 1.1 Introduction

Developing and improvement of functional coatings has been an undertaking in the scientific community for many years, with the main thrusts being anticorrosion, antifouling, and chemical resistance or some combination thereof. Current and forthcoming regulations for volatile organic compounds (VOC) emissions has forced development of new coating systems in efforts to meet and/or exceed requirements for minimizing VOC emission.<sup>1</sup> The release of VOCs into the environment has become a major issue of public interest due to the effects VOCs exhibit when present in the environment.<sup>2</sup> The automotive industries' current method for vehicle painting releases VOCs into the environment from the overspray in paint spray booths and solvent evaporation in the drying ovens. The solvent present in overspray and emissions from the drying ovens constitute one of the major sources of VOC contamination in the United States.<sup>3</sup> Research into multifunctional powder coatings has become paramount to alleviate the introduction of VOCs from solvent based coatings into the environment. Prior efforts toward VOC emissions reduction in liquid coatings has been through the introduction of waterborne coatings and/or the utilization of solvents exempted from regulations set forth by the Environmental Protection Agency.<sup>1</sup> As an alternative to solvent based coatings, powder coatings eliminate the use of solvent completely, thereby reducing the introduction

of VOCs into the atmosphere. Other incentives for utilization of powder coatings in place of liquid coatings include quicker curing times, thicker coatings and higher film durability.

### **1.2** Powder Coatings

Powder coatings are 100% solid, solvent free coating materials consisting of a polymeric binder system with addition of pigments and extender materials as shown in Figure 1-1. Liquid coatings consist of an equal ratio of the polymeric binder to the pigment and extender materials because the viscosity of the formulation is determined by solvent. Powder coatings behave as non-Newtonian fluids in molten form, requiring a minimum shear stress to be exceeded (yield value) prior to flowing and wetting the substrate. The yield value of a powder formulation is dependent upon inter and intra molecular interactions between the polymeric materials within the binder system, the pigments and the extender materials.<sup>4</sup> Formulations with excessive pigment and extender materials, high pigment to volume concentration (PVC), have increased yield values due to a greater number of intermolecular interactions leading to poor flow and substrate wetting.



**Figure 1-1**. Graphical comparison of compositions for standard liquid coatings and powder coatings.

### **1.3** Functional Coatings

In the past, standard liquid coatings have been subjected to the addition of additives to impart additional functionality such as low reflectivity and/or biological and chemical decontamination capabilities beyond those of the original design.<sup>5-11</sup> Successful addition of both ionic<sup>7</sup> and non-ionic<sup>12</sup> surfactants to exhibit control over morphology at the surface of numerous polymeric materials, and subsequently increasing surface roughness,<sup>13,14</sup> has been performed in prior studies; however, these techniques have not been effective at significantly reducing gloss. Targeted application such as low reflectivity or corrosion resistance will help determine the properties needed in the final coating design to meet the specific needs required from the system. Specific control of surface chemistry and morphologies of coatings is of great importance to the development of functional exterior coatings and finishes.<sup>15</sup> The chemistry and topography of the surface plays an important role in the development of coatings and can influence fouling adhesion,<sup>16,17</sup> surface energy<sup>18-20</sup> and appearance.<sup>21,22</sup> In contrast to liquid coatings, powder coatings behave differently when additional materials are incorporated into the formulation; therefore, imparting additional functionality becomes extremely challenging in the development of novel powder coatings.

### **1.4 Polymer Blends**

The critical pigment to volume concentration (CPVC) plays an important role in functionalization of polymeric coatings.<sup>23</sup> The CPVC for a polymeric coating is the concentration of additives within the system at which the behavior of the polymeric

coatings are vastly different from those of the unmodified polymer. Coatings with a PVC below the CPVC (PVC < CPVC) are composite materials with random orientation and placement of additives within a continuous polymer matrix. Coatings with PVC above the CPVC (PVC > CPVC) are no longer continuous polymer networks because of insufficient volumes of polymeric materials.<sup>24</sup> The CPVC for a powder coating is approximately a 3:1 polymeric binder to pigment ratio (**Figure 1-1**). In order to circumvent increasing the PVC with additives and subsequently increasing the yield values, polymer blends have been utilized in powder coatings to tailor functionality through *in situ* generation of a composite material.<sup>25-27</sup>

New functional materials developed through blending polymer systems has gained momentum in the past few decades, with the goal of being able to tailor new materials to fit the requirements for specific applications. The combinatorial effects from blending basic materials has already been used for other products, such as the development of carbides of steel and tungsten, which display improved impact resistance and strength in the form of new materials.<sup>28</sup> The same concept applied to polymer systems through the incorporation of additives or blending polymers can lead to the development of materials with a range of properties such as increased compatibility, durability and thermomechanical properties for certain applications.<sup>23,24,29-32</sup> The utilization of immiscible polymer blends for thin film and coating applications has produced methods for generating ordered patterns and unique surface structures without the use of lithography.<sup>33-39</sup>

One of the biggest undertakings in developing new polymer blends is understanding the macromolecular interactions and/or reactions which take place between

the individual polymers within the blend. The generation of polymeric domains due to phase separation of various magnitudes on the nano, micro and macro scales in the films could potentially provide avenues for a variety of end user applications. Utilization of phase separation and understanding how to predict intermolecular incompatibilities based upon polymeric design is also a topic of great interest within polymer physics. The ability to tune phase separation would allow for the capability of modulating the hydrophobicity, cleaning, vibrational dampening, and tuning of optical properties of the coated surfaces. Research focused on polymer blending within simple systems of polystyrene (PS) and poly(methyl methacrylate) (PMMA) have been performed to identify the domain compositions as well as understanding how domain morphologies are controlled.<sup>34,37</sup> Based upon the physical-chemical properties of the individual polymeric materials within the blend and the reaction conditions, phase separation occurred due to low entropy of mixing which drives the component polymers within the blend to phase separate.<sup>33</sup> The polymers within the blend will therefore segregate based upon the most favorable interactions in order to lower the free energy of the entire system.<sup>37,40</sup>

### **1.5** Polymer Solubility

Thermodynamics plays an important role in the generation of blended materials. In every system, mixing is entropically favored because of the increase in disorder of the system. This is the general case for polymer solutions and blends, however, there are some molecular interactions that have greater influence on the thermodynamics of mixing due to the size of the polymer molecules in question. Therefore, the thermodynamic parameters for polymer solutions or blends have different influences on the system and whether or not polymer miscibility or phase separation occurs.<sup>41,42</sup> A basic model for interactions observed in regular solutions, polymer solutions and polymer blends was developed by Flory and Huggins<sup>43,44</sup> which confines molecules into a lattice that exhibits no volume change upon mixing. **Figure 1-2** represents a random mixing of 100 molecules of A and B confined in a Flory-Huggins lattice.



Figure 1-2. Flory-Huggins lattice representation for a regular solution.

The Flory-Huggins lattice theory then reduces the intermolecular interactions to neighboring lattice sites, thus simplifying the approach to understanding molecular interaction in solutions and blends. The regular solution of components A and B will try to minimize the Gibbs free energy of the solution within the lattice by increasing the entropy of the system through mixing. The Gibbs free energy of the solution ( $\Delta G_{mix}$ ) (Equation 1-1) is determined by the enthalpy ( $\Delta H_{mix}$ ) and entropy ( $\Delta S_{mix}$ ) of mixing as a function of temperature.

Equation 1-1 
$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$$

Expansion of the entropy ( $\Delta S_{mix}$ ) term in Equation 1-1 illustrates that the total entropy of the system is a function of the composition ratios ( $\phi_A$  and  $\phi_B$ ) and molecular weights of the species (N<sub>A</sub> and N<sub>B</sub>) in the lattice.

Equation 1-2 
$$\Delta \overline{S}_{mix} = -k \left[ \frac{\varphi_A}{N_A} ln \varphi_A + \frac{\varphi_B}{N_B} ln \varphi_B \right]$$

In organic or aqueous small molecule solutions, the molecular weight terms in Equation  $1-2^{41}$  are relatively low (close to one), therefore the equation reduces to become dependent upon ratios of the individual species ( $\varphi_A$  and  $\varphi_B$ ) in the solution.

$$\Delta \overline{S}_{mix} = -k(\varphi_A ln \varphi_A + \varphi_B ln \varphi_B)$$

Equation 1-3

The incorporation of a macromolecular species such as a polymer in solvent gives a polymer solution (**Figure 1-3**) which places restrictions on lattice site occupations due to

covalent bonding. The entropy calculation for a polymer solution using Equation 1-2 then includes the high molecular weight ( $N_A$ ) of the polymer species leading to Equation 1-4.<sup>41</sup>

$$\Delta \overline{S}_{mix} = -k \left[ \frac{\varphi_A}{N_A} ln \varphi_A + \varphi_B ln \varphi_B \right]$$

Equation 1-4



Figure 1-3. Flory-Huggins lattice representation for a polymer solution.

The increase in molecular weight of the polymer species leads to a significant reduction of the entropy of mixing, therefore reducing the Gibbs free energy of mixing. The promotion of mixing for a polymer solution then becomes more reliant on the intermolecular interactions occurring between adjacent lattice sites. Similar to the polymer solution, a polymer blend (**Figure 1-4**) will replace all the small solvent molecules with a second polymer species.



Figure 1-4. Flory-Huggins lattice representation of a polymer blend.

The entropy of mixing for a polymer blend is then represented by Equation 1-2. The molecular weights (N<sub>A</sub> and N<sub>B</sub>) of both polymer species then become relevant in order to determine the entropy of the blend. Based upon Equation 1-2, the entropy of a polymer blend is then further reduced from that of a polymer solution, which means that molecular interactions of the polymers becomes highly important in the calculation of the Gibbs free energy of mixing. Polymer characterization therefore becomes an important factor in the development of polymer blended systems. Understanding the inter- and intra-molecular interactions will play an important role in the determination of polymer systems utilized for blended polymer films.

Analysis of the inter- and intra-molecular interactions of the polymers in the blend can be performed through the use of Hansen solubility parameters. The total solubility parameter ( $\delta$ ) takes into account three major interaction components developed by Hansen: dispersion forces ( $\delta_D$ ), polar forces ( $\delta_P$ ) and hydrogen bonding ( $\delta_H$ ).<sup>45</sup>

Equation 1-5 
$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

Through the use of Hansen solubility parameters, polymer systems can be chosen based upon their miscibility, or lack thereof, to target the film properties of the greatest interest. Modifications to certain structural properties and pendant groups will allow for changes to the total solubility parameter which affects how the polymeric materials will interact in the lattice system and influence miscibility or phase separation.

### **1.6** Coating Properties

The primary purpose of any coating is the creation of a desired visual appearance and a protective barrier for the underlying substrate from the surrounding environment. Modifying surface chemistry and/or topography through the addition of nanoparticle,<sup>46,47</sup> surfactants,<sup>7,9,12,48</sup> and fluorinated polymeric materials<sup>19</sup> have been attempted in order to modulate interfacial properties for contamination prevention and appearance modulation. Lithography and machining have also been attempted to produce ordered surface structural characteristics to modulate hydrophobicity and surface energy.<sup>49-51</sup> With this in mind, several factors for developing barrier coatings from blended polymeric system need to be considered including: mechanical integrity, chemical composition and surface characteristics.

Blending of polymers has been utilized in the past for the development of new materials with broad characteristics in the bulk of the new material through influences from the individual components.<sup>28-30</sup> The end application of the new blended polymeric material will determine the targeted characteristics for the design and formulation of the blend. Coatings used as exterior top coats require specific appearances based upon the substrate. Exterior topcoats for automobiles are preferentially high gloss coatings with smooth surfaces having minimum defects to promote the reflection of incident light; whereas top coats for appliances and interior walls are generally semi-gloss or matter respectively. In conjunction with appearance, the functionality of the coating needs to be considered in order to protect the underlying substrate.

The modulation of physical-chemical properties derived from crosslink functionality, polymer backbone structure and isocyanate selection makes thermoset polyurethane systems an ideal platform for durable multifunctional coatings. A polyurethane thermoset coating is comprised of a polymeric material bearing multiple hydroxyl functional groups which are reacted with multi-functionalized isocyanates. By varying the degree of hydroxyl group functionality, the crosslink density can be increased or decreased to modulate the thermal and mechanical properties.

