THE EFFECT OF CHANGES IN CHEMISTRY AND CERAMIC SLURRY PROCESSING ON ALUMINA GREEN TAPES

by

PAUL ROBERT NAHASS

S.B. Chemical Engineering, Massachusetts Institute of Technology (1984)
S.M. Chemical Engineering Practice, Massachusetts Institute of Technology (1984)

Submitted to the Department of Materials Science and Engineering in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Ceramics at the Massachusetts Institute of Technology February, 1990

$^a$Charles Stark Draper Laboratory, Inc., 1990
All Rights Reserved.

Signature of author

Department of Materials Science and Engineering
January 12, 1990

Approved by

William L. Robbins
Charles Stark Draper Laboratory
Technical Supervisor

Certified by

H. Kent Bowen
Ford Professor of Engineering
Thesis Supervisor

Accepted by

Linn W. Hobbs
Professor of Materials Science and Engineering
Chairman, Departmental Committee on Graduate Students
THE EFFECT OF CHANGES IN CHEMISTRY AND CERAMIC SLURRY PROCESSING ON ALUMINA GREEN TAPES

Paul R. Nahass

Submitted to the Department of Materials Science and Engineering on January 12, 1990
in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Ceramics

ABSTRACT

Tape-casting formulations were developed which do not require organic solvents or soluble, high molecular weight polymers in the slip. One formulation utilized monomeric, polymerizable, n-butyl methacrylate in place of the media for tape-casting barium titanate. Polymerization was accomplished in situ, immediately after casting. The organo-titanate dispersant synthesized for this study had the capability of attaching to the ceramic surface and bonding to the polymer, forming a continuous composite matrix in the green tape. The other formulation was aqueous-based, using a proprietary acrylic emulsion polymer as the binder in the aluminium oxide tape-casting system. The emulsion formed a continuous film of binder surrounding the ceramic particles upon drying, but the slip required surfactant addition in order to achieve similar mechanical properties to green tapes from solvent-based, soluble-polymer slurries using the same acrylic binder.

Green tapes from the formulations developed were strong and flexible. Processing was physically easier to accomplish due to the absence of high molecular weight polymers which caused extremely high slip viscosities. The absence of volatile solvents allowed safer handling of slurries and more precise compositional control due to the reduced rate of evaporation of water and the monomeric solvent during processing. A direct comparison of green tape properties was made using the aqueous, emulsion slurry and one utilizing the same polymer dried and redissolved in an equimass mixture of toluene and ethanol. Several green tape properties were evaluated.

Green tapes from the solvent-based slurry were substantially less dimensionally stable over time than aqueous-based samples and experienced more shrinkage anisotropy due to orientation of the soluble polymer chains during casting. Treatments to improve dimensional stability had a more dramatic effect on solvent-based tapes, enabling samples to experience linear shrinkage of <0.15% over 35 days of aging with no measurable anisotropy. These results were reproducible for tapes cast from different batches. The most effective treatments involved heating plus swelling of the tape by saturated vapor of either water or toluene, causing the polymer phase to have high mobility, thereby facilitating relaxation. Shrinkage was found to be inversely proportional to the ratio of the amount polymer phase attached to ceramic particles compared to that in the bulk. This correlation was independent of the slurry system and any stabilization treatment used, and is consistent with observations and theory in
the literature for behavior of similar, filled-polymer systems.

Firing shrinkage behavior was similar to that for green shrinkage of samples from the solvent-based slurry only. Green tape stabilization treatments reduced firing shrinkage and essentially eliminated shrinkage anisotropy during firing. Aqueous-based tapes experienced less linear shrinkage on firing but more in-plane anisotropy, with shrinkage in the casting direction less than that in the transverse direction for treated and untreated samples. These results were also reproducible for tapes prepared from different batches of slurry. The reason for this behavior may be due to the point at which polymer adsorption on ceramic particles occurs: probably before casting in the solvent-based system; and after film-formation in the aqueous system, when drying is mostly complete. This causes different rheological behavior in each system and allows latex particles and ceramic particles to be distributed differently in the aqueous, emulsion-based slurry.

The emulsion polymer used for this comparison was likely a high molecular weight random copolymer of ethyl acrylate (EA) and methyl methacrylate (MMA), in a ratio near 2:1, EA:MMA, based on analysis. Polypropylene glycol, the plasticizer used, was found to be mostly soluble in the polymer at the concentration used (29 wt%), over the temperature ranges scanned by dynamic mechanical analysis (DMA). However, in the presence of ceramic particles, it seems plasticizer was rejected from the binder above 30°C. This phenomenon was completely reversible in green tapes and caused rigidity due to the component segregation. DMA was found to be a useful tool for evaluating and uncovering subtle mechanical property differences in green tapes, and from these and other results it was concluded that the polymer phase was physically and chemically the same even if different solvents were used or stabilization treatments performed. Theory would predict that a correlation should exist between DMA behavior and observed shrinkage in green tapes because damping is significantly affected by the ratio of adsorbed to bulk polymer in filled systems. However, due to instrument shortcomings and and sampling difficulties, DMA was not able to provide a good correlation.

Thesis Supervisor: H. Kent Bowen
Title: Ford Professor of Engineering
### TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>1</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>2</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>4</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>5</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>9</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>11</td>
</tr>
<tr>
<td><strong>Chapter 1</strong></td>
<td></td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>12</td>
</tr>
<tr>
<td><strong>Chapter 2</strong></td>
<td></td>
</tr>
<tr>
<td>DEVELOPMENT OF TAPE-CASTING FORMULATIONS WITHOUT VOLATILE SOLVENTS OR SOLUBLE POLYMERS IN THE SLIP</td>
<td>15</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>15</td>
</tr>
<tr>
<td>II. BACKGROUND</td>
<td>16</td>
</tr>
<tr>
<td>III. TAPE-CASTING BARIUM TITANATE USING \textit{in situ} POLYMERIZATION</td>
<td>28</td>
</tr>
<tr>
<td>IV. AN AQUEOUS TAPE-CASTING SLURRY FOR ALUMINA</td>
<td>50</td>
</tr>
<tr>
<td>V. CHAPTER SUMMARY</td>
<td>65</td>
</tr>
<tr>
<td><strong>Chapter 3</strong></td>
<td></td>
</tr>
<tr>
<td>COMPONENT INTERACTIONS, DIMENSIONAL STABILITY AND FIRING BEHAVIOR OF ALUMINA GREEN TAPES WITH DISPERSED AND SOLUBLE ACRYLIC BINDER</td>
<td>67</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>67</td>
</tr>
<tr>
<td>II. BACKGROUND</td>
<td>68</td>
</tr>
<tr>
<td>III. EXPERIMENTAL</td>
<td>74</td>
</tr>
<tr>
<td>IV. RESULTS</td>
<td>83</td>
</tr>
<tr>
<td>V. DISCUSSION</td>
<td>115</td>
</tr>
<tr>
<td>VI. CONCLUSIONS</td>
<td>134</td>
</tr>
<tr>
<td>VII. FUTURE WORK</td>
<td>137</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>141</td>
</tr>
<tr>
<td>BIOGRAPHICAL NOTE</td>
<td>146</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

CHAPTER 1

Figure 1.1. Schematic diagram of doctor-blade tape-caster [Mistler, 1978].

Figure 1.2. Schematic view of a laminated cofired multilayer ceramic substrate [Young, 1986].

CHAPTER 2

Figure 2.1. Thermal gravimetric analysis of various binders used in ceramics processing [Gurak, 1984].

Figure 2.2. Viscosity v. concentration of: (▲)ethyl cellulose in aqueous emulsion, (●)ethyl cellulose in alcohol solution, (■)methyl cellulose aqueous solution [Onions, 1986].

Figure 2.3. (a) Aqueous dispersion deposited on a substrate; (b) evaporation of water; (c) close-packed spheres with water filling voids; (d) further evaporation of water and polymer deformation; (e) continuous coating [Onions, 1986].

Figure 2.4. Coalescence of polymer spheres in an evaporating water film [Allyn, 1976].

Figure 2.5. Diffusion of plasticizer into latex particles (from Onions [1986]).

Figure 2.6. Domains of steric interaction: (a) non-interpenetrational (d>2L); (b) interpenetrational (L<d<2L); and (c) interpenetrational-plus-compressional (d<2L) [Napper, 1983].

Figure 2.7. Reaction pathway for bonding long chain oleates to alkoxytitanate [Parish, 1985].

Figure 2.8. Mechanism for bonding of alkoxytitanante to BaTiO₃ surface [Parish, 1985].

Figure 2.9. Replacement of isopropoxy groups on titanium tetraisopropoxide with carboxylic acids [Bradley, 1978].

Figure 2.10. Predicted structure of ITODM dispersant.

Figure 2.11. Schematic for tape-casting process with in situ polymerization.
Figure 2.12. Two-blade casting head [Mistler, 1986].

Figure 2.13. Sediment densities for BaTiO₃ in n-butyl methacrylate with different dispersants (dispersant structures included).

Figure 2.14. Structures of triglycerides: (a) glyceryl trioleate, and (b) typical Menhaden oil triglyceride.

Figure 2.15. TGA plots for a green tape cast by *in situ* polymerization under ambient conditions.

Figure 2.16. Scanning electron micrographs of a green tape cast by *in situ* polymerization under ambient conditions: (a) top, (b) bottom.

Figure 2.17. TGA plot for top and bottom of a tape cast by *in situ* polymerization in nitrogen.

Figure 2.18. Scanning electron micrographs of a green tape cast by *in situ* polymerization in nitrogen: (a) top, (b) bottom.

Figure 2.19. TGA for BaTiO₃ powder with ITODM bonded to the surface, and green tape without cross-linking agent, after acetone extraction. Difference between these two plots represents the amount of polymer cross-linked with ITODM.

Figure 2.20. Scanning electron micrographs of top surfaces of BaTiO₃ tapes fired at 1450°C for 30 min: (a) prepared with ITODM dispersant; (b) prepared with organo-Ba/Ti dispersant.

Figure 2.21. Scanning electron micrographs of fracture surfaces of BaTiO₃ tapes fired at 1450°C for 15 min: (a) prepared with ITODM dispersant, (b) prepared with organo-Ba/Ti dispersant.

Figure 2.22. Scanning electron micrographs of fracture surfaces of BaTiO₃ tapes fired at 1450°C for 45 min: (a) prepared with ITODM dispersant, (b) prepared with organo-Ba/Ti dispersant.

Figure 2.23. Particle size distribution of alumina powders determined by Horiba CAPA 500 analyzer.

Figure 2.24. Settling densites of AKP-30 alumina in water.

Figure 2.25. Particle size distribution of Rhoplex B-60A dispersed latex particles and of AKP-30 alumina particles (determined by Horiba CAPA 500).

Figure 2.26. Film-formation models for green tapes: (a) powder content below CPC, (b) powder content above CPC.
Figure 2.27. Design of: (a) overall tape-casting system, and (b) drive system for casting head.

Figure 2.28. Processing steps for tape-casting aqueous slurries.

Figure 2.29. Porosity v. ceramic packing density in green tapes.

Figure 2.30 TGA for a green tape cast from aqueous slurry: (a) slice taken from top surface, (b) slice taken from bottom surface.

CHAPTER 3

Figure 3.1. The broadened glass-transition of filled polymers (am. and amorph. mean amorphous). From Struik [1978].

Figure 3.2. Settling densities for AKP-30 alumina powder in different solvents and with different dispersants.

Figure 3.3. Punch pattern for green tape shrinkage determination.

Figure 3.4. Linear shrinkage over time for untreated green tapes.

Figure 3.5. Linear shrinkage over time for treated green tapes: (a) from solvent, (b) from aqueous emulsion.

Figure 3.6. Reproducibility of shrinkage in green tapes cast from solvent: (a) untreated; (b) treated, solvent-exposure; (c) treated, humidity.

Figure 3.7. Shrinkage for green tapes after 35 days: (a) from solvent, (b) from aqueous emulsion.

Figure 3.8. Complex modulus and damping (tan δ) for Rhoplex B-60A film measured by Dynamic Mechanical Analysis (DMA).

Figure 3.9. DMA of B-60A film, unplasticized green tape.

Figure 3.10. DMA of B-60A/PPG films.

Figure 3.11. DMA of untreated green tapes.

Figure 3.12. DMA for treated, solvent-based green tapes: (a) longitudinal direction, (b) transverse direction.

Figure 3.13. DMA for treated tapes from aqueous emulsion: (a) longitudinal direction, (b) transverse direction.

Figure 3.14. Sample elongation as a function of temperature during DMA.
Figure 3.15. Peak height vs. retention volume for GPC analysis of dried Rhoplex B-60A dissolved in THF.

Figure 3.16. Transmission FTIR spectra for films of acrylic polymers: (a) poly(ethyl acrylate), from Pouchert [1985]; (b) poly(methyl methacrylate), from Higgins [1990]; and (c) Rhoplex B-60A.

Figure 3.17. Prediction of B-60A composition by FTIR absorbance peak ratio comparison to PMMA and PEA.

Figure 3.18. Prediction of B-60A composition using relations for MFT, $T^*$.  

Figure 3.19. Correlation of shrinkage in green tapes to amount of organics attached to alumina particle surfaces.

Figure 3.20. Correlation of green tape shrinkage with modulus drop over the glass-transition region (from DMA).

Figure 3.21 Correlation of firing shrinkage to the amount of organics attached to alumina particle surfaces (in green tapes).
LIST OF TABLES

CHAPTER 2

Table 2.1. A typical tape-casting system [Mistler, 1978].
Table 2.2. Methacrylate monomers and polymers [Brandup, 1975].
Table 2.3. Tape-casting slip formulation used in this study.
Table 2.4. Dispersion results for BaTiO₃ powder in various solvent/dispersant systems.
Table 2.5. Physical properties of BaTiO₃ green tapes prepared by the in situ polymerization process.
Table 2.6. Physical properties of alumina powders tested.
Table 2.7. Physical properties of dispersants tested.
Table 2.8. Physical properties of binders tested.
Table 2.9. Surface tension measurements for aqueous tape-casting slurry components.
Table 2.10. Compositions for tape-casting aqueous slurry.
Table 2.11. Physical properties of green tapes cast from aqueous slurries with acrylic emulsion binder.

CHAPTER 3

Table 3.1. Surface tension measurements for solvents and polymer/solvent mixtures.
Table 3.2. Slurry formulations for aqueous, emulsion-based system and conventional, solvent-based, soluble-polymer system.
Table 3.3. Physical properties of green tapes for comparison.
Table 3.4. Approximate composition of green tapes used for this study.
Table 3.5. Linear shrinkage incurred by green tapes during stabilization treatments (%).
Table 3.6. Glass-transition ranges (°C) for cast samples based on damping peak from DMA.

Table 3.7. FTIR spectra peaks (in wavenumbers) measured for Rhoplex B-60A and literature values for acrylic polymers [Pouchert, 1985].

Table 3.8. Dissolution behavior of polymer films and alumina green tapes in the presence of various solvents.

Table 3.9. Organic content of green tapes before and after solvent extraction in toluene (wt%).

Table 3.10. Linear firing shrinkage (%) of green tape layers; all layers were aged 40 days prior to firing unless otherwise noted.

Table 3.11. Green tape shrinkage incurred on treatment, broken down into mechanistic causes.
ACKNOWLEDGEMENTS

I am grateful to the Charles Stark Draper Laboratory for the financial support for this thesis research. Draper supplied my research assistantship for the past 4-1/2 years, all the tape-casting equipment, and dimensional stability analyses. Thanks also to the MIT Ceramics Processing Research Laboratory for the materials and supplies necessary for work done at MIT, and access to all the analytical equipment. The U.S. Army Natick Development Laboratory provided a great service, allowing me to invade their lab and take over the DMA for about a month and a half. Specific gratitude to John Song at Natick Labs, who spent many hours helping me get my samples running and fixing the apparatus when I broke it. Materials samples for this research were provided by Rohm and Haas, Sumitomo Chemical, R.T. Vanderbilt, Dow Chemical, and Ceralox.

Technical support was provided by many great minds. My deepest indebtedness is to Dr. Richard Pober, without whom I might still be wallowing around the lab; or proofreading, for that matter. His suggestions of experiments, calculations and analyses were invaluable; lest I not forget the experience and wit he shared. Dr. Wendell Rhine was always available to listen to an idea and add his chemist’s perspective. I wish I would’ve been able to bother Prof. Paul Calvert more because he had excellent intuition about this work and suggested simple, yet extremely useful techniques and analyses. Thanks to my thesis advisor, Prof. H. Kent Bowen for, among other things, telling me people were interested in what I was doing, and always being encouraging about my research progress and my professional development. Bill Robbins, my Draper supervisor, pushed me to always remember the practical side to things, and guided the project to a more complete end. I hope Prof. Michael Rubner wasn’t bored by all this, because he was really the only one available to help add some semi-serious polymer science to this study. Prof. Michael Cima provided excellent engineering advice and enthusiasm whenever I bothered him, and always made time for me in his frantic schedule. The most amazing feat was getting all those people together for meetings; I appreciate the extra time they put in to try to make sense of this potential mess. Essential aid was provided by John, Gerry, Barbara, Lenny and Linda at MIT, and Todd, Nancy, Brian, and the Inspection Lab at Draper.

Personal support was, no doubt, that without which all else could not have proceeded. My wife, Jennifer, has endured my PhD program with me from the application process through courses, generals, tie-dying, and thesis. The last months were the toughest and she really came through for me, taking care of everything I needed outside the thesis and even doing an excellent job of proofreading. Thanks to my parents for always being supportive and extremely patient about this whole thing, I hope I can finally pay them back for everything they’ve done. Finally, thanks to all my friends, inside and outside of MIT for companionship, laughs, and stimulation.
CHAPTER 1

INTRODUCTION

Tape-casting is a process in which a ceramic-containing slurry is spread out in a thin layer by passage under a doctor-blade to form thin flexible sheets. This process is illustrated in Figure 1.1 [Mistler, 1978]. After drying, cast green tapes or green sheets are blanked, punched, metallized, stacked, laminated and fired to produce electronic packaging devices, the most advanced of which is IBM’s Thermal Conduction Module (TCM), shown schematically in Figure 1.2 [Young, 1986]. These modules are multifunctional, providing power to and dissipating heat from high density computer chips. A single TCM contains up to 33 ceramic layers, 130 m of wiring, and 100-118 chips. The complexity of this package indicates the importance of materials and process control, and the need to improve these as future information processing requirements will necessitate more layers, connections, and circuitry in the package [Tummala, 1989].

Figure 1.1. Schematic diagram of doctor-blade tape-caster [Mistler, 1978].
Figure 1.2. Schematic view of a laminated cofired multilayer ceramic substrate [Young, 1986].

Typically, tape-casting slurries consist of ceramic powder (usually aluminum oxide for packaging applications, and barium titanate for multilayer ceramic capacitors), dispersion media (usually an organic solvent), a high molecular weight polymer to provide strength to the film, a plasticizer for flexibility, and a deflocculant for the powder. Young indicates several qualities which are required of green sheets made by tape casting: (1) high strength, (2) sufficient flexibility for handling and machining, (3) dimensional stability over time, (4) uniform density, (5) absence of defects and asperities, (6) capability of laminating to itself, (7) stability of the binder, (8) absence of pinholes after solvent evaporation, and (9) capability of shrinking reproducibly during firing.

The tape-casting process, and materials preparation and batching for it have an
immense impact on the properties of green tapes. Though it seems there are many properties to optimize, there are even more variables to control during processing. The influence each variable has on a property can be easily obscured due to the interaction of the materials and process variables. This thesis attempted to assess effects of variation of the solvent in the tape-casting slurry formulation and, to a lesser extent, the binder. The properties of specific interest are dimensional stability over time, binder-plasticizer compatibility and stability, and firing behavior. These were assessed quantitatively while all the other properties mentioned above were maintained.

Since non-proprietary literature directly related to the tape-casting process is very limited, an extensive section of literature review was not necessary or available. However, each topic covered in this thesis includes literature pertinent to that area. Chapter 2, mainly experimental in nature, describes novel formulation methods for tape-casting without using volatile organic solvents or soluble polymeric binders in the slip. Chapter 3 compares the aqueous slurry with acrylic emulsion binder (developed in Chapter 2) to a conventional organic solvent slurry with the same binder dissolved in the solvent. Component interactions in the green tapes are compared for these slurry systems in detail; the dimensional stability of samples produced will be assessed and the firing behavior of green sheets produced from different slurry formulations will be observed. The major conclusions for the thesis are given at the end of Chapter 3 along with the description of specific experiments capable of verifying unconfirmed hypotheses or uncovering valuable information about the tape-casting process and how it might be controlled to produce desirable green sheets.
CHAPTER 2

DEVELOPMENT OF TAPE-CASTING FORMULATIONS WITHOUT VOLATILE SOLVENTS OR SOLUBLE POLYMERS IN THE SLIP

I. INTRODUCTION

The development of the multilayer ceramics market and fabrication technologies for these products have progressed rapidly over the few decades since their inception. Aside from market and fabrication desires deemed necessary by the microelectronics industry, environmental concerns exist which may shift the direction of process development for multilayer ceramics. Processes which do not expel large amounts of organic solvents will be preferred if devices produced perform as well or even nearly as well as those from existing, environmentally-harmful processes. Similarly, labor concerns are less of a problem when using process ingredients that do not produce potentially harmful vapors.

