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Study on the dispersion of surface treated titanium dioxide in various media

Lee, Young-Jin, Ph.D.

Case Western Reserve University, 1993
STUDY ON THE DISPERSION OF SURFACE TREATED TITANIUM DIOXIDE IN VARIOUS MEDIA

BY

YOUNG-JIN LEE

Submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

Thesis Advisors: Ica Manas-Zloczower
Donald L. Feke

DEPARTMENT OF MACROMOLECULAR SCIENCE
CASE WESTERN RESERVE UNIVERSITY
May, 1993
We hereby approve the thesis of

Young-Jin Lee

candidate for the Ph. D.
degree.*

(signed) 

(chair)

Bruce R. Palmer

J. Calvin Manning

Alger C. Lane

Shih-Fu Chang

date __/__/19__

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Lee Young Jin
STUDY ON THE DISPERSION OF SURFACE TREATED TITANIUM DIOXIDE IN VARIOUS MEDIA

ABSTRACT

by

YOUNG JIN LEE

The purposes of this study were 1) to develop the tools to characterize surface treated titanium dioxide powders, 2) to elucidate the dispersion mechanism in low viscosity solvents and high viscosity polymeric melts, and 3) to investigate the dispersion-compound property relationships.

Characterization of various grades of surface treated titanium dioxide powders was performed using Inverse Gas Chromatography, electrophoretic mobility measurements, and cohesivity measurements. These measurements quantified various components of the overall interaction, namely dispersive interactions, acid/base interactions and electrostatic interactions. To quantify cohesivity, tensile strength and compression stress were measured using a split cell and a penetrating cone respectively.

Dispersibility in low viscosity solvents was studied using a sedimentation test. Here, dispersibility was interpreted in terms of the wetting properties (quantified in terms of heat of mixing) and by the colloidal stability as governed by van der Waals attractive and electrostatic repulsive forces. Maps of the dispersibility of titanium
dioxide powders in donor number and acceptor number coordinates were found to be useful.

In high viscosity media, the titanium dioxide agglomerates primarily dispersed by an erosion mechanism in which small fragments detached from the surface. The kinetics of the process was found to be dependent on agglomerate porosity, the cohesive strength of agglomerate, the magnitude of applied shear stress and agglomerate-medium interactions. In this work, dispersion was performed in a rotating cone-and-plate device equipped for in situ observation of the dispersion process in polydimethylsiloxane, a liquid polymer at room temperature. Also the device was set in a temperature controlled oven for dispersion studies into low density polyethylene melt. Studies of the medium penetration were performed in order to gauge the influence of the medium on the effective cohesivity of the agglomerates. A model linking together all of these results was proposed.

The degree of dispersion was found to affect the properties of resulting compounds. Optical properties (light transmittance and gloss) and mechanical properties (yield stress and elongation at break) were correlated with dispersion time, filler loading and interfacial interactions. Dynamic mechanical properties such as storage modulus and mechanical damping were also investigated and analyzed in terms of quality of dispersion and interfacial interactions.
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I thank God for keeping my family without any problems during my Ph.D. study and to make my lovely daughter, Ji-Won and bright son, Chul-Won be good children. I thank my wife, Myoung-Ock. Without her devoted support and encouragement this work could not be finished.

Finally, I dedicate this work to SKC Limited and its employees who permitted and supported my studies at CWRU in spite of the company's difficulties.
TABLE OF CONTENTS

ABSTRACT .......................................................................................................................... ii
ACKNOWLEDGMENTS ......................................................................................................... iv
TABLE OF CONTENTS .......................................................................................................... v
LIST OF TABLES .................................................................................................................. viii
LIST OF FIGURES ............................................................................................................... ix
1. INTRODUCTION ............................................................................................................. 1
2. CHARACTERIZATION OF TITANIUM DIOXIDE POWDER AND AGGLOMERATES ......................................................................................... 11
   2.1. SYNOPSIS ................................................................................................................. 11
   2.2. EXPERIMENTAL PROCEDURE .............................................................................. 12
       2.2.1. MATERIALS ...................................................................................................... 12
       2.2.2. INVERSE GAS CHROMATOGRAPHY .................................................................. 13
       2.2.3. ZETA POTENTIAL MEASUREMENTS .................................................................. 16
       2.2.4. TENSILE STRESS MEASUREMENTS ................................................................. 17
       2.2.5. COMPRESSION STRESS MEASUREMENTS ...................................................... 17
   2.3. RESULTS AND DISCUSSION .................................................................................. 20
       2.3.1. SURFACE PROPERTIES ................................................................................. 20
       2.3.2. COHESIVITY ................................................................................................... 31
   2.4. CONCLUSIONS ......................................................................................................... 38
3. DISPERSION OF TITANIUM DIOXIDE POWDERS IN SOLVENTS

3.1. SYNOPSIS

3.2. EXPERIMENTAL PROCEDURE

3.2.1. MATERIALS

3.2.2. SEDIMENTATION TESTS

3.3. RESULTS AND DISCUSSION

3.3.1. POWDER-SOLVENT INTERACTIONS

3.3.2. POWDER-POWDER INTERACTIONS

3.3.3. OVERALL DISPERSIBILITY

3.4. CONCLUSIONS

4. MECHANISM OF TITANIUM DIOXIDE AGGLOMERATE DISPERSION IN HIGH VISCOUS MEDIA

4.1. SYNOPSIS

4.2. EXPERIMENTAL PROCEDURE

4.2.1. AGGLOMERATE PREPARATION

4.2.2. MEASUREMENT OF MEDIUM INFILTRATION

4.2.3. SHEARING EXPERIMENTS

4.3. RESULTS AND DISCUSSION

4.3.1. MODE OF BREAK UP

4.3.2. PARAMETERS AFFECTING AGGLOMERATE BREAK UP

4.4. CONCLUSIONS
5. ANALYSIS OF TITANIUM DIOXIDE AGGLOMERATE DISPERSION IN LINEAR LOW DENSITY POLYETHYLENE MELT AND THE RESULTING COMPOUND PROPERTIES...80

5.1. SYNOPSIS.................................................................80

5.2. EXPERIMENTAL PROCEDURE.........................................81

5.2.1. SHEARING EXPERIMENTS IN LLDPE.........................81

5.2.2. SAMPLE PREPARATION FOR PROPERTY MEASUREMENT........83

5.2.3. SAMPLE TESTING..................................................84

5.3. RESULTS AND DISCUSSION...........................................85

5.3.1. AGGLOMERATE BREAK UP IN LLDPE..........................85

5.3.2 EFFECT ON COMPOUNDS PROPERTIES.........................89

5.4. CONCLUSIONS.......................................................107

6. SUMMARY AND FUTURE WORK..........................................110

6.1. OVERVIEW..............................................................110

6.2. SUGGESTIONS AND FUTURE WORK...............................112

7. REFERENCES............................................................114
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Properties of Titanium Dioxide Powders</td>
<td>12</td>
</tr>
<tr>
<td>2-2</td>
<td>Properties of Solvents</td>
<td>14</td>
</tr>
<tr>
<td>2-3</td>
<td>Dispersive Component of Surface Tension</td>
<td>20</td>
</tr>
<tr>
<td>2-4</td>
<td>Specific Free Energy of Powders, $\Delta H_p$ KJ/mole</td>
<td>22</td>
</tr>
<tr>
<td>2-5</td>
<td>Acceptor and Donor Numbers of Powders</td>
<td>25</td>
</tr>
<tr>
<td>2-6</td>
<td>Zeta Potential of Powders in Organic Solvents</td>
<td>27</td>
</tr>
<tr>
<td>2-7</td>
<td>Parameters for Zeta Potential Correlation</td>
<td>28</td>
</tr>
<tr>
<td>2-8</td>
<td>Cohesivity Characteristics of Powders</td>
<td>33</td>
</tr>
<tr>
<td>3-1</td>
<td>Properties of Titanium Dioxide Powders</td>
<td>41</td>
</tr>
<tr>
<td>3-2</td>
<td>Comparison of Acid/Base Parameters</td>
<td>54</td>
</tr>
<tr>
<td>4-1</td>
<td>Comparison of Effective Pore Size</td>
<td>70</td>
</tr>
<tr>
<td>5-1</td>
<td>Interaction Parameter and Work of Adhesion</td>
<td>106</td>
</tr>
<tr>
<td>5-2</td>
<td>Tan $\delta_c$ and Tensile Strength of Powder</td>
<td>108</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1-1  Electron micrographs of two (out of four) titanium dioxide powders used in this study. (top) Ti-A: non-treated grade, (bottom) Ti-D: highly silica treated grade. Illustrating particle size and morphology of powder surface.  

Figure 1-2  Photographs of naturally formed agglomerates of titanium dioxide, (top) Ti-A: non-treated grade, (bottom) Ti-D: highly silica treated grade.  

Figure 1-3  Photograph of well dispersed titanium dioxide agglomerates PDMS. Size of fragments are on the order of 1 μm.  

Figure 2-1  Schematic of the tensile strength measurement apparatus and split cell. (a) split cell; (b) separation plate; (c) powder; (d) connector; (e) epoxy impregnated string; (f) fixed roller; (g) moving plate; (h) force transducer; (i) inchworm transducer; (j) speed controller; (k) recorder.  

Figure 2-2  Schematic of the apparatus used to measure compression strength. (a) sample cell; (b) sample cylinder; (c) compression bar; (d) powder; (e) penetrating cone; (f) force transducer; (g) moving plate; (h) inchworm transducer; (i) recorder; (j) speed controller.  

Figure 2-3  Free Energy of adsorption versus $a(y_H)^{0.5}$ for Ti-D(a) and Ti-A(b).  

Figure 2-4  Specific free energy of adsorption versus temperature for Ti-A. Key: • tetrahydrofuran; ○ diethylether; ■ chloroform; □ benzene; + acetone.  

Figure 2-5  Determination of $D_{NP}$ and $A_{NP}$ according to equation 5. Key: • Ti-A; ○ Ti-B; ■ Ti-C; □ Ti-D.  

Figure 2-6  Zeta Potential as a function of pH for titanium dioxide powders. Key: • Ti-A; ○ Ti-B; ■ Ti-C; □ Ti-D.
Figure 2-7  Zeta potential, measured and correlated by equation 8.  
(a) Ti-A; (b) Ti-B; (c) Ti-C; (d) Ti-D.  29

Figure 2-8  Correlation of $K_o$ with the isoelectric point for the various 
titanium dioxide powders.  30

Figure 2-9  Tensile stress as a function of reduced compact density, 
$\phi/(1-\phi)$, for various titanium dioxide agglomerates. 
Key: (a) Ti-A; (b) Ti-B; (c) Ti-C; (d) Ti-D.  32

Figure 2-10  Normalized force, $F/(\gamma \phi)$ as a function of normalized interparticle distance, $t/d$, for Ti-A agglomerates. Key:  
●  less than 0.001 vol% moisture, ○ 0.0087 vol% moisture.  34

Figure 2-11  Uncorrected compression stress as a function of reduced compact density, $\phi/(1-\phi)$, for various titanium dioxide agglomerates. Key:  
● Ti-A; ○ Ti-B; ■ Ti-C; □ Ti-D.  35

Figure 2-12  Uncorrected compression stress as a function of reduced compact density $\phi/(1-\phi)$, for various titanium dioxide moisture contents. 
Key: ● 1.820 wt%; ○ 0.213 wt%; ■ less than 0.001 wt%.  37

Figure 2-13  Zeta-potential mapping on a qualitative plot of solvent and powder acid/base characteristics.  39

Figure 3-1  Classification of the various solvents used in this study in terms of their donor and acceptor numbers based on Jensen.  
Abbreviation for the solvents are listed in Table 2-2.  46

Figure 3-2  Dispersibility map based on the critical heat of mixing.  
(a) Ti-A; (b) Ti-B; (c) Ti-C; (d) Ti-D.  
Key: ● Stable, ○ moderately stable, × unstable.  48

Figure 3-3  Correlation between the dimensionless potential energy number and the quality of the dispersion.  
Key: ● Stable; ○ moderately stable; × unstable (due to poor energy of incorporation into the dispersion media);  
■ unstable (due to particle agglomeration).  52
Figure 3-4  Overall Dispersibility map. Key: (a) Ti-A, (b) Ti-B, (c) Ti-C, (d) Ti-D. Key: ● Stable; ○ moderately Stable; x unstable. 53

Figure 4-1  Schematic of the cone-and-plate device for the hydrodynamic shear experiments; (a) motor; (b) speed controller; (c) cone; (d) agglomerate; (f) transparent glass plate; (f) mirror. 59

Figure 4-2  Photographs of small particle erosion from agglomerate surface. Eroded particles follow the trajectory of flow. (top) porosity 0.696, (bottom) porosity 0.574. 61

Figure 4-3  Photographs of ruptured surface of agglomerate. Ruptured surface shows planar surface and sharp edges. (top) Ti-A. 5,000 cS, 37.5 sec⁻¹, 1.5 min. (bottom) Ti-A, 60,000 cS, 78 sec⁻¹, 3 min. 62

Figure 4-4  Agglomerate size reduction as a function of dimensionless shearing time for titanium dioxide agglomerates. Key: (●) 188 Pa; (○) 375 Pa; (■) 1,125 Pa; (□) 2,250 Pa. 63

Figure 4-5  Erosion rate as a function of reduced compact density, \(\Phi/(1-\Phi)\) for Titanium dioxide agglomerates. When \(\Phi/(1-\Phi)\) approaches 0.4 (dotted line), the erosion rate increases rapidly due to the weakened cohesivity of the agglomerates. 65

Figure 4-6  Agglomerate size reduction as a function of a dimensionless shearing time for Titanium dioxide agglomerates. Key: (●) Ti-A; (○) Ti-B; (■) Ti-C; (□) Ti-D. 66

Figure 4-7  Erosion rate constant as a function of work of adhesion for titanium dioxide agglomerates. 68

Figure 4-8  Agglomerate size reduction as a function of shearing time for various moisture contents. Key: (●) 1.820 wt%; (○) 0.213 wt%; (■) less than 0.001 wt%. 69

Figure 4-9  PDMS penetration depth as a function of time for titanium dioxide agglomerates. Key: (●) Ti-A; (○) Ti-B; (■) Ti-C; (□) Ti-D. 71
Figure 4-10 Comparison of the erosion rate and penetration rate for titanium dioxide agglomerates.

Figure 4-11 Photographs of eroded fragments from Ti-A at the initial stage of shearing as a function of agglomerate porosity. (a) 0.690; (b) 0.645; (c) 0.574; (d) 0.499.

Figure 4-12 Structural models for high and low porosity titanium dioxide agglomerates.

Figure 5-1 Schematic of the cone-and-plate device for the hydrodynamic shear experiments in high temperature: (a) insulated oven; (b) motor; (c) cone; (d) plate; (e) support; (f) guide ring; (g) positioning knob; (h) controller.

Figure 5-2 Photographs of erosion of titanium dioxide agglomerate in LLDPE melt. Observed after applying 19.5 sec\(^{-1}\) shear rate for 30 sec at 170 °C. (a) surface; (b) tail.

Figure 5-3 Agglomerate size reduction as a function of dimensionless shearing time for titanium dioxide agglomerates in LLDPE melt.

Figure 5-4 Work of adhesion corrected erosion rate constant as a function of shear stress for titanium dioxide agglomerates in PDMS (●) and LLDPE (■).