Surface topography on various size scales has been reported to influence key surface interfacial properties such as gloss.<sup>15,52-54</sup> Reflectivity of a standard solvent borne polymer film is typically controlled through the addition of flattening agents. Commercially available silica, polymeric waxes and polymeric beads are products used as flattening agents for solvent borne coatings. Polymeric beads based upon polyurea (Pergopak) and polyurethane (Decosoft) chemistries are available to provide uniform size and shape distributions for flattening in liquid systems. The flattening agents are utilized to produce micro-texture at the surface upon film shrinkage, which occurs during solvent evaporation and subsequent curing.<sup>22</sup> This micro-texture reduces the amount of incident light reflected (**Figure 1-5**), which leads to the appearance of a matte finish.<sup>55</sup>



**Figure 1-5**. Representation of incident light reflected from a glossy surface (left) compared to the incident light reflected from a matte surface (right).

The creation of necessary surface topography for producing matte surfaces from a solvent free system requires a different strategy from that employed in typical solvent based system. The omission of solvent leads to a different curing process where standard flattening agents become detrimental to the cured film durability.<sup>56-58</sup> Standard methods used to a produce matte finish in solvent free thermoset coatings include: inorganic fillers, matting agents, organic waxes, and dry blending of multiple resins.<sup>26,27,55-57,59</sup>

The use of inorganic fillers, such as silica, as matting agents in powder coatings is analogous to that in liquid coatings for the generation of surface roughness. However, the use of inorganic fillers is limited due to the detrimental loss to film durability with increased additive concentrations. During powder coating processing (extrusion), the viscosity of the materials are reduced and flow and melt mixing occurs between 90 and 120 °C. After electrostatic application of the powder coating, the substrate is wet-out and thermoset cross-linking reactions begin to proceed between 140 and 200 °C. Due to the

high oil absorption of silica/silicate flattening agents, high concentrations of these additives in a powder formulation will disrupt the flow of the polymeric material leading to poor substrate wetting and inconsistencies within the cured film.<sup>56,57,60</sup> Flow inhibition leading to inconsistencies in the film thickness will reduce durability and chemical resistance of the cured coating.

The addition of organic waxes to powder formulations has also shown promise in producing matte finished coatings. Incompatible organic waxes are incorporated within the powder formulation which surface segregate during the curing process. The surface segregated wax creates roughness at the coating-air interface which reduces the gloss of the finished coating.<sup>55,59</sup> However, reproducibility becomes a problem because of compatibility issues and alterations of wax particle sizes due to extrusion. The use of polymeric beads is also problematic when the coatings are subjected to curing temperatures at or above which the polymeric beads degrade.

The final approach for generating surface topography discussed in the literature involves the blending of two polymer systems with different reactivity or compatibilities producing micro structure based upon reaction rates and polymer-polymer miscibility.<sup>26,55,57</sup> Reactivity differences between resins produces incompatible domains based upon differences in the cross-link density as a function of curing time with respect to increases in the viscosity. A slower reacting resin will flow to a greater extent prior to the completion of the cross-linking reactions due to limited increases to the viscosity as a function of slower increase in the cross-link density. The phase separated domains produced by the resin with faster increases in the cross-link density and viscosity will

afford the microstructure necessary to reduce the gloss of the coated surface.<sup>26,55,57</sup> Phase separation based upon incompatibility occurs when polymeric resins segregate due to differences in polymer-polymer intermolecular interactions. Polymer-polymer incompatibility results in the formation of domains composed of individual resins, which then cross-link. Phase separation by either mechanism therefore results in the formation of domains composed of the individual polymeric materials in defined locations within the films.

Incompatible polyester resins with large differences in hydroxyl content have been blended; upon curing the resins phase separated to form a heterophase structure which remained after full cure.<sup>25</sup> Blends of high and low carboxyl functionalized polyester resins have also produced low gloss powder coatings using the same principle of induced phase separation and domain formation.<sup>26,27</sup> In addition to gloss reduction, there are other industrial interests for coatings generated from immiscible polymer blends. Resin blended coatings provide a method for producing very finely dispersed microstructures which can significantly enhance mechanical properties such as scratch/mar resistance and adhesion durability.<sup>61,62</sup>

Tailoring a polymer blended film composition which can afford a matte finished appearances reproducibly from a powder coating system would be highly beneficial. Such a system would result in a reduction of VOC emission as well as eliminate the utilization of extra additives, which are needed in solvent borne systems. **Table 1-1** illustrates typical gloss requirements for topcoats in various commercial market applications.<sup>26,55</sup> Gloss reduction for powder coatings is a major topic of interest because the capability to lower

gloss reproducibly without loss of coating durability would open avenues for low VOC emission coatings in every targeted commercial application in the coating industry.

Table 1-1.	Gloss definitions	based upon the 60°	reflection	measurements	with substrate
examples.					

Gloss Levels at 60° Viewing Angle	Example	Gloss Measurement
High Gloss	Automotive Exterior	>90%
Gloss	Floor finishes	75-90%
Semi-Gloss	Door Trim, Refrigerator	25-75%
Matte	Wall paints	10-25%
Flat	Handheld electronics	<10%
Air Force Camouflage	Military Fixed Wing Aircraft	<3%
Army/Navy Camouflage	Vehicles, Helicopters	<1%

### 1.7 Materials Processing and Coating Application

Processing and application techniques play an important role in the generation of film characteristics with high reproducibility from batch to batch. Therefore, an understanding of the materials history is necessary for generating a reliable polymer blend for coating purposes. Typically, starting materials such as resins, hardeners, pigments and additives are weighed, premixed, extruded, milled and then separated by size through a cyclone filtration system and sieve as shown in **Figure 1-6**.<sup>63</sup>



Figure 1-6. Illustration of general powder coating production.

Premixing of the starting materials is performed to ensure a uniform distribution of all the individual components prior to extrusion. The extrusion process is a hot mixing step which helps to uniformly distribute the pigments, fillers, and additives within the polymeric material to ensure uniform pigmentation and filler dispersion prior to milling. Typically, a single or double screw extruder, as illustrated in **Figure 1-7**<sup>64</sup>, is employed.



**Figure 1-7**. Diagram of a twin screw extruder with an inset illustration of the screw configuration.

The extruder houses one or two screws inside a barrel, which can be temperature controlled during the extrusion process. The mixed starting materials enter the barrel through the feeder and are ground, melt mixed and forced in the direction of the die. The melt mixed material exits the barrel through the extrusion head as a viscous material and is subsequently cooled, thereby creating a solid block of material. The increased temperature conditions, due to friction inside the barrel, are sufficient enough to prepolymerize (cross-link) some of the starting materials without extensive deblocking from cooling the barrel during the extrusion process. Therefore, the extrusion process acts as a method for uniform pigment and filler dispersion as well as a pre-polymerization step in the creation of the powder coating. The material exiting the extruder is a viscous mixture

of the polymeric resins with the fillers and pigments incorporated. The viscous material exiting the extruder is then cooled, forming a solid material, which is then milled to generate the fine powder for coating application. The milled powder materials are classified (sifted) to isolate distinct particle size distributions, to provide uniform particle sizes for application, using a cyclone filtration and sieve system. The final milled powder product with typical particle size distribution of 30 to 50  $\mu$ m is then packaged and utilized as a powder coating.<sup>65</sup> Small scale powder coating operations utilize the same processes, however, smaller scale milling and sieving are performed to produce test batches as shown in **Figure 1-8**.



**Figure 1-8**. Small scale powder processing operation. A twin screw extruder with screw configuration for melt mixing the raw materials (A and B). Raw materials are extruded and exit the barrel as a viscous material (C) which is cooled and compressed through chilled rollers (D) forming a brittle solid which is then milled (E) and sieved for particle size selection (F).

The standard application method for a powder coating utilizes an electrostatic attraction between the grounded substrate and charged powder particles. Using a powder application gun, as shown in **Figure 1-9**, a charge is applied to the powder particles as they exit the gun, causing an electrostatic attraction between the charged powder and the grounded substrate. The electrostatic attraction causes the powder to stick to the substrate surface, creating a layer of powder particles, which will eventually become the protective coating upon curing.<sup>65</sup>



**Figure 1-9**. Electrostatic application of powder coating materials to a grounded substrate using a corona-charge application gun.

There are two types of powder application guns currently available: the tribo-charge and the corona-charge guns.<sup>66</sup> **Figure 1-9** illustrates the application of a powder coating using a corona charge gun, which applies a negative charge to the powder particles as they enter the electric field created by the electrode at the tip of the gun. The tribo-charge gun has a polytetrafluoroethylene (PTFE) barrel and applies the charge to the powder particles through friction interactions as the powder moves through the PTFE barrel.<sup>65</sup> There are other application techniques available for powder coatings, however, the electrostatic application is the most commonly employed. Therefore, the other techniques will not be discussed further.

Once the powder is applied to the substrate, the coating is cured through completion of the crosslink reactions resulting in the thermoset film. The curing of a powder coating occurs at elevated temperatures and can be summarized by the following phases: melting, flow/leveling, and crosslinking.<sup>67</sup> The formation of a consistent film from an applied powder coating occurs when the powder particles melt, flow and form a level film over the substrate. In order for the crosslinking reaction to occur, the reactive chemical moieties must come into contact with one another to promote the forward chemical reaction. As the powder particles melt, the intimate contact between reactive chemical moieties becomes possible and reactions can occur.<sup>65</sup> In some powder coating formulations, the curing temperature is regulated through the use of blocking agents which are utilized to obstruct the reactive moieties until the deblocking temperature is reached. Blocking agents play an
important role in processing and curing parameters for a powder system and will be discussed in the subsequent section.

#### **1.8 Blocking Agents**

The polymeric resin systems used in powder coating formulations are similar to those utilized in standard solvent-borne coatings: acrylics, polyesters, epoxies and polyurethanes.<sup>65</sup> However, the processing parameters, such as elevated temperatures during extrusion, typically promote the polymerization of the milling mixture. Therefore, a control mechanism is needed to limit the polymerization/crosslinking reactions prior to application and subsequent cure.<sup>65,68</sup> Polyurethane chemistries in coatings are highly utilized because of great durability and protective strengths provided from the simple urethane linkage shown in **Figure 1-10**.<sup>68-70</sup>

HO-R-OH + O=C=N-R'-N=C=O 
$$\longrightarrow$$
 HO-R-O-C-N-R'-N=C=O  
(1) (2) (3)

Figure 1-10. Formation of the urethane linkage from a diol and a diisocyanate.

The formation of the urethane linkage is a favored exothermic reaction; therefore, in order to prevent the reaction shown above from proceeding to completion during the extrusion process, blocking agents are employed. Blocking agents are reacted with the isocyanate functional groups to prevent the spontaneous formation of the urethane linkage from occurring in the presence of reactive alcohols in the resin systems. Although there are dozens of blocking groups available, ε-caprolactam is commonly utilized as a blocking agent for isocyanates in powder coatings because the group is thermally removed above 170 °C, as is shown **Figure 1-11**.<sup>65,70-73</sup> An extrusion process (melt mixing) is utilized in powder processing to uniformly disperse all of the starting materials within the powder formulation at an elevated temperature, typically 120 °C. In the absence of the blocking group extensive premature crosslinking would occur during the extrusion process possibly destroying the extruder.



**Figure 1-11**. Formation of blocked isocyanate (6) from  $\varepsilon$ -caprolactam (4) and free isocyanate (5). Deblocking reaction of  $\varepsilon$ -caprolactam blocked isocyanate (6) to form  $\varepsilon$ -caprolactam (4) and free isocyanate (5).

The isocyanate blocking reaction shown in **Figure 1-11** is the formation of a urea linkage between  $\varepsilon$ -caprolactam and the isocyanate functional group. The urea linkage

formation reaction is reversible upon the addition of heat; therefore,  $\varepsilon$ -caprolactam is an ideal blocking agent for powder coatings which are heated to cure the applied coating. Alternatively internally blocked isocyanate functional groups can be utilized in polyurethane chemistry to eliminate the use of external blocking agents. Internal blocking of isocyantes is performed via dimerization of two isocyanate functional groups to form an uretdione (**Figure 1-12**).<sup>68,70,73</sup>

$$2\left(O=C=N-R-N=C=O\right) \xrightarrow{\mathsf{PBu}_3} O=C=N-R-N \xrightarrow{O}_{O} N-R-N=C=O$$
(2)
(2)
(7)

**Figure 1-12**. Formation of internally blocked isocyanate via dimerization of diisocyanate to form the uretdione.

The isocyanate dimerization equilibrium reaction to form the uretdione, shown in the above scheme, is catalyzed by trialkyl phosphine catalysts. The uretdione is isolated through the deactivation of the trialkyl phosphine catalyst with an alkylating agent, such as benzyl chloride. The uretdione formation reaction leads to a polyisocyanate adduct, which can be utilized as a low emission powder coating curative with low free isocyanate content. Free isocyanate can be regenerated from the uretdione through heating and subsequent rearrangement of the highly strained four member uretdione ring.<sup>73</sup> The utilization of the uretdione species is a desirable method for the production of polyurethane powder coatings because of the low free isocyanate content and no blocking group emission upon curing.

