CONTROLLING NANOPARTICLE DISPERSIONS FOR NANOSCOPIC SELF-
ASSEMBLY

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Master of Science in Polymers and Coatings

by

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ABSTRACT

Controlling Nanoparticle Dispersions for Nanoscopic Self-Assembly

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Nanotechnology is the manipulation of matter and devices on the nanometer scale. Below the critical dimension length of 100nm, materials begin to display vastly different properties than their macro- or micro- scale counterparts. The exotic properties of nanomaterials may trigger the start of a new technological revolution, similar to the electronics revolution of the late 20th century. Current applications of nanotechnology primarily make use of nanoparticles in bulk, often being made into composites or mixtures. While these materials have fantastic properties, organization of nano and microstructures of nanoparticles may allow the development of novel devices with many unique properties. By analogy, bulk copper may be used to form the alloys brass or bronze, which are useful materials, and have been used for thousands of years. Yet, organized arrays of copper allowed the development of printed circuit boards, a technology far more advanced than the mere use of copper as a bulk material. In the same way, organized assemblies of nanoparticles may offer technological possibilities far beyond our current understanding.

In the first project, 1D assemblies of nanoparticles were explored. 1D anisotropic assemblies of nanoparticles are the simplest organized nanostructures which may be fabricated. One of the greatest difficulties in developing commercial products is in the transfer of a process from the laboratory to manufacturing scale. While many techniques may be used to develop 1D assemblies in lab, simple techniques are needed to allow the

fabrication of these assemblies on a large, cost effective scale. Use of shear, shown previously to induce colloidal ordering in solutions, is a technique that may be readily adapted from the coatings industry as a process for forming 1D assemblies, if the optimal conditions can be found. Atomic force microscopy was used to study the role of shearing forces produced by drawdown and spraying application in the formation of 1D assemblies of nanoparticles. Formation of 1D strings was observed to increase with greater application of simple shear, but greater spraying forces were found to decrease formation of strings. This is explained in terms of greater simple shear providing a greater driving force for string formation, while greater spraying shear acted to irreversibly disperse the particles.

The second project focused on the development of a learning module for education of students at various academic levels on the significance of the surface area of nanomaterials. This project was commissioned by the Global Waste Research Institute, a multidisciplinary organization based at Cal Poly, concerned with performing research and education in areas related to waste management, particularly of emerging waste streams. As nanotechnology and nanoparticles become more prevalent in consumer products and industrial processes, the volume of nanowaste is increasing rapidly. To address challenges associated with processing this unique form of waste, understanding of the fundamental processes controlling the unique properties of nanoparticles is necessary. A learning module was developed using a laboratory demonstration and video presentation to illustrate concepts related to differences in the properties between microparticles and nanoparticles. The laboratory demonstration was designed to be simple to understand, and quick, simple, and inexpensive to perform. The video presentation was designed to

be a 15 minute presentation relating the concepts of nanotechnology, nanoparticles, surface area, and fundamental differences as compared to conventional materials.

Dispersions of particles within aqueous media were used as a framework for the discussion, in a manner comprehensible by students ranging from 12th grade high school students to graduate students in relevant programs.

The third and final project focused on self-assembly of particles in nematic liquid crystalline colloids. Dispersions of colloidal particles in liquid crystals (LCs) are a relatively new set of composite materials, host to a variety of interactions not seen in colloids in isotropic media. Presence of colloidal particles disrupts the local nematic director, resulting in a loss of long-range elastic energy. Interactions between particles and LC molecules results in dipolar or quadrupolar defects, depending on the nature of the interactions between particle and LC. The loss of long-range elastic energy can be minimized through aggregation of particles. The defects formed by interactions between particles and LC stabilize these aggregations as linear chains, either along the nematic director in the case of dipolar defects, or at an offset angle in the case of quadrupolar defects. Dispersions of silica microspheres in the nematic phase of a thermotropic liquid crystal were studied using polarizing light microscopy. Strong homeotropic anchoring was observed, indicated by the abundant formation of hedgehog defects. These defects were found to play a role in self-assembly of particles along the nematic director, resulting aggregates containing up to a dozen aligned particles. In addition, particles were observed to aggregate in chains along grain boundaries in the liquid crystal, acting to stabilize the high energy interface between different grain directions, an effect not previously reported in the scientific literature for nematic colloids.

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1. Introduction

1.1. Nanotechnology

1.1.1. Definition

Nanotechnology may be loosely defined as technology which operates materials and devices on the length scale between 1-100 nanometers (nm) (“Nanotechnology Definition” 2000). Manipulation of matter on this scale differs fundamentally from that on classically sized systems. Many unique properties arise when materials are fabricated on the nano scale, presenting both opportunities and challenges in exploiting them for technological gain.

Whether a technology may be considered “nanotechnology” may become ambiguous when specific applications are considered. The term is an all-encompassing description of technology at very small sizes, across a broad range of industries and academic disciplines. While the critical dimension size of 1-100 nm is considered a very popular definition, some place additional restrictions on what may truly be considered nanotechnology from a more fundamental point of view: behavior dominated by properties intrinsic to small size, the emergence of quantum effects, or properties driven by the enormous surface-area-to-volume ratio of extremely small objects (Schattenburg 2001). Further complications occur when factors significant to differentiating the nano and micro scales of technology may not be consistent across different disciplines. For example, a biological application may involve engineering a fullerene particle as a vector for targeted drug delivery, while an electronic application may involve manipulation of individual atoms.

The conceptual underpinning of nanotechnology is that the operation of technology is fundamentally different than operation at larger scales (“Definition- What is Nanotechnology?” n.d.). Merely shrinking the size of objects is not sufficient, and redesign is necessary to maintain functional viability. An example of this is that despite electronic transistor designs involving dimensions well below 100 nm, these devices are not considered nanotechnology, because operation is fundamentally the same as classically-sized transistors, though the specific device design is different. Regardless of the precise definition of nanotechnology, exploitation of unique and exotic behaviors which begin to manifest at very small length scales is the key to technological advancement.

1.1.2. History of Nanotechnology

The conceptual origins of nanotechnology are popularly credited to physicist Richard Feynman, as delivered in his now-famous lecture, “There’s Plenty of Room at the Bottom”, in 1959 (Milburn 2008). Feynman pondered the logical extremes of the miniaturization of technology. In particular, he considered the technological implications of the ability to manipulate matter on the atomic scale. For example, if text from an encyclopedia could be written using individual atoms, he calculates that 24 million books’ worth of text, each book the size of an encyclopedia, could be written on matter the size of a speck of dust (Feynman 1959). Feynman’s vision was ahead of its time, with response within the scientific community being lackluster until nanotechnology became popularized in the 1990s, following the publication of Eric Drexler’s book, *Engines of Creation: The Coming Era of Nanotechnology* (Tourney 2008).

Advancements in imaging and manipulation of matter occurred over several decades following Feynman's speech, particularly with the 1981 invention of the scanning tunneling microscope (STM), which allowed imaging of individual atoms. Later, in 1989, a technique would be found using the device which allowed atoms to be manipulated individually. Nanoparticle colloids quickly became a significant sub-field of nanotechnology. The study of nanoparticles as dispersions existed as early as the beginning of the 20th century. Improvements in manufacturing techniques, allowing particles to be mass-produced in uniform sizes, aided the development of cost-effective commercial applications ("Chapter 1" n.d.).

1.1.3. Modern Nanotechnology

Modern nanotechnology primarily makes use of nanoparticles in bulk form, added to other materials to provide enhanced performance or properties compared to traditional materials. While several different patents were filed through the mid to late 20th century, the first commercialization of nanotechnology was produced in the form of a nanocomposite by the Toyota Corporation ("Nanocomposites- A Little" 1999). In 1988, Toyota patented the process to produce a nanocomposite of nylon-6 and montmorillonite. Three years later, in 1991, the nanocomposite was used to produce timing belt covers for cars. This material boasted properties considerably improved compared to pure nylon-6, including 70% increased tensile modulus, 125% increased flexural modulus, reduced gas permeability, and increased heat distortion temperature. Since then, many applications have been developed for a wide variety of industries, including textiles, cosmetics, sporting goods, and electronics ("Analysis" n.d.).