Figure 5-5 Photographs of dispersed small agglomerates from Ti-A as a function of shearing time. (a) t=0; (b) t=10 sec; (c) t=30 sec; (d) t=60 sec; (e) t=300 sec; (f) t=600 sec; (g) t=1200 sec.

Figure 5-6 Transmittance of titanium dioxide-LLDPE compound film as a function of dispersion. Key: (●) 19.5 sec\(^{-1}\); (■) 8.3 sec\(^{-1}\).

Figure 5-7 Specula gloss of titanium dioxide-LLDPE compound coated glass as a function of dispersion time. Key: (●) 19.5 sec\(^{-1}\); (■) 8.3 sec\(^{-1}\).

Figure 5-8 Tensile stress - strain curve of titanium dioxide-LLDPE compound film for different dispersion time. Key: (●) 0 sec; (○) 10 sec; (■) 30 sec; (□) 60 sec; (×) 300 sec.
Figure 5-9  Yield stress (a) and elongation at break (b) of titanium dioxide-LLDPE compound sheet as a function of dispersion time.  
Key: (●) 19.5 sec⁻¹; (■) 8.3 sec⁻¹.  
98

Figure 5-10  Tensile stress - strain curve of titanium dioxide-LLDPE compound sheet for different filler loading.  
Key: (●) 0 wt%; (○) 5 wt%; (■) 10 wt%; (□) 20 wt%.  
99

Figure 5-11  Yield stress (a) and elongation at break(b) of titanium dioxide-LLDPE compound sheet as a function of dispersion time.  
Key: (●) 5 wt%; (■) 10 wt%.  
100

Figure 5-12  Yield stress (a) and elongation at break(b) of titanium dioxide-LLDPE compound film as a function of filler loading for different grade of titanium dioxide used.  
(- - -) refers value of pure LLDPE sheet.  
102

Figure 5-13  $E'$ (a) and tan $\delta$ (b) of titanium dioxide-LLDPE compound sheet as a function of dispersion time.  
Key: (●) 5 wt%; (■) 10 wt%.  
104

Figure 5-14  $E'/\varepsilon$ as a function of titanium dioxide vol %.  
Key: (●) Ti-A; (○) Ti-B; (■) Ti-C; (□) Ti-D.  
106

Figure 5-15  Tan $\delta$/tan $\delta$ as a function of titanium dioxide vol %.  
Key: (●) Ti-A; (○) Ti-B; (■) Ti-C; (□) Ti-D.  
107
CHAPTER 1

INTRODUCTION

The term dispersion refers to the process of incorporating a powder into a medium and controlling the particle size and distribution throughout the medium\(^1\). The properties and quality of materials that incorporate fillers in their manufacture are affected by the degree of dispersion of agglomerates into the background. Understanding the mechanism of agglomerates dispersion into a medium is of fundamental concern and it has also practical and technological significance.

Titanium dioxide is one of the important fillers used in many industrial applications such as coating, painting, rubber and thermoplastic industries. Two of the commercial titanium dioxide powders used in this study are shown in figure 1-1. The electron micrographs show that the primary particles are spherical, and the morphology of the surface is affected by the type of titanium dioxide. The primary particle size is on the order of 1 \(\mu\)m. The primary particles are packed either dense or loosely and make agglomerates shown in figure 1-2. The size of the agglomerates found in commercial powders can range from 1 to 10 mm depending on the powder grade. Figure 1-3 shows the final state of subdivision into which titanium dioxide agglomerates can be dispersed in polydimethylsiloxane (PDMS). The fragments obtained are of the order of 1 \(\mu\)m.

The dispersion process consists of three steps\(^1\).

1. Wetting of the solid by the fluid
2. Disruption of agglomerates and distribution of separated
Figure 1-1  Electron micrographs of two (out of four) titanium dioxide powders used in this study. (top) Ti-A: non-treated grade, (bottom) Ti-D: highly silica treated grade. Illustrating particle size and morphology of powder surface.
Figure 1-2 Photographs of naturally formed agglomerates of titanium dioxide, (top) Ti-A: non-treated grade, (bottom) Ti-D: highly silica treated grade.
Figure 1-3  Photograph of well dispersed titanium dioxide aggregates in PDMS. Size of fragments are on the order of 1 μm.
aggregates (or particles)

(3) Stabilization of aggregates (or particles) against (re)agglomeration

These three steps are quite different in nature but occur simultaneously and are not easy to separate.

Depending on the medium in which titanium dioxide is dispersed, the processing conditions will vary. For instance in the case of paint vehicles of viscosity 1-100 Pa.s the shear rate used in the dispersion process is of the order of 100-1000 sec\(^{-1}\), whereas in the case of the thermoplastic materials\(^2\) (of viscosity 10\(^2\)-10\(^5\) Pa.s) the shear rate used vary between 100 and 5000 sec\(^{-1}\).

The dispersion of agglomerates in low molecular weight solvents is mainly affected by the stabilization step rather than the wetting or the disruption steps. Titanium dioxide agglomerates are easily dispersed into small agglomerates (or primary particles) under weak external agitation in most solvents. The stability of the dispersion is governed by the balance of attractive forces and repulsive forces between the powder and the medium. Attractive forces can be defined in terms of different types of interactions. The first is a dispersive interaction which can be quantified in terms of a Hamaker constant\(^3\) or the dispersive component of the surface tension\(^4\). The second is an acid/base specific interaction which affects the energetics of the dispersion process. Repulsive forces usually come from the electrostatic repulsion resulting from the formation of a double layer\(^5\,^6\). Derjaguin-Landau-Verwey-Overbeek (DLVO) theory is used to quantify these forces. In aqueous media, the charge of solid particle-liquid interface can be attributed to adsorption or desorption of ions and/or to dissociation of surface groups\(^5\). For non-
aqueous media, the charging mechanism includes preferential adsorption of cation or anion and dissociation of surface groups 7-8. Verwey9 attributed the charging of solids in organic media to acid/base chemistry at the interface. Fowkes, et al. 10 used the acid/base concept to explain the surface processes including adsorption and adhesion phenomena. Recently Williams, et al. 11-12 showed the charging of solids can be related to the Lewis acid/base chemistry. Adduct complexes formed between a solid interface and an organic medium can lead to interface charging. The sign and magnitude of the charge indicate the direction of electron transfer and magnitude of transfer between solid and organic molecules. Good correlation was found between the isoelectric point of the powder and a donicity scale which is based on the Gutmann's donor number (DN)13. Dispersion behavior of powders in solvents can be characterized by a combination of an effective Hamaker constant for the system which represents attractive interactions and the electrostatic repulsive interactions resulting from the formation of a double layer.

Dispersion of agglomerates in high viscosity media such as polymer melts is governed by the wetting and disruption processes. Particles once separated are unlikely to coalesce due to the high viscosity of the medium. Research related to the dispersion of agglomerates in high viscosity media is more oriented towards the disruption process. Parker, et al.14 proposed the occurrence of two distinct breakage mechanisms which can generally be applied to a variety of agglomerate dispersion processes; large scale splitting and fine particle erosion. Mason, et al.15-16 studied the erosion of cohesionless clusters of spherical particles and found that the agglomerate radius follows a zeroth-order rate law with a rate constant that is independent of the shear stress applied to the cluster. Spielman, et al.17 found cohesive agglomerates to
split into a few fragments whose size and origins were thought to be affected by the shape and internal structure of the parent agglomerate. Rwei, et al.\textsuperscript{18-19} observed both mechanisms occurring in the dispersion of carbon black in polydimethylsiloxane (PDMS). In that work, the ratio of applied stress to agglomerate cohesivity was found to be an important parameter in modeling the dispersion process. Shiga and Furuta\textsuperscript{20} proposed a so-called "onion peeling" mechanism of carbon black dispersion in elastomers in which the dominant mechanism of dispersion is the scraping of the individual constituent particles off the surface of agglomerates. There are several other models\textsuperscript{21-24}. Most of these models are mainly concerned with the structure of the agglomerates and the external flow field but they did not emphasize the importance of the interfacial interactions between the agglomerates and the medium. Also medium infiltration into the agglomerates was seldom considered.

It is well known that the degree of dispersion and the interactions between the powder and the medium alter the performance and properties of the compounds. Agglomerates increase the viscosity and yield stress of polymeric melts\textsuperscript{25}. These tendency is more pronounced as the particle size is getting smaller. Agglomerate size and size distribution affect the packing characteristics of pigments in paint vehicles and change the critical pigment volume concentration (CPVC) which represents the discontinuity in paint properties (e.g. density, transport, mechanical and optical properties)\textsuperscript{26}. Improvement in dispersion increases the CPVC in general\textsuperscript{27}. Color, opacity and gloss can be correlated with the degree of dispersion of titanium dioxide in a paint film\textsuperscript{28}. Opacity and gloss decrease with pigment flocculation and color shifts to reddish. Enhanced interfacial interactions improve the effectiveness of applied energy in the dispersion process\textsuperscript{29}. This effect is more illustrated in highly
acidic polymers than in neutral polymers. Mechanical properties of the compound such as tensile strength, Young's modulus and elongation at break increase with the dispersion time, therefore, with the decreasing agglomerate size\textsuperscript{30-32}. The conductivity of carbon black filled PVC composites increases with increasing the milling time up to a certain optimum milling time\textsuperscript{33}. Many of the previous studies dealt with the effect of interfacial interactions between powder and medium on processability\textsuperscript{34}, mechanical and rheological properties of polymeric melts\textsuperscript{35-36} and mechanical and dynamic mechanical properties of polymeric solids\textsuperscript{37-42}. Schreiber, et al. studied the role of acid/base interactions at the interface on mechanical and dynamic mechanical properties of polymers. They found that acid/base interactions immobilize the polymer in the vicinity of solid particles and increase the effective particle dimensions improving mechanical properties\textsuperscript{43-46}. Some studies were conducted to determine the effect of acid/base interactions on the dispersibility and properties of coatings such as gloss and hiding power\textsuperscript{47}. In order to improve the properties of filled polymers, a decrease in the agglomerate size and in the void concentration \textsuperscript{48}, as well as an enhanced adhesion between the filler and the matrix are needed. Two methods are used to get these goals; (1) increase the local shear stress to break down the agglomerates, and (2) optimize the adhesion characteristics to improve the degree of dispersion and interactions.

Through \textit{in situ} observation of the dispersion process of titanium dioxide agglomerates, we found that titanium dioxide agglomerates from different grades behave differently. The interactions of titanium dioxide powder with itself and with the fluid medium govern the state of dispersion and ultimately the quality and performance of materials into which the titanium dioxide is incorporated. In general,
titanium dioxide is modified through the use of organic or inorganic surface coatings in order to reduce the photocatalytic effect in paint and to enhance the dispersibility into binders. The resulting surface composition, morphology and its interfacial characteristics in a medium depend on the nature and composition of the treatment applied and the method of treatments. Commercial titanium dioxide powders are commonly treated with silica and/or alumina.

The surface characterization of powder plays an important role in studies which aim to explain the behavior of titanium dioxide in different applications. In the chapter 2 of this thesis, characteristics of differently treated titanium dioxides, which could affect the interfacial interactions with the medium, were investigated. The dispersive component (\(\gamma^d\) or \(\Delta G^d\)) and a non-dispersive or specific component (\(\gamma^s\) or \(\Delta G^s\)) were investigated to evaluate the interfacial interactions. To avoid the complexity of contact angle measurement analysis due to the presence of irregularities and pores, Inverse Gas Chromatography (IGC) was used in the characterization. Using Gutmann's approach, we quantified the specific surface properties of the powder in terms of the donor number (DN) and acceptor number (AN). Additional information about acid/base interactions were obtained from the zeta potential measurement of the powder dispersed in various media owing to the differences in the isoelectric point of coating materials. The surface charge of powder in different media was explained based on acid/base interactions. The cohesivity of powders also affects the dispersion of agglomerates. The cohesivity was evaluated from tensile strength and shear strength measurements using a tensile strength apparatus with a modified cylinder cell and a penetrating cone test, respectively.
Chapter 3 presents the experimental results of titanium dioxide dispersion in various solvents. Due to the relatively easy disruption process, much attention was focused on the stability of the resulting suspensions. The stability of the suspensions for various grades titanium dioxide was explained by using a dispersibility map plotted in terms of the acceptor and donor numbers of the solvents.

In chapter 4 the dispersion mechanisms for titanium dioxide agglomerates in viscous media were discussed based on the observation of break-up in a controlled flow field (simple shear flow). Several factors affecting dispersion, such as the cohesivity of the agglomerates, the applied shear stress, and interfacial interactions between the agglomerates and the medium were examined. A model for dispersion was proposed in terms of the various physical and interfacial characteristics that determine the overall dispersion behavior.

In chapter 5, the analysis was extended to the dispersion of titanium dioxide agglomerates in polymeric melts under controlled flow conditions. Correlations between the degree of dispersion and properties of the compound such as optical properties (transparency and gloss), mechanical properties (yield stress, elongation at break) and dynamic mechanical properties (\(E', E''\) and \(\tan \delta\)) were established.

Chapter 6 contains a summary of the work and recommendations for future work.
CHAPTER 2

CHARACTERIZATION OF TREATED TITANIUM DIOXIDE POWDERS: COHESIVITY AND SURFACE PROPERTIES

2.1. SYNOPSIS

Characterization of surface properties and cohesivity of the powders is important for understanding their dispersion behavior. Four grades of titanium dioxide powders which were surface treated differently were selected. The dispersive component of surface tension, \( \gamma_d \), and acid/base parameters, DN and AN were determined by using an inverse gas chromatography technique. Specific acid/base interactions between powder and solvent were found to be very sensitive to powder surface composition. For particles with rough or irregular surfaces, the non-specific, dispersive interaction is also very much dependent on surface composition. Specific interactions were also determined using zeta potential measurements of the powder in aqueous media. The isoelectric point (i.e.p.) was found to vary with surface treatment. Good correlations were obtained between the acid/base characteristics of the powders as measured with IGC and microelectrophoresis. A qualitative diagram for the possible acid/base interactions between the powder and the medium was proposed.

The cohesiveness of powder was quantified using both a tensile and a compression test method. In general, the surface treated powders showed weak tensile strength. The compression strength was found to be higher than the tensile strength. The compression strength is significantly dependent on powder
morphology.

2.2. EXPERIMENTAL PROCEDURE

2.2.1. MATERIALS

The powders used in this study were four types of pigment grade rutile titanium dioxide supplied by the Kerr-McGee Corporation. For convenience, the powders will be denoted Ti-A through Ti-D. Average particle size was measured using scanning electron microscopy with image analysis. Ti-A is essentially a pure rutile which includes only a small amount of SiO₂ and other metal oxides as impurities. As noted in table 2-1, the other powders contained higher levels of secondary surface species. Figure 2-1 shows scanning electron micrographs of Ti-A

<table>
<thead>
<tr>
<th>Table 2-1</th>
<th>Properties of Titanium Dioxide Powders</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powders</td>
<td>Ti-A</td>
</tr>
<tr>
<td>Particle Size, μm*</td>
<td>0.167</td>
</tr>
<tr>
<td>Aspect Ratio*</td>
<td>1.127</td>
</tr>
<tr>
<td>BET Surface Area, m²/g **</td>
<td>9.4</td>
</tr>
<tr>
<td>Absolute Density, g/cm³ **</td>
<td>4.1</td>
</tr>
<tr>
<td>Surface Treatment **</td>
<td>None</td>
</tr>
<tr>
<td>Si/Al **</td>
<td>-</td>
</tr>
<tr>
<td>Moisture Content ***</td>
<td>0.213</td>
</tr>
</tbody>
</table>

* Measured by SEM and Image Analyzer, ** Measured by Manufacturer, *** Weight loss after 48 hr drying at 200 °C under vacuum.
and Ti-D. Note the differences in powder morphology, with Ti-A showing a smooth surface and Ti-D a much rougher morphology. Surface treatment on titanium dioxide increases the specific surface area as measured by the BET method. The water content was measured by determining the weight loss of powders at 200 °C and vacuum conditions.