Formation of a trimer from three isocyanates occurs if the reaction above is performed at higher temperatures. The isocyanurate, shown in **Figure 1-13**, is a thermally stable trimer which will not decompose to the free isocyanate under curing condition.



Figure 1-13. Trimerization of isocyanate functional groups forming the six membered ring isocyanurate.

Blocking group selection and deblocking reactions are extremely important in the formulation of powder coatings because the curing temperature dependence is based upon the generation of the isocyanate group *in situ*. Other blocking agents are available and outlined in the literature, however, they are less relevant to this effort.<sup>73</sup>

# 1.9 Concluding Remarks

Based upon the limited substrate applications for powder coating technologies most of the work within the field has focused upon alterations to the curing mechanism for low temperature applications.<sup>68,74</sup> Most powder technologies currently available are cured between 160 and 200 °C, which limits utility of the powder coatings and provides significant roadblocks for understanding reaction mechanisms.<sup>74</sup> Previous studies have focused upon development of low gloss from powder technologies through resin blending. However, characterization is limited, due to the complexity of powder coatings from processing the starting materials through application and film formation.<sup>57</sup>

#### Chapter 2 : Thesis

The objective of the proposed research is to use incompatible polymer blended systems to generate film formulations for utilization as multifunctional powder coatings. The *in situ* generation of polymeric domains will be utilized to generate composite materials with interacting polymeric domains to enhance physical-chemical properties without compromising film durability. Through the utilization of blended polymers, the goal is to generate coating with the capabilities of tuning bulk properties as well as surface morphologies. The standard methods for the generation of surface morphologies for appearance control in liquid coatings is detrimental to overall coating durability when applied to powder coatings. The approach taken herein, via the synthesis of the polymeric resins with tailored properties for blends, will be performed. The goal is to tailor polymers with specific chemical and physical characteristics to influence solubility parameters, modulate durability and compatibility as the films cures. Controlling the chemistry, and thus the compatibility of the polymers within a blend, allows for an avenue to generate films with distinct surface features for appearance as well as providing a combination of physical and chemical properties of two distinct polymer networks. The identification of factors which influence the coating properties such as gloss reduction, chemical resistance and film durability will be assessed. Synthesized resins, formulated powders and cured sample films have been fully characterized using a variety of techniques for bulk and

surface properties including: surface energy measurements, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, laser scanning confocal microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). At the conclusion of the research, a method for formulating and screening durable polymer blended systems with control over physical-chemical characteristics will be generated.

# **Chapter 3 : Experimental**

# 3.1 General Statement

Unless otherwise noted, all chemicals used in these experiments were of reagent grade and used without additional purification. Curing studies were performed by removal of coated substrate from the oven at various time intervals during the cycle and either quenching in ice water (initial experiments) or on a cooled metal surface to terminate thermal reactions.

### **3.2** Coatings and Sample Preparation

Circumvention of PVC issues associated with increased additive concentrations in powder coatings was performed through the *in situ* generation of polymeric domains. The preparation of a low gloss pigmented coating was executed using hydroxyl group functionalization mismatching of acrylic polymeric resins (**Figure 3-1**). Acrylic resins were obtained from Estron Chemical Inc. (Calvert City, KY) with hydroxyl group content within the range of 20 to 400-OH group functionality.



Figure 3-1. Generic polymeric resin structure.

Blending of a low hydroxyl functionalized resin with a high hydroxyl functionalized resin was undertaken to induce polymeric phase separation upon curing. The blends of the low and high hydroxyl functionalized resins were cross-linked using  $\varepsilon$ -caprolactam externally blocked aliphatic polyisocyanate. Levelling and degassing agents typical in thermoset coating formulations were added at < 1% w/w. Commercial matting agent, carbon black, and black iron oxide pigments were each added at various weight percentages to provide color and enhance gloss reduction of the coating formulation. Control clear coatings were prepared using the same acrylic resins without the additions of the matting agent and pigments. Alternative crosslinking agents, curatives, (**Table 3-1**) were also utilized within the study to understand reaction conditions and curative chemistry with respect to film formation and the development of the coating physical chemical properties.

Curative	Base Structure	Blocking Group	Deblocking Temp (°C) TGA
А	Aliphatic	ε-caprolactam	173
В	Aliphatic	Triazole	161
С	Cycloaliphatic	ε-caprolactam	180

Table 3-1. Curative information.

Raw materials were manually dry-blended, then melt mixed using a 30 mm twin screw extruder through increasing zone temperatures of 40, 90, and 120 °C. The extruded material was compressed into sheets through chilled rollers and the cooled material was ground rotor mill. The ground powder was further classified by using a 106 µm (140 mesh) sieve. Powder formulations from above were electrostatically applied to substrates using a standard gravity fed powder coating cup gun. Coatings were then cross-linked in an oven at 400 °F for 12 minutes to generate the thermoset films. Temperature and catalysis effects on film formation were also performed through curing films with and without the incorporation of low concentrations of catalyst at 375, 350 and 325 °F for 22, 30 and 40 minutes respectively.

Initial epoxy embedded cross-section samples were prepared from coatings on steel or aluminum release foil substrates placed in small clips without sample disbonding. Samples were embedded in a 2:1 ratio of EpoThin<sup>TM</sup> epoxy resin with EpoThin<sup>TM</sup> epoxy hardener under vacuum. The cured epoxy puck with coating samples embedded was then subjected to the polishing process in stages of Al<sub>2</sub>O<sub>3</sub> sand paper: 120, 400, 800, and 1200 grit. Following the 1200 grit  $Al_2O_3$  sand paper, the polishing media was switched to polishing cloths and diamond solutions/suspensions starting with a 3 µm diamond solution, then moving to 1  $\mu$ m and 0.25  $\mu$ m diamond suspensions. Polyester embedded cross-section samples were prepared by embedding the sample specimens within Bio-Plastic acquired from Ward's Science, New York. The Bio-Plastic composition prior to curing was 50% polyester, 40% styrene monomer, and 10% methyl methacrylate. Upon curing, the samples were cut into blocks approximately 1" x 1" x 0.5", which were then subjected to either dry polishing or microtome cross-sectioning. Dry polishing was performed using specialized MOPAS-XS hand-polisher (Jaap Enterprise, Amsterdam, Netherlands) on ultra-fine abrasive cloths to a one micron finish. Microtome cross-section samples 80 nm thick were prepared for transmission electron microscopy (TEM) analysis using a Leica EM UC7 Ultra-microtome (Wetzlar, Germany) using a diamond sectioning blade. Heavy metal staining for enhanced contrast from TEM was performed using a 2 wt% solution of uranyl acetate (SPI Supplies/Structure Probe Inc.) in methanol and a 0.3 wt% solution of lead citrate (Electron Microscopy Sciences) in water. Sectioned samples were first submerged in the uranyl acetate methanol solution for 10 minutes. The sectioned samples were then submersed in the lead citrate water solution for 3 minutes. Microtome cross-section polishing for atomic force microscopy (AFM) analysis was performed using a Leica EM UC7 Ultra-microtome using a glass sectioning knife.

### 3.3 Coating Analysis

Analysis of coating properties was performed to fully characterize the resin blended systems in order to understand the unique properties afforded. Surface characterization was utilized to correlated observed gloss values to observed surface morphologies exhibited in pigmented films and to domain structures and surface morphologies in clear films. Thermal and mechanical analysis were performed to understand and characterize phase separation with respect to the thermal stability and durability of the blended coatings. Chemical analysis was performed to fully characterize and differentiate domain structures within clear films for better understanding of coating properties.

#### 3.3.1 Laser Scanning Confocal Microscopy (LSCM)

Laser scanning confocal microscopy (LSCM) was used to provide information on surface characteristics of the sample coatings. LSCM measurements were performed on an Olympus LEXT OLS4000 using the LEXT software package. Images were acquired using a laser source at 405 nm with 50x optics providing 1076x magnification of the coating surfaces. The LEXT software package allowed stitching of four magnified images together to provide measurements over 483  $\mu$ m x 485  $\mu$ m surfaces. Images were taken every 0.06  $\mu$ m along the z-axis and compiled to create a 3D image of the coating surfaces. Surface roughness parameters, depth profiling and macro size domain measurements were performed using the LEXT software package.

# 3.3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) provided information on surface characteristics of the new coatings below the magnification range of the LSCM. SEM imaging was performed using a Carl Zeiss SMT Supra 55 scanning electron microscope with the accelerating voltages set between 3 and 5 kV for imaging. Powder coating samples were sputter coated with gold using a Cressington 108 auto sputter coater equipped with a

Cressington MTM-20 thickness controller. A 3 nm layer of gold was applied to each coating surface prior to SEM analysis to reduce charging upon exposure to the electron gun. SEM images were used to monitor domain size distributions on the coated surfaces using open source image analysis software *ImageJ*.

#### 3.3.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) was utilized to provide domain identification and distribution throughout the bulk of the film using selective staining with uranyl acetate and lead citrate solutions. TEM experiments were performed using a FEI Bio TwinG2 Transmission Electron Microscope. The TEM was equipped with an AMT XR-60 CCD digital camera system for image collection. Bright field imaging measurements were performed at an accelerating voltage of 80 keV.

#### 3.3.4 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) provided thermal stability data of the polymer films analyzed. TGA analysis shows the sample degradation with increasing temperature at a given rate under controlled conditions. Powder coating formulations which contain an isocyanate with an external blocking agent were analyzed for the removal of the blocking group with respect to temperature as well. TGA experiments were performed on a TA Instruments Q50 TGA instrument using a platinum sample pan. The analyses were carried out in the presence of nitrogen. Nitrogen was also used as the purge gas for the balance. Thermal stability experiments were recorded from ambient temperature to 600 °C at 5 °C/min. Deblocking reactions experiments were recorded from ambient to 600 °C at 10 °C/min ramp to characterize alternative curatives. Plots of percent weight loss versus temperature and weight loss versus time were generated in order to analyze the data.

## 3.3.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature ( $T_g$ ) of the polymer resins, powder formulations and cured films. The  $T_g$  is the temperature at which a polymer transitions from a glassy state to a rubber state. DSC measurements were performed using a TA Instruments Q20 DSC instrument equipped with the DSC Refrigerated Cooling System (RCS) and a purge gas of nitrogen set to 50 mL/min. Samples of approximately 1-2 mg were placed into TA Instrument Tzero<sup>TM</sup> Aluminum pans, and an empty Tzero<sup>TM</sup> aluminum pan was used as reference. Powder and free film samples were analyzed using a cyclic method including an initial run from 30 °C to 85 °C at 10 °C/min, followed by two consecutive cycles from -30 °C to 220 °C at 10 °C/min. DSC experiments were used to monitor the changes of the glass transition temperature as a function of formulation and oven curing. The T<sub>g</sub> for the samples were determined from data in the second ramp cycle. Based on this data, glass transition temperatures were found using the TA Universal Analysis program.

# 3.3.6 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) provided complimentary thermal and mechanical data for fully cured films. DMA analysis was performed using a TA Instruments Q800 Dynamic mechanical analyzer equipped with a gas cooling accessory (GCA) and film tension clamp. Free film samples were analyzed from 0 °C to 250 °C at a

ramp rate of 3 °C/min to thoroughly analyze the mechanical properties before and after the glass transition. Mechanical data was collected at an oscillation frequency of 1 Hz.

### 3.3.7 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transformed infrared spectroscopy was used to provide broad chemical information of neat polymer resins and cured films by monitoring various peaks before, during, and after oven curing. FTIR spectra were recorded on a Thermo Scientific Nicolet 6700 with the Omnic software package. The Nicolet 6700 was equipped with a Smart Performer ATR attachment, and germanium or a diamond crystal was used. Air was employed as the background and each sample was subjected to 32 scans for each ATR-FTIR spectra.

### 3.3.8 Raman Spectroscopy

Raman spectroscopy and chemical mapping was performed using a Thermo Nicolet Almega Raman Spectrometer equipped with a 785 nm laser with a spot size of  $3.1 \ \mu m$  Thermo Fisher Scientific Inc. (Waltham, MA). Individual Raman spectra were collected over 96 iterations at 3 second intervals.

### 3.3.9 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) provides information on the surface and mechanical characteristics of the new coatings to reinforce the LSCM and SEM data. AFM measurements were performed using a Cypher Atomic Force Microscope from Asylum Research, operating in contact and tapping mode. Commercial dataprobe, rectangular silicon cantilevers made by Micromasch (225 x 40 x 7.0  $\mu$ m<sup>3</sup>) were used with a nominal spring constant of 40 N/m and a resonance frequency of 170 kHz.