The paint industry responded to this problem long ago, primarily because laborers and (especially) consumers became physically irritated during and shortly after application. Water-based formulations have since been developed for many paint applications. Many similarities exist between the contents of paint formulations and tape casting slurries. However, the microelectronics industry’s manufacturing processes do not expose many consumers to direct irritation, therefore the driving forces for process change have been limited to organized labor and (recently) environmental concerns. These forces do not seem to be losing momentum on their mission for safer chemicals in industry.
The objective of this chapter is to discuss tape-casting formulations which produce quality green sheets for microelectronics applications but do not involve the use of volatile solvents. Application of these techniques would reduce costs incurred for solvent-vapor treatment as well as those for operator safety, such as ventilation and protective gear. Greater process control due to the absence of solvents, may also allow the operator more freedom in customizing the slurry for specific product needs. Further, the inherent nature of polymerizable and emulsion-based binders could yield products which have some superior properties to those made from existing state-of-the-art formulations.

II. BACKGROUND

Tape-casting is the preferred method for depositing two-dimensional ceramic films with thickness ranges of 20 to 1200 μm. A thorough treatise has been written [Mistler, 1978] on the tape-casting process and its requirements, omitting the necessity for a detailed description here. Some of the ideas more relevant to this work will be presented here, as necessary.

Polymers in the Tape-casting Process

The binder in a tape-casting slurry has several requirements, including its ability to form a tough, flexible film at concentrations as low as 10 wt %. Usual binders are long-chain polymers with sufficient structural flexibility to prevent rigidity of the green tape. Plasticizers are usually added to enhance tape flexibility and can actually be found in greater amounts than the binder. Binder technology is changing rapidly; the more popular binders currently being examined are poly(vinyl butyral) and
poly(alkyl methacrylates). Poly(alkyl methacrylates) are widely studied because of their relatively simple polymerization process, relatively efficient burnout (as seen in Figure 2.1) and the variety of properties available from different methacrylate polymers.

Though soluble polymers have traditionally been used in tape casting formulations, at least two other potential means of binder implementation exist: (1) stable emulsion polymers, and (2) curable, monomeric systems. These are common methods employed by the paint industry [Allyn (1976), Gurak (1987), Martens (1964), Onions (1987)]. Both systems allow the same amount of binder (or vehicle) in the final product while drastically reducing the solvent content necessary to provide usable viscosities. A typical tape-casting system (Table 2.1) has a viscosity of ~2000 cp.

Figure 2.1. Thermal gravimetric analysis of various binders used in ceramics processing [Gurak, 1986].
Table 2.1. A typical tape-casting system [Mistler, 1978].

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Function</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>ceramic</td>
<td>59.6</td>
</tr>
<tr>
<td>Magnesia</td>
<td>grain growth inhibitor</td>
<td>0.15</td>
</tr>
<tr>
<td>Menhaden fish oil</td>
<td>dispersant</td>
<td>1.0</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>solvent</td>
<td>23.2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>solvent</td>
<td>8.9</td>
</tr>
<tr>
<td>Poly(vinyl butyral)</td>
<td>binder</td>
<td>2.4</td>
</tr>
<tr>
<td>Octyl phthalate</td>
<td>plasticizer</td>
<td>2.1</td>
</tr>
<tr>
<td>Poly(ethylene glycol)</td>
<td>plasticizer</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Figure 2.2. Viscosity v. concentration of: (▲)ethyl cellulose in aqueous emulsion, (●)ethyl cellulose in alcohol solution, (■)methyl cellulose aqueous solution [Onions, 1986].
Synthetic emulsion polymers are referred to as latexes if the product was prepared by emulsion polymerization. This technique involves emulsifying a monomer or monomer-blend in aqueous media with anionic or non-ionic surfactants and polymerizing this emulsion (Allyn [1976] and Martens [1964] provide excellent detail). Latex systems have the ability to form dispersions with high concentrations of high molecular weight polymers at viscosities several orders of magnitude lower than soluble systems with the same polymer content, as shown in Figure 2.2.

Film-formation properties of latex systems need to be addressed to provide continuous films necessary to achieve tough green tapes. Emulsion film-formation occurs in three steps, which are illustrated in Figure 2.3 (and on a smaller scale in Figure 2.4): (1) particle contact, (2) particle deformation, and (3) particle fusion. Several models have been put forth to explain the forces present during latex particle coalescence (many of which are reported by Onions [1987]). Brown [1956] indicates that capillary forces have the largest effect on film formation. The Laplace equation,

\[ P = \frac{2 \gamma}{r} \]  

(2.1)

where \( \gamma \) = interfacial or surface tension, and \( r \) = particle radius, can be used to calculate the pressure particles must exert on each other to coalesce. Since the interfacial tension (water/polymer) in commercially-available latexes is usually low due to the surfactants present, surface tension is the principle actor in determining particle coalescence in emulsion formulations of this type.

Solubility of the plasticizer (if used) in the polymer is another important consideration for film-formation in latex systems. Sears [1982] describes several theories of polymer-plasticizer compatibility, the most popular and widely-accepted of those utilize the Hildebrand solubility parameter, \( \delta \), and the Flory-Huggins interaction
Figure 2.3. (a) Aqueous dispersion deposited on a substrate; (b) evaporation of water; (c) close-packed spheres with water filling voids; (d) further evaporation of water and polymer deformation; (e) continuous coating [Onions, 1986].

Figure 2.4. Coalescence of polymer spheres in an evaporating water film [Allyn, 1976].
parameter, $\chi$. Though neither parameter for predicting compatibility works for all cases, the Flory approach is more widely used [Onions, 1986]. It is an empirical quantity which takes into account specific properties of the system, such as polar interactions and hydrogen-bonding, and can be determined by various methods (generally, a smaller $\chi$ value indicates better compatibility). The literature does not contain values of $\chi$ for every system [Brandrup, 1975], and since accurately obtaining the parameter is not trivial, there are practical limitations to the theory.

Plasticizer distribution in a dispersion is affected by its chemical structure and molecular weight [Sears, 1982], and can alter film-formation characteristics. Thermodynamically, a constant amount of plasticizer will dissolve in the polymer particles while the rest remains dissolved in the media, according to the equilibrium constant for the system. This behavior is evidenced by swelling of the latex particles over time, as shown in Figure 2.5. Kinetic considerations indicate the time-scale for equilibrium swelling may be several days, even for sub-micron emulsion particles. Turbidity measurements have been used [Gravier 1983] to assess plasticizer diffusion. Bradford [1963] found, by centrifugal separation, that different plasticizers took from a few seconds to 23 days, to be completely absorbed by the same latex. This phenomenon revealed itself by the different morphologies of films cast from systems which had been aged for different periods.

Free radical polymerization is the most common method for producing bulk, non-crystallizing polymers of alkyl methacrylates [Odian, 1981]. This process is a chain reaction of three steps: initiation, propagation, and termination. Initiation consists of decomposition of an initiator molecule into free radicals and subsequent addition of this radical to a monomer unit thereby initiating a polymer chain.
Figure 2.5. Diffusion of plasticizer into latex particles [Onions, 1986].

Propagation involves sequential addition of large numbers of monomer units to the chain. Propagation of the chain ceases at some point and terminates when two radicals come in contact or by the attack of terminating species (such as oxygen). Mechanical properties and reaction times can be tailored through polymerization kinetics by controlling the initiator concentration. For example, a fast polymerization can be achieved using a high concentration of initiator; while a high molecular weight, tougher product is obtained using a smaller amount of initiator.

Table 2.2 lists some of the wide range of methacrylate monomers which are commercially available and relevant properties. Copolymerization of these monomers results in copolymers having physical properties varying with the amount of that monomer added, enabling precise tailoring for individual applications. Methacrylates
with acid groups might be added to enhance affinity for oxide surfaces.

Dimethacrylates may be added for cross-linking when a tough, solvent-resistant product is desired or the chain lengths attained are too short to achieve the desired mechanical strength. Excessive cross-linking results in an inflexible polymer, but this can be avoided by increasing the distance between cross-linking sites on the monomer.

Two common initiating systems for methacrylates are benzoyl peroxide and azoisobutyronitrile (AIBN), which both decompose at above 60°C to form free radicals. Benzoyl peroxide also has the attractive feature of decomposition at room temperature by the addition of aromatic amines. The concentration of these reaction accelerators can be varied to control the rate of polymerization and the rate of heat evolution. AIBN on its own and benzoyl peroxide in the presence of an activator,
will decompose upon exposure to UV light enabling photo-polymerization.

**Dispersion of Powders for Casting**

Dispersion of the ceramic powder in a tape-casting slurry is of maximum importance for achieving a dense, uniform green microstructure which can maintain dimensional stability through the post-casting handling processes and lead to reproducible sintering behavior. The forces responsible for powder dispersion are either electrostatic (in polar solvents) or steric (in nonpolar solvents), or possibly a combination of the two [Hiemenz, 1977; Pugh, et.al. 1983]. Electrostatic forces result from association of like charges around the oppositely-charged particle surface (not unlike the phenomenon of capacitance), forming a layer which is electrically repulsive to particle coagulation. This process is therefore enhanced in solvents having high dielectric constants. Steric repulsive barriers are difficult to achieve in aqueous dispersions of oxide powders due to the hydrophilic nature of both the solvent and the particle surfaces and subsequent competition for dispersant affinity.

Steric stabilization results from molecular attachment (usually by polymers or oligomers) to particle surfaces enabling an osmotic repulsion which opposes the usual attractive forces between particles. Figure 2.6 shows the three domains of close approach of sterically-stabilized surfaces. This interaction involves mixing free energy and elastic free energy terms [Napper, 1983]. The mixing term arises from an increase in local polymer concentration when particle surfaces approach closer than twice the length of the adsorbed species (Fig. 2.6b). Chain-chain interactions are unfavorable if the polymer is soluble in the solvent (the demixing condition) resulting in a positive free energy change of mixing and particle repulsion. Insolubility of the
Figure 2.6. Domains of steric interaction: (a) noninterpenetrational ($d > 2L$); (b) interpenetrational ($L \leq d \leq 2L$); and (c) interpenetrational-plus-compressional ($d \leq L$) [Napper, 1983].

adsorbed species invites chain-chain interaction leading to system flocculation. The elastic free-energy dominates when particles approach closer than one length of adsorbed species (Fig. 2c). Chain compression lowers local entropy, hence increasing free energy and resulting in particle repulsion. Since organic components are critical to the proposed tape-casting process, steric stabilization will be the dominant mechanism for preventing flocculation.

The degree of steric stabilization achieved by a system is a function of three parameters: (1) solvent-particle interactions which are related to wetting; (2) free energy of interaction between the dispersant and the solvent; and (3) attachment of the dispersant to particle surfaces [Hiemenz, 1977]. The first two conditions require that
the free energies of interaction between the particle-solvent and dispersant-solvent are not so high as to cause the dispersed phase to aggregate. Dispersant structures can be examined to determine if the molecules are likely to fully extend into the solvent; dispersants and solvents having similar functional groups are favored for this condition [Napper, 1983].

There are three modes of attachment of a polymeric dispersant to a ceramic particle surface: physical adsorption, hydrogen bonding, and covalent bonding [Laible and Hamann, 1980]. The ceramic oxides of interest tend to be hydroxylated surfaces. Physical bonding is due to Van der Waals interactions, the potential reversibility of which in the presence of an additional solvent can cause ceramic suspensions to flocculate. Surface hydroxyl groups are capable of strong hydrogen bonding with dispersants having polar end-groups, such as amines, resulting in a stable dispersion. The equilibrium nature of hydrogen bonding may cause displacement by additives and impurities. Covalently-bonded dispersants are less sensitive to being displaced by impurities, and can be carried through several solvents for different processing steps while remaining anchored to the particle surfaces.

Parish [1985] successfully bonded the end group of an alkoxytitanate oligomeric dispersant to barium titanate. Long chain oleates are added to the alkoxytitanate via the reaction shown in Figure 2.7 to create a "steric barrier" (Napper's theory, which applies to polymer chains, predicts that these oligomer chains are too short for steric stabilization). The alkoxide starting material is also a precursor for titania production [Barringer and Bowen, 1985] and easily bonds to the similar surface of the oxide as shown in Figure 2.8. This product is difficult to isolate or characterize fully due to the transient nature of the alkoxides [Nahass, 1985]. It is thought that oleate groups
Figure 2.7. Reaction pathway for bonding long chain oleates to alkoxytitanate [Parish, 1985].

will add selectively to the first two functionalities of the alkoxide because the size of the oleic acid makes replacement of the third and fourth alkoxy groups kinetically unfavorable [Parish, 1985]. The hydrocarbon tail of this dispersant would indicate the use of a hydrocarbon solvent to achieve maximum dispersion. Indeed, hexane was shown to be an excellent solvent for this system.

Figure 2.8. Mechanism for bonding of alkoxytitanate to BaTiO₃ surface [Parish, 1985].
III. TAPE-CASTING BARIUM TITANATE USING *in situ* POLYMERIZATION

Historically, tape-casting of barium titanate has been a reliable, efficient method for producing thin sheets for multilayer ceramic capacitors, ferroelectrics, thermistors, and other insulating devices [Howatt, 1947; Buchanan, 1986]. These devices have properties which are often very sensitive to chemical composition and microstructure. Second phases which can drastically alter dielectric properties can be found in grain boundaries of undoped barium titanate having cation stoichiometry deviations less than 0.1 mol % from 1.000, less than most known analytical techniques can measure [Negas, et.al, 1974; Hu, et.al, 1985]. Similarly, different amounts of dopant ions such as Nb, La, Ta and their distribution can cause significant microstructural and dielectric property changes [Kahn, 1971; Buessem and Kahn, 1971]. Manufacturing rejects due to electrical property non-specification is normally caused by poor microstructure which often originates from chemical inhomogeneity or improper firing conditions.

The tape-casting process in this work involves replacing the binder with monomeric solvents and dispersants that polymerize after casting. This has several potential advantages over conventional processes: (1) the solvent-drying step of the process is eliminated, saving the atmosphere and operators from undesirable organic solvents while allowing the tape to cure without a large volume change (which can lead to cracking); (2) electrical properties and microstructure of the final ceramic can be controlled by minor chemical alterations such as addition of metal-containing polymerizable dispersants without changing processing conditions (casting, drying, forming); (3) cross-linking of the polymerized solvent to the dispersant and the chemical bonding of the dispersant to the particle surfaces can increase the green strength of the tape while allowing the use of less binder; (4) the tape can be cured
with a protective carrier on top increasing the homogeneity of the tape and the similarity of the top and bottom surfaces; (5) selective patterning of ceramic materials can be achieved by ultraviolet or laser-induced polymerization techniques [Lee, et.al, 1986]; and (6) this method is applicable to extrusion, injection molding and other conventional forming processes.

PROCEDURE

The first step in development of the in situ polymerization process was the choice of starting materials and optimization of the slurry recipe. Butyl methacrylate (bp=160°C) was chosen as the monomeric solvent for this process because it forms a tough, rubbery polymer with a relatively low glass-transition temperature (T_g=20°C). In a free radical polymerization oxygen or any impurity will cause premature termination of polymer chains, therefore polymerizations of this type do not usually achieve high molecular weight chains without strict control of reaction conditions, namely purity and atmosphere. This effect was reduced by using a comonomer, diethylene glycol dimethacrylate to induce cross-linking in the system, improving mechanical properties. Too much cross-linking, however, makes chains inflexible and the material brittle; diethylene glycol dimethacrylate contains a spacer group (C-C and C-O bonds) between cross-linking sites, giving the resultant polymer some flexibility. Dioctyl phthalate was used to plasticize the system. Benzoyl peroxide was chosen to initiate the reaction by its decomposition by heat at >60°C or at room temperature by N,N, dimethyl-p-toluidine.

The choice of dispersants effective in polymerizable solvents such as butyl methacrylate is very limited. A new organotitanate dispersant, isoproxytitanium
oleate dimethacrylate (i-PrOTi(O₂C(CH₂)₇CH=CH(CH₂)₇CH₂)₂) was synthesized by the stepwise replacement of isopropoxy groups on titanium tetraisopropoxide with carboxylic acids [Bradley, et.al., 1978]. This reaction is illustrated in Figure 2.9.

In this process the oleic acid (Alfa Products, Danvers MA; bp 286°C/100mm), titanium tetraisopropoxide (Alfa Products, Danvers MA; bp 58°C/1mm), and methacrylic acid (Aldrich, Milwaukee WI; bp=160°C) were first purified by distilling under reduced pressure. Oleic acid (1 mol) was then added dropwise to titanium tetraisopropoxide (1 mol) under nitrogen. The mixture was stirred and heated to 50°C for 1 h. The isopropanol byproduct was removed under reduced pressure and trapped in liquid nitrogen. Methacrylic acid (2 mols) was added dropwise under nitrogen to the reaction product (triisopropoxytitanium oleate). The reaction mixture was stirred for another hour, and the isopropanol byproduct was removed again, as above. The product was a viscous, brownish-orange liquid, the predicted structure of which is

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_7\text{CH} - \text{CH} = \text{CH}(\text{CH}_2)_7\text{COOH} + \text{Ti(Oi-Pr)}_4 & \rightarrow \text{CH}_3(\text{CH}_2)_7\text{CH} - \text{CH}(\text{CH}_2)_7\text{COOTi(Oi-Pr)}_3 + \text{i-PrOH} \\
\text{oleic acid} & \text{titanium tetraisopropoxide} \\
\text{CH}_3(\text{CH}_2)_7\text{CH} - \text{CH}(\text{CH}_2)_7\text{COOTi(Oi-Pr)}_3 + 2\text{CH}_2 = \text{CMcCOOH} & \rightarrow \\
\text{methacrylic acid} & \\
\text{CH}_3(\text{CH}_2)_7\text{CH} - \text{CH}(\text{CH}_2)_7\text{COOTi(Oi-Pr)}(\text{O}_2\text{CMcC—CH}_2)_2 + 2\text{i-PrOH} & \text{isopropoxytitanium oleate dimethacrylate (ITODM)}
\end{align*}
\]

Figure 2.9. Replacement of isopropoxy groups on titanium tetraisopropoxide with carboxylic acids [Bradley, 1978].
shown in Figure 2.10.

A quantitative determination of the isopropanol byproduct using standard aqueous \( \text{K}_2\text{Cr}_2\text{O}_7 \) (in 12.5% \( \text{H}_2\text{SO}_4 \)) [Bradley, 1978] indicated that although the oleic acid replacement was complete, only 1.3 of the 2 moles of methacrylic acid had reacted with the isopropoxytitanate. The replacement of the third isopropoxy group on titanium tetraisopropoxide was therefore incomplete. The unreacted methacrylic acid and the isopropyl ester, which is known to form as a decomposition product in isopropoxytitanium carboxylates, were not separated from the organotitanate in this study. An infrared spectrum of the organotitanate gave the following peaks: IR \( \nu \) (cm\(^{-1}\)) 2925, 2850 (C-H); 1732 (C=O, ester); 1705 (C=O, acid); 1645 (C=C); and 1550 (C=O, Ti carboxylate).

The effectiveness of the organotitanate dispersant was determined from

Figure 2.10. Predicted structure of ITODM dispersant.
dispersion tests. These tests were carried out in 10 ml graduated tubes on 6.0 g of BaTiO$_3$ in 5.0 g methacrylate solvent (4.5 g butyl methacrylate and 0.5 g diethylene glycol dimethacrylate) containing organotitanate. The suspensions were ultrasonicated, and allowed to stand undisturbed for at least one day before the precipitate volumes were measured. In these tests isolated, non-interacting particles will precipitate to a high density, whereas agglomerated particles will form loosely packed sediments [Parish, et.al., 1985]. The observed sediment density therefore provides a qualitative estimate of the extent of flocculation.

The dispersants used for comparison included oleic acid, methacrylic acid, azelaic acid, monomethyl ester, threo-9,10 dihydroxystearic acid, linoleic acid (all from Aldrich Chemical Co., Milwaukee, WI), an oxidized form of Menhaden fish oil (Defloc Z3, Spencer Kellogg Division of Textron, Inc., Buffalo, NY), and prepared ITODM (Landham, 1987). All dispersant amounts were 1 wt% of powder except for the ITODM, which had 0.4 wt% reacted with the powder surface (this pretreated powder had been prepared several months earlier).

Table 2.3 gives the experimental batch recipe for the tape-casting process. The commercial BaTiO$_3$ powder (HPB grade; TAM Ceramics Inc., Niagara Falls NY) was dried at 60$^\circ$C under vacuum prior to use. The powder surface area (B.E.T. N$_2$ [g] adsorption) was 3.6 m$^2$/g, the density (stereopycnometer He [g] displacement) was 6.04 g/cm$^3$, and the particle size distribution (Sedigraph) was 0.4-2.5 μm with an average particle size of 1.4 μm. Butyl methacrylate was distilled under reduced pressure to remove hydroquinone inhibitor. Benzoyl peroxide (50%), diethylene glycol dimethacrylate (Alfa Products, Danvers MA), dioctyl phthalate (Alfa Products, Danvers MA) and N,N-dimethyl-p-toluidine (99 %, Alfa Products, Danvers MA) were used as
Table 2.3. Tape-casting slip formulation used in this study.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Function</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Titanate</td>
<td>ceramic</td>
<td>67-77</td>
</tr>
<tr>
<td>Butyl methacrylate</td>
<td>solvent/binder</td>
<td>21-25</td>
</tr>
<tr>
<td>Organotitanate (ITO−DM)</td>
<td>dispersant/coupling agent</td>
<td>0.4-7.0</td>
</tr>
<tr>
<td>Diethylene glycol dimethacrylate</td>
<td>crosslinking agent</td>
<td>0.0-2.0</td>
</tr>
<tr>
<td>Dioctyl phthalate</td>
<td>plasticizer</td>
<td>0.0-5.2</td>
</tr>
<tr>
<td>Benzoyl peroxide</td>
<td>initiator</td>
<td>0.6</td>
</tr>
<tr>
<td>N,N-dimethyl-p-toluidine</td>
<td>accelerator</td>
<td>0.6</td>
</tr>
</tbody>
</table>

received.