To minimize the effect of adsorbed water, powders were dried under vacuum at 200 °C for at least two days. Dried solids were subsequently stored in a desiccator prior to use. The various organic solvents used in this study were spectroscopic or analytical grades. Their properties are summarized in table 2-2. Distilled and deionized water (16 MΩ-cm) was also used.

2.2.2. Inverse Gas Chromatography

IGC measurements were carried out using a Hewlett Packard model 5880 gas chromatography equipped with a flame ionization detector. The dried titanium dioxide was packed into a stainless steel column of 0.4 m length and 4.4 mm inner diameter. The total weight of the solid was in the range of 3.9-5.9 g. The helium carrier gas was adjusted to 20±1 cm³/min. The injector temperature was set at 200 °C while the detector was at 250 °C. All columns were conditioned for 24 hr at 300 °C prior to the first use. Between runs, the column was purged for 10 min to 2 hr at 300 °C.

To make a run, 5-10 µl of the vapor of a specific probe was injected into the column and retention times were measured. The net retention volume, \( V_N \) is given by

\[
V_N = jD(t_r - t_o)
\]

where \( t_r \) is the retention time of the probe, \( t_o \) the retention time of marker (in this
### Table 2-2 Properties of Solvents

<table>
<thead>
<tr>
<th>Solvent (symbol)</th>
<th>Viscosity $25 \degree C$ a</th>
<th>Dielectric constant b</th>
<th>Surface area c</th>
<th>Surface tension d</th>
<th>Donor number e</th>
<th>Acceptor number f</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane (C6)</td>
<td>0.3 eP</td>
<td>1.89</td>
<td>51.5</td>
<td>18.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Heptane (C7)</td>
<td>0.39 eP</td>
<td>1.92*</td>
<td>57.0</td>
<td>20.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Octane (C8)</td>
<td>0.51 eP</td>
<td>1.95*</td>
<td>62.8</td>
<td>21.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Nonane (C9)</td>
<td>0.68 eP</td>
<td>1.97*</td>
<td>68.9</td>
<td>22.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone (AC)</td>
<td>0.32 eP</td>
<td>20.7</td>
<td>42.5</td>
<td>20.8*</td>
<td>17.0</td>
<td>12.5</td>
</tr>
<tr>
<td>Benzene (Bz)</td>
<td>0.61 eP</td>
<td>2.3</td>
<td>46</td>
<td>26.7</td>
<td>0.1</td>
<td>8.2</td>
</tr>
<tr>
<td>Diethylether (DEE)</td>
<td>0.22 eP</td>
<td>4.3</td>
<td>47</td>
<td>15.0</td>
<td>19.2</td>
<td>3.9</td>
</tr>
<tr>
<td>Tetrahydrofurane (THF)</td>
<td>0.76 eP</td>
<td>7.6*</td>
<td>45</td>
<td>22.5</td>
<td>20.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Chloroform (Ch)</td>
<td>0.54 eP</td>
<td>4.8</td>
<td>44</td>
<td>25.0</td>
<td>0.0*</td>
<td>23.1</td>
</tr>
<tr>
<td>i-Propanol (i-PrOH)</td>
<td>2.08 eP</td>
<td>18.3</td>
<td></td>
<td></td>
<td>36.0</td>
<td>33.5</td>
</tr>
<tr>
<td>Ethanol (EtOH)</td>
<td>1.10 eP</td>
<td>24.3</td>
<td></td>
<td></td>
<td>32.0*</td>
<td>37.1</td>
</tr>
<tr>
<td>Methanol (MeOH)</td>
<td>0.55 eP</td>
<td>32.6</td>
<td></td>
<td></td>
<td>19.0*</td>
<td>41.3</td>
</tr>
<tr>
<td>Water (W)</td>
<td>0.89 eP</td>
<td>80.4</td>
<td></td>
<td></td>
<td>18.0</td>
<td>54.8</td>
</tr>
<tr>
<td>Acetic acid (AcOH)</td>
<td>1.15 eP</td>
<td>6.2</td>
<td></td>
<td></td>
<td>10.5**</td>
<td>52.9</td>
</tr>
<tr>
<td>Dimethylsulfoxide (DMSO)</td>
<td>1.96 eP</td>
<td>46.6</td>
<td></td>
<td></td>
<td>29.8</td>
<td>19.3</td>
</tr>
<tr>
<td>Dimethylformamide (DMF)</td>
<td>0.80 eP</td>
<td>36.7*</td>
<td></td>
<td></td>
<td>26.6</td>
<td>16.0</td>
</tr>
<tr>
<td>Benzylaldehyde (BA)</td>
<td>1.23 eP</td>
<td>17.8*</td>
<td></td>
<td></td>
<td>16.0*</td>
<td>12.8*</td>
</tr>
<tr>
<td>Nitrobenzene (NB)</td>
<td>1.98 eP</td>
<td>34.8</td>
<td></td>
<td></td>
<td>11.0*</td>
<td>14.8</td>
</tr>
<tr>
<td>Nitromethane (NM)</td>
<td>0.62 eP</td>
<td>35.9*</td>
<td></td>
<td></td>
<td>2.7</td>
<td>20.5</td>
</tr>
</tbody>
</table>

---

* Measured by Ostwald Viscometer, b From ref. 55, except * from ref. 56, c From ref. 54, d From ref. 54, except * from averaging values in ref. 57 and ref. 58, e From ref. 13, except * from ref. 59 and ** from ref. 60, f From ref 13, except * from ref. 60.
case, air, which is essentially non-interacting with the powder). D is the temperature corrected flow rate, and j is the correction factor for gas compressibility.

The volatiles used in the IGC experiments were the non-specific interacting n-alkanes (hexane through nonane), CHCl₃ and benzene as acidic probes, ether and tetrahydrofurane (THF) as basic probes, and acetone as an amphoteric probe. The experiments involving each combination of powder and probe were usually repeated three times; variation in the measured retention time was at ±9% about the mean.

The dispersive component of the surface energy for each powder, γₚᵈ, can be obtained from a plot of the results of experiments with the n-alkanes. Retention volumes calculated from equation 1 are plotted against the product of the specific area, a, and the square root of the surface energy, γₕ of the probe molecule, according to

\[ RT \ln V_N = 2N(\gamma_p^d)^{0.5}a(\gamma_H)^{0.5} + K \]  

[2]

Here, N is Avogadro's number, R is the gas constant, T is the temperature and K is a constant for a given chromatographic column. If the results fall on a straight line, the n-alkanes are confirmed to be non-interacting.

The free energy of the specific interaction, ΔGₛ, can be calculated for the other probe molecules relative to the line given by equation 2. In this case,

\[ \Delta G_s = RT \ln \frac{V_N}{V_N^{ref}} \]  

[3]

where \( V_N \) is the actual retention time for the probe as calculated by equation 1, and \( V_N^{ref} \) is calculated from equation 2 using the values of a and γₕ for the probe molecule and the value of K fit to the results for the n-alkanes.

The enthalpy of the specific interaction was determined by studying the variation of ΔGₛ with temperature using...
\[ \Delta G_{sp} = \Delta H_{sp} - T \Delta S_{sp} \]  

[4]

Following Papirer's approach\textsuperscript{61}, the enthalpy of the specific interactions was correlated with the acid/base characteristics of the powder using Gutmann's acceptor number and donor number:

\[ \frac{\Delta H_{sp}}{AN_s} = AN_p \frac{DN_s}{AN_s} + DN_p \]  

[5]

where the subscript s and p refer the solvent (probe) and powder respectively.

2.2.3. Zeta-Potential Measurements

Measurements of electrophoretic mobility were carried out in a Rank Brothers microelectrophoresis apparatus. Dilute suspensions of the powders were made by ultrasonically dispersing 10 ppm solids in aqueous (0.001 M KCl) or organic media. These suspensions were prepared immediately before measurements using dry glassware to avoid moisture contamination. Measurements of the migration velocity at the stationary level were carried out within 2 min of applying the driving voltage to avoid cell polarization. Henry's equation\textsuperscript{62}

\[ U^E = \frac{2 \varepsilon \varepsilon_0 \zeta}{3 \eta} F(\kappa \alpha, K') \]  

[6]

was used to compute the zeta-potential, \( \zeta \), from the observed mobility, \( U^E \). In equation 6, \( \varepsilon \) and \( \eta \) are the dielectric constant and viscosity of the fluid medium, \( \varepsilon_0 \) is the permittivity of free space, and \( F(\kappa \alpha, K') \) is a correction factor for ionic strength of the fluid medium and the conductivity of the solids. In the present case, the powders are non-conductive so \( K'=0 \). Assuming \( \kappa \alpha=1 \) in organic media\textsuperscript{10,63-64} the correction factor is 1.03, while for the aqueous media used, the correction factor is 1.28.
2.2.4. TENSILE STRESS MEASUREMENTS

A split cell tensile stress apparatus\textsuperscript{65} was used to measure the cohesivity of powder compacts. A modified split cell was designed and built for these experiments (figure 2-1). The powder compacts were prepared by compressing 20 g of powder in the split cell for 5 minutes using a press. The compact density was controlled by changing the volume of the compact. To avoid moisture adsorption, experiments were done within 10 min. A constant speed of 3.75 mm/min was used in all experiments. Aging of the compact up to 1 day and variation of the compression speed up to 10 mm/min were not found to affect significantly the results.

2.2.5. COMPRESSION STRESS MEASUREMENTS

A schematic of the apparatus used in compression test is shown in figure 2-2. Powders compacts were formed within a 50 mm diameter and 20 mm depth compaction cell under unidirectional compression for 5 minutes. The compact density was controlled by varying the weight of powder charged to the cell. The penetrating cone was constructed of nickel-plated iron, had an angle of 5°, and 45 mm long. A constant insertion rate of 3.75 mm/min was used in all experiments. (Insertion speed up to 10 mm/min did not affect the results.) Since the size of the failure produced by the cone (about 10 mm) was far smaller than the diameter, the assumption of an unconfined sample is valid. The force F necessary to advance a penetration depth, d, was measured by a load cell. The experiments were terminated when the cone reached an insertion depth of approximately 10 mm.

The uncorrected unconfined compression stress, \( f_c \), is obtained from\textsuperscript{66}

\[
f_c = a f_c \frac{F}{d^2}
\]  

[7]
Figure 2-1  Schematic of the tensile strength measurement apparatus and split cell. (a) split cell; (b) separation plate; (c) powder; (d) connector; (e) epoxy impregnated string; (f) fixed roller; (g) moving plate; (h) force transducer; (i) inchworm transducer; (j) speed controller; (k) recorder.
Figure 2-2  Schematic of the apparatus used to measure compression strength
(a) sample cell; (b) sample cylinder; (c) compression bar; (d) powder;
(e) penetrating cone; (f) force transducer; (g) moving plate; (h)
inchworm transducer; (i) recorder; (j) speed controller
where $a_\phi$ is a proportionality coefficient which depends on both the internal friction coefficient and the internal friction angle of the powder. Since these parameters are not strongly sensitive to characteristics such as particle size and cohesivity\textsuperscript{66}, $a_\phi$ was assumed constant. It has been shown that using $a_\phi=1.4$ results in a good correlation between unconfined compression stress and shear stress\textsuperscript{66}.

2.3. RESULTS AND DISCUSSION

2.3.1. SURFACE PROPERTIES

Plots of $RT \ln V_N$ versus $a (\gamma_H)^{0.5}$ for two of the powders are shown in figure 2-3. The dispersive component of the surface energy obtained from these plots is reported in table 2-3, for all four of the powders studied. Also in table 2-3 are the values of $\gamma_p^d$ for pure rutile and silica as determined from adsorption studies\textsuperscript{4}. The value of $\gamma_p^d$ for alumina was calculated from the reported value of Hamaker constant\textsuperscript{67} (1.45\times10^{-12} \text{ erg}) assuming an interparticle distance of 2.2 Å. The results in table 2-3 indicate that the various surface treatments alter $\gamma_p^d$ for the powders.

However none of the $\gamma_p^d$ measured for titanium dioxide powders exactly matches

<table>
<thead>
<tr>
<th>Powder</th>
<th>Ti-A</th>
<th>Ti-B</th>
<th>Ti-C</th>
<th>Ti-D</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Tension</td>
<td>111.8</td>
<td>149.6</td>
<td>77.5</td>
<td>69.7</td>
<td>140</td>
<td>286</td>
<td>67</td>
</tr>
<tr>
<td>$\gamma_p^d$, mJ/m$^2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 2-3  Free Energy of adsorption versus $a(\gamma_h)^{0.5}$ for Ti-D(a) and Ti-A(b).
that of the pure rutile, silica or alumina. This is evidence of the heterogeneous nature of the treated titanium dioxide powders. The trends exhibited qualitatively correlate with the nature of the surface treatment. Also note that the measured $\gamma^d$ for the heavily silica treated powder, Ti-D, nearly matches that of pure silica. The high degree of roughness of this powder contributes toward $\gamma^d$ being strongly influenced by the surface character. Also presented in figure 2-3 are the results of the IGC experiments with the specifically interacting probes. The variations in $\Delta G_{wp}$ with temperature are shown for Ti-A in figure 2-4. From these data, the enthalpy of the specific interaction can be calculated according to equation 4. These results are shown in table 2-4. The powder with the highest level of silica (Ti-D) shows strong interactions with the basic solvents (ether, THF). The more basic powder (Ti-B) shows stronger interactions with the acidic solvents (CHCl$_3$, CsH$_6$).

The results of fitting these data to equation 5 are shown in figure 2-5. These results are summarized in table 2-5. The powder with little surface treatment (Ti-A) shows relatively high values of both $\Delta N_p$ and $\Delta N_p$ indicative of its amphoteric.

<table>
<thead>
<tr>
<th>Solvent/Powder</th>
<th>Ti-A</th>
<th>Ti-B</th>
<th>Ti-C</th>
<th>Ti-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>17.9</td>
<td>17.8</td>
<td>17.14</td>
<td>12.8</td>
</tr>
<tr>
<td>Benzene</td>
<td>8.7</td>
<td>9.2</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Acetone</td>
<td>42.2</td>
<td>26.1</td>
<td>29.9</td>
<td>55.7</td>
</tr>
<tr>
<td>Tetrahydrofurane</td>
<td>35.0</td>
<td>26.2</td>
<td>39.5</td>
<td>63.5</td>
</tr>
<tr>
<td>Diethylether</td>
<td>31.5</td>
<td>23.1</td>
<td>29.4</td>
<td>54.8</td>
</tr>
</tbody>
</table>
Figure 2-4  Specific free energy of adsorption versus temperature for Ti-A.
Key:  ● tetrahydrofurane;  ○ diethylether;  ■ chloroform;  □ benzene;  + acetone
Figure 2-5  Determination of $D_N_p$ and $A_N_p$ according to equation 5.
Key: • Ti-A; ○ Ti-B; ■ Ti-C; □ Ti-D.
Table 2-5  Acceptor and Donor Numbers of Powders

<table>
<thead>
<tr>
<th>Solvent\Powder</th>
<th>Ti-A</th>
<th>Ti-B</th>
<th>Ti-C</th>
<th>Ti-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acceptor Number, $AN_p$</td>
<td>34.3</td>
<td>24.1</td>
<td>34.0</td>
<td>65.8</td>
</tr>
<tr>
<td>Donor Number, $DN_p$</td>
<td>24.1</td>
<td>20.6</td>
<td>18.1</td>
<td>16.8</td>
</tr>
<tr>
<td>kcal/mole</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

character. The alumina treated powder (Ti-B) has a considerably small acceptor number, and a slightly lower donor number. The more pronounced shift in the acceptor number resulting from the surface treatment indicates the basic nature of the powder. The two silica treated powders (Ti-C and Ti-D) show a more acidic character than Ti-A, with Ti-D showing much more acidity than Ti-C due to the higher silica content.