# 3.3.10 Contact Angle Analysis

The literature suggests that the surface energy of a coating is directly related to the ability of coatings to withstand chemical and environmental conditions. The contact angle of various solvents provided useful information for calculating values of surface energy for coatings. Contact angle measurements were performed to determine the critical surface tension by utilizing a VCA 2500 video contact angle system by AST Products, Inc. Multiple probe liquids such as triple distilled water, diiodomethane, and *n*-hexadecane were employed.

#### **Chapter 4 : Results and Discussion**

Analysis of powder coating formulations has been performed to develop a fundamental understanding of film properties with respect to processing parameters and reaction conditions. Surface, thermal, mechanical and chemical properties were monitored to develop methods for analyzing powder formulations and cured films to determine properties leading to durable high performance low reflectance coatings. This study was performed to correlate and facilitate the chemistry of the powder formulations, processing parameters and curing stages to aid in the development of applicable low VOC emission powder coatings.

# 4.1 Initial Film Analyses

Matte finished coatings are generated when surface features disrupt and scatter the reflection of incident light off the surface as depicted in **Figure 1-5**. The observation of ample gloss reduction from several resin blended powder coating formulation with minimal flattening agents has generated interest in the physical-chemical characteristics of resin blended systems. The cured powder coatings from the resin blended systems exhibited low reflectance capabilities that met Army/Navy Camouflage gloss specifications (**Table 1-1**). The blended coatings were formulated from a combination of high and low hydroxyl content acrylic polyol resins. Surface topography and roughness characterization were performed using LSCM to quantify and correlate surface structure with the observed gloss

reduction. Topography analysis shows random surface features were exhibited by the powder coating formulation (**Figure 4-1**).



**Figure 4-1**. Laser scanning confocal microscopy image illustrating the surface structure of a low reflectance powder film.

The surface topography of a film can be dissociated into two elements: waviness and roughness as shown in **Figure 4-2**. The waviness profile describes the wide spaced surface irregularities whereas the roughness is the closely spaced surface irregularities. As previously mentioned, the structural profile of the surface plays an important role in the development of gloss controlled coatings.



**Figure 4-2**. Illustration of the primary surface structure profile (top) dissociated into the waviness (middle) and roughness (bottom) profiles.

The root mean square (RMS) surface roughness ( $S_q$ ) was calculated using Equation 4-1. The RMS value  $S_q$  is calculated for an M by N surface like that shown in **Figure 4-1** over all points (k, l) in the *xy*-plane to generate a value of roughness for the surface being analyzed.

on 4-1 
$$S_q = \sqrt{\frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} [z(x_k, y_l)]^2}$$

Equation 4-1

Two film formulations meeting the Army/Navy Camouflage specification for reflectance were examined for surface topography and roughness (**Table 4-1**). Duplicate panels for each of the formulations were analyzed and exhibited similar randomized surface topography to that shown in **Figure 4-1**. Roughness analysis shows comparable RMS S<sub>q</sub> values for each of the four films analyzed (**Table 4-1**). Reproducibility of low gloss from a powder coatings is a major challenge in powder coating formulations. The reduction of the gloss for two formulations with duplicate panels indicated the viability of using a resin blend approach to generating low gloss powder films.

Formulation (Panel)	Gloss 60°/85°	Sq (µm)
Formulation – 1 (1)	0.4/3.0	2.533
Formulation – 1 (2)	0.4/3.0	2.619
Formulation – 2 (1)	0.8/2.2	2.942
Formulation – 2 (2)	0.6/1.9	3.565

**Table 4-1**. Coating gloss and RMS surface roughness  $(S_q)$  data for films meeting Army/Navy Camouflage reflectance specifications.

Through a systematic approach, experimental films were created to try and isolate the film components giving rise to composition changes that lead to the gloss reduction observed from the acrylic polyol blended films. Films generated from the individual constituent resin were assessed with the incorporation of full pigmentation and matting agents to determine if either of the constituent resins were capable of producing ample low reflectance films.



**Figure 4-3**. Surface topography images of the individual constituent resin films with the incorporation of pigments and matting agents.

The visual appearance and topographical analysis of the individual constituent resin films indicated that neither of the acrylic polyol resins with pigments and matting agents produced the desired low gloss observed for the blended system. Calculated  $S_q$  values for the individual constituent resin coatings were observed to be an order of magnitude lower than the blended coatings at 0.396 µm and 0.131 µm (60° gloss of 16.5 and 66 respectively) for the left and right films respectively (**Figure 4-3**). Gloss reduction, due to the incorporation of the matting agents and pigments, from the individual resin films was expected. However, the significant difference in surface roughness and resultant gloss from the individual resin films as compared to the blended film was not predicted. The results indicates that an individual resin alone in combination with the matting agent and pigments were not able to generate the necessary surface roughness for gloss reduction below a matte appearance (**Table 1-1**). The individual resin films are prime examples that the additive capacity within a powder formulation is a major road block in the development of high performance low reflectance coatings. Increasing the amount of flattening agent may reduce the gloss in the individual films however, the compromised film durability then becomes a major issue.

Analysis of one of the resin blended formulations was further performed via the systematic exclusion of the pigments followed by the matting agent. Based upon the fully formulated blends in comparison to the individual resin films, a combinatorial effect of resin blending with addition of pigments and matting agents leads to significant gloss reduction. Random surface topography with a high  $S_q$  value of 2.553 µm, similar to the pigmented film (**Figure 4-1**), was observed in the clear film with the addition of the matting agent (**Figure 4-4**A).



**Figure 4-4**. Surface topography analysis of a resin blended formulation with (A) and without (B) matting agent.

The exclusion of the matting agent led to a clear film with minimal surface topography and a low  $S_q$  value of 0.204 µm (**Figure 4-4**B). Therefore, it can be surmised that resin blending alone does not produce the surface topography and roughness responsible for gloss reduction observed for the pigmented films. The addition of matting agent into the resin blended formulation appears to induce a synergistic effect which led to enhanced surface morphologies and produced the low gloss coatings.

The surface analysis indicates that the resin blended system with the addition of matting agent produced random surface morphologies. The random morphologies resulted in the consistent reduction of reflected incident light which led to low gloss coatings. The

resin blended and individual constituent resin films were then subjected to thermal analysis via differential scanning calorimetry (DSC) to help determine a correlation between resin blending and the generation of low gloss.



**Figure 4-5**. Differential scanning calorimetry thermogram of the initial low gloss full pigmented films.

The DSC thermal analysis showed two distinct glass transition temperatures (**Figure 4-5**) which are indicative of polymeric phase separation within the resin blended formulation.<sup>75</sup> DSC thermal analysis of the individual constituent resin films revealed only

single glass transitions (**Figure 4-6**), which further indicated polymeric phase separation within the blended film.



**Figure 4-6**. Differential scanning calorimetry thermograms of the fully formulated individual constituent resin films.

DSC analysis of the coatings as the pigments and the matting agents were removed systematically, remained consistent with the observations made for the pigmented coating (**Table 4-2**). The thermal analysis, in conjunction with the initial coating deconstruction, indicates that polymer phase separation plays a key role in the generation of surface topography and roughness leading to low gloss surfaces. A synergistic effect was observed

between the phase separation exhibited by the blend of the high and low hydroxyl content acrylic polyol resins and the incorporated matting agent, which produced much lower reflectance than the matting agent in combination with either resin alone.

**Table 4-2**. Glass transition temperature comparison of film formulations with systematic removal of pigments and fillers.

Formulation	T <sub>g</sub> (°C)	T <sub>g</sub> '(°C)
Full Formulation	69.34	141.73
Filler and No Pigment	67.88	157.15
No Filler or Pigment	65.11	153.64

# 4.2 Initial Cure Ladder Study

The initial analysis of the powder coating formulations revealed that polymeric phase separation plays a vital role in the development of low reflectance coatings. Therefore, a blended acrylic polyol system without pigments and fillers was analyzed to monitor physical-chemical property changes as a function of curing time. Powder coating films were cured at 400 °F and the thermoset crosslinking reactions were thermally quenched at various time intervals. Sample films cured at various time intervals were then analyzed for surface, thermal and chemical property alterations as a function of curing times.

Differential scanning calorimetry (DSC) was performed on samples cured at various time intervals at 400 °F to observe the evolution of the glass transition temperature  $(T_g)$  as a function of curing time. The DSC analysis indicates that the sample film cured for three minutes developed a secondary  $T_g$  as shown in **Figure 4-7**. The data also indicates that as the curing time increases past three minutes, both the primary and the secondary  $T_g$ 's increase, indicating further crosslinking throughout the curing cycle. These data suggest that phase separation occurs as early as three minutes into the curing cycle and continues to develop until the cycle is completed.



**Figure 4-7**. Glass transition temperature data from coating samples at different curing time intervals at 400 °F.

Thermal gravimetric analysis (TGA) was also performed, under an inert nitrogen atmosphere, on the samples cured for different time intervals to monitor the reaction progression within the films (**Figure 4-8**). The temperature of degradation onset increased as the curing time increased, thereby indicating greater thermal stability and reduced amounts of isocyanate blocking agent within each subsequent film. The TGA results are consistent with the expected deblocking reaction for shorter curing times and increased crosslink density at longer curing times (**Figure 1-11**). Films cured for shorter time lengths show the expulsion of the  $\varepsilon$ -caprolactam blocking group via lower onset temperatures of degradation. A significantly higher crosslink density was observed for films cured for longer time lengths via increased onset temperatures of degradation and increased thermal stability.



**Figure 4-8**. Thermal gravimetric analysis for films cured at various time intervals with inset of initial 20% mass loss.

Along with monitoring the glass transition temperatures and the thermal stability in the experimental films, the progression of the deblocking and crosslinking reactions were also monitored using attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR). Free isocyanate displays a distinct stretching mode at approximately 2250 cm<sup>-1</sup> which is generated by the loss of the blocking group  $\varepsilon$ -caprolactam above 170 °C (**Figure 1-11**). The isocyanate functional group is then capable of reacting with the hydroxyl groups of the polyol resins to crosslink and form the film of interest. The presence of free isocyanate is detected with ATR-FTIR as early as one minute into the curing cycle via the peak at 2250 cm<sup>-1</sup> (**Figure 4-9**). After three minutes, the observed free

isocyanate peak has decreased noticeably and continues to decrease as the curing time increases. In conjunction with the presence and reduction of free isocyanate within the film, the peak intensity at 1698 cm<sup>-1</sup> is also reduced over the course of the curing cycle. The peak at 1698 cm<sup>-1</sup> is a vibration associated with the blocking group  $\varepsilon$ -caprolactam. As the curing time increases the 1698 cm<sup>-1</sup> evolves from a defined peak to a shoulder after three minutes of curing time indicating the loss of the blocking group within the films structure.



Figure 4-1. ATR-FTIR spectra of the blended polymer films at various cure time intervals.

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Surface analysis of the cure ladder samples at various time intervals is highly important in the effort to understanding the evolution of the surface morphologies associated with polymeric domain formation as a result of phase separation. The RMS surface roughness was measured for each of the coatings at three locations; the average and standard deviation values are reported in **Table 4-3**.

**Table 4-3**. Root mean square surface roughness for cure ladder samples monitoring the evolution of surface roughness as a function of curing time.

Cure Time Interval (min)	AVG RMS Sq (µm)	STDEV RMS Sq (µm)
1	0.077	0.010
1.5	0.033	0.003
2	0.041	0.002
2.5	0.061	0.012
3	0.103	0.003
4	0.107	0.010
5	0.122	0.012
6	0.136	0.024
8	0.139	0.035
10	0.165	0.014
12	0.162	0.042

The surface analysis shows an overall increasing trend of surface roughness as films are cured for longer periods of time. The films cured less than three minutes displayed relatively smooth surfaces with roughness values less than 0.100  $\mu$ m. The roughness data indicates that, at 1.5 minutes, the powder coating appeared to have had ample time and heat to exceed the yield value. This is significant because the powder coating must exceed the yield value in order to wet out the substrate and produce a level film prior to development of significant phase separation. At 3 minutes, significant phase separation and domain formation were observed (see **Figure 4-10**) as the surface roughness rapidly increases above 0.100  $\mu$ m. A correlation can be drawn between the surface roughness data in **Table 4-3** and the development of surface features observed in the scanning electron microscopy (SEM) images in **Figure 4-10**.



generation of surface morphologies Figure 4-2. Scanning electron microscopy images of the films at different curing time intervals which show the

# 4.3 Initial Attempted Domain Identification

Polymer phase separation has been confirmed as a major influencing factor in the generation of low reflectance in the experimental films. Thermal (**Figure 4-5**) and visual (**Figure 4-10**) data support the hypothesis that the polymeric resins phase separate in these experimental films; however, understanding and identifying the phases which were present in the films has proven difficult. In the films containing pigments and matting agents, the visual observation of phase separation is hindered due to the random surface structures with no distinct features that would indicate polymeric domains (**Figure 4-1**). Upon the removal of the matting agent, the random surface morphologies were eliminated. This process allowed for observation of polymer-polymer interactions without interference from the random surface morphologies. Characterization of the interactions of the acrylic polyol resins and the curatives through the curing process led to the visual observation of distinct polymeric domains (**Figure 4-10**).