The tape-casting process currently used is illustrated schematically in Figure 2.11. ITO−DM was synthesized from purified oleic acid, methacrylic acid and titanium tetraisopropoxide. Powder was mixed with 5 wt % ITO−DM dispersant and toluene and refluxed at the boiling point of toluene (110°C) to increase the rate of the

Figure 2.11. Schematic for tape-casting process with in situ polymerization.
reaction between the dispersant and the powder surface. Reaction times of at least 8 hours were used. This mixture was then centrifuged and decanted, and fresh toluene was added. After repeating the centrifugation procedure, the amount of dispersant on the surface was measured by thermal gravimetric analysis (TGA). The powder with dispersant bonded to the surface is mixed with butyl methacrylate (polymerizable solvent), cross-linking agent and plasticizer. After preparation, the slurry was put into a nitrogen-atmosphere dry box, where it was then poured into the casting head and cast onto glass plates with an appropriate carrier film (to facilitate easy removal). The two-blade casting head (Figure 2.12) was designed for this research based on the uniform thickness it provides [Mistler, 1986] and the predictability of green tape thickness [Otsuka, et.al., 1986]. No automatic casting equipment was available for use inside a dry box, therefore tapes were cast by hand.

Figure 2.12. Two-blade casting head [Mistler, 1986].
RESULTS AND DISCUSSION

The ideal dispersant for the in situ polymerization system must: (1) form tapes with high packing density, (2) incorporate metal alkoxides that covalently bond to particle surfaces, (3) allow for a variable dopant concentration, and (4) cross-link into the polymer matrix. Unfortunately, the organotitanate dispersant explored thus far, isopropoxy titanium oleate dimethacrylate (ITODM), may need modification for optimal use in the in situ polymerization process. ITODM may not be the most effective dispersant for this system because methacrylate solvents are not completely compatible with the hydrocarbon tail of oleic acid in ITODM, possibly preventing its full extension. The most effective dispersant for BaTiO₃ in an ester solvent would probably be a molecule with a hydrophilic group (i.e., an acid) on one end and an ester on the other. Molecules of this type are not readily available.

Table 2.4 gives dispersion test results for barium titanate powders with organometallic coupling agents; using a solvent (toluene) known to provide good

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Defloculant</th>
<th>Sediment Density (% of theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>none</td>
<td>9</td>
</tr>
<tr>
<td>n-butyl methacrylate</td>
<td>none</td>
<td>15</td>
</tr>
<tr>
<td>toluene</td>
<td>7% ITODM</td>
<td>50</td>
</tr>
<tr>
<td>n-butyl methacrylate</td>
<td>7% ITODM</td>
<td>37-40</td>
</tr>
<tr>
<td>n-butyl methacrylate</td>
<td>7% organo Ba/Ti</td>
<td>42</td>
</tr>
<tr>
<td>n-butyl methacrylate</td>
<td>0.4% ITODM(reacted w/surface)</td>
<td>43</td>
</tr>
<tr>
<td>n-butyl methacrylate</td>
<td>0.4% ITODM(reacted w/surface)*</td>
<td>44</td>
</tr>
</tbody>
</table>

*Sized powder used

Table 2.4. Dispersion results for BaTiO₃ powder in various solvent/dispersant systems.
dispersion [Parish, et.al., 1985] to compare dispersion quality with n-butyl methacrylate
as solvent. These results illustrate several points about the dispersion of the barium
titanate powders used: (1) the amount of ITODM dispersant necessary for optimal
dispersion is decreased by more than 15 times if the refluxing procedure is used; (2)
the amount of ITODM dispersant anchored to the powder surface is consistent and
independent of the amount initially in the mixture (if excess is available); (3) an
organo-Ba/Ti dispersant worked at least as well as the organotitanate; and (4) sized
powder does not disperse significantly better than unsized powder. These results are
significant because powder dispersion one process variable which is known to strongly
affect packing density in green tapes.

Figure 2.13 shows the sediment densities achieved with each dispersant and the
chemical structure of the dispersant. ITODM was used as a control and reference
point for the other dispersants. Its performance was very reproducible. Menhaden
fish oil was found to result in the highest sediment density of all the dispersants
tested: over 45% of theoretical BaTiO₃ density. Azelaic acid, dihydroxystearic acid,
and methacrylic acid did not yield high sediment densities. Oleic acid and linoleic
acid resulted in the same sediment densities as ITODM.

Some conclusions can be drawn about the dispersion of BaTiO₃ powder in
n-butyl methacrylate solvent with a dispersant. First, the presence of double bonds on
the dispersant molecule seems to be absolutely necessary for the dispersant to be
effective. This is shown by the performance of the azelaic and dihydroxystearic acid
dispersants and has also been discussed in the literature [Parish et al., 1985]. Second,
the presence of free acid in ITODM preparation may limit the effectiveness of
ITODM as a dispersant, as shown by the low sediment density achieved with
Figure 2.13. Sediment densities for BaTiO$_3$ in n-butyl methacrylate with different dispersants (dispersant structures included).
methacrylic acid as a dispersant. Free oleic acid gave the same density as ITODM. Improved ITODM preparation should therefore use less methacrylic acid. Third, oxidized glyceryl trioleate has been found to be a close pure chemical analog to fish oil [Calvert et al., 1986] with a mixture of long-chain acid and ester groups (Figure 2.14). This would explain its effectiveness in dispersing BaTiO₃ in the methacrylate solvent.

Linoleic acid (CH=CHCH₂CH=CH(CH₃)₇COOH) does not form as densely packed sediments as fish oil, but may have the capability to extensively cross-link with polymer chains after casting due to the presence of two carbon-carbon double bonds on its long-chain functionality. Linoleic acid also appears likely to behave like oleic acid in replacing alkoxide side chains to form an organometallic dispersant.

Figure 2.15 is thermal gravimetric analysis showing the weight loss from thin slices taken by razor blade of the top and bottom of a green tape cast in air and subsequently placed into a nitrogen atmosphere to facilitate complete polymerization.

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_{18}\text{COOCH}_2 \\
\text{CH}_3(\text{CH}_2)_{17}\text{COOCH} & \quad \text{CH}_3(\text{CH}_2)_{18}\text{COOCH}_2 \\
\text{CH}_3(\text{CH}_2)_{17}\text{COOCH} & \quad \text{CH}_3(\text{CH}_2)_{17}\text{COOCH} \\
\text{CH}_3(\text{CH}_2)_{17}\text{COOCH} & \quad \text{CH}_3(\text{CH}_2)_{18}\text{COOCH} \\
(a) & \quad (b)
\end{align*}
\]

**Figure 2.14. Structures of triglycerides:** (a) glyceryl trioleate, and (b) typical Menhaden oil triglyceride.
Figure 2.15. TGA plots for a green tape cast by *in situ* polymerization under ambient conditions.

The top of the tape shows a lower weight loss than the bottom because it has less organics due to evaporation of the monomer. This data is supported by the SEM photos in Figure 2.16 revealing more polymer in the bottom of the tape than in the top. Figure 2.17 shows the weight loss from a tape-cast in nitrogen. This TGA shows no difference in weight loss, and thus organic content, between the top and bottom of the tape. Support is again provided by SEM photos in Figure 2.18, showing similar amounts of polymer on each surface. However, it appears from these photos as if the top surface is a continuous matrix of particles with polymer interspersed to hold them together, while the bottom surface appears to be a continuous polymer matrix with a dispersed phase of particles. This may be due to wetting phenomena between the polymer and the carrier material (aluminum in this...
Figure 2.16. Scanning electron micrographs of a green tape cast by in situ polymerization under ambient conditions: (a) top surface, (b) bottom surface.
Figure 2.17. TGA plot for top and bottom of a tape cast by *in situ* polymerization in nitrogen.

case); the surfaces could be made similar by curing the polymer with a protective coating on top. Casting in a nitrogen atmosphere produced uniform tapes because the evacuation process used upon entering the dry box was performed on a beaker of slurry, not a cast slurry with large surface area. Monomer evaporation was small in this case (compare TGA wt. loss with recipe quantities) and any inhomogeneities due to evaporation were mixed into the entire slurry prior to casting, yielding a homogeneous tape. These phenomena also indicate that there is no particle settling upon casting, indicating that the degree of dispersion provided by the system is good.

Another advantage to casting in nitrogen is that polymer chains can grow longer. Oxygen poisons chain growth causing weaker, short-chain polymers to form. Nitrogen casting allowed tapes to be formed to a reasonable strength without a
Figure 2.18. Scanning electron micrographs of a green tape cast by *in situ* polymerization in nitrogen: (a) top surface, (b) bottom surface.
cross-linking agent. Tapes cast in air could not be cured to a solid polymeric film without using some cross-linking agent. The amount of cross-linking between the particles, ITODM dispersant, and polymer in a tape-cast in air was measured by first washing the tape in acetone to dissolve all non-cross-linked polymer, then centrifuging and analyzing the sediment by TGA. Figure 2.19 shows that after washing, there was some evidence of polymer cross-linked to the dispersant. Calculations based on the amount of polymer and dispersant in the slurry indicate that 7% of the available polymer cross-linked with the dispersant. This figure might be increased by heating.

Table 2.5 summarizes the physical properties of green tapes prepared by the in situ polymerization process. Sized powder enabled fabrication of a tape with powder

![Figure 2.19](image.png)

**Figure 2.19.** TGA for BaTiO₃ powder with ITODM bonded to the surface, and green tape without cross-linking agent, after acetone extraction. Difference between these two plots represent the amount of polymer cross-linked with ITODM.
loading of 84 wt%, equal to a green density of 47%. Slip viscosity remained low at 700 cp (compared to 2000 cp for a typical alumina slurry [Mitsler, et.al, 1978]) for a 74 wt% powder slurry. Tapes as thin as 3 mil (75 μm) were produced and these tapes sintered to 2 mil (50 μm) thick at 1275°C.

Green tapes were prepared from the recipe in Table 2.3 with different cations in the dispersant. One tape (sample B5) contained 7 wt % of ITODM while the other (sample B6) contained 7 wt % of an organo-Ba/Ti dispersant, prepared from a Ba/Ti double alkoxide with oleic and methacrylic acids added as described above. The original purpose of this experiment was to curb the effect of additional titanium incorporated by ITODM into the BaTiO₃ system. Though quantitative chemical analysis has not been performed on the organo-Ba/Ti dispersant, its cation content is believed to be stoichiometric. After casting, microstructural evolution was studied at 1450°C.

Figure 2.20 shows scanning electron micrographs (SEMs) of the top surfaces of Samples B5 and B6 fired for 30 min. There is a difference in grain size of nearly

Table 2.5. Physical properties of BaTiO₃ green tapes prepared by the in situ polymerization process.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>POWDER LOADING IN SLIP</td>
<td>67 - 84 wt-%</td>
</tr>
<tr>
<td>SLIP VISCOSITY</td>
<td>320 - 700 cp</td>
</tr>
<tr>
<td>TAPE THICKNESS</td>
<td>3 - 25 μm</td>
</tr>
<tr>
<td>PACKING DENSITY</td>
<td>29 - 47 %</td>
</tr>
<tr>
<td>TENSILE STRENGTH</td>
<td>3.2 - 6.5 MPa</td>
</tr>
</tbody>
</table>
Figure 2.20. Scanning electron micrographs of top surfaces of BaTiO$_3$ tapes fired at 1450°C for 30 min: (a) prepared with ITODM dispersant; (b) prepared with organo-Ba/Ti dispersant.
an order of magnitude between these two samples: Sample B5 had an average grain size of about 50 µm while Sample B6 had an average grain size of less than 10 µm. Another difference evident in the figure is the possible presence of a second phase in the grain boundaries of Sample B5, though its presence or composition has not been verified by quantitative means.

Figures 2.21a-b and 2.22a-b are SEMs of the fracture surfaces of the same tapes as in Figure 2.20, fired at 1450°C for 15 and 45 min, respectively. Sample B5 sintered to its final density by 15 min at 1450°C; samples sintered for longer times did not yield significant density differences. The microstructures of the B5 samples did not change much over the firing times studied except for some pore growth (note the pores 10-20 µm in diameter in Fig. 2.20(a)). Final densities (after firing 45 min) were measured by mercury porosimetry and ranged from 83-92% of theoretical density. Sample B6 showed continued shrinkage even after firing for 45 min, and its microstructure changed significantly over the range of firing times studied. Final densities were 73-80% of theoretical. The microstructure of Sample B6 evolved with uniform pore shrinkage, and pores were only 1-3 µm in size (Figure 2.20 (b)). Chemical analyses were not performed on these samples.

The mechanism for the change in microstructural development caused by the dispersant is not defined, but there is an important conclusion to be made. Dopants or additives may be added to this slurry in the form of a dispersant if the alkoxide molecule of the desired metal atom can be synthesized. This procedure does not change any physical properties of the pure powder used, therefore all knowledge of the surface properties of the undoped powder can be utilized to prepare fired pieces of a doped ceramic. Alteration of microstructure by the dispersant is a side effect that
Figure 2.21. Scanning electron micrographs of fracture surfaces of BaTiO$_3$ tapes fired at 1450°C for 15 min: (a) prepared with ITODM dispersant, (b) prepared with organo-Ba/Ti dispersant.
Figure 2.22. Scanning electron micrographs of fracture surfaces of BaTiO$_3$ tapes fired at 1450°C for 45 min: (a) prepared with ITODM dispersant, (b) prepared with organo-Ba/Ti dispersant.
could be extremely useful when understood completely.

FUTURE WORK

The ITODM dispersant synthesized for this study could be modified, replacing oleic acid with linoleic acid to possibly provide higher green densities. Dispersants might then be prepared with commercially available Ba, Nb, and Ta alkoxides. A premise of this is that these dispersants need not change processing conditions (except for firing schedule) while altering properties of the ceramic.

Powders might be prepared for casting with various dopant concentrations. One monolayer of coverage of powder surface sites by each dispersant yields a fixed cation concentration (for constant surface area powders). Preliminary calculations indicate one monolayer of ITODM dispersant changes the Ba/Ti ratio of the powder used by about 0.2%. Adjustment of the concentration below one monolayer coverage can be accomplished by partial substitution of the organic long-chain moiety for the organo-metallic dispersant. Increasing dopant cation concentration above one monolayer is achieved through synthesis of organo-metallic methacrylate monomers (to supplement the organo-metallic dispersant) which would be compatible with the slip and evenly distributed throughout the tape.
IV. AN AQUEOUS TAPE-CASTING SLURRY FOR ALUMINA

Materials and Methods

Considerable literature is available on solvent-based tape casting of alumina [Mistler, 1978]. Aqueous tape casting recipes have not received much attention in the literature and formulation of an optimal recipe for these systems was begun without a reference point.

Table 2.6 shows properties of two alumina powders which were evaluated for use in this study, AKP-30 (Sumitomo Chemical USA, New York) and MPA-4 (Ceralox Corp., Tucson, AZ). The mean diameters of the as-received powders differed somewhat, but the large surface area difference indicates that the MPA-4 powder probably consists of small, high-surface-area particles agglomerated to over 0.5 μm.

These powders were suspended in water with 1.0 wt % Darvan®C (R.T. Vanderbilt Company, Norwalk, CT) and dispersed for one minute by an ultrasonic probe (400 W Ultrasonic Disperser, Harvey Scientific). The particle size distribution for each powder was then measured by absorption of light during centrifugation and is

<table>
<thead>
<tr>
<th>PHYSICAL PROPERTIES*</th>
<th>AKP-30+</th>
<th>MPA-4#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity (%)</td>
<td>99.99</td>
<td>99.90</td>
</tr>
<tr>
<td>Mean Diameter (microns)</td>
<td>0.30</td>
<td>0.52</td>
</tr>
<tr>
<td>Surface Area (m²/g)</td>
<td>6.4</td>
<td>13.0</td>
</tr>
</tbody>
</table>

* Information supplied by manufacturer
+ Sumitomo Chemical Company of America Inc., New York, NY.
# Ceralox Corporation, Tucson, AZ.
reported in Figure 2.23. As expected, the MPA-4 alumina contained many small as well as large particles. AKP-30 had a much narrower particle size distribution (though the mean diameters were equivalent at 0.33 μm) and was chosen for use in this study so that green tapes with high densities might be fabricated.

Properties of two dispersants tested are given in Table 2.7. Settling tests were performed to evaluate dispersant effectiveness. This involved adding 20 g of AKP-30 alumina to about 30 g DI water with dispersant already dissolved in it. The mixture was stirred then dispersed with ultrasonic probe for 3 min, or longer if dispersion was not visibly complete. This mixture was poured into a graduated test tube and allowed to settle; the powder volume was recorded every few days. Settling tests were performed using different amounts of dispersants, the results are plotted in Figure

![Graph of particle size distribution](image)

Figure 2.23. Particle size distribution of alumina powders determined by Horiba CAPA 500 analyzer.

51
Table 2.7. Physical properties of dispersants tested.

<table>
<thead>
<tr>
<th>Property</th>
<th>Darvan C</th>
<th>Darvan 821A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>amber fluid</td>
<td>pale yellow liquid</td>
</tr>
<tr>
<td>% Solids</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>pH</td>
<td>7.5 - 9.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Viscosity (25°C, cps)</td>
<td>75</td>
<td>50</td>
</tr>
<tr>
<td>Stability</td>
<td>alkaline</td>
<td>acidic, alkaline</td>
</tr>
</tbody>
</table>

*Information supplied by manufacturer, R.T. Vanderbilt Company, Norwalk, CT.

2.24. Darvan°C, an ammonium salt of poly(methacrylic acid), and Darvan°821A, a similar ammonium polyelectrolyte (both from R.T. Vanderbilt Co., Norwalk, CT) were found to give stable dispersions of AKP-30 in water with powder settling densities

![Diagram](image)

Figure 2.24. Settling densities of AKP-30 alumina in water.
near 50% of theoretical after 30 days. Darvan*821A provided higher settling densities but tapes made with this dispersant experienced component segregation during drying. Nitric acid was also tested as a dispersant and it did not provide stable dispersions of AKP-30 in water, therefore Darvan*C was the dispersant chosen for this formulation.

Binders from two general classes were tested for use in water-based tape-casting systems: standard water-soluble polymers and stable polymer emulsions dispersed in water. Properties of the binders tested are given in Table 2.8. Rhoplex B-60A, a non-crosslinking, proprietary formulation of acrylic polymers, yielded a tougher, more flexible film than self-crosslinking Rhoplex HA-8 (both from Rohm and Haas, Philadelphia, PA). Both emulsion formulations were much easier to process than Methocel (cellulose ether; Dow Chemical, Midland, MI) at similar polymer concentrations. Rhoplex B-60A has a continuous phase of approximately 54 wt% water and the emulsion is stabilized at pH 9.0 by an ammonium salt (<0.1 wt%)

Table 2.8. Physical properties of binders tested.

<table>
<thead>
<tr>
<th>Description</th>
<th>Methocel*</th>
<th>Rhoplex B-60A#</th>
<th>Rhoplex HA-8#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>cellulosic polymer, water-soluble white powder</td>
<td>acrylic emulsion, water-dispersible milky-white liquid</td>
<td>acrylic emulsion, water-dispersible milky-white liquid</td>
</tr>
<tr>
<td>pH</td>
<td>--------</td>
<td>9.4</td>
<td>3.0</td>
</tr>
<tr>
<td>Viscosity (cps)</td>
<td>~100,000</td>
<td>1900</td>
<td>1000</td>
</tr>
<tr>
<td>Crosslinkable</td>
<td>no</td>
<td>no</td>
<td>heat, catalyst</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>N/A</td>
<td>16</td>
<td>-14</td>
</tr>
</tbody>
</table>

*Dow Chemical Company, Midland, MI.  
Rohm and Haas Company, Philadelphia, PA.
present). The emulsion affords very high loadings of polymer (nearly 50 wt %) at viscosities 2 to 3 orders of magnitude less than similar concentrations of aqueous polymer solutions. This property is especially desirable for tape casting; low solvent content keeps drying times short and can lower the large volume reduction (as high as 70%) encountered on drying, thus reducing cracking in green tapes.

The potential drawback of an emulsion for tape casting is discontinuous film formation. Onions [1986] describes general film-forming properties and behavior of these latex films. Characterization of films [as described by Bierwagen, 1983] indicated that polymer dispersions filled with TiO₂ formed uniform films if the particle concentration was lower than the critical pigment concentration (CPC); above this level of particle filling, the morphology of the film may reflect the emulsion latex

![Graph](image)

**Figure 2.25.** Particle size distribution of Rhoplex B-60A dispersed latex particles and of AKP-30 particles (determined by Horiba CAPA 500).
particle size and significant porosity may result in the green tape. Figure 2.25 compares the particle size distribution of Rhoplex B-60A emulsion droplets and AKP-30 powder particles. The mean diameter of AKP-30 particles is ~2.5 times that of the latex, revealing the size of the defects which might be incurred above the CPC, as shown by the model in Figure 2.26.