In general, the dispersive component of the surface energy is a longer range interaction than the specific acid/base interaction. Thus, $\gamma^d$ should be sensitive to the composition of the particle core as well as its surface regions. However, in the case of very rough or irregular particle morphology, both the dispersive and specific interactions may be primarily determined by the composition of the interface.

Specific interactions can also be examined through zeta-potential measurements. Figure 2-6 shows the variation in the zeta potential with pH in aqueous media. The variation in the observed isoelectric point (i.e.p.) reflects the nature of the surface treatment. Note that silica treatment results in a more acidic nature (low i.e.p.) while alumina treatment results in a more basic powder (high i.e.p.)

$^{68}$
Figure 2-6  Zeta Potential as a function of pH for titanium dioxide powders.
Key: ● Ti-A; ○ Ti-B; ■ Ti-C; □ Ti-D.
## Table 2-6  Zeta Potential of Powders in Organic Solvents

<table>
<thead>
<tr>
<th>Solvent\Powder</th>
<th>Ti-A</th>
<th>Ti-B</th>
<th>Ti-C</th>
<th>Ti-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso-propylalcohol</td>
<td>-81.7</td>
<td>-70.8</td>
<td>-81.2</td>
<td>-71.2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>-48.7</td>
<td>-76.4</td>
<td>-42.4</td>
<td>-79.2</td>
</tr>
<tr>
<td>Methanol</td>
<td>-43.6</td>
<td>-14.0</td>
<td>-43.9</td>
<td>-100.3</td>
</tr>
<tr>
<td>Water (pH=7)</td>
<td>-57.0</td>
<td>8.0</td>
<td>-50.0</td>
<td>-90.0</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>18.7</td>
<td>101.2</td>
<td>22.2</td>
<td>-10.6</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>-88.3</td>
<td>-75.9</td>
<td>-67.3</td>
<td>-91.0</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>-45.7</td>
<td>-61.8</td>
<td>-77.7</td>
<td>-75.0</td>
</tr>
<tr>
<td>Acetone</td>
<td>-37.5</td>
<td>-47.8</td>
<td>-64.0</td>
<td>-101.3</td>
</tr>
<tr>
<td>Benzylaldehyde</td>
<td>-50.1</td>
<td>-28.5</td>
<td>-54.4</td>
<td>-78.3</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>-43.2</td>
<td>-43.6</td>
<td>-25.4</td>
<td>-22.6</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>31.6</td>
<td>35.5</td>
<td>11.1</td>
<td>-9.7</td>
</tr>
</tbody>
</table>

In order to analyze the dependence of various physico-chemical properties of suspension on the solvent, Koppel and Palm\(^69\) proposed an empirical correlation in the form:

\[
P = P_0 + \alpha D N_s + \beta A N_s + \gamma \delta_s^4
\]  \[7\]

where \(P\) is the property of interest, \(P_0\) is the value of the property in some reference state, and \(\alpha, \beta, \text{ and } \gamma\) give the relative sensitivity of the property to solvent acidity, basicity, and dispersive forces, respectively. Generally, if acid/base interactions dominate, the last term in equation 7 can be ignored. Thus we write

\[
\zeta = \zeta_0 + \alpha D N_s + \beta A N_s
\]  \[8\]
Table 2-7 Parameters for Zeta Potential Correlation

<table>
<thead>
<tr>
<th>Solvent\Powder</th>
<th>Ti-A</th>
<th>Ti-B</th>
<th>Ti-C</th>
<th>Ti-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Sensitivity, $\alpha$ mV.mol/kcal</td>
<td>-2.89</td>
<td>-4.16</td>
<td>-2.61</td>
<td>-2.12</td>
</tr>
<tr>
<td>Acid Sensitivity, $\beta$, mV</td>
<td>0.40</td>
<td>1.92</td>
<td>0.76</td>
<td>0.15</td>
</tr>
<tr>
<td>Reference, $\zeta_0$, mV</td>
<td>5.71</td>
<td>2.66</td>
<td>-12.73</td>
<td>-28.36</td>
</tr>
<tr>
<td>Correlation Coefficient</td>
<td>0.679</td>
<td>0.858</td>
<td>0.728</td>
<td>0.386</td>
</tr>
</tbody>
</table>

Table 2-6 shows the measured zeta potential for powders in various organic solvents. A least squares linear regression was used to fit these data to equation 8; the fit parameters are listed in table 2-7 while the linear fits are shown in figure 2-7. The correlation is reasonably good in comparison to similar attempts.$^{69}$

The value of $\zeta_0$, which represents the zeta potential under conditions of zero net specific interactions is related to the i.e.p. The values of $\alpha$ and $\beta$ reflect the relative tendencies of the powders to exchange charge with the suspending media.

To further link the results of the IGC studies to the electrophoretic characterizations, we define a relative acidity parameter, $K_0$, by

$$K_0 \equiv \frac{AN_p}{DN_p}$$

which can be obtained directly from the IGC results. As shown in figure 2-8, there is a strong correlation of $K_0$ with the observed i.e.p's. of the four powders.
Figure 2.7  Zeta potential, measured and correlated by equation 8.
(a) Ti-A, (b) Ti-B, (c) Ti-C, and (d) Ti-D.
Figure 2-8  Correlation of $K_o$ with the isoelectric point for the various titanium dioxide powders.
2.3.2. COHESIVITY

Tensile strength results for the surface treated titanium dioxide powders are shown in figure 2-9. The tensile strength for the various powders seem to follow Rumpf's model with respect to the compact solid volume fraction, \( \phi \). Ti-A shows the highest strength. Ti-A is the least treated powder and shows a smooth surface. The low tensile strength of other three powders are believed to be related to the high surface roughness and imperfect contacting between particles in the compact.

From the results of tensile strength measurements, the Hamaker constant was evaluated by using Hartley's Model.

\[
R = \frac{T}{(\rho / \rho_s)/[1 - (\rho / \rho_s)]} = \frac{9}{4} \frac{(d + t)(t_o - t)}{d^2} \frac{A}{t_o^3} \Phi \tag{10}
\]

\[
t = d \left[ \left( \frac{0.74}{\rho / \rho_s} \right)^{1/3} - 1 \right] \tag{11}
\]

where \( R \) is the reduced interparticle stress, \( T \) is the tensile stress required to fracture the compact, \( \rho \) is the compact density, \( \rho_s \) is the solid density, \( t \) is the surface separation distance, \( t_o \) is the separation distance at the packing density corresponding to a compact of zero strength, \( A \) is the Hamaker constant, and \( \Phi \) is the ratio of the geometric portion of the Hamaker expression evaluated at a surface separation distance \( t \) to that expression evaluated at the \( t_o \). The results are compared with the reference value for pure titanium dioxide (3.10x10^{-19} J) and the calculated value from the dispersive component of surface tension, \( \gamma_p^d \) of powders (table 2-8).

The results in table 2-8 seems to indicate that not only van der Waals attraction forces are responsible for powder cohesivity. Capillary forces due to
Figure 2-9  Tensile stress as a function of reduced compact density, $\phi/(1-\phi)$, for various titanium dioxide agglomerates.
Key: (a) Ti-A; (b) Ti-B; (c) Ti-C; (d) Ti-D.
Table 2-8  Cohesivity Characteristics of Powders

<table>
<thead>
<tr>
<th>Powder</th>
<th>Ti-A</th>
<th>Ti-B</th>
<th>Ti-C</th>
<th>Ti-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hamaker Constant, $\times 10^{-19}$ J</td>
<td>117.4</td>
<td>23.2</td>
<td>23.1</td>
<td>65.4</td>
</tr>
<tr>
<td>Dried powder/Non-dried powder</td>
<td>125.3</td>
<td>46.7</td>
<td>43.4</td>
<td>57.6</td>
</tr>
<tr>
<td>Separation Distant, $t_0$, $\mu$m</td>
<td>0.089</td>
<td>0.076</td>
<td>0.074</td>
<td>0.087</td>
</tr>
<tr>
<td>Dried powder/Non-dried powder</td>
<td>0.065</td>
<td>0.062</td>
<td>0.067</td>
<td>0.069</td>
</tr>
</tbody>
</table>

* Hamaker constant from $\gamma^d$ pure titanium dioxide is $3.10 \times 10^{-19}$ J.

Condensed moisture may affect powder cohesivity. This assumption is confirmed not only by the higher values of the effective Hamaker constants for the non-dried powders in Table 2-8, but also by the correlations in Figure 2-10 between the normalized cohesive force and the normalized interparticle distance. The graph in Figure 2-10 indicates higher values for the cohesive forces and the interparticle distance for the non-dried powders, in accordance with the existing models for liquid bridges between particles in powders\textsuperscript{72-73}.

The cohesivity of the agglomerates can be also evaluated by using a penetrometer technique which measures the unconfined compression strength of a powder compact. Figure 2-11 shows that the measured uncorrected unconfined compression stress has a linear relationship with the agglomerate density parameter, $\phi/(1-\phi)$ ($\phi$ is the volume fraction of solids within agglomerate). These results are consistent with the prediction of tensile strength from Rumpf's model\textsuperscript{70}. Over a narrow range of porosity, the tensile strength is proportional to the shear strength, which in turn has a linear correlation with the compression strength for a
Figure 2-10  Normalized force, $F/(\gamma p^2)$ as a function of normalized interparticle distance, $t/d$, for Ti-A agglomerates.

Key: • less than 0.001 vol% moisture, ○ 0.0087 vol% moisture.
Figure 2-11 Uncorrected compression stress as a function of reduced compact density, $\phi/(1-\phi)$, for various titanium dioxide agglomerates. Key: ● Ti-A; ○ Ti-B; ■ Ti-C; □ Ti-D.
given powder. Note that Ti-A, Ti-B and Ti-C show similar magnitudes of cohesivity, while Ti-D shows a comparatively high cohesivity.

Figure 2-12 shows the dependence of uncorrected unconfined strength on the moisture content of compacts of Ti-A. The magnitudes shown suggest that capillary forces could be responsible for the compression strength. However, since the variation of compression strength with moisture content is relatively small in comparison to the differences between the compression strengths of the various powders, there are other factors contributing to the agglomerate strength. Furthermore, the high compression strength of Ti-D cannot be explained solely on the basis of capillary forces. The van der Waals interactions for different powders can be compared using the dispersive component of surface tension, $\gamma^d$. However, as table 2-3 shows, the high compression strength of Ti-D cannot be explained just in terms of $\gamma^d$ either. The high compression strength of Ti-D can also be attributed in part to the faceted shape and surface structure of the primary particles within the agglomerate.

Powder surface treatment affects differently the two cohesivity measurements. Surface roughness decreases the tensile strength, but increases the compression strength. Whereas the tensile strength is diminished by the reduced contact area due to an irregular structure, the compression strength is enhanced by mechanical locking. Note also that the uncorrected unconfined compression strength is always higher than the tensile strength of powder agglomerates.

Overall, the cohesivity of surface treated titanium dioxide agglomerates is determined by van der Waals interactions, capillary forces and mechanical locking.
Figure 2-12  Uncorrected compression stress as a function of reduced compact density $\phi/(1-\phi)$, for various titanium dioxide moisture contents. Key: • 1.820 wt%, ○ 0.213 wt%; ■ less than 0.001 wt%.
2.4. CONCLUSIONS

The shifts in dispersive and specific interactions of various grades of titanium dioxide with solvents were evidenced through IGC and zeta potential measurements. The results of the measurement of the dispersive component indicates the heterogeneity of the powders. The assessment of specific interactions with liquid solvents through electrophoretic characterization can be directly linked to the measurement of the interactions with the same molecules in the gas phase through IGC studies. Selection of good dispersion media for a particular powder depends both on the acid/base characteristics of powder as well as the magnitude of surface charge generated on the solids. A qualitative diagram that indicates possible acid/base interactions is shown in figure 2-13. Near the zero zeta potential line in Figure 2-13, there will be insufficient electrostatic stabilization to prevent agglomeration. The relative acidity of the dispersion solvent should be chosen such that it is well above this line (giving a negative charge to the solids) or well below this line (so that the solids acquire sufficient positive charge).

Powder cohesivity is affected by surface treatment. Surface roughness decreases the tensile strength by decreasing the contact area but increases the compression strength through an enhanced mechanical locking. Agglomerate cohesivity consists of three components, namely van der Waals interactions, capillary forces due to liquid bridging and mechanical locking. Adsorbed moisture increases both tensile strength and compression strength.
Figure 2-13  Zeta potential mapping on a qualitative plot of solvent and powder acid/base characteristics.
CHAPTER 3

DISPERISON OF TITANIUM DIOXIDE POWDERS IN SOLVENTS

3.1. SYNOPSIS

The dispersion behavior of titanium dioxide powders having surfaces modified with silica and/or alumina has been studied in various media. The results are characterized in terms of the individual effects of powder-solvent interactions and powder-powder interactions. Acid/base interactions predominantly determine the energetics of the incorporation of the powder into the dispersion medium. Dispersibility maps plotted in terms of acceptor and donor number coordinates enable classification of solvents as poor and good dispersion media. The boundary between stable and unstable dispersions is identified by a critical heat of dispersion curve. However some solvents provided a dispersion environment that apparently contradicts this categorization. In this cases, the magnitude of powder-powder interactions was examined. Superposition of a zero zeta potential line on the dispersibility map augments the interpretation of dispersion stability. Shifts in the dispersibility windows with surface treatment of the powders are described.
Table 3-1  Properties of Titanium Dioxide Powders

<table>
<thead>
<tr>
<th>Powders</th>
<th>Ti-A</th>
<th>Ti-B</th>
<th>Ti-C</th>
<th>Ti-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Size, μm*</td>
<td>0.167</td>
<td>0.161</td>
<td>0.156</td>
<td>0.118</td>
</tr>
<tr>
<td>BET Surface Area, m²/g **</td>
<td>9.4</td>
<td>14.7</td>
<td>12.8</td>
<td>36.7</td>
</tr>
<tr>
<td>Surface Treatment **</td>
<td>None</td>
<td>Al</td>
<td>Al+Si</td>
<td>Al+Si</td>
</tr>
<tr>
<td>Si/Al **</td>
<td>-</td>
<td>0.0</td>
<td>1.07</td>
<td>2.43</td>
</tr>
<tr>
<td>Surface Tension, γv, dyn/cm *</td>
<td>111.8</td>
<td>149.6</td>
<td>77.5</td>
<td>69.7</td>
</tr>
<tr>
<td>Donor Number, DNP, kcal/mole *</td>
<td>24.1</td>
<td>20.6</td>
<td>18.1</td>
<td>16.8</td>
</tr>
<tr>
<td>Acceptor Number, ANp *</td>
<td>34.3</td>
<td>24.1</td>
<td>34</td>
<td>65.8</td>
</tr>
<tr>
<td>Ko (ANp/DNP), mole/kcal</td>
<td>1.4</td>
<td>1.2</td>
<td>1.9</td>
<td>3.9</td>
</tr>
</tbody>
</table>

* Measured by SEM and Image Analyzer, ** Measured by Manufacturer,
*** Using IGC measurement in chapter 2

3.2. EXPERIMENTAL PROCEDURE

3.2.1. MATERIALS

Organic solvents used in this study were of spectroscopic or analytical grade; their properties are summarized in table 2-2. Distilled and deionized (16 MΩ-cm) water was also used.