Polymeric domain structures were observed in the first generation of polymer blended films. However, a second generation of polymeric resins and films were generated to improve film durability and modify polymeric incompatibility. Increasing polymeric incompatibility resulted in enhanced domain structures for which a comparative analysis of the individual domains could be performed. Increases to the hydroxyl group content for both the high and low hydroxyl content resins was performed to increase the polar ( $\delta_P$ ) and hydrogen bonding ( $\delta_H$ ) solubility parameters (Equation 1-5), thereby altering the polymer's miscibility which led to improved phase separation (**Figure 4-11**). Greater hydroxyl group content of both resins also resulted in increased crosslink density within the thermoset film which led to increased film durability.



**Figure 4-11**. Surface topography mapping of first generation (A) and second generation (B) polymer blended films.

In order to identify the polymeric domains in the second generation films, AFM techniques were utilized in an effort to mechanically differentiate the polymeric materials in the observed phase domains. The AFM mechanical analyses were performed using a nano-indentation force mapping technique illustrated in **Figure 4-12**.<sup>76</sup>


**Figure 4-12**. General illustration of an AFM probe interactions during nano-indentation experiments.

The nano-indentation force mapping technique generates force distance curves (**Figure 4-13**) for each approach/retract interaction with the surface in question over a specific grid identified in the experimental parameters. The upper portion of the retract (unloading) curve was then analyzed to determine the elastic modulus using a method developed by Oliver and Pharr.<sup>77</sup>



Figure 4-13. Representation of a force distance curve associated with an indentation measurement.

The Oliver and Pharr method for analysis of force distance curves utilizes the slope of the initial portion of the retract curve (S) and the area of projected elastic contact (A) to calculate the reduced elastic modulus (E<sub>r</sub>) using the following equation.

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A}$$

Equation 4-2

The reduced elastic modulus could then be used to determine the actual Young's modulus of the material (E) using the Poisson ratios of the material (v) and the indenter ( $v_i$ ) in the following equation.

Equation 4-3 
$$\frac{1}{E_r} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i}$$

Initial measurements for the current polymeric domain analysis focused upon the calculation of the reduced elastic modulus (E<sub>r</sub>) because the Poisson ratio for these materials was unknown. However, the literature does state that the Poisson ratio for polymeric materials can be estimated at 0.35 for analysis purposes.<sup>78</sup> The second generation coating examined in **Figure 4-14** exhibited large phase domain separation, which was ideal for nano-indentation analysis.



Figure 4-14. Laser scanning confocal microscopy topography image of a coating exhibiting phase separation

Nano-indentation measurements were taken for the film in **Figure 4-14**. Measurements were taken from an area on top of one of the visible domains and from an area within the continuous polymer matrix surrounding the domains to determine the differences in the mechanical properties from each area. Slope data analysis from the area from on top of one of the visible domains is tabulated in **Table 4-4**.

			MPa	339		Pa	N/m <sup>2</sup>	3.39 x 10 <sup>8</sup>	Modulus		2.249	Std Dev
							m²	2.62 x 10 <sup>-14</sup>	Area		61.965	Average
63.122	64.105	63.613	64.832	63.574	64.079	61.620	63.669	61.263	60.146	59.848	60.478	12
62.510	60.873	60.240	59.429	62.056	59.897	61.091	60.512	60.089	61.549	59.742	64.593	11
65.529	65.763	64.957	63.829	60.435	62.253	63.710	64.063	58.085	62.759	63.589	62.594	10
65.478	60.065	60.242	61.322	59.320	63.814	60.347	60.485	63.344	63.163	62.779	61.608	9
64.000	59.562	61.591	59.937	62.689	62.362	59.916	62.899	61.662	62.978	64.231	59.836	8
66.906	58.520	59.362	60.620	61.492	62.857	63.274	62.462	59.675	60.502	60.006	62.847	7
71.824	68.210	61.757	61.254	61.958	62.410	61.894	59.287	59.570	63.541	61.936	64.034	6
66.713	59.633	62.983	60.008	62.338	60.633	63.800	61.617	61.225	64.904	61.682	61.568	5
65.656	62.362	64.050	64.451	61.480	60.774	62.525	63.536	62.404	60.672	61.888	61.514	4
59.398	61.495	57.975	62.670	64.025	58.128	60.074	58.374	58.904	61.608	56.729	64.165	3
63.599	65.223	61.801	62.451	61.348	59.566	57.137	62.583	62.231	61.096	62.375	59.670	2
62.077	63.493	59.622	60.368	63.848	63.497	61.715	59.496	63.125	62.631	61.624	59.174	1
63.295	66.684	65.060	59.102	62.509	58.953	58.885	62.789	61.616	56.964	63.976	64.718	0
11	10	9	8	7	6	5	4	3	2	1	0	Line
Point	Point	Point	Point	Point								

 Table 4-1. AFM nano-indentation slope data and analysis from an area on top of a surface morphology



the surface morphology Figure 4-3. Atomic force microscopy amplitude images before and after nano-indentation of the location on top of

**Figure 4-15** depicts the area of interest before and after indentations were performed. Clear marks are observed in the AFM image on the surface of the film indicating that indentations actually occurred. The area associated with each of the indentations was estimated based upon higher magnification images for these indentations. The area of indentation, estimated to be  $2.62 \times 10^{-14}$  m<sup>2</sup>, was substituted into Equation 4-2 for calculation of the reduced Young's modulus. The estimated indentation area afforded a reduced modulus of  $3.39 \times 10^8$  N/m<sup>2</sup> (339 MPa) for the area analyzed on top of the surface morphology. Indentations were then taken in a valley between the surface morphologies to determine if there is a mechanical difference between the two areas. The slope data analysis for the indentations taken in the continuous polymer matrix are tabulated in **Table 4-5**.

	Point	Point	Point	Point	Point	Point	Point	Point	Point	Point	Point	Point
Line	0	-	2	3	4	y,	6	7	8	9	10	=
0	59.794	62.301	61.906	61.519	64.447	58.651	60.059	60.406	62.244	64.481	58.180	56.785
1	62.632	60.352	60.841	61.650	61.507	59.831	62.103	60.429	59.360	61.830	59.226	60.391
2	61.992	61.550	60.828	60.249	62.609	63.794	62.034	61.810	60.458	61.363	59.097	64.174
3	61.061	64.887	60.286	61.809	61.840	63.089	59.612	57.302	61.307	58.592	59.905	55.819
4	63.965	58.646	60.480	61.714	59.638	63.431	62.269	61.222	61.088	59.043	61.615	61.704
5	62.913	63.761	62.894	59.740	56.866	58.445	61.565	57.326	59.538	59.799	62.325	63.163
6	62.481	64.715	60.287	62.609	60.180	59.408	61.996	61.080	57.478	59.635	60.021	58.977
7	63.471	58.843	57.279	59.929	60.902	59.101	61.792	61.235	61.310	60.743	60.659	58.477
8	63.563	63.189	59.481	59.347	62.788	60.556	60.428	56.369	62.874	61.136	60.344	60.908
9	59.994	61.613	64.301	62.465	63.704	63.362	61.564	59.450	58.316	61.063	60.567	58.516
10	57.395	60.642	60.380	61.291	62.068	56.164	62.834	59.146	61.178	60.494	63.011	62.101
11	65.288	63.857	60.515	59.491	65.017	61.863	59.551	62.216	56.914	59.979	60.472	60.047
12	60.255	61.689	58.220	57.732	63.185	63.155	61.880	62.247	61.384	58.612	61.624	58.568
Average	60.888		Area	2.35 x 10 <sup>-14</sup>	m <sup>2</sup>							
Std Dev	1.962		Modulus	3.52 x 10 <sup>8</sup>	N/m <sup>2</sup>	Pa		352	MPa			

hology	Table 4-2.
	AFM nano-indentation slope data and analysis from an area in the continuous polymer matrix between the



polymer matrix between the surface morphology Figure 4-4. Atomic force microscopy amplitude images before and after nano-indentation of a location in the continuous

**Figure 4-16** depicts the surface of the continuous polymer matrix before and after the indentations were performed. Again, clear marks are observed where the AFM tip interacted with the surface, which then allowed for an estimation of the area of interaction between the AFM tip and surface. Higher magnification images were utilized to calculate the area of interaction at  $2.35 \times 10^{-14}$  m<sup>2</sup> for these indentations. Substitution of the area and the average slope into Equation 4-2 then afforded a reduced modulus of  $3.52 \times 10^8$  N/m<sup>2</sup> (352 MPa).

The nano-indentation experiments indicate that the reduced Young's modulus for the continuous polymer matrix was slightly higher than that of the domain at  $3.52 \times 10^8$ N/m<sup>2</sup> (352 MPa) and  $3.39 \times 10^8$  N/m<sup>2</sup> (339 MPa), respectively. The AFM nano-indentation results illustrate the difficulty in analyzing these complex systems, with the calculated moduli results being too similar to differentiate the polymeric domains.

## 4.4 Polymeric Domain Identification

The initial studies revealed that polymeric phase separation, in conjunction with the addition of matting agents, produced ample gloss reduction to meet Army/Navy Camouflage specifications. The surface roughness and thermal properties have been characterized and correlated with the increased crosslink density expected within the first and second generation films. Chemical differentiation of the visually observed domains have proven problematic in the first and second generation polymer blended films. The heterogeneous composition of the pigmented samples make them ideal candidates for Raman spectroscopy. However, laser induced fluorescence, which was caused by the

matting agents and pigments, was 10<sup>6</sup>–10<sup>8</sup> times greater in intensity than the Raman signal of interest and afforded non-analytical results. Spectral absorption in pigmented samples also led to sample degradation, although this risk was somewhat mitigated using NIR lasers.<sup>79</sup> One of the pigments utilized in these coating formulations is carbon black, which has very strong spectral absorption properties and high blackbody output. These spectral properties thereby rendered Raman spectroscopy unreliable for analytical analysis of the pigmented films.<sup>80</sup> Attempted characterization of domains with AFM nano-indentation provided inconclusive results for polymeric domain identification within the film structure. Therefore, other avenues were pursued to identify the polymeric domains within the resin blended films.

Polished cross-section samples were generated in an effort to characterize the polymeric domains within the clear film structure using FTIR, Raman and AFM. Initial epoxy embedded cross-section samples (**Figure 4-17**) were polished using a semi-automatic polisher and aluminum oxide and diamond paste polishing materials. The polishing procedure utilized produced cross-section samples contaminated with aluminum oxide leading to spectral artifacts hindering domain identification.



**Figure 4-17**. Epoxy embedded cross-section sample with contamination from aluminum oxide polishing media.

The domain features were clearly observed within the cross-section sample in **Figure 4-17**. AFM imaging analysis was performed in an effort to generate a phase contrast image for domain identification based upon the probe interactions with the surface.<sup>14</sup> The generation of a phase image from the epoxy embedded sample could not be performed due to large height variations observed from the protruding domains and the presence of paraffin wax contamination on the surface of the coating. The AFM height image (**Figure 4-18**) showed that, after polishing, the domains within the continuous polymer matrix protruded from the polished surface hindered the generation of a reliable AFM phase image.



**Figure 4-18**. AFM height image (left) and height profile (left) from the epoxy embedded cross-section sample.

In order to eliminate the contamination from the aluminum oxide grit, samples were embedded within a polyester potting resin and then subjected to the dry polishing process down to a 1 µm finish. Microscopy analysis of the polyester embedded cross-section samples revealed that the polished surfaces were not as smooth from the dry polishing procedure (**Figure 4-19**) compared to that achieved from the wet polishing procedure (**Figure 4-17**). However, the surfaces afforded from dry polishing were uncontaminated by extraneous polishing materials and suitable for spectroscopic analysis.