Polypropylene glycol (PPG), molecular weight 1200 (Fluka Chemical Corp., Hauppauge, NY) was used as plasticizer because dioctyl phthalate was completely immiscible with the acrylic emulsion, and polyethylene glycol yielded a nonuniform film due to phase separation on the millimeter scale. PPG 1200 is a liquid of relatively low viscosity at room temperature and was very easy to use for tape casting.

Cracking was common in many water-based casts. Garino [1987] found that principal factors responsible for cracking in ceramic slurries were binder content, surface tension, solids content, and film thickness. Since desired film thickness and binder content were not independent variables for this study, cracking was deterred by

![Figure 2.26. Film-formation models for green tapes: (a) powder content below CPC, (b) powder content above CPC.](image)
increasing solids content (actually lowering the amount of solvent) and reducing surface tension in the slurry. Slurries containing powder, dispersant and solvent were centrifuged at 1500 x gravity for >30 min to remove excess water not necessary for powder dispersion. Usually 60-70% of the water necessary for initial dispersion could be decanted after centrifugation while flow properties were maintained.

Surface tensions of water and Rhoplex/water mixtures were measured to determine the effect of adding surfactant to the slurry. These results are given in Table 2.9. A Rosano Surface Tensiometer (Bilor Corp., North Grafton, MA) which employs the Wilhelmy Plate principle of surface tension measurement was used. Pine oil was recommended as a surfactant by the binder manufacturer for Rhoplex acrylic latexes for use in pigment-filled films [Allyn, 1969]. Significant reduction in surface tension of water was achieved with small additions of pine oil to the emulsion. At levels of surfactant near 1 wt% (too much according to Allyn), more pine oil did not reduce the surface tension of water or water and binder to near that of the solvent.

<table>
<thead>
<tr>
<th>Solvent Comparison</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>73.3</td>
</tr>
<tr>
<td>water + 0.1% pine oil</td>
<td>46.6</td>
</tr>
<tr>
<td>water + 0.5% pine oil</td>
<td>41.9</td>
</tr>
<tr>
<td>water + 1.0% pine oil</td>
<td>40.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent + Binder</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>water + Rhoplex B-60A Emulsion</td>
<td>45.0</td>
</tr>
<tr>
<td>&quot;</td>
<td>+ 0.1% pine oil</td>
</tr>
<tr>
<td>&quot;</td>
<td>+ 0.2% &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>+ 0.3% &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>+ 0.5% &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>+ 0.9% &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>+ 1.2% &quot;</td>
</tr>
</tbody>
</table>

Table 2.9. Surface tensions of aqueous tape-casting slurry components.
system, but 0.1 wt% seemed to eliminate cracking in tapes.

Ball-milling was added as a process step to intimately mix the components immediately prior to casting. This step enabled tapes with low polymer concentrations to have high strength and toughness, whereas without milling the same slurries formed brittle tapes. Ball-milling was carried out on a roller mill in porcelain jars filled to the height of the slurry with alumina media. The minimum milling time required to overcome brittleness in most tapes was 4 h.

A tape-casting system was designed because no commercially-available system suited the project needs sufficiently. The overall system is shown in Figure 2.27 (a). The glove box (VAC Atmospheres, San Diego, CA) enables control of moisture, solvent and oxygen content, and atmosphere. A close-up of the tape-casting unit is shown in Figure 2.27 (b). The Anorail-5 drive system (Anorad, Hauppauge, NY) uses a magnetic field to propel the casting head along rails. The drive is controlled by a simple microprocessor operated from outside the glove box, providing velocities from 2 to 2000 cm/min ± 0.1% accuracy. This drive system enables constant-velocity, bump-free travel over 100 cm. Float glass plates were used as substrates for casting and sat atop an H-beam which was added to the system for stabilization (see Figure 2.27(b)). A plexiglas cover was added to the caster to enable more control of drying and to keep foreign objects away from freshly-cast tapes during drying.

Slurries were prepared outside the glove box, then entered into the box through the ante-chamber for casting. After casting, tapes were stored on shelves inside the box until sufficiently dry, at which time they were taken back through the ante-chamber and removed from the glass plates.

The process and composition for tape casting water-based slurries was
Figure 2.27. Design of: (a) overall tape-casting system, and (b) drive system for casting head.
investigated. The tape-casting formulations used are given in Table 2.10 and the process in Figure 2.28. To cast tapes, lecithin (capsules, CVS Drug Stores, Woonsocket, RI) was applied to a glass plate, buffed with a Kimwipe® to give an even coating and allowed to dry. Dispersant was dissolved in the solvent and then added to the powder. This mixture normally took about a minute to disperse and was stirred with a glass rod until fluid. A plastic beaker was normally used for this step as the slurry wet it much better than glass or metal containers. This mixture was sonicated for 3 to 7 min. using a 400 W Ultrasonic Disperser with 1/2 in. probe (Harvey Scientific, Buffalo, NY) at a setting of about 40 W. More solvent was added if the rheological properties were unsuitable for sonication. This process continued until no visibly undispersed ceramic particles remained in the slurry. This mixture was centrifuged and redispersed to remove excess solvent, then added to a beaker of

<table>
<thead>
<tr>
<th>Component</th>
<th>Function</th>
<th>Wt. % in Slurry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>Ceramic</td>
<td>59-72</td>
</tr>
<tr>
<td>Deionized Water</td>
<td>Solvent</td>
<td>10.4-17.5</td>
</tr>
<tr>
<td>Darvan C, 821A</td>
<td>Dispersant</td>
<td>0.73-0.81</td>
</tr>
<tr>
<td>Rhoplex B-60A*</td>
<td>Binder</td>
<td>12-21</td>
</tr>
<tr>
<td>PPG-1200</td>
<td>Plasticizer</td>
<td>2.5-4.8</td>
</tr>
</tbody>
</table>

**SOLIDS 28-40 vol.% (excluding binder)**

**VISCOSITY 600-2000 cps. (Brookfield)**

*(54% water)*
Figure 2.28. Schematic of tape-casting process using aqueous slurry.
the binder-plasticizer mixture (with a small amount of water necessary for miscibility) on a magnetic stirrer and allowed to stir for at least 10 min. The slurry was filtered through a 400-mesh stainless steel screen to remove any large particulates and bubbles. The slurry viscosity was measured using a Model RVT synchro-lectric viscometer (Brookfield Inc., Stoughton, MA) at several spindle speeds. Some slurries were de-aired at -25 in of Hg vacuum for 1 min in a vacuum and cast. Casting was accomplished at speeds of 80 to 150 cm/min using a dual-blade casting head (Figure 2.12). Casting conditions were 23±2°C and humidity of 5 to 100 % RH inside the glove box. The plastic cover was placed over the cast tape to allow it to dry slowly.

After casting, water-based slurries were allowed to dry at least 24 h at room conditions: 23 ± 2°C and 50 ± 7% relative humidity (RH). Shorter drying times enabled by controlled low-humidity atmospheres (<10% RH) always caused tapes to crack severely on drying. Drying cracks were observed to occur parallel to the direction of the cast while cracks due to tape brittleness (i.e. low binder content) usually occurred normal to the casting direction. Tapes were removed from the glass plates with a wide razor blade and cut into appropriate sizes for analysis.

Green tapes were analyzed by several techniques. Weight loss was measured by thermal gravimetric analysis (TGA) on a 7 Series Thermal Analysis System (Perkin Elmer, Norwalk, CT) at a constant heating rate of 10°C/min to 500°C. Thickness was measured mechanically using an Ono Sokki measurement device. Bulk green densities were measured dimensionally. Bulk porosity was calculated from green density measurements and TGA results and was defined by:

\[
\text{Porosity} = 1 - \frac{\rho_{\text{measured}}}{\rho_{\text{calc}}} \tag{2.1}
\]
where $\rho_{\text{calc}}$ is calculated from the manufacturer-supplied densities of the materials:

$$\rho_{\text{calc}} = \rho_{\text{alumina}}\Phi_{\text{alumina}} + \rho_{\text{organics}}\Phi_{\text{organics}}$$

where $\Phi$ is the volume fraction of the component in the green tape. Strengths were measured at a crosshead speed of 2 mm/min using an Instron Model 1122 Mechanical Tester (Instron Corp., Canton, MA). "Dogbone"-shaped stencils were used to cut pieces for strength measurements.

Results and Discussion

Table 2.11 summarizes the physical properties of green tapes cast from water-based slurries. TGA weight loss represents the amount of organics and other components which decompose at temperatures less than 500°C. Green tape thicknesses were averaged from 50 to 75 points over the entire cast (15 x 100 cm) excluding 5 cm from the beginning and end of the cast and 1 cm from the side edges. The

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA Weight Loss</td>
<td>10.5 - 21.0</td>
<td>%</td>
</tr>
<tr>
<td>Thickness</td>
<td>6 - 12</td>
<td>1/1000 &quot;</td>
</tr>
<tr>
<td>Std. Dev. of Thickness</td>
<td>4 - 16</td>
<td>% from mean</td>
</tr>
<tr>
<td>Green Density*</td>
<td>49.8 - 53.4</td>
<td>% of theoretical</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.3 - 35.1</td>
<td>vol. %</td>
</tr>
<tr>
<td>Yield Strength</td>
<td>105 - 195</td>
<td>PSI</td>
</tr>
</tbody>
</table>

*Geometric, measured dimensionally.
standard deviation of thickness was very low and larger deviations could usually be attributed to changes in the hydrostatic pressure in the slurry reservoir due to operator error. Ceramic packing densities in green tapes were as high as 53% of the theoretical density of alumina.

The huge variation in porosity may give an indication of the film-formation properties of Rhoplex B-60A with high concentrations of ceramic particles present. All the tapes with very low porosities (less than 2 to 3%) had powder volume fractions less than 53%, which happens to correspond to the highest green density attained. These results are illustrated graphically in Figure 2.29. This phenomenon may be related to the critical pigment concentration (CPC) for this system, above which powder loading green tapes do not have higher green densities but simply

![Graph showing porosity and ceramic packing density vs. weight percent alumina in green tapes.]

Figure 2.29. Porosity and ceramic packing density v. wt% alumina in green tapes.
higher porosities (hence lower bulk densities). The reason that the correlation of porosity and density isn’t better is that tapes were prepared using different compositional slurry formulations and processing conditions.

Figure 2.30 is a TGA plot for the top and bottom surfaces of a green tape. Slices taken manually with a razor blade were used for TGA samples. The difference in weight loss between the top and bottom surfaces of the green tape indicates that there is a particle concentration gradient (albeit very small) in the thickness direction of the tape. This usually results from particle settling during drying of the tape (drying times for water-based tapes were on the order of 24 to 30 h).

Green tapes were sintered for 1 h at 1500°C in air. A porous coverplate was placed on the sample during sintering to ensure flatness of the sample. Densities of the samples were measured using the Archimedes method with t-butanol as the solvent. All samples had densities above 93% of theoretical, with some thinner ones at nearly 99%. Sintering temperature and time were not optimized, as the purpose of this experiment was to show that these water-based tape-casting slurries could form dense ceramic layers. Variation in density may have been related to thickness variation of tapes from different casts.

V. CHAPTER SUMMARY

Tape-casting slurry formulations were developed which do not include volatile, organic solvents or high molecular weight, soluble polymers in the slip. The absence of volatile solvents allows for safer handling of slurrys and reduces evaporation normally encountered during processing of solvent-containing slurries. The low viscosity nature of these formulations allows for high powder loadings in the slip
Figure 2.30  TGA for a green tape cast from aqueous slurry: (a) slice taken from top surface, (b) slice taken from bottom surface.

while maintaining good rheological properties. Green tapes prepared from these formulations were strong, flexible, uniform, and sintered to high densities.

A formulation for tape-casting barium titanate was developed using in situ polymerization of the monomeric, n-butyl methacrylate dispersion media used in the slip. The distribution of organics from top surface to bottom in this system was excellent, due to the rate of the polymerization relative to that of particle settling. The organo-titanate dispersant used was found to attach to ceramic particle surfaces as well as bond to some of the poly(butyl methacrylate) binder. The dispersant was also found to affect the microstructure of fired samples by altering the barium/titanium ratio in the system. Therefore, an organo-Ba/Ti dispersant was synthesized and samples made with it had reduced grain size after firing. Precise microstructural and
stoichiometric control in this system may be achieved by inserting dopant atoms into the dispersant.

An aqueous slurry formulation was developed for tape-casting alumina, using a proprietary acrylic emulsion formulation for the binder. This system was very easy to process due to its very low viscosity, and without the need for dissolving the binder in the solvent. However, deviation from precise slurry compositions often caused a cast to have visibly noticeable problems such as cracking, component segregation or brittleness. Cracking was one of the major obstacles to overcome for this system; it was controlled by solids content, surface tension, and drying rate. Water content in the slurry was reduced by centrifugation of ceramic/dispersant/solvent dispersions; only 30% of the initial water used for dispersion was required for rheological properties to be maintained. The system utilized the aid of a surfactant for good emulsion film-formation; this reduced the surface tension of the solvent about 30%. Drying conditions significantly affected cracking in tapes, as all those subjected to very low humidity (<10%) during drying severely cracked. Simultaneous control of these three variables alleviated cracking in green tapes.

Green tapes had very uniform thickness over the entire cast (save the edges). Packing densities of green tapes were as high as 53% of the theoretical value for alumina. This value seems to correspond to the critical pigment concentration for this system, above which packing level the density did not increase, only porosity did. Samples sintered at 1500°C for 1 h in air all reached densities >93% of theoretical, with some as high as 99%.
CHAPTER 3  
COMPONENT INTERACTIONS, DIMENSIONAL STABILITY, AND 
FIRING BEHAVIOR OF ALUMINA GREEN TAPES WITH 
DISPERSED AND SOLUBLE ACRYLIC BINDER

I. INTRODUCTION

Tape-cast ceramic green sheets for multilayer electronics applications are generally punched, screened, stacked, and laminated prior to firing. The punch step usually involves mechanical perforation of vias through each layer which are subsequently filled with conductor pastes to interconnect the circuitry between layers. Aside from exhibiting strength and flexibility sufficient for subsequent handling and processing steps, green sheets must exhibit excellent dimensional stability over time to ensure accurate interlayer registration upon lamination [Schwartz, 1984]. Even slight variations from design tolerances can lead to device rejection. As ceramic components become more densely loaded with circuits, the necessity for maintaining precise device tolerances becomes of the utmost importance [Tummala, 1989].

Ceramic green sheets used immediately after casting and drying are not allowed sufficient opportunity to undergo significant dimensional changes, but aging for any length of time results in changes in green sheet dimensions unacceptable for use in multilayer electronic component applications [Hait, 1976]. Hait goes on to assess the cause for dimensional change as stresses which develop during green sheet formation. Another factor which is thought to contribute to dimensional change in green sheets is solvent evaporation over time. These mechanisms are generally accepted in the industry and widely observed in the polymer literature, though they are not directly
documented for the ceramic green sheet system. Aside from simple dimensional change over time, the industry generally observes anisotropic dimensional changes in green sheets. Anisotropic stresses are thought to develop in green sheets due to polymer or ceramic particle orientation due to the shear induced by the doctor blade during tape-casting. Particle number density can be significantly lower (on a microscopic scale) in the casting direction than in the direction normal to cast. Since volume fraction of each material in a composite is known to be a significant factor in determining stresses incurred on film formation [Boriek, 1988], directional particle number density differences, even on a microscopic (as opposed to bulk) scale, might cause stress variations which could lead to anisotropic dimensional changes in green sheets over time.

The objective of this investigation was to develop formulations for tape-casting alumina using aqueous slurries, and to compare slurry processing and green tape properties to those for conventional, solvent-based systems. Considerations involve selection of compatible materials to effect a valid comparison and evaluation of processing steps necessary for each system. Green tape comparisons with regard to physical and mechanical properties, dimensional stability upon aging, response to stabilization treatments, and firing shrinkage behavior will be addressed.

II. BACKGROUND

Literature regarding properties of ceramic green tapes and their relationship to slurry components is scarce. According to several sources [Mistler, 1987; Bowen, 1988; Cima, 1989], the reason for this lack of scientific information is that many of
the processing-property relationships made for green tape manufacture are entirely empirical in nature, based on statistical analysis of large amounts of data. The aim of this chapter is to assess some component interactions in the tape-casting process and in green tapes. Specifically it will document dimensional change in ceramic green sheets over time, establish treatments to reduce the magnitude and anisotropy of dimensional change, and attempt to understand this phenomenon by additional experimentation combined with literature available on similar materials systems. Mechanical properties of green tapes will be used to analyze physical and chemical differences incurred by component interactions at different processing steps.

Aging of Polymers

The concept of aging of polymers and polymer systems is the subject of many works by Struik [1978, 1987, 1987]. Amorphous polymers experience aging only below their glass-transition temperature and defines aging as the process of approaching thermodynamic equilibrium. Glasses, for example, are known to undergo dimensional change on very long timescales. Polymers in the rubbery state (above \( T_g \)) are able to achieve equilibrium very quickly (essentially faster than measurement can detect), and are therefore considered (by Struik) not to age. Semi-crystalline polymers and rubbery polymers filled with carbon black were found to age at temperatures above their \( T_g \). The hypothesis for this phenomenon is that polymeric material near or attached to the surface of the particle or crystallite behaves as part of this rigid matrix while that material further away from particle surfaces behaves as amorphous polymer. The composite system cannot achieve equilibrium rapidly due to the lowered mobility of the attached polymer due to constraint by the rigid filler/attached-polymer matrix.
and the broadened glass transition of the amorphous phase. The model proposed by Struijk (illustrated in Figure 3.1) was verified by correlations of aging with particle size of the filler.

The driving force then, for aging in filled polymer systems is internal stress in the system. Stresses are generated when polymer chains are constrained by the matrix, usually due to processing. Therefore, it can be seen that two factors influence aging in these systems: (1) the degree of stress in the system, or how far it is from thermodynamic equilibrium determines the magnitude of the conformational changes which might occur; and (2) the mobility of the bulk polymer phase in the matrix will

Figure 3.1. The broadened glass-transition of filled polymers (am. and amorph. mean amorphous). From Struijk [1978].
influence the time-scale at which equilibrium is approached, or the rate of aging.

Polymer mobility is an increasing function of temperature, but Struik argues that regardless of temperature, mobility is proportional to the fraction of free volume present in the system. Free volume is that space which is not occupied by polymer molecules. It increases with temperature as the polymer bulk volume increases and drastically increases with temperature above $T_i$ as does the mobility (hence volume relaxation and aging are rapid above $T_i$). At $T_i$, all polymers are thought to contain the same fraction of free volume, this fraction being about 0.025, from the work of Williams, Landel and Ferry [1955] and Fox and Flory [1950]. Many have challenged the universality of free volume at $T_i$ usually due to their own differing measurements, leading researchers like Struik to disregard quantitative measures of free volume and only utilize the concept of free volume qualitatively until the problem of defining it in terms of measurable quantities is solved.

Having said this, it seems that methods other than temperature increase may be proposed which might increase free volume and hence mobility in a polymer and cause it to relax more rapidly. If these methods (even those including heating) could be accomplished over a relatively short timescale (a few hours) they might be used as stabilization treatments for green tapes, after which they would be very close to equilibrium, the mobility would decrease to negligible, and tapes would not change dimensions. Plasticization by a lower molecular weight species usually increases the number of end groups (those functional groups not in the polymer backbone) which increases free volume. Plasticization however, is a fairly permanent process and might cause increased mobility over the entire aging period. Swelling of the polymer by solvent addition, partial solvation or exposure to saturated vapor would also increase
free volume. The newly-created volume in these systems would probably collapse when the additive was removed, but if the objective were to temporarily increase mobility, such processes might be adequate.

Dynamic Mechanical Analysis of Polymeric Materials

Dynamic mechanical analysis (DMA) has been an efficient and versatile method for obtaining useful information about thermo-mechanical properties of polymers and organic coatings [Koo, 1974; and Varadarajan, 1983; provide excellent reviews]. DMA measures the viscoelastic response of a material to an induced deformation, often applied sinusoidally. Purely elastic materials exhibit strain responses perfectly in-phase with applied stress, enabling recovery of all energy input, while purely viscous materials (ie. some liquids) respond 90° out of phase, dissipating all energy to heat. The angle between stress and strain is, then, a measure of the ratio of viscous to elastic character of a material. The tensile or Young’s modulus is a complex property made up of real and imaginary parts,

\[ E^* = E' + iE'' \]  \hspace{1cm} (3.1)

where \( E^* \) is the complex or Young’s modulus, \( E' \) is the storage or elastic modulus, and \( E'' \) is the loss or viscous modulus, and

\[ E''/E' = \tan \delta \]  \hspace{1cm} (3.2)

is the tangent of the phase angle between the stress response and the applied strain. \( \tan \delta \) is commonly referred to as damping because the higher values indicate more viscous (damped or dissipated) behavior.

DMA has a variety of applications, most notably determination of the glass-transition temperature, \( T_g \), or more appropriately, the glass-transition behavior.
Literature values for $T_s$ do not include the breadth of the transition region, the modulus change over the transition, the sharpness of the damping peak, etc. These are all recorded by DMA and can provide very useful information about differences between similar materials. The glass-transition in a filled polymer, which the green tape system is, is determined by chemical structure, molecular weight, and morphology of the polymer as well as filler properties and polymer-filler interaction. Plasticizers and the presence of residual solvents in films affects transition behavior, and DMA is capable of detecting the effect of these variables in addition to their compatibility over a large temperature range [Grentzer, 1981]. DMA also has the ability to detect differences in thermal history or process condition, such as stress development or drying behavior [Rigdahl, 1984].