Powders used in this study were the same titanium dioxide grades as described in chapter 2. Properties of the titanium dioxide powders are summarized in table 3-1. The powders were dried and kept in a desiccator as described in chapter 2.

3.2.2. SEDIMENTATION TESTS
Suspensions were prepared by dispersing 0.1 g of powder into 40 cm³ of solvent (to yield approximately 0.25 wt% suspension) by 10 min of magnetic stirring and 30 min of sonication with a 20 kHz horn. Powders taken from the desiccator were never exposed to the ambient atmosphere for more than 1 min. These suspensions were sealed in test tubes and were allowed to remain undisturbed for more than 1 day.

The quality of dispersion was judged by observing the clarity of a printed character sighted through the suspension. If the character could not be distinguished after 1 day had passed, the suspensions were judged to be stable. If, owing to settling of the solids, the character was observed within 1 hr, the suspension was considered to be unstable. Moderately stable suspensions were those that did not allow the observation of the character after 1 hr, but had settled sufficiently over the course of 1 day such that the character was visible. The judgment of moderately stable dispersions was somewhat subjective since the method used is sensitive to the solids loading.

3.3. RESULTS AND DISCUSSION

3.3.1. POWDER-SOLVENT INTERACTIONS

(A) MODEL DEVELOPMENT.

To model the energetics of the interaction between powders and solvents, we adopt concepts first proposed to model similar interactions between solvents. The solubility parameter, given by\(^{75}\)

\[
\delta = \sqrt{\frac{\Delta E}{V}}
\]  
[1]
where $\Delta E$ is the interaction energy, and $V$ is the molar volume, is an intrinsic measure of the intermolecular interaction within solvents which can be used to correlate the heat of mixing of solvents ($\Delta H_{\text{mix}}$). For dilute mixtures of solvent 2 in solvent 1

$$\Delta H_{\text{mix}} = V_2 \phi_1^2 (\delta_1 - \delta_2)^2$$

[2]

where $\phi_1$ is the volume fraction of solvent 1. Burrell suggested that the molecular interactions controlling solubility, miscibility, adhesion and dispersion are all similar. Thus, the form suggested by equation 2 has been proposed to model the energetics of the powder dispersion process.

Hansen attributed the solubility parameter to three distinct contributions: dispersive interactions ($\delta_d$), polar interactions ($\delta_p$) and hydrogen bonding interactions ($\delta_h$). Karger et al. added induced dipole ($\delta_i$) and orientation dependent ($\delta_o$) interactions to this list. However, the form of the predicted heat of mixing stemming from these models cannot account for an exotherm which occurs in many instances. For example, Hansen's model predicts

$$\Delta H_{2,\text{mix}} = V_2 \phi_1^2 [ (\delta_{1d} - \delta_{2d})^2 + (\delta_{1p} - \delta_{2p})^2 + (\delta_{1h} - \delta_{2h})^2 ]$$

[3]

which is always positive. To remedy this difficulty, the form of this equation was modified to include the combination of the polar and hydrogen bonding interactions in terms of the donor-acceptor concept advanced by Gutmann. Thus

$$\Delta H_{2,\text{mix}} = V_2 \phi_1^2 (\delta_{1d} - \delta_{2d})^2 + k (AN_1 - AN_2) (DN_1 - DN_2)$$

[4]

allows for either endothermic or exothermic heats of mixing. Here $k$ is a scaling constant. This form can be used to model interactions between powder (component 2) and solvent (component 1). For dilute suspensions it is reasonable to neglect the energetics of powder-powder interactions. Thus, equation 4 becomes:
\[ \Delta H_{p,\text{dis}} = V_p \phi_s^2 (\delta_{pd} - \delta_{pd})^2 + k (DN_s AN_s - DN_s AN_p - DN_p AN_s) \]  

where subscript \( p \) and \( s \) refer to the powder and solvent, respectively. For convenience, we denote the dispersive part of equation 5, \( V_p \phi_s^2 (\delta_{pd} - \delta_{pd})^2 \), as \( \Delta H_d \), while the acid/base component of equation 5, \( k (DN_s AN_s - DN_s AN_p - DN_p AN_s) \), is abbreviated as \( \Delta H_{ab} \).

For good incorporation of the powder into a solvent, \( \Delta H_{p,\text{dis}} \), should be small or negative. Since \( \delta_{pd} \) is in the range 7-9 cal\(^{0.5}\) cm\(^{-1.5}\) for most solvents\(^{80} \), and \( \delta_{pd} \) for metal oxides is in a similar range\(^{81} \), \( \Delta H_d \), is small and should not significantly vary with the suspending medium. Thus, the free energy of dispersion is often determined primarily by \( \Delta H_{ab} \). Accordingly, we postulate that for each powder, there is some fixed \( \Delta H^* \), for which if

\[ \Delta H_{ab} \leq \Delta H^* \]  

there will be favorable powder-solvent interactions that lead to good incorporation of the solids into the dispersion media. Based on the definition of \( \Delta H_{ab} \), the condition expressed by equation 6 can be recast as

\[ DN_s (AN_s - AN_p) \leq \Delta H^*/k + DN_p AN_s \]  

The unknown value of \( \Delta H^*/k \) must be determined empirically.

Provided that dispersive interactions do not control the overall energy of dispersion, the above expression can be used to prepare a dispersibility map for a given powder in terms of coordinates based on acceptor and donor numbers for the solvent. Since the curve that depicts the conditions of equality in equation 7 gives the boundary between good and poor dispersion, it represents the critical energy of dispersion. The intercept of this curve with the \( AN_s=0 \) boundary is given
by $-\Delta H^*/k \cdot AN_p$ while the intercept with the $DN_S=0$ boundary is $-\Delta H^*/k \cdot DN_p$. The ratio of these two intercepts gives $DN_p/AN_p$.

The relations described above lead to an experimental method of assessing the acid/base characteristics of a particular powder. The quality of dispersion of a particular powder can be assessed in a series of solvents. This can be mapped using the acceptor number and donor number of the solvent as coordinates. The region of stable dispersion behavior is depicted by equation 7 while the intercepts of the critical energy can be used to quantify the ratio $DN_p/AN_p$.

(B) DISPERSBILITY MAP

Following Jensen$^{79,82}$, the interaction mapping plane for the solvents used in this study is depicted in figure 3-1. The solvents can be classified into four main categories depending on the combination of their donor and acceptor numbers. Neutral (or non-specific) solvents such as the alkanes, benzene, toluene, and xylene have relatively low acceptor and donor numbers. In this case, the contribution of the acid/base interaction to the overall heat of dispersion is small, leaving the dispersive interaction, which is always positive, to control the dispersion stability. Indeed, the titanium dioxide powders showed unstable behavior for neutral solvents.

Solvents that have large acceptor and donor numbers are termed amphoteric solvents. Such solvents strongly interact with themselves as well as with the powders, thereby diminishing the effect of the acid/base interaction on the overall heat of mixing. Since real solvents have limited acidity and basicity, few solvents fall into this category.

Acceptor (or acidic) solvents are characterized by large acceptor numbers
Figure 3-1  Classification of the various solvents used in this study in terms of their donor and acceptor numbers based on Jensen\textsuperscript{79,82}. Abbreviation for the solvents are listed in table 2-2.
and small donor numbers. Donor (or basic) solvents have large donor numbers, but small acceptor numbers. For these combinations, $\Delta H_{\omega}$, can take on large negative values, indicating an exothermic overall heat of dispersion and the possibility of good interaction between the powders and dispersion media. In general, acidic powders will show better stability in basic solvents and vice versa.

Figure 3-2 shows the dispersibility maps for the four titanium dioxide powders examined. A least squares optimization technique was used to determine the values of $-\Delta H^*/k$, $DN_p$, and $AN_p$, that give the critical energy boundary predicted by equation 7. From the experimental results, those solvents giving unstable dispersions and located closest to the origin on the acceptor/donor number mapping were denoted as key solvents. The selection of key solvents is obvious when well- and poor-dispersing solvents are located close to each other on the dispersibility map. However, in some cases, the location of the critical energy curve might pass through a portion of the dispersibility map sparsely populated by solvents. While the identification of key solvents is more subjective in these cases, examination of the whole dispersibility map will usually enable the reliable selection of the key solvents.

The critical energy curve was assigned to pass near these key solvents on the dispersibility map. To find the optimum fitting parameters, combination of values of $-\Delta H/k$ (0-20 kcal mole$^{-1}$ in increments of 0.1 kcal mole$^{-1}$), $AN_p$, (0-100 in increments of 0.5), and $DN_p$, (0-100 in increments of 0.5 kcal mole$^{-1}$) were used to predict the location of the border curve. The goodness of fit was judged by computing the sum of squared error (deviation between the predicted and actual donor numbers at a given acceptor number) for the key solvents. Variations in the value of $-\Delta H_\omega$ between different solvents were neglected for the purpose of this
Figure 3-2  
Dispersibility map based on the critical heat of mixing. (a) Ti-A, (b) Ti-B, (c) Ti-C, (d) Ti-D. 
Key: ● stable; ○ moderately Stable; × unstable.
calculation. The curves superimposed on the dispersibility maps in figure 3-2 correspond to the globally best fit. The curve-fitting procedure was not overly sensitive to the choice of key solvents.

Since practical solvents have discrete acceptor and donor numbers, and the region through which the critical energy curve passes can be sparsely populated by data points, there is some ambiguity in the determination of the correlation parameters. Nevertheless, the general form given by equation 7 is apparently useful for distinguishing dispersion behavior. However, in some instances (Ti-A in methanol or water, for example) the dispersion behavior cannot be predicted on the basis of the critical energy curve alone.

3.3.2. POWDER-POWDER INTERACTIONS

Some solvents located outside the critical energy curve were poorly dispersing. In this cases, powder-powder interactions can lead to agglomeration, even though the energetics of the dispersion process favor good incorporation of the powders into the solvents. Powder-powder interactions result from a combination of van der Waals attraction and electrostatic double layer repulsion. Sufficient electrostatic interaction, as gauged by the zeta potential of the powders in the solvents, is necessary to insure adequate dispersion stability.

Using standard formulation, it can be shown that the maximum ratio between the magnitude of the electrostatic repulsion and the van der Waals interaction potentials occurs near $\kappa H = 1$ where $\kappa$ is the inverse Debye length and $H$ is the interparticle separation. For organic solvents, we assumed that $\kappa d = 1^{11, 63-64}$ (d is
the particle diameter) since ions have poor mobility in organic media. Using these assumptions, it can be shown that the dimensionless potential energy ratio

\[ N_{dpe} \equiv \frac{edc^2}{A_{pp}} \]  

[8]
scales the maximum ratio of the two types of interparticle interaction energy. In equation 8, \( \zeta \) represents the zeta potential which is assumed to be proportional to the surface potential and \( A_{pp} \) is the effective Hamaker constant. Dispersions will resist agglomeration if

\[ N_{dpe} \geq N_{dpe}^* \]  

[9]
where \( N_{dpe}^* \) is a characteristic of each particular solid.

To obtain parameters for estimation of the powder-powder interactions given by equation 8, we used the standard geometric mean approximation for the effective Hamaker constant:

\[ A_{pp} = (A_{ss}^{1/2} - A_{pp}^{1/2})^2 \]  

[10]
Standard expressions also were used to give the contributions of the solvent\(^{68}\)

\[ A_{ss} = 4.02 \times 10^{-19} \left( \frac{\varepsilon_s - 1}{\varepsilon_s + 1} \right)^2 \]  

[11]
and powder\(^5\)

\[ A_{pp} = 6\pi d^2 \gamma_p d \]  

[12]
to the effective Hamaker constant. Compilation of dielectric constants of solvents\(^{55-56}\) and surface tensions of powders from chapter 2 were used for these purposes.

The zeta potential values for titanium dioxide powders in various solvents are listed in table 2-6. As described in chapter 2, the zeta potential has a linear relationship with the donor and acceptor numbers of the solvent:
\[ \zeta = \zeta_0 + \alpha \Delta N + \beta AN \]  

The related parameters, \( \zeta_0, \alpha \) and \( \beta \) for titanium dioxide powders used in this study are summarized in table 2-7.

3.3.3. OVERALL DISPERSIBILITY

Overall dispersibility can be viewed to result from both powder-solvent interactions and powder-powder interactions. Two conditions must be met for the formation of a stable dispersion. First, there must be favorable energetics for the incorporation of the solid into the solvent. This corresponds to choosing a solvent located outside of the critical energy of dispersion curve on the dispersibility map. Secondly, there must be sufficient repulsive interparticle interaction to counterbalance the attractive van der Waals forces present between the particles. The value of \( N_{4\pi} \) calculated from equation 8 is shown in figure 3-3. Clearly, high values of \( N_{4\pi} \) lead to dispersion that resist agglomeration. The points denoted with filled squares correspond to unstable dispersions in solvents located outside of the critical energy of dispersion curve while those marked with crosses denote unstable dispersions for solvents located inside the critical energy of dispersion curve. The suspensions identified by the squares are unstable due to particle agglomeration while those marked with crosses are unstable due to poor energy of incorporation into the solvent.

Superimposed on the maps in figure 3-2 are lines depicting zero zeta potential from the correlation equation 13 (figure 3-4). The zero zeta potential line for Ti-D (figure 3-4(d)) does not appear since it falls outside the range of AN and DN depicted. Also not shown in the graphs are bands, centered around the zero zeta potential lines, for which \( N_{4\pi} \leq N_{4\pi}^* \). Solvents that fall within the band of low zeta
Figure 3-3  Correlation between the dimensionless potential energy number and the quality of the dispersion. Key: ● Stable; ○ moderately stable; × unstable (due to poor energy of incorporation into the dispersion media); ■ unstable (due to particle agglomeration)
Figure 3-4  Overall dispersibility map. (a) Ti-A, (b) Ti-B, (c) Ti-C, (d) Ti-D.
Key: ● stable; ○ moderately stable; × unstable.
Table 3-2  Comparison of Acid/Base Parameters

<table>
<thead>
<tr>
<th>Powders</th>
<th>Ti-A</th>
<th>Ti-B</th>
<th>Ti-C</th>
<th>Ti-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN\textsubscript{p}/DN\textsubscript{p} (IGC studies) mol kcal\textsuperscript{-1}</td>
<td>1.42</td>
<td>1.18</td>
<td>1.88</td>
<td>3.92</td>
</tr>
<tr>
<td>AN\textsubscript{p}/DN\textsubscript{p} (this study) mol kcal\textsuperscript{-1}</td>
<td>0.90</td>
<td>0.88</td>
<td>1.10</td>
<td>3.33</td>
</tr>
</tbody>
</table>

potential do not provide an adequate environment for the generation of sufficient surface potential to resist agglomeration.