**Figure 4-19**. Microscopy image of a dry polished cross-section sample of the second generation resin blended film.

Raman analysis of the encapsulated domain and the continuous polymer matrix of the film (**Figure 4-19**) was performed through comparison of individual spectra to determine differences between the encapsulated domain and the continuous polymer matrix. A comparison of the spectra acquired from the continuous polymeric matrix and the encapsulated domain showed peaks between 1560 cm<sup>-1</sup> and 1660 cm<sup>-1</sup> that corresponded to differences in the polymer network within the domain, as compared to the continuous polymeric matrix, as shown in **Figure 4-20**.



**Figure 4-20**. Individual Raman spectra comparison of the encapsulated domain (top) and the continuous polymer matrix (bottom) from the second generation resin blended film.

The spectrum for the continuous polymer matrix shows two strong peaks at 1632 cm<sup>-1</sup> and 1605 cm<sup>-1</sup>, with a small shoulder at 1580 cm<sup>-1</sup>; however, for the encapsulated polymeric domain, the peak intensities are highly diminished or absent, which indicated a unique spectral handle for differentiation of the two polymeric domains. Mapping of the peak at 1632 cm<sup>-1</sup> was selected because of the vast intensity difference observed in the spectra from each of the individual regions within the film. The Raman correlation mapping of the peak at 1632 cm<sup>-1</sup> of the cross-section is shown in **Figure 4-21**. The spectral intensity map illustrates the consistent low intensity of the peak at 1632 cm<sup>-1</sup>

moderate and high peak intensities at 1632 cm<sup>-1</sup> are observed throughout the cross-section map, illustrating the spectroscopic difference between the domain and the continuous polymer matrix is consistent.



**Figure 4-21**. False-color map of the Raman peak at 1632 cm<sup>-1</sup>. The black corresponds to the greatest peak intensity and the white corresponds to the lowest peak intensity.

Using this discernable observation from the blended sample, Raman analysis of cross-section samples of the individual resin films was performed to chemically identify the domains within the blended film. Individual spectra recorded from each of the two films are presented in **Figure 4-22**. The Raman spectra for the films, composed of the individual resins (**Figure 4-22**), were almost identical to the observation from the blended

film (**Figure 4-20**) in the region between 1560 cm<sup>-1</sup> and 1660 cm<sup>-1</sup>. Raman analysis clearly identified that the domain within the resin blended film is the high hydroxyl functionalized resin via the absence of the peak at 1632 cm<sup>-1</sup>, whereas the continuous polymer matrix is identified as the low hydroxyl functionalized resin with the presence of a prominent peak at 1632 cm<sup>-1</sup>.



**Figure 4-22**. Individual Raman spectra comparison of films based upon the singular polymeric resins used in the blended film. The high hydroxyl content resin spectra (top) and the low hydroxyl content resin spectra (bottom).

The Raman marker peak at 1632 cm<sup>-1</sup>, utilized for domain identification, originates from infiltration of a contamination species from the polyester embedding process (**Figure 4-23**). The polyester embedding resin utilizes monomeric styrene as a viscosity reducing agent for ease of application. The monomeric styrene appeared to infiltrate the low hydroxyl resin and the continuous polymer matrix upon sample embedding. Therefore, the selective contamination resulted in the presence of the spectroscopic handle utilized for domain differentiation.



**Figure 4-23**. Comparison of Raman spectra from the individual resin in comparison to the polyester embedding resin.

The infiltration of monomeric styrene observed in the cross-section samples utilized for domain identification was thought to be a function of crosslink density differences between the polymeric regions. The high hydroxyl content resin was expected to have a greater crosslink density in comparison to that of the low hydroxyl content resin based upon functional group concentration. Mechanical analysis monitoring the Tan  $\delta$ showed that the high hydroxyl content resin had a higher crosslink density than that of the low hydroxyl content resin as shown in (Figure 4-24). Tan  $\delta$  (E"/E') for a sample is the ratio of the loss modulus (E") and the storage modulus (E') which represents the viscous and elastic responses of the samples to deformation as a function of temperature, respectively. The increased magnitude of the Tan  $\delta$  peak for the low hydroxyl resin indicated that more energy was dissipated as heat lost to molecular motions as the sample went through the glass transition which signified lower crosslink density.<sup>81</sup> The mechanical integrity of the low hydroxyl resin was also significantly reduced after going through the glass transition, resulting in large signal fluctuations in Tan  $\delta$ . Higher crosslink density was thought to restrict infiltration of monomeric styrene within the encapsulated domains, which allowed for successful Raman identification and mapping (Figure 4-21).



Figure 4-24. Dynamic mechanical analysis Tan  $\delta$  plot for the individual resin films

In order to provide complimentary evidence of domain composition, AFM analysis was attempted on cross-section samples prepared from the polyester embedded samples. However, due to the enhanced roughness observed from the dry polishing procedure, complimentary AFM results for domain identification were further hindered. In order to generate a smooth surface for AFM analysis, samples embedded within the polyester were subjected to polishing using a microtome equipped with a glass sectioning blade. LSCM images of the cross-section samples polished with the glass blade revealed distinct ridges within the domains and smooth surfaces in the continuous polymer matrix (**Figure 4-25**).



**Figure 4-25**. Microtome polished cross-section sample of the second generation resin blended film.

AFM imaging of the cross-section sample showed enhanced images of the distinct ridges observed within the domains adjacent to the smooth continuous polymer matrix (**Figure 4-26**). The glass blade appears to stick and slip within the encapsulated domain portions of the film while producing smooth cut surface in the adjacent continuous polymer matrix. The behavior exhibited by the polymer domains and the continuous polymer matrix correlates well with the infiltration of the continuous polymer matrix with monomeric styrene leading to disruption of the hydrogen bonding network, resulting in reduced interaction with the glass sectioning blade. The hydrogen bonding network within

the domains remained intact, which led to a greater interactions with the glass sectioning blade during polishing. The greater interaction with the sectioning blade resulted in a sticking and slipping interaction between the blade and the sample which led to the observed ridge formations.



**Figure 4-26**. AFM image of a domain and portions of the adjacent continuous polymer matrix of the microtome polished cross-section.

Similar behaviors were observed for the individual resin films when polished with the glass sectioning blade confirming the Raman analysis results for domain identification (Figure 4-27). The high hydroxyl content resin shows a distinct rough surface similar to the domains within the blended film in Figure 4-26. The height profile for the polished high hydroxyl shows 250 nm size oscillations, thereby indicating a strong stick slip interaction with the microtome glass sectioning blade. The low hydroxyl content resin shows relatively smooth surface similar to the continuous polymer matrix region in Figure 4-26 with 50 nm size oscillations after polishing indicating minimal interaction with the glass sectioning blade.



**Figure 4-27**. AFM height images and line profiles of the high (left) and low (right) hydroxyl constituent resin microtome polished cross-section samples.

Complimentary transmission electron microscopy (TEM) imaging was also performed in an effort to identify domains. Due to the increased success of cross-section analysis with Raman mapping and the AFM analysis, TEM analysis was pursued in order to fully visualize domains throughout a thin cross-section sample. Contrast observed for bright field TEM is based upon the interactions of electrons as they pass through the sample. Regions with greater interactions induced by greater thickness or larger atomic mass within the regions appear darker while regions with lower interactions appear lighter and areas without sample interactions appear white.<sup>82,83</sup>



**Figure 4-28**. TEM Image of a resin blended film showing domains distributed throughout the bulk of the cross-section.

The contrast observed from TEM analysis within the films provides a promising avenue for future domain identification and distribution analysis. Domains are clearly visible throughout the cross-section sample using TEM without the use of heavy metal staining (**Figure 4-28**). The domains appear darker indicating greater interaction with the electrons being transmitted through the sample, which could be indicative of greater crosslink density. Further contrast from TEM was approached with selective staining with heavy metal solutions uranyl acetate and lead citrate (**Figure 4-29**). The heavy metals

provide enhanced contrast for bright field imaging due to their high atomic mass interacting with the electrons being transmitted through the sample.<sup>82,83</sup>



Figure 4-29. TEM image of polymer blended film stained with heavy metal solutions enhancing contrast

The enhanced contrast associated with staining was readily observed due to the association of the heavy metal compounds with the encapsulated domains (**Figure 4-29**). Domain identification previously performed with Raman spectroscopy, in correlation with the enhanced contrast from TEM, showed that the heavy metal staining had a high affinity for the high hydroxyl content resin domains. The TEM results, in conjunction with Raman

chemical mapping, will allow for easy observation of domain dispersion and identification in future coating formulations based upon resin blending.

## 4.5 **Optimizing Coating Properties**

Polymeric domain identification provided a major step forward in the research and development of powder coatings with low gloss capabilities. Knowledge that the encapsulated domains are composed of the high hydroxyl functionalized resin provides valuable insight into the optimization and down selection for future powder coating materials. A third generation powder coating formulation was prepared by further increasing the hydroxyl content and subsequently the polar and hydrogen bonding solubility parameter of the high hydroxyl resin. The increases to the hydroxyl group content has proven valuable to increase the film durability through increasing crosslink density within the film structure. The crosslink density increases of the three generations of resin blended films are shown in the dynamic mechanical analysis (DMA) in **Figure 4-30**.



Figure 4-30. Comparison of storage moduli for the three generations of polymer blends.

The comparison of the crosslink density between the three generations of resin blended films was performed via monitoring the changes in storage moduli ( $\Delta E'$ ) before and after the glass transition. The film with the largest change in the storage modulus (largest  $\Delta E'$ ) observed from the DMA analysis corresponded to the film with the lowest crosslink density.<sup>81,84</sup> The DMA data (**Figure 4-30**) clearly shows that the first generation film has the largest observed change in storage modulus ( $\Delta E'$ ) of 2817 MPa. The third generation film displayed the smallest observed change in the storage modulus ( $\Delta E'$ ) of 2523 MPa, indicating the highest crosslink density of the three generations of blended coatings. Coating durability was clearly increased in the second and third generation blends as the mechanical properties are stable above the glass transition. The first generation film appears to lose all mechanical integrity at temperatures above the glass transition as shown by the DMA data in **Figure 4-30**. Increasing the mechanical integrity of liquid coatings has been shown by Levine *et al.*<sup>1</sup> to reduce the permeability of coatings to dimethyl methylphosphonate while increasing the glass transition temperature, tensile strength and elastic modulus. Increasing the mechanical integrity of the powder coating helps with weathering and chemical resistance which are important for substrate protection.

The enhancement of surface structure has also been observed in the three generations of resin blended clear films, in conjunction with the observed enhancement to the mechanical properties. The first generation film clearly shows the least amount of phase separation within the clear film, resulting in a relatively smooth surface (**Figure 4-31**). Increasing the polar and hydrogen bonding characteristics, and subsequently increasing the crosslink density, has shown massive improvements to domain formation in the second and third generation clear films (**Figure 4-31**). Distinct domain features (~ 100  $\mu$ m) with a relatively smooth continuous polymer matrix were observed for the second generation films. Upon further increasing the polar and hydrogen bonding solubility parameters for the high hydroxyl content resin in the third generation film, the surface structure becomes more disrupted with smaller surface features observed in between the larger domain features.



**Figure 4-31**. Comparison of the surface topography for the three generations of polymer blended clear films.

Comparative surface energy analysis for each of the three generations of coatings revealed a decrease in the overall approximated surface energy for each subsequent generation. Increasing the polar and hydrogen bonding solubility parameters, and subsequently increasing phase separation and crosslink density led to an overall decrease in the approximated surface energy. As the generations of coatings progressed both the water contact angle and diiodomethane contact angles increased, leading to the observed decrease in the surface energy (**Figure 4-32**). Surface wetting is reduced for both solvents, which is helpful in reducing the spread of chemical contaminants on the surface and absorption of contaminants within the polymer network of the film.<sup>85,86</sup>



**Figure 4-32**. Surface energy and contact angle analysis of the three generations of resin blended films.

Thermal, mechanical and surface analysis has provided valuable information into the optimization of coating properties in the three generations of resin blended films. Enhancement of the thermal and mechanical properties are clearly shown through increased crosslink density and higher T<sub>g</sub> values observed with DMA analysis. Enhancement of surface properties has been consistent throughout the analysis of the three generations of clear coatings. Visual conformation of domain formations were performed with microscopy techniques, and decreases to the surface free energy approximations were calculated through contact angle analysis.