No literature is available on the use of DMA to evaluate green tape properties. For this study, determination of morphological differences of systems cast from different solvents; using dispersed emulsion polymers and soluble polymers; and with the complex rheology of the doctor-blading process; DMA was thought to have the ability to provide insightful clues as to the behavior of this intricate composite system. Of course, DMA alone cannot substitute for other characterization or analytical methods, but it may provide mechanistic details where other methods may only give bulk properties. Perhaps DMA combined with other analyses may remove some of the black art of tape-casting and scientifically explain what has traditionally been evaluated by reams of empirical data.
III. EXPERIMENTAL

Materials and Process Selection for Comparison

Chapter 2 describes aqueous slurry formulations using emulsion binders, the processing methods necessary for these preparations, and properties of tapes produced. This section describes the adaptation of those formulations for comparison to conventional, solvent-based systems. Refer to Chapter 2 for details and descriptions of components used.

Evaluating the effect of changing any one component of a slurry formulation required maintaining all other components as constant as possible, keeping in mind component interactions which may change an important property such as particle packing, slurry viscosity, or polymer morphology.

Sumitomo AKP-30 alumina powder was chosen for use in this study. Rhoplex B-60A aqueous acrylic emulsion was used as the binder for the aqueous system. For solvent-based slurries, B-60A films were dried at 100°C for 24 h. Dried films were then cooled to -5°C to make them more brittle, at which point they were broken up into tiny pieces for dissolution. Small amounts of this polymer did not dissolve in either ethanol or isopropanol, but readily dissolved in toluene and toluene/ethanol mixtures. Toluene/ethanol was considered acceptable as a solvent system which could dissolve the dried B-60A acrylic polymer as well as provide an effective medium for a water-soluble dispersant for AKP-30.

Figure 3.2 summarizes the dispersion behavior for AKP-30 alumina in different solvents. Darvan*C was found to give stable dispersions of AKP-30 in water with powder settling densities near 50% of theoretical after 30 days. Para-hydroxybenzoic acid (p-HBA, MW=138, Aldrich Chemical, Milwaukee, WI) also yielded stable
dispersions with settling densities near 50% in water; however p-HBA seemed to break down the emulsion in Rhoplex B-60A (probably due to its acidity) and therefore could not be used for aqueous slurries. Darvan®C was not soluble in ethanol, eliminating it for use in solvent-based slurries. Dispersion results for p-HBA in toluene/ethanol were not as promising as those in water, but p-HBA in pure ethanol provided adequate settling densities for comparison. The maximum settling density for alumina with the poorer dispersant (p-HBA) occurred at 2.0 wt% (by weight of powder) and was 43% of the theoretical density for alumina. The same settling density was achieved using 1.2% Darvan®C in water, hence these amounts of the different dispersants were used in slurry formulations. Toluene alone was responsible for dissolution of B-60A solids in a toluene/ethanol system; similarly ethanol alone
was probably responsible for dispersant dissolution. A 50/50 mixture of toluene and ethanol (by weight) readily formed a 20 wt% polymer solution and also formed a 10wt% p-HBA solution; therefore this mixture was chosen as the solvent system to be compared with water for casting tapes.

Polypropylene glycol (PPG-1200), was used as plasticizer for both aqueous and organic systems. It is a liquid at room temperature and was readily miscible with water and toluene/ethanol. A solution of lecithin (capsules, CVS, Woonsocket, RI) in isopropanol was applied to tempered glass plates as a release agent for the aqueous-based green tapes. A fluorocarbon dry release was used for the solvent-based slurries (MS-136, Miller-Stephenson, Danbury, CT). Pine oil was added to reduce surface tension and aid in film-formation of aqueous slurries (see Chapter 2), though surface tension in the aqueous system was never quite as low as that for the solvent-based system; these results are shown in Table 3.1. Unless stated otherwise, pine oil was always present in polymer films and green tapes cast from the aqueous emulsion system.

The slurry formulations used for this study are presented in Table 3.2. All components used for this study were from one product batch to reduce extraneous variables. All components had been received 9 to 12 months prior to their use in this

| Table 3.1. Surface tension measurements for solvents and polymer/solvent mixtures. |
|-----------------------------------|--------|
| SOLVENT SYSTEMS                  |        |
| toluene/ethanol                   | 25.7   |
| water                             | 73.3   |
| water + 0.1% pine oil             | 46.6   |
| SOLVENT-BINDER SYSTEMS            |        |
| toluene/ethanol + Rhoplex B-60A solids | 27.9   |
| water + Rhoplex B-60A emulsion    | 45.0   |
| water + Rhoplex B-60A emulsion + 0.1% pine oil | 42.1   |
Table 3.2. Slurry formulations for aqueous, emulsion-based system and conventional, solvent-based, soluble-polymer system.

<table>
<thead>
<tr>
<th>Component</th>
<th>Organic System (g)</th>
<th>Aqueous System (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>Al₂O₃, AKP-30</td>
<td>Al₂O₃, AKP-30</td>
</tr>
<tr>
<td>Solvent</td>
<td>Ethanol/Toluene*</td>
<td>DI Water</td>
</tr>
<tr>
<td>Dispersant</td>
<td>p-HBA</td>
<td>Darvan* C</td>
</tr>
<tr>
<td>Binder</td>
<td>Dried Rhoplex</td>
<td>Rhoplex B-60A-</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>PPG-1200</td>
<td>PPG-1200</td>
</tr>
<tr>
<td>Surfactant</td>
<td>None</td>
<td>Pine Oil</td>
</tr>
</tbody>
</table>

Solids Content (vol%) 10-15 44*  
Slurry Viscosity (cp) ~5000 700  
Surface Tension (dynes/cm²) 29 42  

*40% of this was due to polymer solids in Rhoplex.  
*Equimass mixture used.

study. A detailed description of the tape-casting process for aqueous slurries with emulsion binder is given in Chapter 2. To cast a tape, release agent was applied to a glass plate and allowed to dry. Dispersant was dissolved in the appropriate solvent, to which the powder was added and stirred until fluid. The mixture was sonicated 3-7 min (until no visibly undispersed ceramic particles remained) using a 400-W Ultrasonic Disperser with a 0.5-in probe (Harvey Scientific, Buffalo, NY) set at 40 W. More solvent was added if the rheological properties were unsuitable for sonication. At this point, aqueous dispersions were centrifuged and redispersed using about 1/10 the water initially required for powder dispersion. The dispersion was added to the binder-plasticizer mixture and pine oil was added to the aqueous slurry. A small amount of water was added to enhance emulsion-plasticizer miscibility in the aqueous system. Slurries were then ball-milled for at least 4 h to intimately mix the components. Ball-milling was carried out on a roller mill in porcelain jars filled to

77
slurry height with alumina media. Solvent-based slurries became noticeably more viscous during milling. Slurries were then filtered through a 400-mesh stainless steel screen to remove large particles and bubbles. Solvent-based slurries often required significant pressure for filtration. Slurry viscosity was then measured using a Model RVT Syncho-lectric viscometer (Brookfield Inc., Stoughton, MA). Viscosities were reported at 10 rpm using spindle RVT #3. Slurries were cast inside a glove box: at 50% relative humidity (RH) and 23°C under flowing air for the aqueous system; in pure N₂ for solvent system. The casting head had two blades and was driven by magnetic field along rails at ~2 cm/s. A plastic cover was placed over the cast to slow the drying process. Also, polymer films were made by manually casting mixtures of solvent, binder, plasticizer and surfactant on glass.

Post-Casting Treatments, Sample Analyses and Polymer Characterization

After casting, slurries were allowed to dry at least 24 h with room conditions 23 ± 2°C and 50 ± 7% RH. Tapes were removed from the glass plates with a wide razor blade and cut into two-inch squares, then punched by an automatic programmable punch (Model SK 5470; Schneider & Marquard, Newton, NJ, with model MD5-5 Berger-Lahr controller) with 0.25 cm measurement holes and then subjected to appropriate storage conditions or treatments. Strips of tape and polymer films ~0.5 cm x ~6 cm were cut parallel and normal to the casting direction for directional property measurements.

Punched tape samples and accompanying strips for both aqueous and organic systems (in duplicate) were subjected to one of several treatments in order to understand dimensional change on aging. Sample treatments included: (1) a simple
bake (2 h at 120 °C in flowing air); (2) thermal cycling (-5°C for 30 min, then 120 °C for 30 min, 4 times); (3) solvent exposure (saturated toluene vapor for 1 h at room temperature, then simple bake [Hait, 1976]); (4) humidity (24 h at 100% RH, 80°C, then 24 h at 80°C in flowing air [ASTM, 1983]). Control samples were left untreated. All samples were then stored under controlled conditions, 23 ± 2°C and 50± 7% RH. Positions of punched holes were measured using an optical comparator at 20x magnification with radial viewing template and digital translational readings (to 10⁻⁵ in). The template enabled very precise measurement. Hole positions were measured after punching, immediately after treatments, then every 3 to 5 days during aging, and finally, after firing. Four of the seven holes were used to quantify shrinkage in the casting (x) direction and four were used for the normal (y) direction, as shown in Figure 3.3.

Green tapes were sintered for 30 min at 1500°C in air. Porous alumina coverplates were placed above and below samples during sintering to ensure flatness of the sample while allowing organics to escape. Hole positions were also measured after firing to assess firing shrinkage. Fired densities were measured geometrically and by the Archimedes method with t-butanol as the liquid. Shrinkage in the z-direction was measured by micrometer and was not perfectly accurate due to surface asperities on the samples. Sintering temperature and time were not optimized, as this procedure was meant only to verify the reproducibility of stabilization treatments with respect to firing shrinkage.

Properties of green tapes were analyzed by several techniques. Weight loss was measured by thermal gravimetric analysis (TGA) on a 7 Series Thermal Analysis System (Perkin Elmer) at a constant heating rate of 10°C/min to 500°C. Thickness
was measured mechanically using an Ono Sokki digital-reading measurement device. Bulk and directional green densities were measured geometrically. Bulk porosity was calculated from green density measurements and TGA results (as described in chapter 2). Yield strength was measured using dog-bone shaped samples (cut parallel and normal to the casting direction) on an Instron machine.

Thermo-mechanical properties of green tape strips, Rhoplex B-60A, and plasticized Rhoplex films, cast from aqueous and organic systems were measured by dynamic mechanical analysis on a Rheovibron Direct Reading Dynamic Viscoelastometer (Model DDV-II, Imass, Hingham, MA). The temperature range scanned was -120°C to 150°C at 2°C/min, with an strain oscillation frequency of 11 Hz. The Autovibron software automatically recorded: damping factor (tan δ),
complex modulus ($E'$), storage or elastic modulus ($E''$), loss or viscous modulus ($E'''$), and sample length; every minute (or 2°C).

Polymer and tape samples were placed in several solvents to determine their chemical resistance to dissolution or disintegration. Toluene and THF were organic solvents used; triethylamine, an organic base was added to these solvents to possibly enhance sample dissolution; aqueous sodium hydroxide solution was also used. Samples were observed periodically for one week at room temperature, then were heated for 12 h at 95°C.

In a similar experiment, 0.2 - 0.3 g samples of untreated and treated green tapes were placed in 50 ml of toluene at room temperature for 90 min. Upon removal, samples were placed in 50 ml of fresh solvent to completely wash away any remaining soluble organics. Tape samples were placed in an oven at 60°C under vacuum for 1 h to remove all toluene, and then weighed. After weighing, tape samples were heated to 500°C for 10 min to remove all remaining, insoluble organics, and were then weighed again to determine the amount of insoluble organics in green tapes.

Centrifugation was used to assess diffusion kinetics of PPG in the latex particles. Due to the different physical state of the binder in the aqueous system (0.15 μm particles) and the organic system (dissolved polymer chains), the plasticizer might not completely diffuse into latex particles before the slurry dried (~30 h after mixing) and mobility decreased drastically. A batch of Rhoplex B-60A, PPG-1200 and DI water (in the ratios used in Table 3.2) were covered and placed on a magnetic stirrer with a cooling bath. Samples removed from the mixture after 1 h and after 24 h were centrifuged with a force of 25,000 x gravity for 4 h in a IEC-HT Centrifuge
(IEC Corporation, Needham Heights, MA). The supernatant viscosity was qualitatively compared with water by dripping onto a petri dish. The supernatant from the sample removed after 1 h had a viscosity obviously higher than water, indicating dissolved plasticizer present. The supernatant from the 24 h sample appeared to have a viscosity very similar to water, indicating little to no plasticizer remaining in the water phase but rather all dissolved in the latex particles. This is consistent with the results of Sears [1982] who indicates that emulsion polymers (with similar particle size to those in this system) with plasticizer simply added usually reached equilibrium within 24 h of mixing.

Additional polymer characterization included infrared spectroscopy, molecular weight analysis, and thermal analysis. Transmission Fourier Transform Infrared (FTIR) spectroscopy (IR-44, IBM Instruments) was performed on a transparent, thin (100 μm), air-dried film of Rhoplex B-60A. Polymer and plasticized-polymer films were evaluated by differential scanning calorimetry (DSC) on a DuPont 982 Thermal Analyzer from -150 to 150°C at 10 °C/min. Samples of 8-10 mg were run in duplicate in aluminum pans and the heat flow measured was compared to that from an empty pan. The molecular weight and molecular weight distribution of dried Rhoplex B-60A dissolved in tetrahydrofuran (THF) were analyzed by gel permeation chromatography (GPC). Rhoplex B-60A was dried in an oven at 110°C for 24 h and the resulting polymer was manually broken up for analysis. A polymer solution of 3.8 g/l was prepared using HPLC-grade THF (Aldrich Chemical, Milwaukee, WI). About 50 μl of this solution was manually injected into a Waters Associates GPC II with 6000A solvent delivery system and the retention volume was measured by a differential refractometer, comparing refractive index of the solution to that of the pure
solvent. The GPC columns were standardized with four monodisperse polystyrene standards ranging from 3000 to 200,000 MW to develop a linear correlation between molecular weight and retention volume.

IV. RESULTS

Physical Properties of Green Tapes

Table 3.3 summarizes the physical properties of green tapes. All data in this section are from individual casts of solvent- and aqueous-based slurries unless otherwise specified. Overall, physical and compositional consistency was maintained between the aqueous-based and solvent-based tapes. TGA weight loss represents the amount of organics and other components which decompose at temperatures less than 500°C; there was a slight difference in this value for the two systems due to preparation errors (TGA values were used to calculate the approximate green tape compositions in Table 3.4). Green tape thicknesses were averaged from 50 to 75 points over the entire cast (15 x 100 cm), excluding 5 cm from the beginning and end

<table>
<thead>
<tr>
<th></th>
<th>Organic Slurry</th>
<th>Aqueous Slurry</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA Weight Loss (%)</td>
<td>21.8</td>
<td>21.3</td>
</tr>
<tr>
<td>Avg. Thickness (μm)</td>
<td>239</td>
<td>274</td>
</tr>
<tr>
<td>Avg. Bulk Density (g/cm³)</td>
<td>2.43</td>
<td>2.46</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Yield Strength (MPA)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Casting direction</td>
<td>---</td>
<td>0.98</td>
</tr>
<tr>
<td>Normal to cast</td>
<td>---</td>
<td>1.15</td>
</tr>
</tbody>
</table>
Table 3.4. Approximate composition of green tapes used for this study.

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>SOLVENT</th>
<th>AQUEOUS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>78.2</td>
<td>78.7</td>
</tr>
<tr>
<td>Dispersant</td>
<td>1.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Binder</td>
<td>14.5</td>
<td>14.2</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>5.8</td>
<td>6.1</td>
</tr>
</tbody>
</table>

of the cast and 1 cm from the side edges. Casts were 90 cm long by 13 cm wide. Standard deviations of thickness were low (2-10 %) and green densities were consistent. The low porosity indicates powder concentrations in green tapes were probably below the CPC for each system, hence drastic morphological differences should not be present. There were consistent directional differences in yield strength (which was averaged over several samples) with strength parallel to the casting (or longitudinal) direction lower than those in the normal (or transverse) direction. Both organic and aqueous-based tapes laminated easily top-to-bottom at 120°C for 2 sec at very low pressure (<500 psi). Laminated layers held together well after pressureless sintering of samples.

**Dimensional Stability of Green Tapes over Time**

Linear dimensions of green tapes over time are shown in Figures 3.4 through 3.6. All curves represent the average directional shrinkage from four points on two different samples cut from the same batch of green tape (see Figure 3.3 for measurement technique). Two batches were used for all the data presented: one cast from the solvent-based system and one from the aqueous, emulsion-based formulation;
Table 3.5 lists directional shrinkage of green tapes during each stabilization treatment. The order of severity of treatment was generally the same for both systems: (in increasing severity) bake, thermal cycle, solvent, humidity. The magnitude of the shrinkages between systems varied widely as solvent-based tapes experienced up to 2-1/2 times more shrinkage than aqueous-based samples during each treatment. Anisotropic shrinkage behavior was observed for samples from both systems with shrinkage in the casting (x) direction usually greater than or equal to that in the normal (y) direction. The extent of shrinkage anisotropy varied for each treatment, but it varied consistently for each tape-casting system. Weight losses were observed to be fairly constant at about 1%.

Figure 3.5 displays shrinkage of green tapes which have undergone stabilization treatments; note that Figures 3.5a and 3.5b have different scales. Several things are interesting to note from Figure 3.5a: (1) treatment of solvent-based tapes caused a reduction in linear shrinkage of 63-87% over untreated tapes while the same

Table 3.5. Linear shrinkage incurred by green tapes during stabilization treatments (%).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Solvent-Based</th>
<th>Aqueous-Based</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x y</td>
<td>x y</td>
</tr>
<tr>
<td>Bake</td>
<td>1.14 1.22</td>
<td>0.57 0.63</td>
</tr>
<tr>
<td>Thermal Cycle</td>
<td>1.61 1.67</td>
<td>1.06 0.80</td>
</tr>
<tr>
<td>Solvent</td>
<td>2.04 1.84</td>
<td>0.95 0.87</td>
</tr>
<tr>
<td>Humidity</td>
<td>2.58 2.55</td>
<td>1.16 0.94</td>
</tr>
</tbody>
</table>
Figure 3.5. Linear shrinkage over time for treated green tapes: (a) from solvent, (b) from aqueous emulsion.
treatments performed on aqueous-based tapes only reduced shrinkage by 0-50%; (2) for solvent-based green tapes, the only samples having significant shrinkage anisotropy after treatment were ones which had been baked; (3) solvent-treated and humidity-treated samples cast from the soluble-polymer system experienced <0.2% linear shrinkage after 35 days; (4) tapes exposed to thermal-cycling underwent significantly less shrinkage than those which had been only baked; and (5) the shape of the shrinkage curves for the treated, solvent-based samples resembles that for untreated solvent-based tapes (Figure 3.4).

Behavior of treated, aqueous, emulsion-based tapes are shown in Figure 3.5b. Though the figure appears busy, there are a few worthwhile details to point out: (1) no treated samples experienced significant linear shrinkage anisotropy between x- and y- directions; (2) the only treatment which caused any sample to undergo significantly less aging shrinkage than untreated tapes, was the humidity treatment; and (3) the shape of the curves is similar to those of untreated, aqueous, emulsion-based samples. For both aqueous- and solvent-based tapes, the most severe treatments caused those samples to experience the least dimensional change on aging.

Batch-to-batch reproducibility of shrinkage was addressed by preparing and casting a solvent-based slurry identical to the one in Table 3.2. Samples were cut, punched, and subjected to solvent and humidity treatments. Shrinkage behavior over time was compared to the tape prepared for Figures 3.4 and 3.5(a); the results of the comparison are shown in Figure 3.6. For the untreated tape (Figure 3.6(a)), shrinkage curves identically match for the casting direction, and slightly differ for the normal direction. Samples subjected to the solvent exposure treatment showed essentially the same inter-batch shrinkage behavior (within measurement error). For samples
Figure 3.6. Reproducibility of shrinkage in green tapes cast from solvent: (a) untreated; (b) treated, solvent-exposure; (c) treated, humidity.
subjected to humidity (Figure 3.6(c)), there was a significant difference in the shape of the shrinkage curve, but the absolute value of the shrinkage remained extremely small (<0.1±0.05%).

Differences between batches became more evident for samples having lower magnitude of shrinkage, probably due to the lower signal to noise ratio in dimensional measurement; but that alone cannot account for all differences. Confidence in preparation methods was fairly high, reinforced by the inter-batch reproducibility of untreated samples. Variations in humidity and temperature were present during aging, although they were controlled as well as realistically possible. Temperature variation in the oven could have caused batch-to-batch shrinkage differences during the humidity treatment, leading to these aging results. Evaluation of enough samples to enable statistically-meaningful averages would be necessary to implement these relationships into a manufacturing scheme.