Comparison of the four dispersibility maps illustrates the effect of the surface treatment. Ti-B disperses well in acidic solvents; this is consistent with the alumina surface rendering it a relatively basic character. At the other extreme is Ti-D, which disperses well in basic solvents. This tendency results from the predominance of silica treatment. Both minimally treated Ti-A, and the proportionately treated Ti-C, show intermediate tendencies.

To illustrate the adequacy of using numerical fitting of the critical energy of dispersion curve to predict acidity characteristics of the powders, we compare the ratio AN\textsubscript{p}/DN\textsubscript{p} obtained in this study to those obtained in a complementary study of chapter 2 using IGC in table 3-2. Note that there is semiquantitative agreement between the two sets of results. The discrepancy between the two sets of results can be attributed in part to the minimization of solvent-solvent interactions in the IGC experiments (since the solvents are used in the vapor phase) and the neglect of the dispersion contribution to the heat of mixing in the dispersibility studies.
3.4 CONCLUSIONS

The dispersibility of titanium dioxide powders was investigated in terms of powder-solvent and powder-powder interactions. The usefulness of depicting good and poor dispersing solvents on a mapping of donor and acceptor numbers was established. The boundary between the two regions could be used to establish estimates of the relative acidity (AN/DN) of the powders. These results compared well with independent measurements of the same ratio using inverse gas chromatography. Superposition of lines of zero zeta potential on these dispersibility maps further completes the description of powder dispersibility. These techniques are sensitive to the modifications in the surface acidity of the powders.
CHAPTER 4

MECHANISM OF TITANIUM DIOXIDE AGGLOMERATE DISPERSION IN HIGH VISCOSITY MEDIA

4.1. SYNOPSIS

The dispersion behavior of titanium dioxide agglomerates in viscous media has been studied. Under application of simple shear within a cone-and-plate device, the titanium dioxide agglomerates primarily dispersed by an erosion process in which small fragments separate from the surface. In some cases, the shear stress necessary to produce erosion was found to be an order of magnitude smaller than the measured cohesivity. Medium infiltration within agglomerates was assessed through observation of penetration of the medium into powder compacts. The kinetics of the erosion process was highly sensitive to the overall property of the agglomerates. In the case of high porosity agglomerates, the erosion rate depends on the speed of medium infiltration within the agglomerate, and the strength of the applied shear stress. A relatively wide size distribution of fragments was observed. For low porosity agglomerates, the erosion process depends on the magnitude of shear stress, the cohesive strength of the agglomerates, and agglomerate-medium interactions. A narrower distribution of fragments, having smaller mean size, was observed. Based on the experimental analysis, a model for dispersion is proposed in terms of the various physical and interfacial characteristics that determine the overall dispersion behavior.
4.2. EXPERIMENTAL PROCEDURE

4.2.1. AGGLOMERATE PREPARATION

Agglomerates were prepared from the four different grades of rutile titanium dioxide analyzed in chapter 2. Agglomerates of these powders were prepared by a compaction and shaping technique. First, the as-received powders were sieved with a 50 mesh screen to eliminate large agglomerates. These screened powders were compacted in a mold; the compacts were fractured to produce irregular pieces which were typically larger than 3 mm in size. By vibrating these pieces on screens for extended periods of time, a nearly spherical shape was produced. Agglomerates taken for the dispersion studies were collected between 7 mesh and 8 mesh screens (to give agglomerates in the size range of 2.4 - 2.8 mm). These agglomerates were dried at 200 °C under vacuum for 48 hr and stored in a desiccator to prevent moisture adsorption. Subsequent exposure to air during preparation for a shearing experiment was not more than 1 minute.

The porosity of the prepared agglomerates measured through pycnometry was consistent with the value calculated on the basis of the weight of powder charged to the mold before compaction. Usually, 80 % of the prepared agglomerates had a porosity within ± 5% of the average. The porosity of these prepared agglomerates was found to be 50 to 60 % of the porosity of agglomerates found in samples of the as-received powder.

4.2.2. MEASUREMENT OF MEDIUM INFILTRATION
The apparatus used for medium penetration measurements consisted of a graduated horizontal tube (10 mm I.D., 150 mm length) of which one side was capped with a glass filter. After packing a fixed amount of powder into the tube, the tube was connected by a rubber tube to a 50 ml reservoir of medium (PDMS of 500 to 60,000 cS). The progression of the medium into the powder compact was monitored at room temperature for 48 hr.

To measure the effective pore size of the agglomerates, a low viscosity fluid (hexane) was also used to infiltrate the powder compacts.

4.2.3. SHEARING EXPERIMENTS

Shearing experiments were performed in a rotating cone-and-plate device having a 4° cone angle, as depicted in figure 4-1. By controlling the rotation rate of the cone, shear rates up to 90 sec⁻¹ could be produced. In most experiments, two titanium dioxide agglomerates were placed into the apparatus at positions 10 - 15 mm apart from the walls. Shearing was applied after agglomerates were fully engulfed by the medium. Preparation of these experiments took not more than 1 min so as to avoid moisture adsorption by the agglomerates. PDMS fluids of 5,000 to 60,000 cS were used as media. Shearing experiments were performed at room temperature. Through the transparent glass plate, agglomerate breaking was observed in situ.

The fragments produced after 30 s of shearing were observed using a microscope. The mass of fragments produced (Wi) was quantified by comparing the UV absorbance of the sheared suspension (after extracting the parent agglomerates)
Figure 4-1  Schematic of the cone-and-plate device for the hydrodynamic shear experiments; (a) motor; (b) speed controller; (c) cone; (d) agglomerate; (f) transparent glass plate; (f) mirror.
to that of calibration standards. By difference, the radius of the diminished parent agglomerate (R) can be calculated from

\[
\frac{R(t)}{R_0} = \left( \frac{W_0 - W_r(t)}{W_0} \right)^{1/3}
\]  

[1]

where \( R_0 \) and \( W_0 \) indicate the initial radius and mass of the parent agglomerate, respectively.

4.3 RESULTS AND DISCUSSION

4.3.1. MODE OF BREAK-UP

In all but five out of more than 200 dispersion experiments, erosion was the predominant dispersion mechanism. Usually fine particles eroded from the surface formed a long tail that marked the trajectories of the flow as shown in figure 4-2. For the agglomerates that dispersed by a rupture mode, the fracture surface was always planar as shown in figure 4-3. These rare rupture events may be due to a heterogeneous structure which decreases the strength of agglomerates\(^{21,83}\).

The fragments produced by erosion were qualitatively different depending on the porosity of the agglomerates. For highly porous agglomerates, large fragments were eroded while uniformly sized small fragments were produced from low porosity agglomerates.

4.3.2. PARAMETERS AFFECTING AGGLOMERATE BREAK-UP

(A) EFFECT OF PROCESSING CONDITIONS

Figure 4-4 shows the observed size of Ti-A agglomerates as a function of the shearing time, \( t \), made dimensionless on the shear rate \( \dot{\gamma} \). These experiments were
Figure 4-2  Photographs of small particle erosion from agglomerate surface. Eroded particles follow the trajectory of flow. (top) porosity 0.696, (bottom) porosity 0.574
Figure 4-3  Photographs of ruptured surface of agglomerate. Ruptured surface shows planar surface and sharp edges. (top) Ti-A, 5,000 cS, 37.5 sec\(^{-1}\), 1.5 min, (bottom) Ti-A, 60,000 cS, 78 sec\(^{-1}\), 3 min.
Figure 4-4  Agglomerate size reduction as a function of dimensionless shearing time for titanium dioxide agglomerates. Key: (●) 188 Pa; (○) 375 Pa; (■) 1,125 Pa; (□) 2,250 Pa.
performed in four different PDMS fluids and only short shearing times were used. These data fit well the functional form predicted by Mason, et al.\textsuperscript{16}

\[
\frac{R_o - R(t)}{R_o} = k \gamma t
\]

where \( k \) is the erosion rate constant. However, in contrast with Mason's results\textsuperscript{17} for cohesionless clusters, the titanium dioxide agglomerates show that the erosion rate does depend on the magnitude of the applied shear stress which indicates that the agglomerates are cohesive.

\( \text{(B) INFLUENCE OF COHESIVITY} \)

Figure 4-5 shows the erosion rate for agglomerates of different porosity. Two different erosion regimes are seen. For low porosity agglomerates ( \( \Phi/(1-\Phi) \geq 0.55 \) ) the erosion rate has a weak dependence on porosity while a strong dependence is noted for highly porous agglomerates ( \( \Phi/(1-\Phi) \leq 0.55 \) ). Since \( \Phi/(1-\Phi) \) has a linear relationship with the strength of agglomerates as described in chapter 2, the erosion rate constant, \( k \), in equation 2 has an inverse dependence on cohesivity.

Note also that the magnitude of shear stress necessary to produce erosion of the parent agglomerates is generally an order of magnitude lower than the cohesive strength as gauged by the tensile strength or the uncorrected unconfined compression stress. It is reasonable to believe that the wetting of the solids by the fluid matrix substantially diminishes the shear strength of the agglomerates.

\( \text{(C) INFLUENCE OF AGGLOMERATE-MEDIUM INTERACTIONS} \)

Figure 4-6 compares measured erosion rates for low porosity agglomerates of the four different grades of titanium dioxide. Despite their similar cohesivity, Ti-A,
Figure 4-5  Erosion rate as a function of reduced compact density, $\Phi/(1-\Phi)$ for Titanium dioxide agglomerates. When $\Phi/(1-\Phi)$ approaches 0.4 (dotted line), the erosion rate increases rapidly due to the weakened cohesivity of the agglomerates.
Figure 4-6  Agglomerate size reduction as a function of a dimensionless shearing time for Titanium dioxide agglomerates.
Key: (●) Ti-A; (○) Ti-B; (■) Ti-C; (□) Ti-D.
Ti-B, and Ti-C show different erosion rates while Ti-D, the strongest powder shows by far the smallest erosion rate. To interpret these results, a modified erosion rate constant, \( k' \) defined as

\[
k' = \frac{k}{I_c}
\]

is plotted in figure 4-7 as a function of the work of adhesion, \( W_a \), expressed as

\[
W_a = 2 \sqrt{\gamma_{1d} \gamma_{p}^d} + W_{1p}^{sp}
\]

for the four powders. Here \( \gamma^d \) is the dispersive component of the medium surface tension, and \( W_{1p}^{sp} \) is the specific interaction between the powder and medium. For 10,000 cS PDMS, \( \gamma^d \) is 18.4 mJ/m². Since PDMS is virtually neutral, \( W_{1p}^{sp} \) is negligible. A good correlation is found between the two variables indicating that \( W_a \) is a useful parameter for gauging the erosion of low porosity titanium dioxide agglomerates.

Adsorbed water also affects the agglomerate-medium interactions. For water \( \gamma^d \) is 21.6 mJ/m². Since this is less than \( \gamma_p^d \) for the dried titanium dioxide powders (\( \gamma_p^d \) of Ti-A is 111.4 mJ/m² in table 2-3), increasing moisture content will result in a decreasing \( \gamma_p^d \). According to equation 4, this results in a smaller \( W_a \), and correspondingly, a smaller erosion rate is expected. This was confirmed by conducting experiments using different moisture contents as shown in figure 4-8. These results emphasize the importance of agglomerate-medium interactions in agglomerate dispersion.

(D) EFFECT OF MEDIUM PENETRATION
Figure 4-7  Erosion rate constant as a function of work of adhesion for titanium dioxide agglomerates.
Figure 4-8  Agglomerate size reduction as a function of shearing time for various moisture contents. Key: (●) 1.820 wt%; (○) 0.213 wt%; (■) less than 0.001 wt%.
Table 4-1  Comparison of Effective Pore Size

<table>
<thead>
<tr>
<th>Powders</th>
<th>Ti-A</th>
<th>Ti-B</th>
<th>Ti-C</th>
<th>Ti-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective Pore Size, μm *</td>
<td>7.54</td>
<td>11.8</td>
<td>6.56</td>
<td>&lt; 1.0</td>
</tr>
</tbody>
</table>

* Measured at 0.75 porosity using hexane

Infiltration of the matrix fluids used in this study is expected to be slow even for the most highly porous agglomerates. The rate of medium infiltration is highly sensitive to the pore size and pore size distribution within agglomerates (or the compacts used in the medium penetration tests). For structures of high porosity, medium penetration is expected to be relatively fast because of the larger pores, and vice-versa. Figure 4-9 shows results of PDMS penetration experiments for compacts of the four grades of titanium dioxide having the same porosity. In all cases, the penetration followed the Washburn equation\(^{87}\)

\[ l^2 = \frac{r^2}{4\eta} \left( \frac{2\gamma_{lv}\cos\theta}{r} + \Delta p \right) t \]  \[ [5] \]

where \( l \) is the depth of penetration into the compact, \( r \) is the effective pore radius, \( \eta \) is the viscosity of the medium, \( \gamma_{lv} \) is the surface tension of liquid, \( \theta \) is the contact angle at the powder-medium interface (assumed to be 0), \( \Delta p \) is the total driving pressure (nil in the case of horizontal orientation of the column). Ti-A, Ti-B, and Ti-C all show similar infiltration rates while the penetration rate for Ti-D is much less due to the smaller effective pore size shown in the table 4-1.

(E)  STRUCTURAL MODEL FOR TITANIUM DIOXIDE DISPERSION
Figure 4-9: PDMS penetration depth as a function of time for titanium dioxide agglomerates. Key: (●) Ti-A; (○) Ti-B; (■) Ti-C; (□) Ti-D.
We postulate that there is a direct relationship between the porosity and structural heterogeneity of the titanium dioxide agglomerates used in this study. The heterogeneity of the agglomerates affects both the kinetics of the infiltration of the matrix medium into the agglomerate as well as the size of the fragments produced by the erosion process. The speed of matrix infiltration has direct bearing on the erosion process since wetting of the solids is responsible for reduction of the cohesive strength of the agglomerates compared to that exhibited in the dry state.

Figure 4-10 compares the results of PDMS infiltration and agglomerate erosion as a function of the porosity of solids \( = 1 - \Phi \). Infiltration rates for powder compacts having a porosity less than 0.72 were small and could not be reliably measured. The abrupt break in the erosion curve (at 0.65 porosity) is presumed to occur at a porosity corresponding to a structure that allows significant medium infiltration within the agglomerate. For agglomerates having a porosity larger than this critical value, the erosion rate parallels the dependence of the rate of matrix infiltration on porosity. Negligible infiltration of PDMS into the agglomerates is expected if the porosity is less than the critical value.

As indicated earlier, the size of fragments produced by dispersion were found to be correlated with the porosity of the parent agglomerates. Photographs illustrating this dependence are given in figure 4-11. The largest fragments observed from parent agglomerates having a porosity of 0.696 was about 100 \( \mu m \). For parent agglomerates with smaller porosity, the largest fragment size was correspondingly smaller.