1.2. Nanoparticles

1.2.1. Definition

Nanoparticles are defined analogously to nanotechnology: particles with a dimension on the 1-100 nm length scale. Particles at this scale may begin to exhibit behavior different from those at micro or macro sizes, as effects of surface interactions or quantum mechanics increase relative to bulk properties (Sato 2008). Nanoparticles occur in a variety of shapes, including spheres, tubes, and sheets. Some nanoparticles, such as those from the fullerene family of materials, may be held together entirely by covalent bonds. Fullerenes are a family of molecules consisting entirely of carbon atoms, and include carbon nanotubes and buckyballs. While individual molecules are generally not considered nanoparticles, certain notable exceptions exist for macromolecules, including fullerenes and polymers. Many nanoparticle materials, such as those of titanium dioxide (TiO_2), are simply clusters of small molecules stuck together as a single unit (Sato 2008).

1.2.2. History of Nanoparticles

While precision manufacturing and characterization of nanoparticles are modern developments, nanoparticles themselves are naturally occurring materials, and may be generated inadvertently through relatively simplistic techniques. It has been discovered that 9th century Mesopotamian artisans used copper and silver oxide nanoparticles to create a glittering effect on the surface of ceramic pots (“Nanoparticles” 2012). Artisans from other cultures made use of other techniques, discovered through trial and error, to produce similar effects, though they didn’t understand the true nature of these materials

(Rawson 1984). Michael Faraday made the first scientific description of the source of the unique optical properties observed in these ancient artifacts, attributing the properties to the same phenomena as observed due to the extremely small size of particles in gold solutions he studied (Faraday 1857).

The first measurements of the sizes of nanoparticles were enabled with the invention of the immersion ultramicroscope in 1912, which enabled indirect visualization of particles smaller than 4 nm in diameter (Mappes 2012). This device led to developments in colloidal science which resulted in work culminating in multiple Nobel Prizes. The study of fundamental properties of nanoparticle colloids was a key step in the developing the knowledge base that eventually led to commercially-viable nanotechnologies.

Composite materials were the first applications in which nanoparticles were intentionally formulated into a product to enhance the properties of the matrix material (“Nanoparticles- A Little” 1999). Hybrids of nylon-6 and montmorillonite nanoclay were developed by Toyota Central R&D Laboratories in the late 1980s (Hussain 2006). Similar to the addition of additives to metals to enhance certain properties, small amounts of nanoclay added to plastics were found to provide significant property enhancements: improvements to mechanical and thermal properties, as well as gas barrier and flame resistance, with essentially no negative side-effects.

1.2.3. Nanoparticle Properties

Modern uses of nanoparticles include a number of commercial applications, both industrially and in consumer products (“Nanotechnology Information Center” 2011).

While new applications are continually being found, most involve new ways to use a few popular nanomaterials with relatively well-understood properties, such as carbon or metal oxide nanostructures, or gold and silver nanoparticles (“The National Nanotechnology Initiative” 2008). While many of the basic properties of nanoparticles are well characterized, the unpredictable nature of nanoscale materials complicates the design of new nanotechnology, while leaving open the door for revolutionary developments.

1.2.3a Surface Area Properties

The most direct and obvious effect of shrinking a particle size into the nano region is the dramatic increase in specific surface area (SSA), the surface area per unit of mass of a substance (“IUPAC” 1997). This occurs due to the increase in surface-area-to-volume ratio of geometric objects as dimensions shrink, while density remains constant. Simple shapes, such as spheres, cylinders, or cubes, offer good approximations for the shapes of real particles. Therefore, the approximate ratio of surface-area-to-volume can be predicted using geometric formulas for surface area (SA) and volume (V) of a given shape. This is most conceptually useful when considering cubes and spheres, which involve only a single dimensional quantity involved in the respective formulae, as shown in table 1.

Table 1: Surface-area-to-volume ratios of simple geometric objects

Shape	Surface Area	Volume	$\frac{SA}{V}$
<div>Cube</div>	$6s^2$	s^3	$\frac{6}{s}$
<div>Sphere</div>	$4\pi r^2$	$\frac{4}{3}\pi r^3$	$\frac{3}{r}$

The presence of the dimensional quantity in the denominator results in the increase in the ratio SA/V as the value of that quantity decreases (reflecting smaller particle size). Nanoparticles involve extremely small dimensional sizes. This causes the ratio of surface-area-to-volume to increase enormously for a given mass of material. For spherical and cubic particles, the change in surface area is inversely proportional to the change in particle size, such that decreasing particle size from micron-sized to nano-sized may increase the surface area by orders of magnitude.

Behaviors of micro- and macro- scale objects are determined primarily by properties of the bulk material (Fernando 2009). This occurs because the fraction of atoms (or molecules) of a substance on the surface of the object is trivial compared to the fraction of in the bulk. The atoms on the surface of a particle form an interfacial layer which interacts with the particle's surroundings, contributing to surface-based properties. For a particle large enough to be seen by the naked eye, the fraction of atoms forming the interfacial layer may be a very small fraction of a percent (Fernando 2009). Nanoparticles, however, are small enough that the surface fraction is non-trivial, and most or all of the atoms may be able to form part of the interfacial layer. For example, a 10 x 10 atom particle consisting of atoms which form an interfacial layer one atom thick contains 36 atoms able to interact at the interface with other materials, so that 36% of the atoms exist at the interfacial layer, as shown in figure 1. However, in a 2x2 atom particle of the same substance, all 4 atoms, 100%, exist at the interface. When placed in the same chemical environment, they may behave very differently.

Figure 1: Smaller particles have a much higher portion of interfacial atoms (red).

1.2.3b Cluster Chemistry

Nanoparticles may exhibit size-dependent properties as a result of the changing fraction of atoms on the surface. Atoms on the surface of a particle behave differently

than atoms in the bulk, such that collective phenomena such as “solid” or “liquid” break down (Berry n.d.). The fundamental study of this type of phenomenon is known as cluster chemistry. Cluster chemistry is the study of particles consisting of approximately $5\text{-}10^5$ atoms (Mingos 1990). The term “cluster”, therefore, occasionally overlaps with the term “nanoparticle” in scientific literature (Schmid 2010). A classic example of breakdown in phenomena at small cluster sizes is found in magnetism. Ferromagnetism, the most commonly felt type of magnetism (for example, in refrigerator magnets), is a collective phenomenon which results from aligned electron spins throughout a bulk material. However, this phenomenon breaks down as cluster sizes get very small, and clusters (or nanoparticles) of a ferromagnetic material behave as superparamagnets instead (Kostakis 2010). In this way, many unique properties may be found in nanoparticles which are not found in conventional materials, opening the door for exotic applications.

1.2.4. Modern Nanoparticle Applications

Many applications of nanotechnology are ubiquitous with applications of nanoparticles, since many forms of nanotechnology use nanoparticles deposited on a surface or dispersed in some other medium or matrix, particularly polymeric materials (“History and Future” n.d.). The physical incorporation of nanoparticles into a particular technology may or may not pose a considerable challenge, or require modifications to existing techniques.

The first commercial nanocomposites were composites of nylon-6 and nanoclay. To make this material, a process was designed in which the nanoclay was combined with

the nylon-6 polymer *in-situ* during the polymerization process. While synthesis of nylon-6 was a well-established procedure, synthesis in the presence of nanoclay required significant effort due to the complicated interactions involved, including the difficulty in maintaining effective dispersion throughout the process (“Nanocomposites- A Little” 1999). This type of technique has become refined, however, and remains useful for producing a variety of nanoparticle-infused materials. For example, PMMA-grafted nanoclay has been synthesized using *in-situ* techniques for use as dental fillings (Atai 2009). The technique can also be used for such purposes as effective dispersion of silver nanoparticles throughout a wool matrix, as the resulting material has potential applications as an improved antibacterial fabric (Barani 2012).