Dimensional stability results for all green tapes are summarized and compared in Figure 3.7; estimated error of linear shrinkage measurement was 0.05% for all data. Untreated solvent-based samples exhibited anisotropic shrinkage on aging, with longitudinal shrinkage significantly greater than normal shrinkage. During stabilization treatments, solvent-based tapes experienced up to 3% linear shrinkage, with all solvent-based samples shrinking more in the casting direction. The bake treatment caused significantly lower shrinkage than all other treatments. After completion of treatment, all solvent-based tapes underwent significantly less shrinkage than untreated tapes and showed little or no anisotropy. Samples which underwent the bake shrunk the most of all treated solvent-based samples after treatment and had the most anisotropy while samples which underwent the solvent and humidity treatments had
Figure 3.7. Shrinkage for green tapes after 35 days: (a) from solvent, (b) from aqueous emulsion.
less than 0.2% linear shrinkage after 35 days and essentially no anisotropy, with all humidity-treated samples changing dimensions by < 0.15%.

Untreated aqueous-based green tapes shrunk less than solvent-based tapes on aging. All aqueous-based tapes experienced significantly less shrinkage during stabilization treatments than solvent-based samples did. After treatment, little change was observed in the magnitude of shrinkage from that of untreated samples, though anisotropy was lowered. As in the solvent system, the humidity treatment caused the most dramatic difference in shrinkage behavior.

Green tapes from the two systems did exhibit some similar behavior. Samples within each slurry system showed wide variations in overall shrinkage (combining shrinkage during and after treatments) which were accompanied by green density differences of similar proportions, most likely due to solvent evolution during treatment. Densities of treated samples remained stable on aging. No quantitative correlation could be made between green density and shrinkage, however, due to the comparatively low accuracy of density measurement capability. Weights of all samples did change during treatments, but only untreated samples experienced weight changes greater than 0.1% on aging. This result is significant because it may be surmised that shrinkage of treated samples must be compensated for by an increase in thickness in order to preserve volume, assuming volume stays constant with mass for this system (see Discussion for assessment of this assumption).

**Dynamic Mechanical Analysis of Polymer Films and Green Tapes**

Results of dynamic mechanical analysis are illustrated in Figures 3.8 to 3.13. Figure 3.8 is the DMA for Rhoplex B-60A film cast from the as-received emulsion.
Figure 3.8. Complex modulus and damping (tan δ) for Rhoplex B-60A film measured by Dynamic Mechanical Analysis (DMA).

The data is smooth; there is a clear, sharp damping (tan δ) peak at 40°C. For convention, this will be called the dynamic glass transition, which falls 28°C above the manufacturer’s Tg value for B-60A, obtained by DSC (such differences are normal). The small hump in the damping curve between 0 and 10°C may be due to temperature increases caused by Rheovibron heaters turning on at that temperature (Note the increase in spacing of datapoints at 0°C. The Autovibron collected data every minute with the heater programmed for a specific rate.). This artifact obstructs quantitative data interpretation, especially since many samples go through their glass-transition peak in this temperature range. The complex modulus (E*) changes little until the transition region, then drops sharply and levels off about three orders of magnitude.
lower. The actual value of the modulus may differ slightly from the value on the graph because it is inversely proportional to the sample length and cross-sectional area entered manually by the operator.

The effect of adding filler to the polymer film is shown in Figure 3.9, DMA of a green tape sample prepared without plasticizer and cast from solvent. The modulus value starts significantly higher than that for the unfilled polymer and drops less than an order of magnitude over the transition region. The onset temperature of the modulus drop is 10°C higher than that of the unfilled system, and the breadth of the transition is lowered. The damping peak occurs at a slightly lower temperature but is an order of magnitude lower in value, less sharp, and skewed to the right compared to the unfilled polymer. Data collection ceased as the sample broke (~60°C). These results generally indicate that the polymer in the tape had a lower mobility in the

![Figure 3.9. DMA of B-60A film, unplasticized green tape.](image-url)
highly-constrained, filled system than the same polymer in the unfilled state.

Figure 3.10 displays curves for plasticized B-60A films: (1) from dried polymer dissolved in toluene, (2) from the emulsion, and (3) from the emulsion with pine oil added. As these were cast manually with a glass rod, significant anisotropy in mechanical properties was not observed; therefore only one sample from each system was presented. A significant modulus increase was observed compared to that for the unplasticized polymer (Figure 3.8), except for the emulsion film without pine oil (indicating the necessity of pine oil in order to form films similar enough to the soluble system for to enable a valid comparison). The onset temperatures, slopes and amount of modulus drop through the transition region are very close to each other with the transition range shifted 30°C lower by plasticizer addition. The damping peaks of all three samples reach very similar maxima at temperatures within 1 or 2°C of each other. The most significant difference between plasticized and unplasticized films’ behavior is the small damping peak at -70°C. This corresponds to literature values for the Tg of PPG (-80 to -72°C [Macchi, 1986, II]), and reveals the existence of free plasticizer present in the polymer system at low temperatures. The size of the peak indicates that the amount of free plasticizer is probably small.

Figure 3.11 illustrates DMA behavior for untreated green tapes, again showing the effect of adding filler to the polymer system; in this case the polymer system is B-60A/PPG. The four curves represent samples cast from solvent and water, with tape strips in longitudinal and transverse directions for each system. The modulus values are close and the onset points of the modulus drop are within a few degrees, except for the longitudinal, solvent-based tape sample which shows a broader transition region and greater modulus drop over the region. The damping behavior is
Figure 3.10. DMA of B-60A/PPG films.

Figure 3.11. DMA of untreated green tapes.
similar for all samples. Tan δ peaks are very broad over the transition, skewed to the
right, and lower in magnitude than those for the unfilled polymer system; identical to
the comparison of filled and unfilled samples in the unplasticized system. There seem
to be several small damping humps (as opposed to peaks) through the transition region
for all samples, though the small peak at -72°C is not present. This occurs either
because dilution of the polymer with a filler lowers the damping signal of that peak
below detection limits or improves polymer-plasticizer compatibility. No significant
systematic differences between samples cast from each solvent system or those
analyzed in different directions were evident, except that damping values below -60°C
were consistently lower for solvent-based tapes.

A most interesting phenomenon occurred in the modulus behavior above 25 or
30°C. The modulus of green tapes significantly increased in all samples, those cast
from solvent or emulsion, parallel or normal to the cast. This behavior was not
observed for B-60A, filled B-60A, or B-60A/PPG films. Some multiple component
interaction must exist which caused green tapes to become more rigid just above room
temperature, and this phenomenon requires the presence of binder, plasticizer and
ceramic particles to manifest itself. Modulus drops for green tapes (taken from
temperatures below the transition region to those above the modulus increase point)
were nearly identical to that of the unplasticized green tape (shown in Figure 3.9).

DMA behavior of treated green tapes is shown in Figures 3.12 and 3.13. The
complex modulus and damping resemble those for untreated tapes, including the
modulus increase above room temperature. This is significant because it shows that
the modulus increase in green tapes is reversible, or at least that it occurred in
samples which had been thermal cycled from -5 to 120°C four times. Though the
Figure 3.12. DMA for treated, solvent-based green tapes: (a) longitudinal direction, (b) transverse direction.
Figure 3.13. DMA for treated, aqueous-based green tapes: (a) longitudinal direction, (b) transverse direction.
data contain significant variation and even different curve shapes, no systematic differences can be deduced between treatment type, solvent system or directional differences. One variation can be noted between untreated and treated tapes cast from the solvent-based slurry: damping values are consistently higher for treated samples than those for untreated samples. Glass-transition ranges obtained from DMA of all samples is summarized in Table 3.6.

Figure 3.14 plots sample elongation during DMA as a function of temperature for three films, all of which were cast from the solvent-based slurry. The purpose of this plot was to determine differences between green tape; which consists of ceramic, binder and plasticizer; films without plasticizer; and films without ceramic. The dynamic $T_g$ is noted in the figure for each sample, at which point the slope of the elongation curve increases. Only the curve for the plasticized green tape shows

![Diagram showing sample elongation as a function of temperature during DMA.](image)

**Figure 3.14. Sample elongation as a function of temperature during DMA.**
inflection above $T_g$. The temperature of the inflection corresponds to that of the modulus increase evidenced by DMA curves (Figures 3.11 through 3.13).

DMA results for polymer films and green tapes are summarized in Table 3.6. The general conclusions which can be drawn from the data are: (1) PPG certainly acts to plasticize B-60A and green tapes based on its ability to lower $T_g$ by 30 to 40°C; (2) untreated and treated green tapes in the longitudinal and transverse directions did not differ substantially in mechanical properties or glass-transition behavior, based on damping peaks for these samples; and (3) a multicomponent interaction phenomenon exists in green tapes resulting in a modulus increase at ~30°C.

**Polymer Characterization and Binder-Plasticizer Compatibility**

Little is known about Rhoplex B-60A except that it is an acrylic emulsion with aqueous continuous phase and <0.1% ammonium salt stabilizer. The average particle size of the latex particles is ~0.15μm (see Chapter 2), the glass-transition temperature is 12°C [Kligerman, 1989], and the formulation is 46.5 wt% solids, as received. Standard polymer characterization techniques were employed to assess the chemical and physical make-up of Rhoplex B-60A solids.

**Table 3.6. Glass-transition ranges (°C) for cast samples based on damping peak from DMA.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass Transition Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aqueous-Based</td>
</tr>
<tr>
<td></td>
<td>Solvent-Based</td>
</tr>
<tr>
<td>B-60A Film</td>
<td>40</td>
</tr>
<tr>
<td>B-60A/PPG-1200</td>
<td>0-2</td>
</tr>
<tr>
<td>Green Tape</td>
<td>0-13</td>
</tr>
<tr>
<td>Green Tape w/o PPG</td>
<td>---</td>
</tr>
<tr>
<td>Green Tape after Treats</td>
<td>-2-17</td>
</tr>
<tr>
<td></td>
<td>30-33</td>
</tr>
<tr>
<td></td>
<td>0-15</td>
</tr>
</tbody>
</table>
Figure 3.15 represents the molecular weight distribution of the B-60A sample, obtained by GPC, relative to the polystyrene standards. A calibration equation relating the retention volume to molecular weight was derived from the standards. Peak heights reflect the number of polymer chains having a given molecular weight. From Figure 3.15, the weight-average molecular weight, $M_w$, and the number-average molecular weight, $M_n$, were computed. For the B-60A sample, $M_w = 298,000$ g/mol and $M_n = 222,000$ g/mol. The ratio $M_w/M_n$, called the polydispersity, is equal to 1.34 for this sample. A monodisperse polymer (that is, one having all chains the same length) has a polydispersity of near 1.0, indicating that the termination mechanism during polymer synthesis was size-exact in its chain-stopping. A polydispersity of <1.5 usually indicates a polymer which was synthesized by addition polymerization with termination by a coupling mechanism [Collins, 1973]. Emulsion polymerizations rarely produce polymers with polydispersity <1.5, therefore Rhoplex B-60A should be

![Graph showing peak height vs. retention volume for GPC analysis of dried Rhoplex B-60A dissolved in THF.](image-url)
considered to have a narrow molecular weight distribution, especially for its class. GPC is not perfectly accurate for all polymers because calibration is usually made with polystyrene and the retention volume may differ for other polymers in the same solvent (THF in this case), often due to molecular shape differences. Billmeyer gives a thorough treatise on methods and analysis of molecular weight determination of polymers [1973].

The transmission FTIR spectra for a B-60A film is shown in Figure 3.16. The spectrum was compared to those of many acrylate and methacrylate polymers and most closely resembled those of poly(methyl methacrylate) and poly(ethyl acrylate). FTIR spectra for PMMA and PEA films are also shown in Figure 3.16. The resolvable absorption peak values (in wavenumbers) are given for FTIR of a B-60A film in Table 3.7. Literature values for PMMA and PEA spectra are also given in

Table 3.7. FTIR spectra Peaks (in wavenumbers) measured for Rhoplex B-60A and literature values for acrylic polymers [Pouchert, 1985].

<table>
<thead>
<tr>
<th>RHOLEX B-60A</th>
<th>PMMA</th>
<th>PEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>2983</td>
<td>----</td>
<td>2982</td>
</tr>
<tr>
<td>2953</td>
<td>2953</td>
<td>----</td>
</tr>
<tr>
<td>1726</td>
<td>1730</td>
<td>1733</td>
</tr>
<tr>
<td>1465</td>
<td>----</td>
<td>1462</td>
</tr>
<tr>
<td>1447</td>
<td>1448</td>
<td>1447</td>
</tr>
<tr>
<td>1382</td>
<td>1387</td>
<td>1382</td>
</tr>
<tr>
<td>1330</td>
<td>----</td>
<td>1330</td>
</tr>
<tr>
<td>1298</td>
<td>----</td>
<td>1297</td>
</tr>
<tr>
<td>1253</td>
<td>----</td>
<td>1257</td>
</tr>
<tr>
<td>1239</td>
<td>1240</td>
<td>----</td>
</tr>
<tr>
<td>1176</td>
<td>----</td>
<td>1175</td>
</tr>
<tr>
<td>1160</td>
<td>----</td>
<td>1159</td>
</tr>
<tr>
<td>1099</td>
<td>----</td>
<td>1097</td>
</tr>
<tr>
<td>1067</td>
<td>1068</td>
<td>----</td>
</tr>
<tr>
<td>1024</td>
<td>----</td>
<td>1025</td>
</tr>
<tr>
<td>992</td>
<td>989</td>
<td>----</td>
</tr>
<tr>
<td>853</td>
<td>----</td>
<td>853</td>
</tr>
</tbody>
</table>
Figure 3.16. FTIR spectra for films of acrylic polymers: (a) poly(ethyl acrylate), from Pouchert [1985]; (b) poly(methyl methacrylate), from Higgins [1990]; and (c) Rhoplex B-60A solids.
Table 3.7 [Pouchert, 1985]. All peaks found in the Rhoplex sample were also found in the PEA or PMMA spectra or both. It is possible that Rhoplex B-60A is a copolymer of methyl methacrylate and ethyl acrylate, based on the spectra.

Beer's Law linearly relates absorbance of infrared peaks to species concentration:

$$A = \log_{10} T = mC$$  \hspace{1cm} (3.3)

where A=absorbance units, T=transmittance units, C=concentration in mole fraction, and m=slope. This relation may be used to calculate composition of a copolymer. The spectrum used for PEA was from Pouchert [1985] and for PMMA, from Higgins [1990]. Higgins' spectrum was obtained from the same instrument as that for B-60A, therefore relative peak heights and positions should be very close for those spectra. Since sample preparation for this analysis was done by different people using different methods and, in one case, different instruments; an analysis slightly more complex than a simple Beer's Law correlation was developed.

For the analysis, the height of a peak common to both homopolymers was compared to a peak contained only in the spectra of one of the homopolymers. Simple comparison of single peak heights was not worthwhile since the detector appears to have saturated for at least two of the samples at the carbonyl peak (1732 cm⁻¹), therefore ratios of peak heights had to be used. The common peak chosen was 1447 cm⁻¹, absorbing between 0.35 and 0.65 for all three samples. The 749 cm⁻¹ peak had strong absorbance in PMMA and weak absorbance in PEA while the 1024 cm⁻¹ peak had very strong absorbance in PEA and very little in PMMA.

The results of the pseudo-Beer’s Law analysis are plotted in Figure 3.17, as the absorption peak ratio as a function of concentration of EA in the copolymer (0=pure
Figure 3.17. Prediction of B-60A composition by FTIR absorbance peak ratio comparison to PMMA and PEA.

PMMA, 1=pure PEA), in mole fraction. Since EA and MMA monomer units both have formula weight equal to 100, weight fraction is equal to mole fraction for this system. Linear relationships were constructed from peak ratios for each homopolymer. Each absorbance ratio should be a linear function of concentration, hence peak ratios for B-60A were interpolated to give a predicted concentration for each line on the graph. The ratio for the 749 cm⁻¹ peak predicts a concentration of 63 wt% EA, 37 wt% MMA; the 1024 cm⁻¹ peak predicts 66 wt% EA, 34 wt% MMA; the results are close to each other. The literature suggests that copolymers of these species, are common in the coatings industry, usually in ratios between 1:1 and 2:1 EA/MMA, depending on product requirements [Allyn, 1973].

The DMA curve for Rhoplex B-60A, shown in Figure 3.8 shows only one
transition for the polymer, indicating only one polymer phase present in the system. If B-60A were indeed a copolymer of methyl methacrylate and ethyl acrylate as hypothesized, it should have a glass transition somewhere in between the values for the homopolymers. Pochan [1979] has developed a relation that can be used to determine glass-transition temperature (in K) in plasticized polymers as a function of composition (by weight or volume percent):

$$\ln T_g = \Phi_1 \ln T_{1g} + \Phi_2 \ln T_{2g}. \quad (3.4)$$

This empirical relation has been found to accurately predict the $T_g$ for copolymers and polymer blends. Figure 3.18 uses equation 3.4 to predict the composition of Rhoplex B-60A. Glass transition values for PEA (-25°C) and PMMA (105°C) were measured by DSC [Brandrup, 1975] while $T_g$ for the Rhoplex film was given by the manufacturer (also determined by DSC [Kligerman, 1989]). The fact that B-60A has a single glass-transition indicates that it must be a random copolymer because block and graft copolymers usually have multiple transitions corresponding to each component [Billmeyer, 1973; Koo, 1974]. The $T_g$ value for B-60A (12°C) predicts a composition of 69 wt% EA, 31 wt% MMA.

Another parameter which may used to correlate composition, related to but different from $T_g$, is called the minimum film forming temperature (MFT), which is the minimum temperature necessary to obtain a continuous film from a polymer emulsion formulation under specific atmosphere conditions [Protzman, 1960]. King [1966] has published a relationship for the (methyl methacrylate)co(ethyl acrylate) system based on experimental determination of MFT as a function of monomer composition. This relationship is also illustrated in Figure 3.18, along with the manufacturer's value for the MFT [Rohm and Haas, 1987]. The composition of Rhoplex B-60A predicted by
MFT is very similar to that predicted by $T_g$: 67 wt% EA, 33 wt% MMA. These values are very close to those predicted by quantitative FTIR. Emulsion coating formulations made with this composition are not out of the ordinary [Johnson, 1979].

Figure 3.10(a) is the DMA plot for Rhoplex B-60A with poly(propylene glycol) plasticizer added in identical proportion to that used in the green tape formulations: 0.71 wt% B-60A, 0.29 wt% PPG. The damping peak occurs at about 1°C; a decrease of nearly 40°C by plasticizer addition. A small damping peak occurs at -69°C, and must be due to a small amount of free PPG in the system since this peak is not present in un-plasticized B-60A (see DMA section). The dynamic $T_g$ for B-60A without plasticizer is 40°C (Figure 3.8). Pochan found equation 3.4 to work especially
well to relate $T_s$ and composition for dynamically determined transition temperatures. Koo [1974] reports that prediction of composition and compatibility of copolymers and polymer blends using DMA is common. In this case, equation 3.4 can be used to assess the compatibility between binder and plasticizer used for green tape formulation. Calculation using vol% based on the composition of Table 3.2 (vol% was calculated from measured polymer densities of 1.15 g/cm$^3$ for B-60A and 1.01 for PPG) and $T_s$ values of the plasticizer and the blend measured by DMA (see Figure 3.10(a), DMA of the unfilled polymer) predicts a $T_s$ of 0.5°C for the film. The $T_s$ measured by the damping peak of DMA was about 1°C, essentially right on the predicted value. This result implies that although some free PPG is present in the polymer blend at -69°C; little or no free PPG is present at the transition temperature of the mixture (near 0°C), and the polymers can be considered to be a compatible system around the glass-transition region. Others have found PMMA/PPG blends in similar proportions to be compatible at these temperatures [Macchi, 1986].

DSC indicated a glass transition region for plasticized B-60A films cast from solvent and emulsion with onset at about -50°C, peak at -13°C, and ending just above 10°C. A sharp endothermic spike, not present in DSC of unplasticized B-60A samples, occurred just over 30°C, well beyond the glass-transition range. The glass-transition peak was shifted ~10°C higher for DSC of green tape samples, and the spike at 30°C was a much more gradual endotherm. Just as in DSC of unplasticized polymer films, green tapes without plasticizer did not show the endothermic spike above 30°C.

Again using the Pochan relation (equation 3.4) and $T_s$ values obtained by DSC for PEA, PMMA, and PPG; the predicted $T_s$ value for this ternary mixture would be -
17°C, not far from the DSC transition peak for the sample (13°C). The data again support the fact that all or nearly all of the plasticizer is compatible or miscible in the polymer matrix in the glass-transition region for the blend.

Chemical Stability of Polymer Films and Green Tapes

Table 3.8 describes the response of polymer films and green tapes when placed in various solvents for several days. Toluene and THF, known solvents for most acrylic polymers, indeed dissolved films the unfilled binder-plasticizer system used in tape formulations when cast from either the emulsion or the soluble system.

Table 3.8. Dissolution behavior of polymer films and alumina green tapes in the presence of various solvents.