## 4.6 Examining Reaction Conditions

The extent of polymer immiscibility for the resins utilized in the third generation coating was examined at 400 °F in the absence of the isocyanate crosslinker. Omission of the crosslinker results in the isolation of polymer-polymer interactions under reaction conditions similar to the simplified Flory-Huggins lattice of a polymer blend (**Figure 1-4**). Polymeric phase separation is readily observed within one minute under reaction conditions with polymeric domains on the order of 100  $\mu$ m (**Figure 4-33**). The extent of polymeric phase separation increased the longer the polymer blend remained at the reaction temperature of 400 °F. The initial polymeric domains appear to coalesce forming larger phases, which become readily observable to the human eye after several minutes.



isocyanate crosslinker Figure 4-5. Polymeric phase separation exhibited by the polymer blend at 400 °F at various time intervals without

In the absence of the crosslinking agent, phase separation of the polymeric resins appeared to occur spontaneously through spinodal decomposition under reaction conditions.<sup>28,33</sup> However, in the presence of the isocyanate curative, the extent of polymeric phase separation appeared to be limited, due to crosslinking and other factors associated with the thermoset reaction. **Figure 4-34** shows films of the third generation polymer blend with curative that have been allowed to cure for one minute (**Figure 4-34**A) and for 12 minutes (**Figure 4-34**B).



**Figure 4-34**. Third generation polymer blend films cured for one minute (A) and 12 minutes (B).

Surface analysis of the third generation films cured at various time intervals show similar results when compared to the initial cure ladder studies performed in Section 4.2 above. The surface roughness is well below 0.100  $\mu$ m before 2.5 minutes of curing time, at which time the surface roughness increases to 0.200  $\mu$ m; it reaches a maximum of 0.430  $\mu$ m at 9 minutes (**Figure 4-35**). Minimal surface topography and a low Sq value of 0.040  $\mu$ m was observed for the film thermally cured for 1 minute. The minimal surface roughness indicated that the polymeric materials wetted the surface and produced a level film without significant domain formation. The fully cured film exhibited an increased amount of phase separation within the film, which resulted in a rougher surface with a high Sq value of 0.340  $\mu$ m (**Figure 4-35**).



Figure 4-35. Root mean square (RMS) surface roughness development for the third generation blend formulation cure ladder study.

The initial surface roughness observed in both cure ladder studies for the first and third generation resin blends indicates that the curative may behave as a solvent in which both the resins become dissolved, thereby generating smooth films in the initial stages of curing. Phase separation appeared to begin within the first 2 minutes as the surface roughness gradually increased from 0.040  $\mu$ m to 0.081  $\mu$ m. Significant phase separation was observed between 2 and 4 minutes when the surface roughness rapidly increased from 0.081  $\mu$ m to 0.326  $\mu$ m in the same two minute time frame. Analysis of solvation effects
of the resins within the blocked isocyanate curative was attempted via utilization of alternative curatives.

#### 4.6.1 Alternative Curatives

Resin solubility within the isocyanate curative was examined through alterations of the blocking agent and the isocyanate base structure. Previous film preparations and cure ladder studies performed in this study utilized an aliphatic polyisocyanate curative blocked with a  $\varepsilon$ -caprolactam blocking agent (**Figure 4-36**).



Figure 4-36. Aliphatic diisocyanate (left) and ε-caprolactam (right) chemical structures.

Alternative blocked isocyanate curatives (Curative B and Curative C) were utilized to alter polymer solubility within the blended powder formulations and monitor the physical-chemical alterations of the resulting thermoset films. Curative B was an aliphatic polyisocyanate curative blocked with a triazole blocking agent, which thermally deblocks above 161 °C (**Table 3-1**). Curative C was a cycloaliphatic polyisocyanate blocked with a ε-caprolactam, which thermally deblocks above 180 °C (**Table 3-1**).



**Figure 4-37**. Surface structure analysis of films cured with different blocked isocyanate crosslinkers A, B and C.

Upon altering the curatives significant surface structural alterations were observed for the fully cured clear films (**Figure 4-37**). The film formulations utilizing Curative B led to a film structure exhibiting minimal phase separation resulting in a smooth coating with a surface roughness value of 0.110  $\mu$ m (**Figure 4-37**B). The solubility of the resins appeared to be enhanced upon switching the blocking agent of the aliphatic polyisocyante subsequently increased the gloss of the pigmented coatings. The film formulations that utilized Curative C resulted in a surface with a large number of randomly dispersed pits across the entire surface (**Figure 4-37**C). The area between the pits appeared smooth possibly indicating enhanced solubility of the resins within the  $\varepsilon$ -caprolactam blocked cycloaliphatic polyisocyante. However, the presence of the random pits across the entire surface was a possible byproduct of significant off gassing of the blocking agent from the coating. The surface analysis results indicated that both the curative base structure and blocking agent play a major role in the development of phase separation within the polymer blended formulations.

Cure ladder studies for the clear film formulations utilizing alternative curatives were performed to monitor the development of the distinct surface features observed in Figure 4-37. An overlay of the surface roughness data for each of the three film formulations is shown in **Figure 4-38**. The surface roughness for the film formulation utilizing Curative A showed minimal surface development within the initial 2 minutes of curing consistent with substrate wetting and leveling accompanied by minor amounts of phase separation. Between 2 and 4 minutes, rapid surface structure development was observed, which indicated significant phase separation within the film. After 4 minutes minimal surface roughness development was observed as the surface roughness plateaued. Surface analysis results for the formulation with Curative B showed a gradual increase in the surface roughness within the initial three minutes of curing prior to a gradual reduction of the surface roughness throughout the remainder of the cure. These results were consistent with the hypothesis of enhanced solubility of the resins within the curative leading to minimal phase separation and smoother coatings. The cure ladder results for the film formulation containing Curative C showed the pitted surface developed rapidly within the initial one and a half minutes of curing which was hypothesized to be a result of rapid off-gassing from within the film structure leaving the pitted surface throughout the remainder of the cure.



**Figure 4-38**. Surface roughness analysis of cure ladder samples of films with alternative curative.

The distinct alterations to the clear film surface structures has led to vast alterations to the observed gloss of both the clear and pigmented formulations. The surface roughness and gloss data for the three curative formulations are shown in **Table 4-6**. The only formulation to meet the Army/Navy Camouflage specification upon pigmentation utilized Curative A. Pigmentation of the film formulations with Curatives B and C led to films with gloss values well above the Army/Navy Camouflage specifications.

Curative	Base Structure	Blocking Group	S <sub>q</sub> (μm)	Clear Gloss 60°/85°	Pigmented Gloss 60°/85°
А	Blocked ALPH	ε-caprolactam	0.400	27/40	0.6/2.7
В	Blocked ALPH	Triazole	0.110	76/87	11/21
С	Blocked CYCLOALPH	ε-caprolactam	0.519	38/70	3.3/8.3

Table 4-6. Gloss and surface roughness data for films cured with various curatives.

Further characterization of the observed changes to the film structure was undertaken through mechanical analysis of the clear films. Comparison of the change in the storage moduli ( $\Delta E'$ ) before and after the glass transition (**Figure 4-39**) for the clear films provided complimentary evidence to the enhancement of solubility of the resins upon switching the isocyanate crosslinking agent. Modulation of the crosslink density was readily observed in the DMA analysis of the storage moduli for the three clear film formulations. The film formulation with Curative A possessed the highest crosslink density, with the smallest observed  $\Delta E'$  of 2523 MPa (**Figure 4-39**). Upon switching the curative, the crosslink density was reduced, leading to larger  $\Delta E'$  values of 2843 MPa and 2737 MPa for formulations with Curatives B and C, respectively. The substantial differences in crosslink density clearly indicated increased solubility of the resins with lower amounts of phase separation and increased co-curing between the two constituent resins.



Figure 4-39. Comparison of storage moduli for clear films cured with alternative curatives.

# 4.6.2 Temperature

Alterations to the reaction conditions has proven to play a vast role in balancing and generating durable coatings with exceptional low gloss. The alterations to the curative demonstrated that, through simple modification to the formulations, the blended system can be altered drastically — further illustrating the complexity of the powder coating systems. Curing temperature, with respect to powder coatings, was another highly important parameter due to limitations of substrate durability at high temperatures.<sup>69,74</sup> Curing profiles were modified to evaluate the resultant coatings physical-chemical characteristics as a function of reaction temperature. The third generation coating formulation was cured at four different temperature and time profiles: 400, 375, 350, and 325 °F for 12, 22, 30, and 40 min respectively. Surface thermal and mechanical properties were monitored for coatings cured at various temperatures. Surface topography and roughness analysis clearly show that, as the reaction temperature is reduced, the surface features become diminished (**Figure 4-40**). The RMS roughness value decreases steadily from  $0.41 \pm 0.02 \ \mu m$  to  $0.25 \pm 0.02 \ \mu m$  for the films cured at 400 °F and 325 °F respectively. The decrease in the surface topography is indicative of reduced amount of phase separation within the film structure over the course of curing at lower temperatures.



Figure 4-40. Surface images of a film formulation cured at various temperatures.

The observed reduction in the surface roughness correlated well with observed gloss measurements taken for each of the films cured at various temperatures (**Figure 4-41**). As the curing temperature was decreased, the surface roughness decreased, which led to a significant increase in the observed gloss from the coatings. Significant alterations to the surface morphologies and roughness in clear coatings has been shown in the previous curative analysis. The resulting alterations to the surface morphologies observed in the

clear coatings were shown to affect the observed gloss for the fully formulated coatings with incorporated pigments and matting agents (**Table 4-6**).



Figure 4-41. Comparison of gloss and surface roughness as a function of curing temperature.

Mechanical analysis was performed to correlate the changes in the storage moduli and the Tan  $\delta$  curve with the altered surface features observed in **Figure 4-40**. The storage moduli changes in **Figure 4-42** for the films cured at various temperatures were consistent with the observed changes in the surface roughness. As the curing temperature was lowered, the crosslink density was also reduced, thereby indicating that phase separation was limited in the films cured at lower temperatures.



Figure 4-42. Comparison of storage moduli for clear films cured at different temperatures.

Higher degrees of co-curing are readily observed in the Tan  $\delta$  plots of the films cured at lower temperatures (**Figure 4-43**). The peaks in the Tan  $\delta$  plots shift to lower temperatures resulting in a reduction in the primary and secondary glass transition temperatures. Tan  $\delta$  plots for samples cured at 350 °F and 325 °F show single broad peaks, indicating heterogeneity of the crosslinks within the film structure. Increased heterogeneity within the films is due to a minimization of phase separation, which resulted in increased co-curing between the two constituent resins.<sup>24,81,84</sup> The peaks in the Tan  $\delta$  plots for the sample cured at 350 °F and 325 °F are larger in magnitude due to a greater

viscous response (E") of both of the samples upon deformation. The increased magnitude of the Tan  $\delta$  peaks indicates that more energy was dissipated as heat lost to molecular motions as the sample goes through the glass transition.<sup>81</sup>



Figure 4-43. Tan  $\delta$  plot of the clear films cured at different temperatures.

Raman analysis was also utilized to provide complementary data on crosslink density, with respect to infiltration of monomeric styrene utilized in domain identification. Raman analysis of cross-section samples prepared through polyester embedding were examined for styrene infiltration within the domains. Samples of films cured at 375 °F,

350 °F and 325 °F were examined for styrene infiltration (**Figure 4-44**). Previous analysis shown in Section 4.4 illustrated that the infiltration of monomeric styrene was based upon the crosslink density differences between the continuous polymer matrix and the encapsulated domains. Mechanical comparison of the individual resin films showed that the crosslink density within the high hydroxyl content was indeed greater than that of the low hydroxyl resin (**Figure 4-24**), which was thought to limit the infiltration of monomeric styrene within the domains.



**Figure 4-44**. Raman mapping of styrene infiltration within domains observed in blended films cured at various temperatures.

The Raman maps clearly show that the lowest peak intensity observed in each map increased as the temperature of reaction was decreased. The increase in peak intensity observed in the chemical map indicated a higher degree of monomeric styrene infiltration within the lowest intensity regions. Domains were still readily discernible in the Raman maps, however, the crosslink density was reduced within the domain regions allowing styrene penetration within the domains.

Reduction of the reaction temperature resulted in a clear reduction of the phase separation within the polymer blended films. Reduction of phase separation within the film structure led to visible alterations to the surface structure (**Figure 4-40**), resulting in decreased surface roughness and subsequently increased gloss (**Figure 4-41**). Thermal-mechanical (**Figure 4-42** and **Figure 4-43**) and spectroscopic (**Figure 4-44**) analyses both show decreased crosslink density as a result of the lowered curing temperature. The results indicated limited diffusion of the materials in the molten phase due to increased viscosities at lower reaction temperatures which led to increased co-curing of the two constituent resins.