A simpler approach to creating nanocomposites is by melt-mixing nanoparticles with a thermoplastic material (Bikiaris 2006). The thermoplastic is melted, and nanoparticles are mixed directly into the material by a combination of high temperature and high shear during mixing. This is a relatively simple brute-force way of making a composite, but only works for thermoplastics, and may be too aggressive for thermally-sensitive materials.

Solution-mixing is another option, in which all relevant materials are dissolved or dispersed in a common medium, allowing homogenous dispersion. When the dispersion medium is evaporated, the remaining material is a well-dispersed nanocomposite (Hussain 2006). While there are a number of disadvantages to this technique (particularly the necessary handling of the dispersion medium), it is particularly important in current nanotechnology applications because it is the method by which nanoparticles are incorporated into paints and coatings. The paints and coatings industry was one of the

earliest adopters of the use of nanoparticles for enhanced product performance, and continues to be one of the leaders in commercial application, as well as research and development (Khanna 2008). Nanoparticles produce a large improvement in the performance properties of protective coatings compared to microparticle additives. In addition, incorporation of nanoparticles is a relatively simple process, as it follows as a natural extension of the methods used to incorporate microparticles (including fillers and pigments). The effects of mechanical shear and dispersion stabilizing additives on dispersions are well-characterized phenomena crucial to the performance of even the most basic coatings or paints, and the same principles may be extended to aid in the stable dispersion of nanoparticles (Fernando 2009).

1.2.5. Safety Concerns Over Nanomaterials

One of the difficulties in bringing new nanotechnology into market is uncertainty over the safety of nanomaterials. Nanotoxicology is an emerging field of study concerned with the toxic effects of nanomaterials (“How Safe is Nano?” 2011). Researching nanotoxicology is an interdisciplinary effort, crossing the fields of physics, chemistry, biology, and others to consider the possible effects that nanomaterials might have on biological systems. Of particular concern is the enormous surface area of nanomaterials, which may invalidate assumptions of traditional dose-effect relationships due to much greater interfacial area between biological systems and the molecules at the surface of the nanomaterial (“Research Investigates” n.d.). In addition, since properties of nanoparticles change fundamentally with particle size, toxicity may increase or decrease with smaller particle sizes.

As nanotechnology becomes more prevalent, nanowaste processing is a significant area of research for the waste management industry (GWRI n.d.). One of the greatest human health risks occurs when toxic materials are not thoroughly extracted from waste streams, resulting in spillage into the environment. Effective removal of nanomaterials from waste streams is crucial to preventing accumulation of toxic nanomaterials in the environment, where they might end up being ingested by humans as they make their way back up the food chain (GWRI n.d.). However, much of this is speculation, as the true health risks of many nanomaterials are unknown, and constant new development of nanotechnology means new risks will arise over time (“Nanoparticles” 2012).

2. Organized 1D Nanostructures

2.1. Background

A natural extension of the bulk use of nanoparticles in composites is controlling the nanostructures they produce. While individual nanoparticles themselves are useful materials due to their unusual behavior, further novel device development will be enabled with production of ordered assemblies into a variety of structures required for advanced function.

2.1.1. Organized Nanoparticle Assemblies

When referring to nanomaterials, different types of assemblies may be distinguished based on the dimensions of their assembly: 0D (individual nanoparticles), 1D (nanowires and similar), 2D (layers or films), or 3D (large networks). Trends in research tend to focus on either individual nanoparticles (0D) or assemblies of multiple (1D, 2D, 3D) (Tang 2005). Creating organized nanoscale assemblies provides ample opportunity for new technological development, by shrinking device sizes and taking advantage of the intrinsic properties of nanomaterials (Pillai 2009). For example, nanoelectronics may enable the creation of devices with higher speeds, higher information storage density, and less power consumption (Vogel 2012). Other applications include photovoltaics, chemical sensors, and more effective catalysts.

Because individual nanoparticles are 0D, creating 1D assemblies of nanoparticles is difficult due to the necessity of creating an anisotropic assembly from an isotropic building block. Due to the necessity of fabricating these structures for creation of several novel devices, considerable research has uncovered several techniques for synthesizing

1D systems (Tang 2005). There are two categories of preparation methods for 1D nanoparticle assemblies- template methods, and non-template methods.

Linear templates provide a straightforward approach to synthesizing 1D assemblies. An existing template molecule or design is created, and then the nanoparticle structure is grown along the template material. Linear polyelectrolytes provide an excellent method of producing metal or semiconductor NP assemblies (Tang 2005). Metal ions can become adsorbed along the charged surface of the polyelectrolyte. When the ions are reduced or chemically combined, nanoparticle growth occurs in a linear fashion along the polymer backbone. Biomolecules, such as DNA, RNA, or amino acid sequences, may be useful for similar reasons. An advantage of a biomolecular template is the wide variety of techniques useful for manipulating such systems, as developed by the biochemical and biological sciences over the course of the last century. Carbon nanotubes and inorganic nanowires also provide excellent templates, and provide the additional opportunity to create hybrid nanomaterials.

Non-template based methods for 1D nanoparticle assembly revolve around exploitation of intrinsic anisotropy of certain types of interparticle interactions (Tang 2005). Alignment of nanoparticles into 1D chains as a result of magnetic dipoles is well known in nature, having been observed in bacteria, and the phenomenon can be reproduced in lab to produce similar results. Electric dipoles may also be used to generate 1D structures, particularly in nanoparticles of semiconducting materials.

One of the greatest difficulties in producing new technology is creating cost-efficient production methods to bring products to a large enough commercial market. While many techniques may be useful for creating laboratory prototypes, production

methods must be robust, reliable, and rapid, and preferably simple. One of the simplest 1D assembly preparation methods reported in literature is based on shear-induced ordering of colloidal systems (Brickweg 2006). If this process could be refined, a number of large scale manufacturing techniques, such as roll coating, may be adopted from the coatings industry with minimal modification.

2.1.2. Shear in Coating Applications

In fluid rheology, shear refers one of the ways stress is applied to a fluid to cause a rate of deformation. The ratio of stress to rate defines the viscosity, or resistance to flow. Shear rate is calculated as a velocity gradient within a flowing material, and is an important parameter to control in the application of thin films through liquid-casting methods (Fernando 2012).

Figure 2: Schematic illustration of shear occurring in an object.

Shear rate between two parallel plates is defined as the velocity gradient, calculated by dividing the difference in flow velocities between the two plates by the distance between them: $\text{Shear rate} = \frac{V_1 - V_2}{d}$. Shear rate is an important parameter in coating science because flow behavior strongly influences many processes from

formulation to application. Many coating formulations are complex non-Newtonian fluids, in which the shear stress is not a linear function of shear rate. In other words, the viscosity of the fluid is dependent on the shear rate. This is intentional in coatings formulations. For example, they must flow rapidly at moderate to high shear rates to ease the application process, but must not drip down the side of the substrate once applied (Fernando 2012). Brushing and rolling are examples of moderate shear rate application methods, while use of a spray gun produces very high shear rate.

Because of the number of variables involved in studying a coating formulation, a consistent method of producing test coatings of a constant thickness is necessary for routine laboratory analysis. A common method used for preparation of test coatings is through the use of a drawdown bar: a precisely machined block of metal designed to prepare a coating of a specific thickness on a test substrate.

Figure 3: Schematic drawing of a drawdown bar.