<table>
<thead>
<tr>
<th>Film Type</th>
<th>Cast From</th>
<th>Toluene</th>
<th>THF</th>
<th>Tol/TEA</th>
<th>NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-60A/PPG</td>
<td>aq. emulsion</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>org. solution</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>----</td>
</tr>
<tr>
<td>Untreated Tape</td>
<td>aq. emulsion</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>org. solution</td>
<td>broke</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Unplastic. Tape</td>
<td>org. solution</td>
<td>broke</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Treated Tapes:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bake</td>
<td>org. solution</td>
<td>no</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>humid</td>
<td>org. solution</td>
<td>no</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>DuPont Tape</td>
<td>?</td>
<td>yes</td>
<td>yes</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>BaTiO₃ (Ch. 2)</td>
<td>monomer</td>
<td>yes</td>
<td>yes</td>
<td>----</td>
<td>----</td>
</tr>
</tbody>
</table>
Dissolution of green tapes can be described as the destruction of all integrity of the matrix composite system, usually leaving what appears to be only ceramic powder (the results of Chapter 2 show that small amounts of binder may still be attached). Two green tape samples which were not fabricated for this study dissolved in toluene: (1) commercially-available DuPont Green Tape (E.I. DuPont & Nemours, Inc., Wilmington, DE), and (2) non-crosslinked barium titanate tape as found in Chapter 2. Green tapes formulated for this study did not dissolve in the presence of any of the solvents listed in Table 3.8. There was, however, some interesting behavior shown by samples of untreated green tape cast from the solvent and unplasticized green tape. These samples broke into small pieces (several mm in diameter) after several days in solvent, but did not dissolve as the other green tape samples had. There were several differences between the alumina tapes made for this study and the DuPont and BaTiO₃ tapes obtained. The DuPont tape included a significant amount of glass in addition to alumina, these together formed the inorganic component. The binder used in this tape formulation was not known. The BaTiO₃ tape, besides obviously using a different ceramic, utilized a poly(n-butyl methacrylate) binder of unknown molecular weight.

The fact that green tapes with Rhoplex B-60A binder did not dissolve is quite interesting. It is easier to explain what did not happen in the system than to isolate exactly what did happen, although it is clear that the binder strongly adsorbed to the ceramic particle surfaces. Though chemical crosslinking of the polymer chains in the binder could account for the observed chemical resistance, this is highly unlikely for two reasons: (1) Rhoplex B-60A is designed by the manufacturer to be a non-crosslinking system and any efforts to cause crosslinking would require specific crosslinking agents (such as dimethacrylates); and (2) the identical polymer system
without alumina particles present was readily soluble at room temperature, and there is no reason alumina particle addition should cause chemical crosslinking to occur in the polymer. The fact that green tapes did not lose their integrity in solvents does not automatically imply that none of the polymer phase was dissolved. Thermal gravimetric analysis indicated that treated and untreated green tape samples lost some of the organics in the system after a 2 h in toluene at room temperature. These results are summarized in Table 3.9. Untreated tapes from the solvent-based formulation had less bound organics, but this value increased for treated tapes, samples of which had the same or more bound species than samples of aqueous-based tapes. The BaTiO₃ tape, which disintegrated, was found to have only about 2 wt% organics remaining after solvent extraction (see Figure 2.19). The molecular weight of the binder and the number of available basic-type surface sites for binder adsorption on barium titanate probably caused this behavioral difference in this similar (oxide/acrylic) system.

Table 3.9. Organic content of green tapes before and after solvent extraction in toluene (wt%).

<table>
<thead>
<tr>
<th>Green Tape</th>
<th>Solvent</th>
<th>Aqueous</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Cast</td>
<td>21.8</td>
<td>21.3</td>
</tr>
<tr>
<td>After extraction:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>untreated</td>
<td>8.9</td>
<td>13.0</td>
</tr>
<tr>
<td>bake</td>
<td>14.1</td>
<td>14.4</td>
</tr>
<tr>
<td>humidity</td>
<td>15.3</td>
<td>14.6</td>
</tr>
</tbody>
</table>
Firing Behavior

Directional linear shrinkage incurred during firing of samples is given in Table 3.10. Each shrinkage value (for in-plane directions) was averaged from two samples, with four data points per sample. Several samples from different slurry batches were fired to check reproducibility of firing shrinkage. All green tapes from the solvent-based slurry had less shrinkage anisotropy on firing, in general. Stabilization treatments performed on solvent-based green tapes reduced the magnitude of firing shrinkage noticeably and consistently except for the humidity treatment, which caused more shrinkage reduction than the other treatments and eliminated anisotropy.

Table 3.10. Linear firing shrinkage (%) of green tape layers; all layers were aged 40 days prior to firing unless otherwise noted.

<table>
<thead>
<tr>
<th>Solvent System: Direction</th>
<th>ORGANIC</th>
<th>AQUEOUS</th>
<th>x/y</th>
<th>parallel</th>
<th>normal</th>
<th>z-dir</th>
<th>x/y</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>parallel</td>
<td>normal</td>
<td>z-dir</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No Treatment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.0</td>
<td>17.6&quot;</td>
<td>1.02</td>
<td>16.5&quot;</td>
<td>17.0</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.0'</td>
<td>17.8</td>
<td>17</td>
<td>1.01</td>
<td>16.9</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.6&quot;</td>
<td>17.3</td>
<td>1.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bake</td>
<td>18.0&quot;</td>
<td>18.4</td>
<td>1.01</td>
<td>16.1</td>
<td>16.7</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>Thermal Cycle</td>
<td>18.6</td>
<td>18.4</td>
<td>17</td>
<td>1.01</td>
<td>16.3</td>
<td>16.8</td>
<td>0.97</td>
</tr>
<tr>
<td>Solvent</td>
<td>18.6</td>
<td>18.4</td>
<td>1.01</td>
<td>16.2</td>
<td>16.6</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>Humidity</td>
<td>17.4</td>
<td>17.4'</td>
<td>1.00</td>
<td>15.9</td>
<td>16.5</td>
<td>18</td>
<td>0.96</td>
</tr>
</tbody>
</table>

| Avg. Density (g/cm³)*   | 87.2    | 86.5   |
| Std. Dev.               | 0.98    | 0.86   |

*Measured geometrically.
*Tape aged 70 days.
*Tape aged 100 days.
Fired densities were measured for all samples by geometric methods and were consistent for all samples. Archimedes measurements gave artificially high results for all samples. The discrepancy between the results from the measuring techniques was attributed to open porosity in films which is known to be present in ceramics below 90% of theoretical density. The same samples re-fired at 1600°C for 1 h sintered to between 99 and 100% of theoretical density (densities were equivalent using both measurement techniques), therefore samples fired to 1500°C for 30 min can be considered to have been under-fired.

The aqueous-based samples shrunk less than the organic, solvent-based samples, in general, and with more shrinkage anisotropy. As in the solvent-based system, treatments lowered the magnitude of firing shrinkage without altering anisotropic behavior. Samples exposed to the humidity treatment underwent the lowest firing shrinkage (as in the solvent-based system) but shrinkage anisotropy remained the same as for all other aqueous samples. Fired densities for aqueous, emulsion-based tapes were again consistent for all samples and were similar to those for solvent-based samples.

Reproducibility of firing shrinkage was investigated by firing samples which were prepared from different slurry batches. These samples had been aged longer before firing (70 or 100 days) than the two batches used for most of the data collection in this study (40 days). The magnitude of the shrinkage for untreated solvent-based samples decreased with aging time, x/y ratio remained constant. The magnitude of the firing shrinkage for the sample which had aged 100 days was nearly identical to that for the humidity-treated sample. The untreated, aqueous-based sample aged 70 days experienced the same shrinkage as tape from a different aqueous slurry.
batch which had been aged only 40 days. The solvent-based sample which underwent the humidity treatment and 70 days of aging had the same shrinkage (within measurement error) same as the humidity-treated sample which had aged only 40 days.

Firing shrinkage in the thickness or z-direction was calculated from the geometric density and the linear shrinkage values for the samples. Samples within each solvent system experienced very similar z-shrinkage, while that for green tapes from the different slurry systems varied. Solvent-based samples shrunk more in the in-plane directions than in thickness during firing, while aqueous, emulsion-based tape samples shrunk more in thickness.

V. DISCUSSION

There are numerous variables present in tape-casting, making complete understanding of a system, from component reproducibility to mechanical properties and firing behavior, impossible. This is a sentiment shared by others in similar areas of research [Glass, 1986]. The results presented here reflect the influences of many parameters simultaneously. For this reason, some of the interpretations discussed will only be valid for this specific system while others may hold for tape-casting systems in general or even for organic coatings in general.

All attempts were made to keep systems as similar as possible in this study, in order to isolate green tape differences due to solvent and those caused by changes in binder states. Processing techniques and formulation compositions needed to be slightly altered for each system to produce samples which would be valid for comparison (see Experimental section). While the results presented are for only one cast for each system, they reflect numerous attempts, as both systems had major
processing difficulties to overcome. The solvent-based slurry, very much more volatile and irritating to process, was relatively insensitive to perturbations; it produced strong, uniform green tapes nearly every time. The aqueous slurry, without dissolved polymer, was easy and not unpleasant to process but had a smaller tolerance to minor changes in drying conditions, casting composition, or film thickness; it produced crack-free, uniform green tapes only when all variables were controlled extremely well.

Effect of Changing Slurry Chemistry on Shrinkage in Green Tapes

It is important to differentiate between shape changes, volume changes, and density changes in green tapes. Only untreated samples experienced weight changes on aging due to residual solvent evolution. Therefore, for all treated samples, in-plane shrinkage must be compensated by an increase in sample thickness in order to preserve volume, since densities did not vary for these samples. Volume preservation is not intuitively valid, however, especially in polymers which are known to contain free volume.

Macchi [1986] determined the amount of free volume in polymer blends of PMMA/PPG by evaluation of coefficients of thermal expansion of the pure polymers and the blends. For molecular weights of PMMA and PPG of 550,000 and 1000 respectively, the free volume at 25 wt% plasticizer was 1.1% of the total volume and PPG addition was found to lower free volume in that system, contrary to results for most plasticized polymers. This value would correspond to linear shrinkage of 0.37% in an unfilled polymer/plasticizer system (based on isotropic shrinkage) if all the free volume of the system were to collapse. Green tapes in this study were approximately
50 vol% polymer, reducing the potential free-volume-shrinkage by half, to 0.19%.
Comparing this value with observed shrinkage in green tapes, which was as high as
2.7% during stabilization treatments and 0.4% on aging of treated samples, it is safe
to say that shrinkage due to free-volume-collapse was a negligible fraction of the total
shrinkage in green tapes but may have contributed to aging shrinkage. The only way
to be certain of this would be to measure the free volume contained in samples, and
given the disputed nature of such measurements, that may not even be adequate.
Sears [1982] indicates that drying of polymer films may create free volume and that
the casting solvent might affect its magnitude. Sears also reports values for free
volume an order of magnitude higher than most other researchers.

Given this analysis, it seems almost certain that green tapes undergo nearly all
of their dimensional change due to stress relaxation of the bulk polymer phase in the
system. This hypothesis is consistent with all the shrinkage data. Samples which
incur the most stress would be those having the slowest relaxation time relative to the
time for the solvent to dry, drastically reducing polymer mobility. This ratio may be
reflected by the Deborah number, the magnitude of which indicates how far samples
are from thermodynamic equilibrium (in this case) after constrained drying occurs by
rs by consideration of viscoelastic behavior of the slurry. A priori, several slurry
differences are known which would affect the Deborah number: (1) toluene and
ethanol have higher vapor pressures than water at room temperature; (2) slurry
viscosity in the soluble-polymer system is several times higher than the dispersed,
emulsion slurry, and (3) the polymer in the aqueous system is in the form of
dispersed spherical particles, giving the slurry little elastic character.

Shear under the doctor-blade during tape-casting causes alignment or
deformation in both polymer systems. Soluble polymer chains become stretched or aligned more in the casting direction and then become frozen in that state by drying, hence more shrinkage occurs in the casting direction. Dispersed latex particles in the emulsion may be dragged along by the doctor-blade, and then in order to form a continuous film, polymer chains must stretch somewhat in the casting direction as the water evaporates, causing anisotropic shrinkage in that system due to the film-formation mechanism. The absolute value % of shrinkage anisotropy (difference between x- and y-shrinkage values) was significantly larger in the solvent-based system, but to argue about the degree of anisotropy in each system would be difficult because each experienced differences between x and y shrinkage of the same percentage of the total. This analysis is consistent with the literature [Blumentritt, 1979].

The shape of the shrinkage curves of untreated tape samples is probably affected by the casting solvent. Tapes cast from toluene/ethanol slurries became dimensionally stable after 20 days of aging, while aqueous-based tapes’ shrinkage curves did not flatten fully even after 35 days. This is possibly due to the residual solvent evaporation behavior over the course of aging. Not only do toluene and ethanol have higher vapor pressures than water (and would therefore tend to evaporate more quickly), but humidity in the atmosphere lowers the concentration driving force for residual water evaporation. Another contribution to differences in the shrinkage curves may originate in lower polymer mobility in aqueous-based tapes due to a higher ratio of adsorbed to bulk polymer in that system (see Discussion).
Correlation of Shrinkage with Amount of Adsorbed Polymer in Green Tape

Figure 3.19 may help to define the shrinkage mechanism in green tapes over time as it linearly correlates the average of x and y shrinkage values in green tapes, over the 35-day aging period (see Figure 3.7), with the amount of organics remaining in green tapes after toluene extraction (Table 3.9). Treated and untreated tapes from aqueous and organic slurries were used for this correlation (with duplicates of three different samples run), which had a linear regression coefficient of 0.996. It can be concluded then, that for the alumina/B-60A/PPG system, green shrinkage is inversely proportional to the amount of adsorbed organic phase, regardless of processing history (i.e. solvent used or state of the binder).

This relation may hold (in some form) for green tape systems with other binders.

Figure 3.19. Correlation of shrinkage in green tapes to amount of organics attached to alumina particle surfaces.
and possibly other ceramics. It might be used to design tapes with given amounts of shrinkage by precisely controlling processing or post-casting treatments to affect the amount of binder adsorbed. One caution worth mentioning is that tapes without any bulk polymer phase (ie. those after extraction) had poor mechanical properties. Attempts to eliminate shrinkage by fabricating tapes with all the polymer adsorbed, or extracting all the bulk organics, might not be fortuitous for further processing steps. Aside from mechanical flexibility required for punching and machining, bulk polymer may be necessary for layers to stick during lamination.

Higgins [1990] found by infrared spectroscopy that PMMA formed strong ionic bonds on alumina surfaces, sometimes displacing other adsorbed species. PMMA adsorption on alumina was observed on the basic, hydroxyl sites on the oxide surfaces. Higgins calculated (by quantitative FTIR) that the number of bonds which functional groups of PMMA had at room temperature was 3.4 per 100 Å² of alumina surface. Comparing this result with the amount of Rhoplex polymer present in this system (15.6 wt% of the green tape), the average molecular weight of Rhoplex chains (M_w=298,000 g/mol), and the surface area of the alumina powder used (6.4 m²/g), there should be approximately 8 bonds per polymer chain. This number would enable most of the polymer chains of the binder present in the green tapes to adsorb to particle surfaces, and would therefore explain why green tapes maintained their integrity in solvents which normally dissolve the polymer. The fact that tapes in the presence of solvents did not dissolve even when heated indicates that polymer chains were not simply tangled in the web of a few adsorbed chains. Heating might enable chains not attached to have higher mobility and solubilize; it could also promote polymer adsorption to alumina hydroxyl sites as Higgins found. It can be concluded
that a continuous matrix of ceramic particles exists, connected by polymer chains bound to their surfaces.

The high molecular weight of the binder facilitates such a matrix, requiring that only a few percent of the monomer units present be bound to oxide surfaces to create particle bridging. The root-mean-square end-to-end distance of an amorphous chain of PMMA or PEA is approximately 800 Å. This distance (coincidentally?) corresponds to the surface separation of alumina particles in dried green tapes, based on the maximum green density achieved in this study (53% of theoretical, see Figure 2.29).

The results of the toluene extraction indicate the amount of adsorbed organics in untreated green tapes varies with the casting system used. After treatments (all of which involved heating) the amounts of insoluble organics were similar in samples from different solvent systems. The composition of the organics remaining in the tape is unknown, though it is safe to assume that nearly all of the plasticizer was probably dissolved, leaving binder and dispersant. Calculation based on this assumption indicates that nearly 100% of the binder was not extracted from treated green tapes. The binder itself was exactly the same in each solvent system, likely a high molecular weight copolymer of ethyl acrylate and methyl methacrylate. The dispersants were para-hydroxy benzoic acid (MW=138) in the organic solvent system and Darvan®C (MW=14,000), poly(methacrylic acid) with ammonium ions in place of some of the acid functional groups, in the aqueous emulsion system. The molar ratio of dispersants used for this study was 160:1, p-HBA:Darvan®C. For p-HBA, this amount of p-HBA equals about 74 times one monolayer of alumina surface coverage based on hydroxyl site surface area of 5.88 Å² [Higgins, 1990]. Dispersant in excess of one
monolayer cannot be attached to particle surfaces unless molecules bond to each other. Therefore, at least in the solvent-based system, most of the dispersant was probably washed away by toluene.

Dispersant differences in the systems do not seem to be reflected in organic content after extraction for treated green tapes, making binder-dispersant interaction an unlikely cause for variation in polymer adsorption in the different solvent systems. A more plausible explanation is that the toluene present during casting the solvent-based slurry dissolved the binder and the system either: (1) reached a thermodynamic equilibrium state with given binder concentrations on the surface and in the solvent; or (2) the drying time relative to the polymer-surface-adsorption time was too small for all the binder to achieve some desired equilibrium state. The higher value for insoluble organics in the untreated aqueous tape over that for the untreated solvent-based tape favors the first argument, thermodynamic limitation. Higgins also indicates that the presence of water (even in very small amounts such as would be present due to room humidity) seems to facilitate polymer adsorption.

A physical basis for correlation of amount of adsorbed polymer with aging shrinkage in this filled-polymer system can be inferred from the work of Struik [1987]. The model discussed earlier (Figure 3.1) for aging in filled-polymer systems indicates that polymeric material near or attached to the surface of the particle behaves as part of the rigid matrix. Mobility is lower in the adsorbed-polymer phase than in the bulk phase. If this is so, it would make physical sense that the system with the highest fraction of its polymer in the adsorbed state would be the most rigid and the least mobile, and would age the least on the timescales observed for this study (assuming constant initial sample composition).
Mechanisms of Stabilization Treatments

Two issues are of interest with regard to stabilization treatments for green tapes: how do they cause shrinkage and how do they facilitate polymer attachment to alumina surfaces? Polymer relaxation and polymer redistribution may not be distinct, independent processes, but they need to be thought of as such in order to assess why the treatments yielded different results.

Table 3.9 indicates that the bake and humidity treatments each caused a significant increase in the fraction of organics which were attached to alumina particle surfaces. Untreated, solvent-based tapes dried in the presence of toluene, which is a good solvent for the binder, causing much of the polymer not to attach due to thermodynamic equilibrium. The treatments seem to have simply caused equilibrium to shift and favor more binder adsorbed to the surface (facilitated by the absence of toluene and the higher temperatures). These results are consistent with those of Higgins’, who observed increased PMMA adsorption on alumina surfaces at higher temperatures.

The results shown in Table 3.5 point out significant variation of shrinkage due to stabilization treatments. This variation was present for samples treated differently within the same solvent system as well as those for different systems subjected to the same treatment. There are certainly different mechanisms acting to induce stress relaxation in green tapes during treatments.

A crude approximation to assess shrinkage mechanisms during treatment can be attempted from simple kinetic principles. The simplest treatment, sample bake, involved heating for 2 h at 120°C. Assuming that simple diffusion and chemical
kinetic processes approximately double in rate for every 10°C of temperature increase (as is generally accepted as a rule of thumb), the bake process was equivalent to aging 2000 h, or 83 days, at room temperature (20°C). After 83 days of aging, extrapolation of shrinkage curves for untreated solvent-based green tapes indicates an average (based on x and y values) of about 25% less shrinkage than the bake process caused. This indicated that another mechanism, in addition to a polymer mobility increase due to heating, operates to cause shrinkage during the bake treatment. The only certain difference between baked and untreated samples is that some residual solvent was still present in untreated samples after 83 days (from sample weight measurements).

The thermal cycle and solvent treatments both consist of the bake treatment plus some other process, therefore the amount of shrinkage due to a mechanism other than solvent evolution and increased mobility (accomplished by the bake treatment) at high temperature, may be determined for those treatments by comparing shrinkage they caused to that of the bake treatment. The humidity treatment may be broken down into two parts: (1) heating for 48 h at 80°C, and (2) 24 h at 100% RH. The thermal part correlates to about 250 days of aging at room temperature. Following extrapolated shrinkage curves for untreated tapes out to 250 days, one can estimate the fraction of shrinkage which was not due to the thermal part of the humidity treatment but rather due to the presence of saturated water vapor. This extrapolation probably contains substantial error.

This analysis is summarized for solvent-based and aqueous, emulsion-based tapes in Table 3.11, using average of x and y shrinkage values for comparison. The numbers are not precise by any means, but are simply intended to indicate why the
treatments work to the extent that they do. The values seem to make more intuitive sense for the solvent-based system, most likely because the shrinkage curves for those samples (which were the baseline for this analysis) were regular and flattened quickly, enabling reliable interpolation and extrapolation. This was not the case for aqueous-based tapes.