# 4.6.3 Catalysis

Addition of catalyst to film formulations was performed to modify reaction conditions to determine the effect of increased reaction rates on the physical-chemical properties of the resulting films. Film formulations with minor additions of catalyst were cured using the same four temperature and time profiles examined in Section 4.6.2 above. Surface and thermal-mechanical measurements were performed to evaluate the catalyzed films for comparative analysis with the non-catalyzed films. The resulting surface morphology for the catalyzed films are shown in **Figure 4-45**.



**Figure 4-45**. Surface images of a film formulation with incorporation of catalyst cured at various temperatures.

Incorporation of the catalyst to the formulation clearly results in faster crosslink formation which resulted in limited phase separation. Limited phase separation and domain formation is clearly observed in the surface analysis of the catalyzed films due to the increased rate of thermoset crosslinking reactions. Smaller domains are clearly visible in all four surface images in **Figure 4-45** as compared to the non-catalyzed films in **Figure 4-40**. As a result of faster reaction rates, the surface roughness of the resulting films was considerably reduced in the catalyzed films as compared to the non-catalyzed films (**Table 4-7**).

Temperature (°F)	Non-Catalyzed Sq (μm)	Catalyzed Sq (µm)
400	$0.41 \pm 0.02$	$0.31\pm0.02$
375	$0.37 \pm 0.02$	$0.29\pm0.02$
350	$0.31 \pm 0.02$	$0.24\pm0.02$
325	$0.25 \pm 0.02$	$0.21\pm0.01$

**Table 4-7**. Surface roughness data for non-catalyzed and catalyzed clear films cured at various temperatures.

The mechanical analysis of the catalyzed films is consistent with the surface analysis results previously presented in **Figure 4-45**. Catalysis of film formation led to significant reduction of the crosslink density (**Figure 4-46**) through minimization of phase separation, similar to the resultant crosslink density alterations as a result of reduction to the reaction temperature reported in the previous section. Distinct crosslink density differences are readily observed when comparing the storage moduli of the non-catalyzed and catalyzed films cured at 400 °F. The change in storage modulus ( $\Delta E'$ ) for the non-catalyzed clear film cured at 400 °F is 2526 MPa (**Figure 4-42**); the catalyzed film had a  $\Delta E'$  value of 3442 MPa (**Figure 4-46**), which was a considerable difference in the crosslink density upon addition of catalyst.



**Figure 4-46**. Comparison of storage moduli for catalyzed clear films cured at different temperatures.

Further control over domain formations and crosslink density within the thermoset coatings has been observed through the addition of catalyst to the formulations. Greater reduction in domain development was readily observed via surface analysis (**Figure 4-45**), which resulted in more co-curing and overall reduction of crosslink density observed in the catalyzed film formulations (**Figure 4-46**). Increased deblocking and crosslinking reaction rates and reduction of temperature have allowed for control over polymeric phase

separation within the resin blended coatings. The combination of these factors allows for tailoring domain formations within the thermoset coatings.

### 4.6.4 Incorporation of the Matting Agent

The matting agent has been determined as working synergistically with the resulting phase separation within the blended coatings to produce random surface structure, which is necessary for gloss reduction (**Figure 4-4**). Cure ladder studies of clear films have been performed on the third generation blended coatings without incorporation of the matting agent. As a result, the surface roughness has been shown to develop as the cure time increases (**Figure 4-35**). A cure ladder study was performed with the incorporation of the matting agent in an effort to determine the development of the full surface structure necessary for gloss reduction, with respect to curing time.



**Figure 4-47**. Root mean square (RMS) surface roughness development for the third generation blend formulation with matting agent.

Surface analysis of cure ladder samples for the film formulation with the inclusion of the matting agent displayed three distinct regions: initial substrate wetting, rapid surface development and static surface structure (**Figure 4-47**). The coating materials appeared to wet the substrate and level within 1.5 min, which produced a film with a relatively low surface roughness value of 0.16  $\mu$ m (**Figure 4-47**). Rapid surface structure development was then observed between 1.5 and 4 min in the curing cycle, increasing from 0.16  $\mu$ m to 2.12  $\mu$ m, respectively. After 4 min at 400 °F, the film surface structure remained relatively constant, with minimal surface structure changes throughout the remainder of the cure. These results confirmed the synergistic effect observed in the first generation coating

analysis between the resin blend and the addition of matting agent. Surface structure develops rapidly after substrate wetting early within the curing cycle, reaching a maximum within 4 min under reaction conditions. The results also indicate the time at which the viscosity of the crosslinked materials become high enough that diffusion of the matting agent and domains within the film become severely hindered locking the film structure in place.

### 4.7 Domain Identification in Pigmented Coatings

Initial analysis of pigmented coating described above revealed random surface topographies via analysis with laser scanning confocal microscopy (**Figure 4-1**) and two distinct glass transition temperatures in the DSC thermal analysis (**Figure 4-5**). Subsequent work in clear films followed in an effort to fully characterize polymeric interactions occurring within the thermoset films. The polymeric domain within the resin blended film were chemically identified via Raman spectroscopy. Raman analysis of monomeric styrene infiltration within the films led to differentiation of the polymeric phases based upon crosslink density. Domain composition was further confirmed with AFM and TEM experiments which correlated well with the Raman analysis. TEM results from the resin blended clear films with (**Figure 4-29**) and without (**Figure 4-28**) heavy metal staining proved promising for possible observation of polymeric domains within the pigmented films. Discernable contrast of the polymeric phases as a product selective heavy metal staining of the encapsulated domains in the clear films should provide the same contrast within the pigmented films.



Figure 4-48. Cross-section TEM image from a pigmented coating with heavy metal staining.

TEM analysis of the pigmented coating proved to be successful and showed the presence of phase separation throughout the extent of the film thickness, with domains of various shapes and sizes (**Figure 4-48**). The domains appeared to sequester the matting agent and pigment materials, which led to the disruption of the standard domain shapes observed in the clear coatings previously examined in **Figure 4-29**. Smaller domains appeared to remain in spherical shapes similar to those observed in the clear coating with small pigment particles present within the domain structures. The larger domains appeared distorted in order to completely envelop the larger matting agent and pigment particles within the domain structures. Correlating SEM cross-section images clearly showed

agglomeration of the pigment materials throughout the film structure without the distinct contrast from TEM imaging (**Figure 4-49**).



**Figure 4-49**. SEM image of a cross-section sample from a pigmented coating showing agglomeration of pigment materials.

Electron microscopy imaging of cross-section samples has proven to show polymeric phase separation throughout the thickness of the pigmented coatings. High contrast for domain formations was afforded by TEM, while high contrast for matting agents and pigments was afforded by SEM, allowing for tandem characterization of the pigmented films. These results further confirmed the synergistic nature of domain formation within the resin blended films and the incorporation of matting agents and pigments. Domain formation and sequestration of the matting agent and pigment particles are key factors in generating high performance low reflectance coatings.

### **Chapter 5 : Conclusions**

The *in situ* generation of polymeric domains within resin blended powder formulations has proven to work synergistically with the addition of matting agents and pigments to afford coatings that meet Army/Navy Camouflage gloss specifications. The subsequent characterization of polymeric behavior in resin blended films has shown that polymeric phase separation was an invaluable approach for new materials development. Custom tailoring of surface and bulk properties from the powder coating was highly desired; however, with the omission of solvent and different processing/curing parameters, new challenges arose which required rigorous characterization for advancement of new solvent free coatings.

Physical-chemical properties have been characterized for films exhibiting polymeric phase separation throughout three generations of resin blended coatings. Through variations in hydroxyl group functionality, the degree of polar and hydrogen bonding solubility influence for individual polymeric resins has been modulated. The modulation of the polymer solubility parameters has allowed for the generation of polymeric films with enhanced surface, thermal and mechanical characteristics due to enhanced polymeric phase separation and increased crosslink density. Increased crosslink density, due to increased hydroxyl group functionality, was clearly observed for each new generation of polymer blends via DMA analysis. Distinct domain features were clearly observed in the second and third generation resin blended films as a result of greater polar and hydrogen bonding characteristics. Greater degrees of phase separation allowed for isolation of individual polymeric domain suitable for independent analysis and subsequent identification.

Utilization of Raman spectroscopy on polished cross-section samples provided conclusive chemical differentiation of the polymeric domains present in the second and third generation clear resin blend films. Spectroscopic differences between the encapsulated domains and the continuous polymer matrix were observed within the Raman shift region from 1560 cm<sup>-1</sup> to 1660 cm<sup>-1</sup>. Infiltration of monomeric styrene into the continuous polymer matrix, as a result of the cross-section embedding process, was observed and identified as a spectroscopic handle for polymer identification within the blended films. Comparison of the Raman spectra acquired from the blends and the individual polymer resin films provided consistent evidence for polymeric phase differentiation. The high hydroxyl functionalized resin film displayed minimal infiltration of monomeric styrene, similar to encapsulated domains within the blended film. The low hydroxyl functionalized resin film displayed significant amounts of styrene infiltration, consistent with the infiltration observed for the continuous polymer matrix. Complementary AFM and TEM analyses of cross-section samples also provided evidence consistent with Raman chemical mapping of monomeric styrene infiltration.

Development of an understanding of the curing mechanism and how phase separation progresses in conjunction with simultaneous thermoset cross-linking reactions posed a significant analytical challenge. Therefore, multiple avenues of analysis and

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various reaction conditions were altered to characterize polymeric behavior within the resin blended coatings. Alterations to reaction conditions has provided valuable insight into film development and phase separation under thermoset reaction conditions. In the absence of an aliphatic polyisocyanate curative, the polymeric resins phase separate instantaneously via spinodal decomposition, resulting in random domain morphologies. However, in the presence of the aliphatic polyisocyanate curative, polymeric phase separation was suppressed due to the curative behaving as a solvent. Significant surface structural development from the resin blend, with the incorporated curative, was observed in the cure ladder studies after 2 min. The use of alternative blocked polyisocyanate curatives modulated the solubility, leading to significant changes in the overall surface, thermal and mechanical properties of the cured films. Increased solubility of the resins within both alternative polyisocyanate curatives led to decreased domain formations, which resulted in higher degrees of co-curing between the two constituent resins and reduced mechanical integrity. Significant off gassing was readily observed for the film formulation with the *ε*caprolactam blocked cycloaliphatic polyisocyante, which led to a pitted surface with reduced film consistency.

Reaction rate effects on film formation were pursued through reduction of the reaction temperature and via the addition of a catalyst to the powder coating formulations. Modulation of the curing temperature and incorporation of a catalyst to the formulation both led to reduced phase separation, which resulted in higher gloss films with reduced crosslink density. Reduction of the curing temperature appeared to limit phase separation and increase co-curing due to increased viscosities of the molten resins within the blend.

The incorporation of the catalyst resulted in an even greater reduction of phase separation due to increased reaction rates. Significant crosslink formation and rapidly increased viscosities, as a result of catalysis, limited the diffusion of the molten resins within the blended film. As a result of limited diffusion within the catalyzed film, significant cocuring was observed, leading to the reduction in the observed mechanical properties.

Surface roughness development for the third generation resin blended film, with the incorporation of the matting agent, was monitored as a function of reaction time. The cure ladder study confirmed the synergistic effect between the incorporation of the matting agent and phase separation of the constituent resins. Three distinct stages of surface roughness development were readily observed: initial substrate wetting, rapid surface development and static surface structure. Surface analysis results showed that the characteristic random surface morphologies were developed within the first four minutes of curing. After four minutes of curing the surface morphologies and roughness remained relatively static while the remainder of the crosslinking reactions proceeded. The changes to the viscosity and subsequently the diffusion rates were readily observed to play a vital role in the surface structure development.

Lastly, domain observations within pigmented films was performed with bright field TEM analysis and heavy metal staining. TEM analysis clearly showed domain formations within the pigmented films with excellent contrast from the heavy metal staining. The high hydroxyl content resins of the pigmented blended film appeared to sequester the pigment and matting agent particles within the domains, which resulted in various domain structures observed within the film. Correlating SEM imaging also showed distinct agglomeration of the matting particles within the cross-section samples which further indicated domain structures within the pigmented films.

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# **Biography**

Spencer L. Giles graduated from Susan B. English High School (Seldovia, Alaska) in 2004. He then attended the University of Alaska Fairbanks (Fairbanks, Alaska), where he received his Bachelor of Science and Master of Science degrees in Chemistry in 2009 and 2011, respectively. While attending graduate school at the University of Alaska Fairbanks, he was a teaching assistant for several general chemistry laboratory courses as well as a sophomore analytical chemistry laboratory course. After receiving his Master of Science degree, he moved to Alexandria, Virginia and enrolled in the doctoral program at George Mason University (Fairfax, Virginia). He pursued doctoral studies while concurrently working at the Naval Research Laboratory (Washington, DC) under the Pathways program in 2011.