While there are some variants on the technique (such as using a wire coil), the use of a drawdown bar to prepare a drawdown is the most straightforward and simple method. Because use of the bar provides coatings with the same thickness across all samples, the shear rate can be controlled simply by controlling the speed that the bar moves as it applies the coating.

Shearing forces during spraying applications are much more complex and chaotic than during drawdown applications. During spraying, the coating formulation is atomized into tiny droplets, which then land on the substrate. While a relationship between rheological parameters and sprayability of a fluid can be quantified, evaluation of secondary effects through empirical research is necessary to correlate other behaviors (Elliott 2007).

2.2. Formation of 1D Strings of Alumina and Silica Nanoparticles in a Coating Formulation Using Shear

2.2.1. Background

One of the greatest difficulties in developing a new technology is to take a working prototype and redesign it to be mass produced. Theoretical demonstrations of working technologies exist long before commercial products are brought to market. One-dimensional assemblies of nanoparticles are a crucial component of many theoretically viable devices which may signal the beginning of a new technological revolution (Tang 2005). However, assembling short strings of nanoparticles imprecisely in a laboratory sample is a long way from mass-production of precision-engineered devices. Exploration of new techniques to generate 1D strings, and examination of the fundamental forces involved, are key first steps to this new generation of nanotechnology.

Previous efforts to create 1D assemblies of nanoparticles using simple, scalable methods have revealed that both simple shear and low-intensity spraying shear may be sufficient in some systems to form strings of nanoparticles oriented along the shear direction (Brickweg 2006). If this method could be refined to form these strings in abundance, it would provide a simple method for generating anisotropic 1D nanoarrays.

2.2.2. Methods and Materials

Joncryl 910 acrylic polyol (BASF), Tinuvin 292 UV stabilizer (Ciba), Tinuvin 1130 UV stabilizer (Ciba), BYK 315 surfactant (BYK), Desmodur N3300A isocyanate (Bayer), silica nanoparticles (BYK 3650, BYK, particle size ~25 nm), and alumina nanoparticles (BYK 3610, BYK, particle size ~25nm) were obtained from respective vendors and used as received. Methyl amyl ketone, p-xylene, n-pentyl propionate, and n-butyl acetate were obtained from Sigma Aldrich.

All coatings were prepared using the formulation provided in table 2. To obtain desired loadings of nanoparticles, 4.0g silica nanoparticles (BYK 3650) or 4.0g alumina nanoparticles (BYK 3610) were added to part A of the formulation. Parts A and B were both mixed thoroughly to ensure homogenous dispersion of all chemicals, and then mixed together to begin the crosslinking reaction of the 2K polyurethane. An induction time of 30 minutes was provided to allow the reaction to proceed to a point to ensure optimal coating performance.

Table 2: Polyurethane formulation used for 1D nanoparticle assemblies.

Part A:	Joncryl 910	47.02
	methyl amyl ketone	20.72
	p-xylene	6.48
	n-pentyl propionate	4.72
	Tinuvin 292	0.48
	Tinuvin 1130	0.32
	BYK 315	0.24
	Part A Total	80.0g
Part B:	Desmodur N3300A	10.9
	n-butyl acetate	9.1
	Part B Total	20g
	Formulation Total	100g

Coatings were applied onto clean glass microscope slides using a 75 μ m cubic drawdown applicator. To study the effect of simple shear rate on the generation of particle string formation, drawdowns were prepared using one of three qualitatively determined shear rates: slow (1.3-4 s⁻¹), medium (13-27 s⁻¹), and fast (>130 s⁻¹).

Air brush films were prepared using a Badger™ 200NH air brush, using a partially depleted can of Badger Propel 15oz as the air source. Coating was applied to glass microscope slides hung vertically within a small spray booth, in a vertical motion, with up to 15 layers of coating applied.

Spray gun films were prepared using a Binks™ Mach 1 SL HVLP spray gun with a 93P air nozzle. A Binks™ Model 80 2 quart pressure pot was used as the reservoir, with a fluid pressure of 40 psi. Coatings were applied using an air atomizing pressure of 6 psi and a flat fan spray pattern. The fluid inlet valve was tuned to optimize the spraying conditions to produce a smooth coating. The spraying was performed such that the flat fan spread vertically, while the gun was moved horizontally back and forth over sample substrates. All coatings were cured at 70°C for 30 minutes, and then allowed to finish drying overnight.

Optical microscopy was performed on a Leica DM 2500 P polarizing light microscope. Images were processed in the Leica Application Suite™ V4.0. Atomic force microscopy was performed on an Asylum Research MFD-3D-SA™ instrument in tapping mode using Asylum AC 240 tips. It was connected to an Asylum Research Molecular Force Probe 300 Controller and noise was dampened by an Asylum TS 150 isolation system. Force and gain settings were varied to produce optimal imaging conditions. Data was analyzed using Asylum Igor Pro 6.22A software.

2.3. Results

2.3.1. Optical Microscopy

Figure 4: Optical microscope image of a silica nanoparticle infused polyurethane coating under 20x magnification prepared as a 5 mil drawdown. Lines are parallel to the direction of shear.

The use of a polarizing light microscope greatly simplified the process of finding nanoparticle arrays on the surface of the prepared coatings. Figure 4 is provided as a representative image demonstrating features visible at 20x magnification, which proved useful for determining the locations of nanofeatures on the coating surface. At a 90° polarization angle, the polyurethane transmits very little light, allowing areas of the film containing visible features to stand out as white spots on the dark background. These spots are believed to consist of the polysiloxane dispersant used in the nanoparticle solution provided by BYK (for both alumina and silica particles), which became dislodged under certain shear conditions. Thus, in areas of the film in which dispersant has formed 1D lines on the microscopic scale, nanoparticles stripped of dispersant form similar lines on the nanoscopic scale.

Evidence that the microscopic features are polysiloxane dispersant is in their apparent volatility. Sections of each slide with abundant microfeatures were marked for future reference. However, subsequent analysis within the marked regions showed no evidence of microfeatures, implying that polysiloxane droplets volatilized over time.

Figure 5: Optical microscope image of an alumina nanoparticle infused polyurethane film as prepared by a) airbrush method at 10x magnification b) spray gun method at 20x magnification.

In comparing the formation of nanoparticle lines in coatings prepared by airbrush vs. spray gun method, the most significant feature is the abundance of lines in the airbrush method compared to the spray gun. Under 10x magnification, a large abundance of lines was observed (figure 2a), filling the entire field of view in some areas of the sample. In contrast, the spray gun produced extremely few visible lines, with only a single highly distinct line being visible given reasonable effort in searching. While this might seem counterintuitive to the hypothesis that the microscopic features are beads of polysiloxane dispersant forcibly removed from nanoparticles under high shear forces, it suggests that the nature of the spraying conditions using the spray gun might be harsh enough that the dispersant is not able to aggregate into features visible by optical

microscopy. In both films, the direction of the lines formed occurred in the direction the application device was moved while applying the coating: top to bottom in (a), left to right in (b).

It is not believed that the absence of visible features under polarizing light is necessarily indicative of failure to generate 1D strings of nanoparticles. However, it is believed that regions of the coating surface which contain microscopic features will contain a higher abundance of nanoscopic features compared to regions of the coating which do not contain them.

2.3.2. Atomic Force Microscopy

Figure 6: a) amplitude image and b) phase image of a polyurethane containing no nanoparticles, as prepared by the drawdown method. c) amplitude image and d) phase image of the same formulation, as prepared by the spray gun method.