In general, part of the energy required for dispersion is expended on overcoming the cohesivity of the agglomerate, and the balance drives the wetting of
Figure 4-10  Comparison of the erosion rate and penetration rate for titanium dioxide agglomerates.
Figure 4-11  Photographs of eroded fragments from Ti-A at the initial stage of shearing as a function of agglomerate porosity. (a) 0.696; (b) 0.645. (continued next page)
Figure 4-11  Photographs of eroded fragments from Ti-A at the initial stage of shearing as a function of agglomerate porosity. (c) 0.574, (d) 0.499.
the detached fragments. Parent agglomerates of low and high porosity are depicted in figure 4.12. Penetration of the medium weakens the interactions between the primary units which initially exists within the agglomerates. Depending upon the extent of penetration, the titanium dioxide agglomerates will exhibit different effective cohesivities.

Agglomerates having porosity lower than the critical value apparently allow penetration of only a thin region at the agglomerate boundary. In this case, the erosion process is affected by the strength of the applied shear stress, the cohesivity of the agglomerate, and the energetics of the agglomerate-medium interaction. Thus, the kinetics of erosion for low porosity titanium dioxide agglomerates can be expressed as

\[
\frac{R_o - R(t)}{R_o} = \frac{k''}{f_c} W_\eta \eta \dot{\gamma} t \tag{6}
\]

where \( k'' \) is a constant that does not depend on the cohesivity of the agglomerates, the strength of agglomerate-medium interactions, or the magnitude of applied shear stress. The structure of these agglomerates are apparently quite homogeneous since fragments produced by erosion were comparable to the primary particles comprising the agglomerates, i.e., \( \sim 1 \) \( \mu \text{m} \).

In the case of agglomerates with porosity higher than the critical value, the erosion process is more dependent on the structure of the agglomerate. In this case the erosion rate is closely linked to the rate of matrix infiltration. As fluid infiltrates within the agglomerate, the strength of attachment of potential fragments near the surface of the agglomerate is significantly reduced. Since less energy per unit mass of solids is required to overcome the residual cohesive strength, erosion rates are high. Also, since these high porosity agglomerates are believed to show more structural
Figure 4-12 Structural models for high and low porosity titanium dioxide agglomerates.
heterogeneity, a wider distribution of fragment sizes may be expected.

(F) COMMENT ON DISPERSION BY RUPTURE

The results presented here are generally different from other studies\textsuperscript{21, 24} in which dispersion by a rupture mechanism was analyzed. In this work, experiments were limited to applied shear stresses that are believed to be below that generally necessary to initiate the rupture process. Those few agglomerates that were found to rupture in our experiments are believed to have several internal flaws that resulted in uncharacteristically low cohesivity.

4.4. CONCLUSIONS

The dispersion of titanium dioxide agglomerates was investigated, and a quantitative analysis of agglomerate breakup was carried out. The following results were obtained:

1. The dispersion of titanium dioxide agglomerates mainly proceeds by an erosion mechanism.

2. The titanium dioxide agglomerates were found to disperse by erosion at applied stresses that were significantly lower than the magnitude of the cohesivity measured for the unwetted powders.

3. For high porosity agglomerates, the infiltration of medium substantially reduces the effective cohesivity at the agglomerate surface, allowing relatively fast erosion to occur. Also, the structural heterogeneity associated with high
porosity agglomerates allows a wide range of relatively large fragments to be produced by erosion.

4. For low porosity agglomerates, the erosion rate is determined by the cohesive strength of the agglomerates and the work of adhesion between agglomerate and medium. The relative homogeneity of the structure results in smaller and more uniformly sized fragments to be produced by erosion.
CHAPTER 5

ANALYSIS OF TITANIUM DIOXIDE AGGLOMERATE
DISPERSION IN LINEAR LOW DENSITY POLYETHYLENE
AND RESULTING PROPERTIES OF COMPOUNDS

5.1. SYNOPSIS

The dispersion of titanium dioxide agglomerates within the melt of LLDPE has been investigated by using the cone-and-plate device installed within a temperature controlled oven. Observation of evolution of fragments from agglomerates indicated that the erosion process was the predominant mechanism. Fragments of narrow size distribution separated from the surface of agglomerate and followed the trajectory of flow. The erosion rate of agglomerates measured in LLDPE melt were consistent with the results of dispersion studies in PDMS. The erosion process was confirmed for the dispersion of agglomerates as small as 150-300 μm size. Effects of dispersion of agglomerates on the optical, mechanical and dynamic mechanical properties of compounds incorporating titanium dioxide powder were investigated. Morphological changes of compounds during dispersion were traced by observing the morphology of quenched and remelted films using a hot stage and microscope. The transparency of films and gloss of coated glass plates were investigated using a spectrophotometer and a gloss meter respectively. Mechanical properties of sheets of the compound, such as yield stress and elongation at break, were investigated by using an Instron type instrument. Dynamic mechanical properties (dynamic storage modulus $E'$ and mechanical damping tan δ) were
assessed using a dynamic mechanical tester operating at a fixed frequency. Property changes were correlated with observed morphology changes to clarify the effect of the degree of dispersion. Effects of powder loading and interactions between the powder and the media on compound properties were also studied.

5.2. EXPERIMENTAL PROCEDURE

5.2.1. SHEARING EXPERIMENTS IN LLDPE

All of the shearing experiments in LLDPE were performed using Ti-A (properties are listed in table 2-1). Agglomerates of 2-4-2.8 mm in diameter were prepared and stored as described in chapter 4.

Shearing experiments were performed in a rotating cone-and-plate device having a 4° cone angle and mounted within a temperature controlled oven (temperature range ~ 220 °C, control accuracy ± 1 °C) as depicted in figure 5-1. Most experiments were performed at 170 °C. By controlling the rotation rate, shear rates up to 90 sec⁻¹ could be produced. However, to insure stable flow conditions, the shear rate was limited to 19.5 sec⁻¹. The device was designed to easily set and remove the cone and plate and to control the distance between them.

Melts of LLDPE (GA 584 from QUANTUM Chem. Corp., 100 Pa.s at 100 sec⁻¹, 170 °C) were used as a suspending medium for the powders. To prepare the LLDPE melt, 20 g of pellets were set onto the plate and were melted in a vacuum oven at 200 °C for 45 min. No bubbles or visible color changes were observed. Two titanium dioxide agglomerates were then placed into the LLDPE melt and the plate subsequently set in the shearing instrument. About 5-10 min is required to perform
Figure 5-1  Schematic of the cone-and-plate device for the hydrodynamic shear experiments in high temperature: (a) insulated oven; (b) motor; (c) cone; (d) plate; (e) support; (f) guide ring; (g) positioning knob; (h) controller.
this operation and to stabilize the oven temperature at 170 °C. During this time interval, the agglomerates became fully immersed in the LLDPE melt, and air bubbles around agglomerates in the melt were eliminated.

The mass of fragments produced by shearing was quantified by comparing the UV absorbance of the LLDPE melt film to that of calibration standards. LLDPE films were prepared in a windowed mold made with two glass plates and a 75 μm polyester film spacer. UV absorbance was measured before the polymer melt solidified. Negligible absorbance change was observed within 3-5 min after the LLDPE melt film was set in the measuring chamber of the UV spectrophotometer. Calculation of the radius change of the agglomerates followed the same method as described in chapter 4.

5.2.2. SAMPLE PREPARATION FOR PROPERTY MEASUREMENT

Compounds were prepared by dispersing the agglomerates into LLDPE matrix. To avoid sample heterogeneity, multiple small agglomerates were used in these experiments. Agglomerates were obtained by screening the as-received titanium dioxide powder with 50 and 100 mesh screens (this yields 150-300 μm agglomerates). The screened agglomerates were dried in a vacuum oven at 200 °C for 48 hr consistent with the procedure outlined in chapter 2.

To get the initial agglomerate-LLDPE blend, a controlled amount of titanium dioxide agglomerates (up to 20 wt% which corresponds approximately to 2,000 agglomerates in one experiment) was dry-blended with LLDPE pellets and charged into the plate of the cone-and-plate device and melted in a vacuum oven at 200 °C for 45 min. These mixtures were set in the instrument, and the temperature was
controlled and stabilized at 170 °C for 5-10 min, before shear was applied. The shear rate varied between 13 and 19.5 sec⁻¹, and the shearing time ranged up to 40 min.

After shearing, the compounds were compression molded and quenched with cold water to give approximately 0.8 mm thick sheets for mechanical and dynamic mechanical property measurement. Samples for optical transparency measurements were prepared with the thin mold to get 0.08 mm thin films. Film thickness varied between 0.075 to 0.085 mm for solidified samples. Samples for optical gloss measurements were prepared by coating the compound melt on the glass plate. The coating was performed by placing a sheet of compound prepared for the mechanical property measurement onto a glass plate and then remelting it at 200 °C vacuum oven for 45 min. A slightly yellowish color change was observed after remelting and quenching in the cold air.

5.2.3. SAMPLE TESTING

Optical transparency was evaluated by measuring the transmitted light intensity of 540 nm incident beam radiation through the thin compound film using the UV spectrophotometer. Air was used to calibrate for 100 % transparency.

Gloss was measured by using the specula gloss meter ( Multi Bykometer manufactured by BYK Chemie, Germany ). A specula angle of 85° was adopted. Details regarding the measurement of specula gloss are given in ASTM D5238.

Mechanical testing was performed using the Instron tester at a cross head speed of 1 mm/min with dog-bone shaped samples. The cross section measurements were 0.8 ± 0.05 mm by 10 ± 0.05 mm.
Dynamic mechanical properties in terms of the dynamic storage moduli $E'$, dynamic loss moduli $E''$, and mechanical damping $\tan \delta$ for the compounds were measured using a dynamic mechanical analyzer (DMA 980 Dynamic Mechanical Analyzer manufactured by TA Instruments). Flexural deformation was done with a 7.26 mm clamp distance and a 10 Hz fixed frequency at room temperature.

Three measurements were made in the mechanical and dynamic mechanical tests. The exact thickness and width of specimens were used in the calculation of mechanical and dynamic mechanical properties.

5.3. RESULTS AND DISCUSSION

5.3.1. AGGLOMERATE BREAK UP IN LLDPE

Fine particles eroded from the surface of agglomerates and made a long tail following the trajectory of flow in LLDPE melts as shown in figure 5-2. The size of fragments is on the order of 1 μm. This is basically the same pattern of dispersion as observed in PDMS and reported in chapter 4.

Figure 5-3 shows the reduction of the size of the parent agglomerate as a function of dimensionless shearing time. The radius of the parent agglomerate decreased linearly as expected from Mason's study15,16 and the dispersion study in PDMS. The erosion rate constant corrected for the work of adhesion compares well with the experimental results obtained using PDMS. Figure 5-4 shows that this corrected erosion rate constant linearly increases with the applied shear stress. Also note that the erosion rate constant measured in LLDPE melts falls on the same line of erosion rates measured in PDMS. This comparison illustrates that the model of
Figure 5-2  Photographs of erosion of titanium dioxide agglomerate in LLDPE melt. Observed after applying 19.5 sec$^{-1}$ shear rate for 30 sec at 170 °C. (a) surface, (b) tail.
Figure 5-3  Agglomerate size reduction as a function of dimensionless shearing time for titanium dioxide agglomerates in LLDPE melt.
Figure 5-4  Work of adhesion corrected erosion rate constant as a function of shear stress for titanium dioxide agglomerates in PDMS (●) and LLDPE (■).
titanium dioxide dispersion in PDMS can be extrapolated to the polymeric melt.

Qualitatively similar dispersion phenomena were observed using multiple small agglomerates in samples prepared for property measurement. Figure 5-5 shows how small agglomerates (150 - 300 μm in size) change under the shearing process in LLDPE melt. The initial agglomerates show irregular and rough surface structures. After 10 sec, 50% of the radius of the initial parent agglomerate was eroded. With increasing the dispersion time, the parent agglomerate size decreased and the concentration of eroded fragment increased. Most radius reduction occurred in the initial 30 sec of each experiment but 30 to 50 μm size fragments were observed even after a 20 min mixing time. This means that the initial agglomerates are heterogeneous in structure and some parts of the agglomerate are very dense or highly cohesive.

5.3.2. EFFECTS ON COMPOUNDS PROPERTIES

(A) OPTICAL PROPERTIES

To evaluate the effect of dispersion on the optical qualities of compounds, opacity of compound films and gloss of compound coatings were investigated.

The light transmission through a film is affected by the surface structure and internal structure. The effect of surface structure in molded samples is minor due to the flat polymer-glass interface. The internal structure composes isotropic and random inhomogeneities. The transmitted intensity obeys the following equation

\[ I_t = I_o \exp(-\tau d) \]

where \( I_t \) is the intensity of the transmitted light through a sample of thickness \( d \) when the incident intensity is \( I_o \), and \( \tau \) is the turbidity. The turbidity is a measure of
Figure 5-5  Photographs of dispersed small agglomerates from Ti-A as a function of shearing time. (a) t=0, (b) t=10 sec, (c) t=30 sec, (d) t=60 sec.
(continued to next page)
Figure 5-5  Photographs of dispersed small agglomerates from Ti-A as a function of shearing time. (e) t=300 sec, (f) t=600 sec, (g) t=1200 sec.
all structure factors. The turbidity has a maximum value for a given wavelength and
dpends on the properties and size of the scattering solids. For small particles turbidity
increases with particle size, however the reverse is true for large particles. The
transmittance changes inversely with turbidity. Figure 5-6 shows the transmittance
change of a thin compound film during dispersion. At low shearing times,
agglomerates are not significantly eroded, and the size of agglomerates is large
compared to the wavelength of the incident light. However, since there are few
agglomerates present, τ is small and I is high. As the parent agglomerates are eroded
into fragments with size comparable to the wavelength of the incident beam during
the initial 30-60 sec, I decreases rapidly as shown in figure 5-5 (a-d). A slow
decrease in transmittance after 1 min shearing time is consistent with the slow change
in dispersion observed in figure 5-5 (e-g). Figure 5-6 also shows the effect of the
shear rate on the optical property of the film. Increased shear rate accelerates the
erosion process, and the transparency drops.

The degree of dispersion also affects the gloss, which is related to the surface
structure of the film. During the sample preparation, melted polymer flowed around
the large agglomerates which protruded through the film. If the surface of the coated
film is rough, the reflected light diverges and specular gloss will decrease. The gloss
of surface was calculated by Bennett and Porteus\textsuperscript{90} and is given by

\[ G = G_T \exp\left(-\frac{4\pi\sigma\cos\theta_i}{\lambda}\right)^2 \]  \hspace{1cm} [2]

where G is the specular gloss, \(G_T\) is the maximum possible theoretical gloss which is
calculated using the Fresnel equations, \(\theta_i\) is the angle of incidence, \(\lambda\) is the wave
length of light used and \(\sigma\) is the root mean square roughness. The critical size of a
Figure 5-6  Transmittance of titanium dioxide-LLDPE compound film as a function of dispersion. Key: (●) 19.5 sec⁻¹; (■) 8.3 sec⁻¹.
defect affecting the gloss was derived by Rayleigh\textsuperscript{91}

\[ D = \frac{\lambda}{8 \cos \theta_i} \]  \[3\]

where \( D \) is the simple step function defect of height \( D \). In our study, \( \lambda \) is 550 nm, \( \theta_i \) is 85° and \( D \) becomes 0.78 \( \mu \text{m} \). Therefore defects smaller than 0.78 \( \mu \text{m} \) in height have little effect on gloss. Figure 5-7 shows the specula gloss of the compounds as a function of dispersion time. At short shearing times, the coating shows low gloss due to the large size of agglomerates and the rough surface structure caused by a poor dispersion. With increasing dispersion time, agglomerates erode, and the volume of fine fragments increases. As a result, the surface of the coating becomes smoother, and the specula gloss increases. After 1 min of dispersion, further dispersion does not affect agglomerate size, and the gloss of the coating becomes constant.