The purpose of the stabilization treatments was to determine their effect on limiting dimensional changes in ceramic green sheets. The bakeout involved heating at 120°C, just above the boiling points of toluene (110°C) and water (100°C). The bake treatment was intended to eliminate all residual solvent that might cause dimensional change over time due to evaporation, and allow the tape to relieve internal stresses incurred during drying. Samples exposed to the thermal cycling

Table 3.11. Green tape shrinkage incurred on treatment, broken down into mechanistic causes.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Total Shrinkage (avg. of x &amp; y)</th>
<th>Estimated Percent of Total Shrinkage Due to:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solvent</td>
<td>Heating</td>
</tr>
<tr>
<td>BAKE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>solvent</td>
<td>1.10</td>
<td>25</td>
</tr>
<tr>
<td>aqueous</td>
<td>0.35</td>
<td>30</td>
</tr>
<tr>
<td>THERMAL CYCLE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>solvent</td>
<td>1.80</td>
<td>15</td>
</tr>
<tr>
<td>aqueous</td>
<td>0.60</td>
<td>15</td>
</tr>
<tr>
<td>SOLVENT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>solvent</td>
<td>2.10</td>
<td>15</td>
</tr>
<tr>
<td>aqueous</td>
<td>0.50</td>
<td>20</td>
</tr>
<tr>
<td>HUMIDITY</td>
<td></td>
<td></td>
</tr>
<tr>
<td>solvent</td>
<td>2.70</td>
<td>10</td>
</tr>
<tr>
<td>aqueous</td>
<td>0.85</td>
<td>10</td>
</tr>
</tbody>
</table>
treatment were more resistant to dimensional change than those exposed to constant temperature treatment for the same total time. Four cycles of 30 min each at -5°C and 120°C were administered alternately to green tapes. The total time at 120°C was equal to the bakeout time, 2 h, but cycling caused continuous volume changes in the sample during treatment. This result is consistent with that of McLoughlin [1952] who found that rapid heating and cooling increased stress relaxation processes in PMMA. Volume change during thermal cycling facilitated configurational changes in the polymer phase and allowed it to approach a relaxed state. Solvent-vapor saturation is believed to relieve residual stresses by substantial swelling which increases free volume thereby enhancing polymer mobility [Struik, 1978]. Since the bake part of the solvent treatment occurred after the solvent exposure, the value for shrinkage attributed to swelling is probably artificially low because most of the relaxation had occurred before heat treatment.

The humidity treatment was taken from an ASTM test [1983] for dimensional testing of plastics after simulated aging conditions. Berry [1984] found that exposure of PMMA to 100% RH induced stress relaxation equivalent to that incurred by raising the temperature of the sample by 90°C, and that humidity treatments can be comparable to or even surpass heating for effectiveness of altering stresses in thin samples of PMMA. This result is consistent with those of this study, as the amount of shrinkage attributed to humidity was approximately equal to that caused by the temperature increase of 60°C during humidity treatment. Berry attributes relaxation to swelling of PMMA leading to free volume and mobility increases, similar to the mechanism proposed for the solvent-vapor treatment.
Correlation of Shrinkage and DMA Behavior

One might expect shrinkage to be related to DMA behavior in filled-polymer systems. After exhaustive data analysis, a correlation between shrinkage and the magnitude of the complex modulus drop over the glass-transition region was developed, and is illustrated in Figure 3.20. Three additional datapoints were omitted as they were off scale and the shape of the modulus curve differed significantly for these samples. Two independent relations seem to exist, one for each solvent system used. Though the correlation is not perfect, there is definitely a trend of samples showing proportionality between modulus drop and shrinkage. Measurement error for modulus drop was estimated from the standard deviation of three identical samples.

Theoretically, DMA behavior should correlate with shrinkage. Damping (tan δ)

![Figure 3.20. Correlation of green tape shrinkage with modulus drop over the glass-transition region (from DMA).](image-url)
is a measure of the ratio of viscous to elastic behavior of a material. As polymers become more rigid by adding filler, they also become more elastic (or less viscous). This effect has been observed by many as flatter, broader damping peaks [Saini, 1986; Bradshaw, 1986]. Similarly, breadth of the glass-transition, and relative rigidity as observed by modulus drop might give an indication as to potential shrinkage behavior of a green tape. Since more rigid tapes (those with more adsorbed polymer) experienced less shrinkage, DMA should be able to reflect potential shrinkage in green tapes.

Why then does no good correlation exist between shrinkage and DMA for green tapes? The two general reasons for this are: (1) problems inherent to the Rheovibron instrument design, and (2) time and labor intensity of sample measurement. Webler [1981] has written a critical analysis of the benefits and shortcomings of commercially-available Rheovibron instruments. The instrument design requires extremely precise measurement of sample thickness and width and accurate alignment of samples in order to obtain reliable and reproducible data. Beyond that, thermal control is not consistent throughout the temperature ranges normally used and was observed to affect measured properties (some of these problems are described in Results).

The best results obtained by Webler, after identifying and controlling these and other problems, showed 5% variation in modulus for runs of essentially identical samples. For this reason, researchers often run DMA of several duplicate samples and average the results. That feat was impossible for this study due to the number of different samples (26) and the amount of operator-attentive time required for each run (3 to 4 h). Due to the long run times, samples from the same batch of green tape
were run over a period of several weeks, during which time shrinkage and relaxation occurred, altering properties significantly and certainly throwing off any correlation that might be attempted. The modulus increase observed in green tapes also impeded precise determination of modulus drop and breadth of transition. Ideally, all samples would have been run on the same day as they were exposed to stabilization treatment, which usually was the day immediately following casting.

**Behavior of the Polymer Phase in Green Tapes**

Though DMA did not provide an excellent shrinkage correlation, it provided other very valuable information about green tapes. Glass-transition peaks were used to assess binder-plasticizer compatibility and understand the effect of plasticization and adding filler to the polymer. DMA revealed interesting modulus behavior found only in measurements of plasticized green tapes. The modulus of these samples increased at ~30°C (observed by DMA) and its value above this temperature was nearly identical to that of unplasticized green tape at similar temperatures. The slope of the sample elongation v. temperature curve became significantly flatter at 30°C. Another result reflecting this phenomenon in green tapes was the endothermic spike of the DSC which occurred at the same temperature. Based on all these results, an argument can be made that phase separation occurs in the B-60A/PPG system just above room temperature, although no visual evidence of it was available. Neither visual observation nor optical microscopy of heated samples revealed hard evidence of phase separation in the polymer blend. Macchi [1986,II] used small-angle x-ray scattering to assess phase separation in a similar polymer system (PMMA/PPG). Gretzner [1981] was able to conclude phase separation from DMA behavior of pigmented organic
coatings. Sears [1982] states that plasticizer evolution (but not necessarily volatilization) is not uncommon just above room temperature and that such phase separation is often reversible (as it is in this study). He indicates that in some cases this is related to the Flory delta temperature for polymers, or the lower critical solution temperature (LCST) of the binary mixture, above which miscibility is not complete.

A model is proposed to explain the observed behavior. Plasticizer leaves the green tape matrix and aggregates in pockets throughout the tape (no tackiness was observed for green tapes above 30°C, therefore significant diffusion of the plasticizer to the surface was unlikely). The resultant matrix becomes much more rigid for two reasons: (1) the plasticizer is no longer functioning as such (determined by comparing the moduli of green tapes above the increase to that of unplasticized green tape at the at the same temperature, Figure 3.9), and (2) most of the binder is bound to ceramic particle surfaces (in all green tape samples analyzed). As with the correlation of shrinkage and adsorbed organics, this phenomenon is also independent of the slurry system used.

This behavior is important because it causes significant property changes in green tapes very close to room temperature. With understanding, such properties might be exploited; for example, the thermal cycle treatment may have been effective because of property changes caused by binder-plasticizer compatibility behavior within the cycled temperature region. Conversely, a process such as lamination might be affected negatively by such an occurrence as exhibited by the polymer phase which plays a critical role in the effectiveness of adhesion of green sheets to one another. Untreated green tapes from both slurry systems laminated readily.
Effect of Slurry System on Firing Shrinkage and Ceramic Particle Packing

Firing shrinkage in a direction is usually a function of ceramic particle spacings in that direction [Kingery, 1976]. The firing results presented, then, infer that slurry alteration caused particle arrangement in green tapes to differ substantially. This assumption is validated by the fact that samples from both systems fired to similar densities at 1500°C (within 1%) and to full density at 1600°C. Specifically, in aqueous-based tapes, particles were slightly closer together in the direction of casting (x) than the normal (y) direction, and both in-plane spacings were lower than those in thickness (z). Conversely, in solvent-based tapes, x- and y-spacings were similar but both were much higher than those for aqueous tapes; and z-spacings were lower than x- and y- in these samples and were also lower than z-spacings in aqueous-based tapes.

Figure 3.21 correlates linear firing shrinkage (average of x and y values) to the amount of adsorbed organics in green tape samples. Unfortunately, the data from different casting systems do not fall on the same curve, limiting the number of datapoints to three for each. The relations do appear very similar for both slurry systems, as the curves are the same shape. However, unlike the correlation of shrinkage in green tapes, firing shrinkage cannot be predicted independently of the slurry system.

Not enough data was generated to fully understand the effect of the solvent and binder on directional particle packing in green tapes. The firing behavior of the organic, soluble-polymer system (Table 3.10) seems to indicate that ceramic particle spacings follow a similar path to those of polymer chains during processing and
Figure 3.21. Correlation of firing shrinkage with amount of organics attached to alumina particle surfaces (in green tapes).

treatment. Based on firing shrinkage data, ceramic particles were spaced relatively far apart in the untreated green tape (in the in-plane directions) with x-spacing > y-spacing. The stabilization treatments caused particles to come closer together during polymer relaxation and green tape shrinkage. The fact that a substantial amount of binder was bound to the ceramic particles, and that the viscosity of solvent-based slips increased substantially on ball-milling (possibly due to polymer adsorption) supports this hypothesis (that particle spacings vary with polymer relaxation), and can be explained by polymer adsorption occurring before casting in this system. The humidity treatment, which caused the polymer phase to relax more than any other treatment, eliminated shrinkage anisotropy on firing as well as that in the green tape. It is possible then, that the relaxed (near-equilibrium) state of green tapes from the
solvent-based casting slurry is that in which particle spacing and polymer configuration are both isotropic. Furthermore, anisotropy is caused by polymer alignment and particle dragging caused by doctor-blade shear combined with an inability for the system to return to equilibrium before slurry drying is complete (high Deborah number).

Aqueous-based green tapes experienced less x-shrinkage than y-shrinkage on firing for both treated and untreated samples, indicating closer particle packing in the casting direction than the transverse direction. This is the opposite result from that for solvent-based samples. A possible mechanism is that rheological properties cause ceramic particle spacings to be larger in the y-direction than the x-direction after casting, but film-formation properties of the emulsion cause the polymer phase to dry in a state further from equilibrium in the x-direction, possibly due to a lower less adsorbed polymer in that direction (orientation due to adsorbed species). Polymer most likely does not become adsorbed until the emulsion film-formation process is underway; many hours after casting (based on no increase in slip viscosity during ball-milling). This would account for observed green shrinkage behavior (\(x>y\)) and firing shrinkage behavior (\(y>x\)). The actual reasons as to why this arrangement might result are not understood.

Differences in z-direction shrinkage between slurry systems results from planes of ceramic particles being further away from each other in the aqueous system. Figure 2.30 (TGA of top and bottom of green tape) indicates that a concentration gradient exists in the z-direction of aqueous-based tapes (no data were generated for comparison with the solvent-based samples, although Mistler [1978] showed the same phenomenon for similar slurry systems). Such gradients can infer that the actual
particle-particle distances do not differ between systems but that the aqueous samples had more polymer towards the top surface of the tape. Firing shrinkage equals that due to binder removal (if particles are not already touching in the green tape, which they are not for this system; see Chapter 2) plus that due to sintering of ceramic particles. Analysis of the shrinkage immediately after binder-burnout would enable confirmation of this mechanism, but this measurement is very difficult because samples have virtually no strength at that stage of the firing process.

VI. CONCLUSIONS

Slurry Processing

Due to significantly lower slip viscosity and the absence of volatile organic solvents, processing of the aqueous alumina tape-casting slurry with acrylic, emulsion binder was physically easier and less unpleasant than preparing a conventional, solvent-based slurry using the same amount of the binder in the soluble state. Binder addition did not alter rheological characteristics of the slip, even after ball-milling, due to the dispersed state of the latex binder.

Shrinkage in Green Tapes

Green tapes from the aqueous, emulsion-based system experienced much less linear shrinkage than those from the solvent-based slurry, under controlled aging conditions for several weeks. Anisotropy of shrinkage was also less for aqueous-based tapes, with samples from both systems experiencing more shrinkage in the casting direction compared to that in the transverse direction.

Shrinkage in green tapes correlated extremely well to the amount of the organic
phase which was attached to alumina particles (all tape samples had the same composition). This correlation was independent of the slurry formulation used to prepare green tapes.

A weaker correlation existed between green shrinkage and the relative modulus change over the glass-transition region, as measured by dynamic mechanical analysis (DMA). This correlation was not independent of the slurry formulation used. Inadequacies of the correlation can be traced to problems inherent to the instrument and sampling errors.

Relaxation of polymer stresses incurred due to: (1) constrained drying, and (2) polymer-ceramic interaction, is the mechanism for shrinkage of green tapes on aging. Free-volume collapse can not account for a significant fraction of shrinkage for most samples. According to this analysis solvent-based, soluble-polymer green tape slurries dried in a less relaxed state (further from thermodynamic equilibrium) than aqueous, emulsion-based tapes. This can be attributed to the high degree of polymer orientation caused by (probably caused by doctor-blade shear) in the solvent-based system.

**Dimensional Stabilization Treatments for Green Tapes**

Some dimensional stabilization treatments caused green tapes to undergo less than 0.15% linear shrinkage after 35 days of aging at controlled-room conditions and experience no shrinkage anisotropy (within measurement limits) after treatment. This result was reproducible.

Stabilization treatments increased the amount of polymer bound to alumina surfaces in green tapes, enabling these treated samples to shrink less on aging.
The mechanism for relaxation of green tapes during treatments was increased polymer mobility and polymer free volume due to thermal energy input and swelling of the polymer. Treatments which involved only thermal energy input were less effective than those involving an additional relaxation mechanism.

**Polymer Phase in Green Tapes**

DMA behavior indicated that no observable changes in the chemical or physical nature of the polymer phase occurred for green tapes regardless of the slurry formulation or stabilization treatment.

The binder and plasticizer were mostly compatible at the ratio used (about 2.5:1, by weight) but phase separation occurred in green tapes above 30°C causing them to behave like unplasticized materials above this temperature. This phenomenon was reversible and independent of the slurry formulation used, but it did not occur unless ceramic, binder, and plasticizer were all present in samples.

Rhoplex B-60A acrylic emulsion is most likely a random copolymer of methyl methacrylate and ethyl acrylate, in a ratio near 1:2, MMA:EA. This conclusion is based on results of FTIR peak height comparison and relationships for glass-transition properties as functions of composition. B-60A solids have weight-average molecular weight (\(M_w\)) of 298,000 and number-average molecular weight (\(M_n\)) of 222,000, indicating a very narrow size distribution for a polymer produced by emulsion polymerization.

**Firing Behavior**

The slurry formulations used had an effect on linear in-plane firing shrinkage.
Tapes from the aqueous system experienced less overall linear shrinkage on firing (than those from the solvent-based slurry) but more shrinkage anisotropy, with shrinkage in the casting (x) direction less than that in the normal (y) direction.

Firing shrinkage in tapes from solvent-based formulations seemed to follow green shrinkage for those samples. Casting-direction shrinkage was greater than that in the y-direction and treatments reduced the magnitude and anisotropy of shrinkage occurring during aging and firing of green tapes.

Firing shrinkage correlated with the amount of adsorbed polymer on alumina surfaces of green tapes, but independent relationships existed for samples from each slurry formulation. This correlation may account for the similarity of green and firing shrinkage behavior in samples cast from the solvent-based slurry, with both based on the amount of adsorbed polymer.

The casting solvents used may have caused shrinkage in the out-of-plane (z) direction to vary for tapes from different slurry formulations. Though thickness could not be measured precisely, aqueous samples seemed to experience more shrinkage in the z-direction than in-plane. This result was reversed for solvent-based tapes, with isotropic shrinkage occurring in samples subjected to the most effective stabilization treatment. This behavior is most likely caused by directional ceramic particle packing variation caused by rheological and drying differences between the slurry systems used.

VII. FUTURE WORK

The aim of this research was to lend some science to what is considered a black art. The many variables of tape-casting are impossible to understand and
control simultaneously, but isolation of a few at a time can lead to some explanations. There are several areas of research which would be very interesting to pursue or might confirm hypotheses made in this thesis.

Studies of green shrinkage were not all-encompassing. Shrinkage might be investigated as a function of the molecular weight of the binder, with the assumption that molecular weight would influence the amount of binder adsorption to ceramic surfaces, and hence influence shrinkage behavior. This could be looked at for soluble and emulsion-based systems using commercially-available products. The effect of green tape thickness was not evaluated; thickness from various slurry systems was held as constant as possible but varied slightly (about 15%). If the effect of thickness on green or firing shrinkage is large over this thickness variation (for samples from the same slurry system), results from this study may need to be corrected slightly. Drying rate of the slurry and its effect on shrinkage was not isolated for this study. This would require utilizing different solvents for the same binder (soluble or dispersed), or varying drying parameters.

The correlation of aging shrinkage and amount of adsorbed species spurs interesting ideas which may uncover some intangibles of tape-casting. First of all, the identity of the adsorbed species should be analyzed. Transmission FTIR on the extracted organics would be a useful analysis, and this might be compared to diffuse reflectance FTIR of the green tape after the extraction. Higgins [1990] found this technique to be extremely valuable to assess the mechanism of attachment of organics to oxide surfaces. The age of the slurry before casting has been found by others to influence shrinkage behavior. This may be related to adsorption of organics during the mixing or milling operations. A study of the rate of adsorption in each type of
slurry system used, keeping in mind the effect of changing solvent (for soluble-polymer systems) and soluble v. dispersed binder, would be advantageous.

The identity of Rhoplex B-60A might be easily verified by more quantitative FTIR studies comparing spectra of known copolymer compositions to that of the Rhoplex formulation. Comparison of proton NMR spectra of known copolymers to that of B-60A might also yield more convincing information, although both methods would require synthesis of copolymers or knowledge of spectral differences between polymer blends and copolymers of the same composition. Binder-plasticizer compatibility without the presence of filler might be assessed as a function of plasticizer content and temperature, by small-angle x-ray diffraction [Macchi, 1986, II].

In hindsight, DMA of green tapes might provide a more accurate correlation to green tape shrinkage if only a few tapes were run, but five to seven times for identical samples of each. If there were a way to analyze all samples from a cast at the same time, that might add to the correlation accuracy. This may be accomplished by not removing green tape from the glass casting surface until treatment and then immediately DMA would be performed for that sample. Some form of stress relaxation might still occur after casting, even on the constrained surface, but this procedure might be useful.

A more detailed analysis of the effect of the slurry system on firing behavior and particle spacings needs to be undertaken before comprehensive understanding of component interactions is accomplished. Aside from the effect of green tape thickness described above, there are several experiments which would aid in quantifying firing shrinkage. Firstly, measuring shrinkage after firing all samples to 100% dense, of course, allows one to put more faith in the reproducibility of shrinkage results.
Quantitative TGA of green tapes as a function of the z-direction might provide helpful information. This would be facilitated by quantitative sample preparation using a microtome or similar device to make uniform, thin slices of green tape (<10μm) for analysis. Particle spacings in the x- and y-directions need to be analyzed, preferably by both bulk and microscopic methods. Dielectric constant of green tapes as a function of direction might give ideas as to relative particle spacings in the bulk material. Similarly, quantitative microscopy (though it may be extremely laborious) could indicate the average and standard deviation of particle-particle spacings as a function of direction. Dielectric constant measurements might give indications as to the morphology of green tapes as a function of direction, as this technique has been used to assess microstructure of polymers, ceramics, and filled polymers [Varadarajan, 1983].
REFERENCES


H.K. Bowen; MIT; Cambridge, MA; personal communication, 1988.


M.J. Cima; MIT; Cambridge, MA; personal communication, 1989.


T.G. Fox and J.P. Flory, *J. Appl. Phys.*, 21, 581, 1950; as found in Macchi [1986].


R.E. Mistler; Keramos Industries; Yardley, PA; personal communication, 1987.


A. onions, "Films from Water-Based Colloidal Dispersions," Manufacturing Chemist, March 1986, p.55; article continued April 1986, p.66.


BIOGRAPHICAL NOTE

Paul Nahass was born in Paterson, NJ in 1961 and raised in the northern New Jersey area. He attended Passaic Valley Regional High School where he graduated 2nd in a class of 446. He went to college at M.I.T. and became a brother of Phi Gamma Delta. After completing his S.B. in Chemical Engineering and S.M. in Chemical Engineering Practice in 1984, Professor H. Kent Bowen offered him a position doing research in the Ceramics Processing Research Laboratory. Before beginning research in ceramics, however, he met his future wife, Jennifer Nahas (yes, that is spelled correctly!), as they were counselors at a summer camp in Pennsylvania. The bug to continue school bit and Paul entered the PhD program in Ceramics at M.I.T. in the Department Materials Science and Engineering. At this point his family began to wonder if he would ever enter the real world, or even leave Cambridge for that matter. Why should he: he had a steady girlfriend (who went on to support them both after graduating from college), a fireplace, a dog, and a lucrative little cottage business (tie-dying shirts and selling them at crafts fairs and Grateful Dead concerts from coast to coast). Paul and Jennifer were married in 1989 and it looked like it was time to graduate. As soon as the newlyweds got home from their honeymoon, the thesis went into full swing and a few months later, it was today. Ten years and five months after entering the Infinite Corridor, Paul Nahass decided it was time to go to work, for Hyperion Catalysis International, of Lexington, MA.