Analysis by AFM to determine the effects of drawdown and spray gun methods was complicated by the difficulty in determining identity of nanoscale features on the surface of the coatings, based on the comparisons of virgin polyurethane coatings (figure 3) with those infused with nanoparticles (figure 4). Coatings not containing nanoparticles showed many visible features rather than a simple flat surface, some of which were aligned in the same way that nanoparticle strings were expected to form. In addition, some coatings containing nanoparticles did not show any features resembling nanoparticle strings or parallel lines. It is most likely that the jagged features observed in coatings not containing nanoparticle are particles of dust or imperfections in the surface of the coating, as they do not appear to be homogenous in size. Thus, it is considered

Figure 7: a) amplitude image and b) phase image for a silica nanoparticle infused polyurethane prepared by the drawdown method. c) amplitude image and d) phase image of the same formulation, prepared by the spray gun method. Shear direction is left to right.

most likely that the lines observed in nanoparticle-infused coatings to be nanoparticles, and that instances of non-nanoparticle surface features could be distinguished from particle strings with reasonable accuracy.

Figure 8: a) amplitude image and b) phase image of alumina nanoparticle infused polyurethane, prepared as a slow drawdown. c) amplitude image and d) phase image of the same polyurethane prepared as a fast drawdown. e) zoomed in amplitude image and f) zoomed in phase image for the fast drawdown. Shear direction is left to right.

With silica nanoparticles, generation of 1D strings was limited, both in the spray and drawdown application methods. While the drawdown method produced some visible

strings, the coatings prepared with the spray gun method did not show any features resembling nanoparticle arrays.

Figure 9: a) amplitude image and b) phase image of alumina nanoparticle infused polyurethane prepared by spray gun method. Spray direction top to bottom. c) amplitude image and d) phase image of the same formulation prepared by air brush method. e) zoomed amplitude image and f) zoomed phase image. Spray direction left to right.

Analysis of alumina nanoparticle infused coatings showed a much greater abundance of 1D string formation. At slow drawdown speeds (shear rate $1\text{--}4\text{ s}^{-1}$), very

little is seen in either the phase or amplitude images. While some vague evidence in the phase image suggests presence of nanoparticles slightly deeper within the coating, it is likely that this is merely a product of scanning conditions. The fast drawdown, however, shows extremely clear abundance of features on the coating surface. Presumably, the larger spheres present in the images are polysiloxane dispersant detached from the nanoparticles, while the smaller spheres are the nanoparticles themselves. Their orientation precisely parallel to the shear direction leaves little doubt about successful generation of 1D nanoparticle arrays.

Spray test results, using both the commercial HVLP spray gun and hobby shop air brush, showed that spraying conditions dramatically affect nanoparticle orientation. Coatings prepared using the spray gun showed very few organized arrangements, and those found were perpendicular with respect to the expected direction. It was expected that in the spray gun coatings, shear caused by forcing the spray pattern into a flat fan would produce shearing forces parallel to the fan direction. The direction of the movement of the spray gun over the sample substrate was perpendicular to the fan direction, as it was not expected that this would be a significant variable. However, these results show particle growth in lines parallel to the movement of the spray gun, not the spray pattern. Thus, it appears that the movement direction of the spray gun is the relevant variable.

With the air brush method, line formation was extremely abundant, with lines approximately parallel to the spray direction. It is assumed that the slight diagonal tilt is due to slight imprecision in spraying technique. Figures 9e and 9f show that the lines are nearly perfectly straight under higher magnification. In addition, particle size is uniform,

providing further evidence that these features are successfully formed 1D strings of alumina particles. An interesting observation is the lack of dispersant droplets visible in the image with the nanoparticles. One possibility is that the separation of dispersant from nanoparticles was more complete than in the drawdown method. As a result, dispersant droplets might not be visible in the same vicinity as nanoparticle features, or may not be visible at all.

A number of differences between the spray conditions for the airbrush and spray gun tests may have contributed to these results. The results of the spray gun test suggest that in addition to minimum shear conditions required to produce nanoparticle alignment, an additional requirement is either remaining below a certain maximum shear, or maintaining a certain degree of order during the shear. In other words, the greater magnitude of forces in the HVLP spray gun may have caused a much greater degree of chaos during the application, preventing nanoparticles from being able to come together in the final coating.

Another difference was in the spray pattern used to produce test samples. While the air brush was only capable of a full cone spray, the spray gun was used to produce a flat fan spray pattern. It was expected that the relevant shear forces would occur in the direction of the fan spray, though it turned out that the direction the spray gun was moved during application, which was different from the fan spray orientation, was more relevant.

The pressure was significantly different for the spray gun and air brush. The spray gun controlled spraying conditions through both air pressure (used to atomize the fluid) and fluid pressure. Both of these settings are tunable to produce different spraying

conditions. In the air brush, however, pressure is provided by a pressurized canister. While the air flow rate can be tuned, it is not quantitative, and there is no method for measuring precise air pressure. In addition, the pressurized canister stores pressure in the condensed state. Thus, the rapid expansion of gas leaving the canister produces significant cooling, lowering the air pressure available to the air brush. There is also no compensation for the natural drop in pressure as the canister becomes empty.

These four factors (spray pattern, application direction, atomizing pressure, fluid pressure) may all influence the final ability of nanoparticles to form 1D strings. It is hypothesized that the formation of the nanoparticle strings occurs when the polysiloxane dispersant used on the nanoparticles is forcibly removed under certain shear conditions. Based on the lack of line formation under the harsh spray conditions used in the spray gun test, it seems formation of 1D strings requires shear conditions to reside within a certain window, rather than passing a critical threshold. It might also be possible that incomplete removal of dispersant from nanoparticles is necessary for array formation in this system. The harsh spray conditions used by the spray gun might have more thoroughly removed the dispersant from the nanoparticle, preventing array formation, and promoting aggregation deep within the coating instead.

The methods used to analyze line formation leave open the possibility that limitations in these methods prevented optimal observation of generated nanostructures. Experimental methodology dictated a search for nanoparticle string formation only in areas of the coating which contained alignment of polysiloxane dispersant droplets visible under polarizing light. A more thorough search for nanoparticle formation might reveal a significant number of features not observed in our results. However, the

difficulty of broadening the search for formations of dispersant or nanoparticle in the film during AFM analysis made this approach impractical. Thus, our results hinge on the assumption that reasonable time and effort invested into searching for nanoarrays resulted in typical observations, and that unusual luck in finding or failing to find features did not compromise our results.

One difficulty in interpreting AFM results of this nature is in distinguishing nanoparticles from small dust particles present on the surface of the coating. Figures 6 and 7 show coatings with similar features, though those in figure 6 contain no nanoparticles. Subtle differences in appearance of these particles suggest that the particles in figure 7 are nanoparticles: they are consistent in size, aligned closer to parallel along the shear direction, and more spherical in nature. However, the potential to mistake aligned dust particles for nanoparticles, or non-aligned nanoparticles for dust particles, partially hinders ability to draw conclusions from this analysis. Thus, a conclusion that this technique produced abundant generation of nanoparticles would require that many strings of nanoparticles be abundantly and clearly visible on the surface, such that their observation could not possibly be a statistical anomaly. However, this is not observed.

It is noteworthy that this AFM analysis is only capable of determining nanoparticle arrangements present on the surface of the coating. It is very possible that more distinct or more abundant arrangements exist deeper in the coating. It is also possible that distinct arrangements of nanoparticles only occur in extremely close proximity to arrangement of dispersant droplets. If this were the case, then nanoparticle strings would only be detected if the observation window happened to be in precisely the right location. The scan window on the AFM instrument could only be controlled within

a 40 μ m by 40 μ m area. Thus, it is possible that the coating surface might not contain an even distribution of nanoparticle strings, and other areas of the coating might contain them in high abundance.