(B) MECHANICAL PROPERTIES

Inorganic titanium dioxide particles dispersed in LLDPE matrix affect the mechanical properties. The yield stress and elongation at break have primary importance, giving information on the maximum allowable load without considerable plastic deformation and the maximum deformation before breaking, respectively. These properties, however, depend in a complex way on the microstructure including particle size, particle size distribution, concentration, shape, properties of particle and matrix and interfacial interactions. Chow\textsuperscript{41} provides a simple model, explaining how mechanical properties depend on these various parameters

\[ \sigma_u = \left[ \left( \frac{12 \gamma E_m}{d} \right) \left( \frac{1}{E_u} + \phi \right) \right]^{1/2} \] \[4\]
Figure 5-7 Specula gloss of titanium dioxide-LLDPE compound coated glass as a function of dispersion time. Key: (●) 19.5 sec⁻¹; (■) 8.3 sec⁻¹.
\[ e_u = \left( \frac{12\gamma}{d E_m E_H (1 + E_H \phi)} \right)^{1/2} \]  

where \( \gamma \) is the interfacial energy per unit area (work of adhesion), \( E_u \) is the longitudinal Young's modulus, \( E_m \) is the Young's modulus of matrix, \( d \) is the particle size of filler and \( \phi \) is the volume fraction of filler in the matrix. From equation 4, the yield stress increases with increasing \( \gamma \) and \( \phi \) but with decreasing \( d \). The elongation at break shows a similar trend except the reverse effect of \( \phi \). Increased filler content increases the rigid portion of the compound and increases yield stress but makes the compound brittle.

Figure 5-8 shows measured tensile stress - strain curves and figure 5-9 shows the change of mechanical properties as a function of dispersion time. Due to large agglomerates present at short shearing times, the yield stress and elongation at break are small but improve with increasing dispersion time through fragmentation of agglomerates. The dispersion process also increases the interfacial area and increases the total work of adhesion. Most of the overall change occurred at the initial stage of dispersion. Theses results are also consistent with the change in the morphology of films as shown in figure 5-5. Higher shear rates also proved to accelerate the dispersion process and improved the mechanical properties.

The effect of filler loading on the mechanical properties is shown in figure 5-10 and figure 5-11 for compounds made from one type of titanium dioxide powder dispersed in LLDPE. The filler loading increases the yield stress and decreases the elongation at break as expected from equation 4 and equation 5.

One important factor governing these results is the interfacial interaction. Depending on the effectiveness of load transfer between powder and matrix, yield
Figure 5-8  Tensile stress - strain curve of titanium dioxide-LLDPE compound film for different dispersion times.
Key: (●) 0 sec; (○) 10 sec; (■) 30; sec:(□) 60 sec; (×) 300 sec.
Figure 5-9  Yield stress (a) and elongation at break (b) of titanium dioxide-LLDPE compound sheet as a function of dispersion time.
Key: (●) 19.5 sec⁻¹; (■) 8.3 sec⁻¹.
Figure 5-10  Tensile stress - strain curve of titanium dioxide-LLDPE compound sheet for different filler loading.
Key: (●) 0 wt%; (○) 5 wt%; (■) 10 wt%; (□) 20 wt%.
Figure 5-11  Yield stress (a) and elongation at break (b) of titanium dioxide-LLDPE compound sheet as a function of dispersion time. Key: (●) 5 wt%; (■) 10 wt%.
stress is affected\textsuperscript{56-46}. The following model was developed to quantify the effect of interfacial interactions\textsuperscript{92}

\[
\sigma_y = \sigma_{y0} \frac{1 - \phi}{1 + 2.5\phi} \text{EXP}(B\phi) \tag{6}
\]

where \(\sigma_y\) and \(\sigma_{y0}\) are the composite and matrix yield stress and \(B\) is the parameter which reflects the effect of the interfacial interactions. The interaction parameter, \(B\), is related to the effective thickness of the interface layer, \(\Delta R\), and is expressed for spheres by\textsuperscript{93}

\[
B = \left(1 + \frac{2\Delta R}{D}\right)^3 \tag{7}
\]

where \(D\) is the diameter of the sphere. Good adhesion (high \(B\)) corresponds to high yield\textsuperscript{94}. Mechanical properties of compound sheets made from different grades of titanium dioxide and subjected to long shearing times are shown in figure 5-12. Regardless of the grade of titanium dioxide, the effect of filler loading on the elongation at break is quite clear. The effect on tensile stress is hard to distinguish among different grades of powders due to the relatively large amount of scatter in the experimental data. One feature is the low yield stress of the compound films comparing to pure LLDPE film. This result can be explained by the presence of undispersed fragments of 30-50\ \mu\text{m} which were found even after long shearing times as shown in figure 5-5 (e-f). These large fragments were observed regardless of the titanium dioxide grade used. Stress concentration at large fragments causes premature failure and reduces the yield stress. It looks unlikely that perfect bonding and flawless compounds can be made.
Figure 5-12  Yield stress (a) and elongation at break (b) of titanium dioxide-LLDPE compound film as a function of filler loading for different grade of titanium dioxide used. (----) refers value of pure LLDPE sheet.
(C) DYNAMIC MECHANICAL PROPERTIES

Since dynamic mechanical measurements are taken at low strain, they are less sensitive to local defects such as agglomerates or flaws which cause crack initiation and premature failure in a high strain measurement. The dynamic mechanical measurement is useful to evaluate various interactions occurring during repeated deformation. The storage modulus, \( E' \) and mechanical damping, \( \tan \delta \) of compound sheets change with dispersion time (or shearing time) as shown in figure 5-13(a). \( E' \) increased with the dispersion time due to the increased interfacial area and decreased size of agglomerates which may behave as defects. Increased \( E' \) with loading can be explained using the relationship

\[
\frac{E_c}{E_m} = \frac{1 + 1.5\phi B}{1 - \phi B}
\]

where \( E_c \) and \( E_m \) are the dynamic storage modulus of compound and matrix respectively, and \( B \) is the interaction parameter defined in equation 7. Increases in \( E_c \) result from increases in the hard filler content, \( \phi \). A relationship for \( \tan \delta \) was also developed:

\[
\tan \delta_c = \tan \delta_m / (1 + 1.5\phi B)
\]

The relationship between \( \tan \delta_c \) and dispersion time is rather complex as shown in figure 5-13(b). The initial decrease in \( \tan \delta_c \) can be explained by an improved adhesion due to the increased interfacial area, (and therefore, improved interfacial interactions) and decreased powder-powder contact. Particle-particle friction is generally assumed to be responsible for an increased damping. At longer times, the increase of damping may be related to a network formation between the dispersed titanium dioxide such as is seen in carbon black dispersed in rubber. The minimum in \( \tan \delta_c \) is thought to indicate a dynamic equilibrium between destruction of
Figure 5-13  $E'$ (a) and $\tan \delta$ (b) of titanium dioxide-LLDPE compound sheet as a function of dispersion time. Key: (●) 5 wt%; (■) 10 wt%.
agglomerates into fine particles and reformation of the network. This tendency is also accelerated by an increasing shear rate.

Figure 5-14 shows the dependence of E' on the filler loading. These data fit the form of equation 8 well. Different grades of titanium dioxide show different slopes, indicating different strengths of interaction. The interaction parameter B is compared with the work of adhesion in table 5-1. The good correlation qualitatively indicates that the high moduli of Ti-A and Ti-B loaded compound sheets is a direct result of the interfacial interactions between particles and matrix.

The measured tan δc of compound sheets is plotted as a function of filler loading in figure 5-15. Tan δc increased with initial loading but decreased linearly with loading above 1 vol %. The slope of each line represents the interfacial interaction between filler and matrix as expected from equation 5-9. The interaction parameter B obtained from the slope coincides with the results from the analysis of storage modulus but is less sensitive to the filler characteristics. Interestingly, the initial increment of tan δc showed a good correlation with the tensile strength of the agglomerates for each powder. This comparison is tabulated in table 5-2. The damping is affected not only by the interfacial interactions but also by the particle-

<table>
<thead>
<tr>
<th>Powders</th>
<th>Ti-A</th>
<th>Ti-B</th>
<th>Ti-C</th>
<th>Ti-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interaction Parameter B</td>
<td>2.62</td>
<td>2.95</td>
<td>1.61</td>
<td>0.66</td>
</tr>
<tr>
<td>Work of adhesion Wc, mJ/m^2</td>
<td>119.6</td>
<td>138.3</td>
<td>99.6</td>
<td>94.45</td>
</tr>
</tbody>
</table>

* Calculated from \(\gamma_p^d\) of powder of table 2-3 and \(\gamma_{LLDPE}^d\) of 32 mJ/m^2.
Figure 5-14  
$E'/E''$ as a function of titanium dioxide vol %.  
Key: (●) Ti-A; (○) Ti-B; (■) Ti-C; (□) Ti-D.
Figure 5-15  Tan δc/tan δm as a function of titanium dioxide vol %.
Key: (●) Ti-A, (○) Ti-B; (■) Ti-C, (□) Ti-D.
particle interactions and the deformation of agglomerates. Mechanical energy is consumed to disperse the remaining agglomerates in the matrix and is dissipated as the powders flow past each other. The stronger the powder-powder interactions, the more energy is consumed, and damping is increased. Another possibility is that some energy may be consumed to break any network present. The strength of network is proportional to the particle-particle interactions, which is represented by the work of adhesion between powders.

The results presented here indicate that whereas $E'$ depends on the dispersion of powder through interfacial interactions, only $\tan \delta$ depends also on the powder-powder interactions or any secondary structure formed in the compound.

5.4. CONCLUSIONS

The dispersion of titanium dioxide agglomerates within polymeric melts occurs by the mechanism of erosion. Experimental measurements of parent agglomerate radius reduction indicate that the dispersion behavior of titanium dioxide agglomerates in LLDPE melt is consistent with the kinetics observed for dispersion of titanium dioxide agglomerates in PDMS.
As indicated by measurements of optical properties, mechanical properties and dynamic mechanical properties, the dispersion quality strongly influences these physical properties. Opacity, gloss, yield stress, elongation at break and storage modulus all increased with increasing dispersion time. Mechanical damping reflects the complexity of interactions in agglomerate dispersion processes. Understanding dispersion mechanism and effects on compounds properties can be applied in modifying powder surface characteristics and optimizing the processing conditions to improve the properties of compounds in which titanium dioxide powders are incorporated.
CHAPTER 6

SUMMARY AND FUTURE WORK

6.1. OVERVIEW

The purpose of this study was 1) to develop the tools to characterize the surface treated titanium dioxide powders, 2) to clarify the dispersion mechanism in low viscosity solvents and high viscosity polymeric melts, and 3) to investigate the dispersion quality-compound property relationship.

The characterization of surface treated titanium dioxide was performed by investigating the interacting forces using IGC, zeta potential measurements and cohesivity measurements. These studies indicate that van der Waals interactions, acid base interactions, electrostatic interactions and mechanical locking are affected by the surface treatment. Si or/and Al treatment on titanium dioxide powders changed the surface characteristics towards those of the corresponding inorganic oxide. Surface treatment also changed the morphology of primary particles which affected the cohesivity of agglomerates made from these treated powders.

Studies on the dispersion mechanism of titanium dioxide powder in low viscosity solvents were performed by the sedimentation test. Stable dispersions are determined by a combination of powder-solvent interactions (as represented by the heat of mixing) and powder-powder interactions (van der Waals interactions and electrostatic repulsion forces). We found that acid/base interactions are important for titanium dioxide powder dispersion in solvents. Acid/base interactions affect the
heat of mixing and the electrostatic repulsions. Using the Gutman's donor and acceptor numbers, dispersion maps were successfully obtained.

Experiments for dispersion of agglomerates in high viscosity media were performed by using a cone-and-plate device having a 4° cone angle. This instrument was used to generate the simple shear flow fields of known strength. PDMS (liquid at room temperature) and LLDPE melts were used as media. The dispersion mechanism of titanium dioxide in high viscosity media was quite different from that in low viscosity solvents. Agglomerates eroded into small fragments under shear flow, and the rate of erosion was accelerated by increasing the field strength. Due to the high viscosity of the medium, coagulation seldom occurred. Cohesivity of agglomerates and interfacial interactions between agglomerates and medium were found to be important factors governing the erosion mechanism. Surface treatment on titanium dioxide altered the erosion rate by changing the interfacial interactions. Porosity and its effect on medium penetration are affecting factors in dispersion of highly porous agglomerates. Fast penetration weakened cohesivity and increased the erosion rate. Based on experimental results, models which include related parameters were proposed. A similar erosion process was observed in small agglomerate (150-300 μm) dispersion experiments. The models developed for the mechanism of titanium dioxide agglomerates in PDMS at room temperature can be extended to polymeric melts. The same dependence of erosion rate to shear forces in PDMS and LLDPE melt was confirmed.

Correlations between physical properties of the compound and the quality of dispersion in terms of distribution of eroded particles have been investigated. Opacity, gloss, yield stress, elongation at break and storage moduls improved with
increasing dispersion time by increasing the fine particle concentration and reducing the agglomerate size. Mechanical damping change during dispersion reflects the complex interactions in the dispersion process. Surface treatment on titanium dioxide also affects the compound properties by changing the interfacial interactions.

6.2. SUGGESTIONS FOR FUTURE WORK

Dispersion experiments were limited to the low shear rate in this study due to constraints of flow stability in the cone-and-plate geometry. The shear stress applied is 1-2 orders of magnitude lower than that in real mixing and compounding operations. The rupture process expected from theoretical studies and from results of previous carbon black agglomerates was not observed. This study can be extended to higher shear stresses by 1) using high viscosity polymers or 2) changing the operation temperature and increasing the viscosity. To do this, modifications would also be required in the cone-and-plate device. Decreasing the cone angle, increasing the radius of cone and improving the accuracy in alignment will provide more stable performances for high shear stress experiments.

Another approach for higher external stress is changing the flow field geometry such as to pure elongation or biaxial extension. The elongational flow fields have proved to be more efficient than simple shear for liquid-liquid dispersion processes both theoretically and experimentally\textsuperscript{100-103}. For solid-liquid dispersion processes, little work has been done experimentally in elongational fields. It is certainly worthwhile to extend the study to elongational fields considering that most real operations occur in a combination of simple shear and elongational flows.
The effect of acid/base interactions during dispersion and on compound properties can be evaluated against more general powder-polymer combinations. In this study, neutral polymers (PDMS and LLDPE) were used, and interactions were limited to van der Waals forces. A broader selection of polymers can be applied to change the acid/base combination. Chlorinated polyethylene can be used as an acidic polymer and acetated polyethylene as a basic polymer. Acid/base interactions have been the focus in adhesion and composite studies for long time\textsuperscript{43-46,61} and have been used to improve the properties. Considering that inorganic surface treatment is most common in powder manufacturing, use of organic treatments through coupling and adsorption of additive may be advantageous.

Finally we suggest that a more thorough study of the agglomerate formation process and agglomerate structure will be very helpful. In our simple shear dispersion process, relatively large size agglomerates survived after long dispersion times. A similar situation is reported in ceramic processing\textsuperscript{104-105}. The strength of ceramic does not rise to the expected level due to flaws formed by agglomeration. Such agglomerates can not be dispersed easily. Probably the manufacturing process can also be controlled to limit agglomerate formation.
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