2.4. Conclusions

Generation of ordered one-dimensional arrays of nanoparticles is much simpler with alumina than silica, though both show evidence of array formation. Very low shear rates performed with a cubic drawdown applicator result in little if any formation of aligned nanoparticles. However, a high shear rate produces nanoparticle alignment in abundance. Differences in spraying conditions produce dramatic differences in the formation of nanoparticle arrays in the coating: air pressure, fluid pressure, spray pattern, and application direction all may affect the final generation of 1D strings. Difficulties in finding strings under optical microscopy imply that a more efficient means of generating consistent, abundant one-dimensional arrays of nanoparticles is necessary. Further characterization, including properties of the generated films, will lead to ambiguous results until the optimal 1D array-forming conditions are found. Fortunately, a large number of variables remain tunable for optimization: shear forces, particle loading, particle size, formulation chemistry, and spraying conditions are all variables which may be tested in the search for greater particle formation.

2.4.1. Safety Concerns

The original intention of this research was to explore the effect of spraying conditions on generation of 1D arrays. However, it quickly became obvious that the

facilities available were not sufficient to provide a safe spraying environment. Attempts to contain polyurethane vapor by performing spraying applications within a fume hood, with the aid of a converted cardboard box, proved insufficient, as solvent odor was still clearly detectable. The health hazards posed by isocyanate fumes, including potentially irreversible lung damage, were deemed too high of a risk to continue activities. Research was therefore abruptly terminated. The difficulties encountered during this research, though important to document, do not seem to be significant hurdles given appropriate time to perform quality research.

3. Developing a Learning Module for Education on Nanowaste

3.1. Background

As nanotechnology becomes more widespread, increasing amounts of waste material are generated containing nanomaterials. Difficulties in processing these materials using conventional methods means that new techniques must be developed in order to meet challenges provided by ever-increasing amounts of nanomaterials emerging in waste streams. Not only must nanomaterials themselves be understood, but so too must the technologies that incorporate them, in order to successfully develop nanowaste solutions.

3.1.1. Dispersions

Successfully incorporating nanoparticles into bulk composite materials depends on successful and thorough dispersion of particles throughout the encompassing matrix. Dispersions of particles are often unstable, resulting in aggregation behavior and compromising the integrity of the resulting composite material (Mackay 2006). As a result, many different strategies for successful dispersion of nanomaterials into a variety of dispersion media are in use for commercial applications.

Dispersions of nanomaterials in coatings formulations are excellent examples of the application of methods involving mechanical and chemical dispersion of particles. Particle dispersion in coatings is a well-studied phenomenon, due to the effect of degree of dispersion of inorganic pigments on the coating performance. Incomplete dispersion may result in a coating with reduced color, gloss, or altered rheological properties (“Dispersing Process” n.d.).

The process of dispersing a nanoparticle in a dispersion medium (or resin solution) for a coating may be broken down into three distinct steps (“Dispersing Process” n.d.). In the first step, particle wetting, particles are introduced to the dispersion medium and the air/particle interface is removed, and replaced by the liquid/particle interface. Incomplete wetting can be severely detrimental to the performance of a nanocomposite. For example, reduced interfacial area between nanoparticle and matrix in the applied film can inhibit the mechanical properties of the composite, and the resulting air voids can compromise visual appearance. The second step is the grinding stage, in which particles are de-aggregated by the application of significant mechanical shearing forces. Aggregation of individual particles is a primary process, thus significant amounts of energy must be applied to the system to disrupt them. The third step is stabilization of the deaggregated particles with chemical dispersing agents (dispersants). Without the use of some agent to stabilize the dispersion, individual particles will spontaneously re-flocculate. Thus, the use of chemical dispersants is an extremely important step in the formulation process (“Dispersing Process” n.d.).

3.1.2. Dispersants

Chemical dispersants are additives which aid in the dispersion of insoluble matter, preventing aggregation and settling (Mackay 2006). Most dispersants are surfactant molecules- amphipathic molecules containing both polar and nonpolar portions, allowing them to interact favorably with both phases of an incompatible system. They find widespread use in a variety of industries, where they are vital components of operating processes or of formulated products. For example, both automotive lubricating oils and

fuel use dispersants to prevent buildup of deposits which may harm key engine parts (“Succinimide Dispersants” 2013). In oil drilling, they are used to disperse solid particles or create stable oil-in-water or water-in-oil emulsions. The surface coatings industry, serving again as an excellent case study, uses dispersants to stabilize the addition of pigment particles and fillers into the dispersion medium. In the coatings industry, the stabilization of dispersions may be accomplished through either steric or electrostatic forces (“Dispersing Process” n.d.).

Pigment particles dispersed in liquid naturally develop charges along the particle surface. Because like-charges repel, this feature can be exploited to create interparticle repulsion great enough to create a stable dispersion. The naturally occurring charges are not sufficient, so electrostatic dispersion additives are used to create an electrical double-layer around the particle surface (“Dispersing Process” n.d.). The thicker the double layer, the greater the repulsion, and thus the more stable the dispersion becomes. Additives used for this purpose are commonly polyelectrolytes, as they contain many like charges in close proximity, and are simple to synthesize.

Figure 10: Electric double layer formed from electrostatic stabilization of dispersions.

Steric dispersion additives tend to be more structurally similar to the classical image of a surfactant, with a head group interacting with the particle, and a tail group which extends into the dispersion medium, and must be fully solvated therein (“Dispersing Process” n.d.). The solvated tails create repulsive forces through a crowding effect: it is extremely entropically unfavorable for many tails of these molecules to attempt to occupy a very small space, as would happen if particles were to aggregate together.

3.2. Global Waste Research Institute (GWRI)

One of the most overlooked problems of the 21st century is the management of waste generated by both industrial byproducts as well as consumer goods (GWRI n.d.). The environmental impact of poor waste management strategies can be devastating to local ecosystems. In addition, failure to conserve and recycle non-renewable resources may have severe long-term ramifications. One of the greatest difficulties in generating new solutions is that strategies for managing waste must keep pace with the development of new technologies, such as use of nanomaterials. Research at both the industrial and academic level is necessary to produce economically and environmentally viable methods of managing the vast amounts of waste produced by modern life. To explore solutions related to waste and industrial byproducts, faculty at Cal Poly have founded the Global Waste Research Institute (GWRI) to tackle the unique issues that 21st century waste management present.

The GWRI is a multidisciplinary collaboration between academic researchers and a number of industrial partners. It is centered at Cal Poly, with most associated faculty being members of the Civil and Environmental Engineering Department. However, a number of faculty from other departments are involved, particularly as issues related to management of waste from specific industries require collaborative input. Departments represented by affiliated faculty include the Orfalea College of Business, Chemistry and Biochemistry, Civil and Environmental Engineering, and Physics.

One of the keys to the success of Cal Poly in producing cutting-edge research and technically proficient graduates is maintaining collaboration with industrial contacts. The GWRI seeks to continue this tradition by establishing connections with industrial partners even from its inception. Seed money for creation of the GWRI was provided by Waste Connections, Inc., a national solid waste management company operating in 27 states across the country. In addition, relations with over a dozen partner organizations were established prior to the creation of the institute. These partnerships exist not only to collaborate on research projects, but also to educate through use of partners' facilities, and collaborative workshops and seminars.

3.2.1. Research and Education

Two of the primary objectives for the GWRI are to contribute to research and education in the field of waste management. Changes in industrial practices and technologies across a variety of sectors in recent decades have changed the way waste is handled, and development of new technologies for handling that waste is crucial for satisfying demand. Common forms of waste include not only municipal solid waste, but

also hazardous materials such as medical or radioactive waste, which require specialized management procedures due to the danger they pose to the environment or to waste handlers, and the expense of dealing with difficult materials. Increased demand for sustainable technologies has also promoted recycling as an alternative to permanent disposal. This provides an additional set of challenges for extracting reusable materials from waste using economic methods. The GWRI maintains interest across a variety of specific focus areas, ranging from fundamental understanding of processes in landfills, to developing preventative solutions for futuristic technologies. A list of thematic research areas, as listed in the original proposal for creation of the GWRI at Cal Pol, is shown in table 3.

Table 3: List of specific research areas of GWRI (Hanson 2008).

- Assessment of trends for generation, recovery, recycling, and disposal of existing, new, and emerging wastes and byproducts.
- Development of methodologies for recovery, recycling, and management of specialized waste streams such as e-wastes, scrap tires, agricultural wastes, military wastes, and high moisture content wastes
- Identification, assessment, and technological development of processes for handling of wastes and byproducts associated with emerging industries such as biotechnology, nanotechnology, and alternative energy.
- Assessment of existing approaches and development of new applications and technologies for use of recyclable materials and byproducts.
- Development of management strategies and engineering/scientific solutions for wastes at various levels of governance.
- Investigation and development of energy recovery and conversion technologies for wastes.
- Investigation of long-term and field-scale performance and effectiveness of existing waste containment systems.

- Investigation of impacts of containment facilities on the global environment including effects on air quality as well as carbon balance in the environment.
- Development of new approaches for management of legacy wastes.
- Development of innovative materials and systems for waste treatment and containment.
- Numerical modeling and model verification of processes and systems related to optimization of waste treatment, conversion, and containment.
- Investigation of post-closure no maintenance (“walk-away”) and perpetual containment systems.
- Development of versatile (e.g., inert, low impact, mobile, low cost) alternatives for diverse waste management and disposal needs (e.g., extreme climates, military activities, remote locations, environmentally sensitive areas, underdeveloped regions).
- Development of specific designs for waste management solutions for developing countries.
- Development of an inventory of instrumented field sites with industrial partners for assessment of various aspects of management of wastes and byproducts.
- Development of manufacturing and processing strategies to minimize waste production.
- Conducting life-cycle assessments for a wide variety of products with regard to environmental impact and resource utilization.
- Investigation of financial impacts associated with reduction, recycling, and reuse of wastes and byproducts on carbon credits trading.
- Investigation of the economic aspects of alternative containment system designs.
- Market development for recycled and reused wastes and byproducts.

Waste management is a specialized subfield of engineering. As a result, issues related to waste and byproduct disposal do not get significant attention outside of specialized coursework. With the increasing complexity of managing these wastes, it is becoming clear that waste management is becoming a subject deserving of study at the academic level, to provide students with an educational background to produce technically proficient graduates. This applies not only at the engineering level, where new waste management technologies must be developed, but also at the management level, where understanding of an increasingly complex world is vital to maintaining effective business practices. To address this academic void, the GWRI is developing coursework and educational initiatives to serve students at Cal Poly, and produce and exchange educational material with academic and industrial institutions around the world at all levels of education. Coursework from several different departments covers issues from many different angles. A list of thematic education areas, as listed in the original proposal for creation of the GWRI at Cal Poly, is shown in table 4.

Table 4: List of thematic education areas of GWRI (Hanson, 2008)

- Facilitating development of extensive course programs, degree alternatives, and research opportunities at Cal Poly in engineered, scientific, and economic management of wastes and byproducts for undergraduate and graduate students.
- Establishment of industry partnerships to develop specific solutions to waste and byproduct related problems using undergraduate and graduate students in a project based learning environment.
- Development of workshops, seminars, training courses at various levels of technical competency for practitioners, regulators, and policy makers.
- Development of course modules for K-12 and undergraduate and graduate education.

- Development of teaching aids for K-12 educators and university professors.
- Development of outreach materials for the general public that can be used by various constituents including regulators, waste management industry, consultants, as well as educational institutions.
- Provision of learning opportunities for developing multidisciplinary solutions to global waste management problems.
- Development of reports, manuscripts, theses, guidelines, standards, databases, and web-based materials for technology transfer.

3.2.2. Commissioning of a Learning Module on Nanomaterials

One issue which demands immediate attention is in the management of nanowaste. With nanotechnology gaining a greater foothold in the commercial market with new applications and products, management of nanomaterials presents a set of challenges distinct from classical materials. For example, current filtering systems designed for water purification cannot effectively filter nanoparticles. Developing solutions to such problems requires fundamental understanding of nanomaterials and how they are used in current technologies. For nanomaterials, understanding size-related properties and dispersion of nanoparticles are two key concepts which much be understood before solutions can be developed. The advantage of a multidisciplinary approach to education here becomes obvious, allowing departments with significant knowledge related to these issues to handle education of this subject, ensuring efficacy and accuracy of material.

Figure 11: Infographic describing the logic path connecting waste management with fundamental understanding of surface area.

For the issue of nanomaterials, Polymers and Coatings program at Cal Poly has an excellent academic background in properties and use of nanoparticles in coatings formulations. The protective coatings industry makes extensive use of both nanoparticles and micron-sized pigment particles, providing excellent opportunity to compare conventional and nano- materials.

The Polymers and Coatings program was therefore commissioned by the GWRI to produce a learning module for fundamental understanding of the significance of surface area in the context of nanomaterials. This was designated to be done through the design of an experimental demonstration, presented to students through a narrated video presentation.

3.3. Design Considerations for Laboratory Demonstration

Drawing on expertise to develop the educational module, it was decided that the best method for conveying the significance of the surface area of nanomaterials was to design a demonstration using one of the most common techniques in coatings science: dispersion of inorganic matter in aqueous media. For this task, it was decided that nanosized and pigment grade titanium dioxide (TiO₂) would be compared side by side,

both qualitatively and quantitatively. TiO_2 is widely used in the paints and coatings industry. It is the most common white pigment, and has excellent hiding power, allowing a coating to hide the surface of the substrate it is applied over. As a result, it is used to some extent in nearly every opaque coating formulation. It is thus an excellent choice of material to use for purposes of maintaining real-world relevance in a laboratory demonstration. Each grade of TiO_2 would be weighed into an empty beaker, and mixed by hand with a sufficient quantity of water. Chemical dispersant would then be added in amounts to elicit a desired change in viscosity. The differences in surface area would be probed by comparing the amount of dispersant required to produce equivalent reductions in slurry viscosity, measured by a laboratory- grade rheometer. Specific parameters would be determined experimentally, such that the final demonstration satisfied a number of design criteria to maximize the effectiveness of the learning module in educating students.

3.3.1. Simplicity

As the learning module was intended for education at the most fundamental level of the subject, simplicity of the resulting demonstration was of the utmost importance for effectively communicating desired concepts to students. So that the demonstration may be repeated in laboratories as an educational tool, minimization of required laboratory skills was desired so that students of all levels of proficiency in chemistry could participate individually. In the event that a single demonstration were to be performed by a professor or teacher's assistant in front of a group of students, minimizing experimental complexity ensures that the demonstration can be seamlessly incorporated into existing

educational structures, eliminating the need for extensive preparation of equipment or reagents. This ensures that the chance of experimental failure due to insufficient preparation or random factors is essentially nil.

The experiment must also be conceptually simple. While many excellent examples of the unique effects of nanoparticles exist, many of them are too complex for new students to appreciate. For example, while the effect of nanoparticle loading on glass transition (T_g) of a polymer nanocomposite may be of significant fundamental and practical value, a student with no background in nanomaterials or polymer science will likely not understand or care about the significance. In contrast, presentation of information on brand-new subjects should begin with the simplest concepts, and make use of simplifying assumptions to allow students to rapidly grasp the new material. Complexities, specific instances, and caveats can be introduced once the basic concepts are well understood. Otherwise, educators run the risk of alienating students, to the detriment of the entire academic system.

Use of a dispersion of TiO_2 in water as an educational tool solves both of these issues. First, by creating a demonstration that requires only the most basic pouring and measuring skills, it is ensured that nearly all students should be able to participate. In fact, even basic experience cooking is sufficient to allow students to flawlessly execute this demonstration. In addition, the use of only three different materials (water, TiO_2 , and chemical dispersant) in a physical mixture maximizes robustness of the experiment. Even if students do not directly participate in the experiment, the simplicity of the procedure ensures that they can clearly understand each step performed by an instructor, and simultaneously ensures conceptual simplicity. As mixture of powder with water is an

event with which most students will have had some sort of prior experience, they will be able to rapidly associate their old experience with the process of dispersing nanomaterials in water.

The use of a particle dispersion offers the additional benefit of scalability of both size and complexity of the experiment. Dispersion can occur with small bench-top samples or large batches, depending on the specific needs or available equipment of the laboratory. The complexity of the experiment can be increased according to the depth of analysis to be performed, including the materials used and types of analyses performed, according to the specific needs of the students. This potentially allows the experiment to range from a 5 minute demonstration up to a multi-day experiment in which students prepare samples, collect data, and write a comprehensive report.

3.3.2. Clarity of Results

The conceptual simplicity of the experiment ties into the necessity of producing an experiment with unambiguous results. For example, while small increases in certain properties of composites might have significant practical implications, students not familiar with typical performance of conventional composites or improvements via addition of nanoparticles might not fully appreciate the property enhancing effects. For a simple demonstration, the effect of particle size should be visually obvious from casual observation, so that students not familiar with the system will clearly notice differences between nano and micro sized materials.

A recent (and amusing) experiment by Harvard researchers tested the observation skills of trained radiologists, using modified image scans which included a small but

noticeable image of a man in a gorilla suit. While radiologists are well-known for being able to spot extremely small details which might have medical significance, it was discovered that 83% of radiologists did not notice the gorilla image. This is known as “inattention blindness”, and the same phenomenon might prevent students from being adequately educated in the event that only subtle differences are used to illustrate a scientific point, because they are not trained to look for those specific differences.

The change in both the visual appearance and viscous response of pigment slurries is extremely dramatic with addition of chemical dispersant. The slurry transforms from a thick goop into a runny fluid with addition of sufficient dispersant. Because the specific surface area of micro- and nano- materials is so different, conditions which turn a microparticle slurry into a runny fluid will hardly influence the nanoparticle slurry- an effect that is obvious both by casual observation, and can be measured by rheological data.

3.3.3. Time Investment

Preventing the experiment from requiring significant amounts of time or waiting periods improves efficiency of time spent in laboratory settings, and prevents lack of student interest due to boredom. While this is unavoidable with certain analysis techniques, the effect can be minimized in instructional settings through careful consideration of the experimental design.

The experiment involving analysis of dispersions can be broken into two distinct phases for instructional purposes: sample preparation, and analysis. Sample preparation is rapid, allowing two different samples to be prepared simultaneously and compared,

uninterrupted, in as little as approximately 2 minutes, while verbal explanation of processes occurring in each step can allow the sample preparation period to be stretched into a 10-15 minute period full of relevant information and visual aids. Because the change in appearance of the powder and slurry is very dramatic, sample preparation can be used without further analysis to illustrate the core concepts of surface area in nanomaterials.

Analysis of samples is an additional layer of complexity and time investment, and requires students to have experience measuring the viscosity of mixtures. The most precise and time-consuming analysis would be performed by a research-grade rheometer. However, even in this case, the experiment can be designed to rapidly analyze each sample, ensuring that the experiment can be performed in a timely matter. In addition, this provides a level of scalability in the complexity of the experiment, where inexperienced students can take advantage of very simple techniques, while experienced students may be able to obtain more precise data.

3.3.4. Expense

As Cal Poly and the GWRI are located in California, recent budget cutbacks have placed efficient use of existing funds at a premium when developing new learning material. Because studying surface area properties of nanoparticles is very fundamental, careful design of this demonstration provides an opportunity to provide a case study in the effective creation of a learning module without significant material costs. This demonstration makes use of commercially available grades of TiO_2 , a very common material used in the coatings industry in a variety of particle sizes, and useful for a

variety of educational purposes beyond this demonstration. As the amount of TiO_2 required can be very little, it is not necessary to seek out cheaper alternatives, though some alternatives may be found. Presumably, other inorganic nanomaterials could be substituted for TiO_2 with minimal effort, so long as both nano and micro sized grades of the material could be located. While the chemical dispersant used can be expensive, free samples are available from manufacturers, and a friendly relationship may be developed to create further educational opportunities at minimal cost.

3.4. Laboratory Demonstration

3.4.1. Methods and Materials

Two grades of TiO_2 powders, one each nano and micro sized, were compared. The nano TiO_2 chosen was TTO 51-A, an ultrafine grade of rutile TiO_2 produced by ISK, LTD. with particle sizes ranging from 10-30nm, surface treated with a thin layer of aluminum oxide. The oil adsorption value is 40-47 g oil/ 100g.

TiPure® R706 is a pigment sized grade of TiO_2 made by DuPont, with a particle size of 360nm, and a thin surface treatment of aluminum oxide. TiPure® is a product line of titanium dioxide pigments by DuPont, any of which could be substituted for R706 with essentially no modification to the experimental procedure. The oil adsorption value is listed at 13.9 g/100g.

The dispersant chosen was DISPERBYK®-190, by BYK. BYK-190 is a VOC and solvent free chemical dispersant solution of a high molecular weight block copolymer with pigment affinic groups at 40% non-volatile matter (NVV) in water. This

dispersant is commonly used for dispersing binder free pigment concentrates, and so is especially useful for this particular demonstration.

Each sample was prepared by weighing 25g of TiO_2 into an empty beaker. Water was weighed into each beaker to produce a slurry of 70 wt.% TiO_2 (TiPure R706) or 50 wt.% TiO_2 (TTO-51A). The slurries were stirred to by hand to homogeneity. To produce visually apparent qualitative results, 2% dispersant (to TiPure R706) or 9% dispersant (to TTO-51A) was added as a weight percent relative to TiO_2 , and each slurry was mixed to homogeneity. To produce quantitative results, dispersant was added incrementally from 0.5%-2.0% in steps of 0.5% (TiPure R706) or 4.5%-9% in steps of 1.5% (TTO-51A), and analyzed between each addition step via rheometry on a Discovery HR-2 series rheometer. All data was analyzed using Trios software (TA Instruments).

3.4.2. Results

Three primary results were obtained from this experiment. All three produce visually apparent results when preparing samples, while one (dispersant concentration) also produces quantitative data to verify the observations. All three occur as direct results of the differences in surface area.

The first result is obtained when TiO_2 samples are weighed out in the first step of the procedure. Here, students will observe differences in bulk density of the two materials: the volume occupied by equal masses of TiO_2 when weighed casually into an empty beaker differs significantly between the micro and nano grades of TiO_2 . Real powders do not pack perfectly, so air voids within a powder contribute to the apparent volume of the powder. Nanoparticles are very small, and so forces such as gravity have

little influence on particle packing, relative to the strong surface interactions which allow particles to resist flowing into more tightly packed structures. The nanoTiO₂, possessing greater surface area than microTiO₂, will resist the tendency of gravity to compress the particle packing and will have greater occupied volume due to decreased bulk packing density. A similar phenomenon can be seen in many other substances, such as sugar, where the phenomenon may be seen when comparing powdered vs. granule sugar.

Figure 12: Packing density differences between equal masses of micro and nano grades of TiO₂.

The greater surface area of the nanoTiO₂ also provides a greater interfacial area between particle and water, resulting in greater adsorption of water within the powder. While 70 wt.% slurries of microTiO₂ are easily prepared, a 70 wt.% mixture of nanoTiO₂ consists of damp and dry powder. This is the reason for the use of a 50 wt.% slurry of nanoTiO₂ in the procedure: a 70 wt.% slurry is not obtainable with nanoTiO₂. However, once sufficient water is present to wet the surface of all of the particles, only a small further addition of water is necessary to produce a slurry.

Figure 13: Comparison of 70 wt.% slurries of micro and nano TiO_2 , showing water absorption by nano TiO_2 .

The final result obtainable from this demonstration is in the difference in dispersant concentration required to transform the thick, viscous slurries of each grade of TiO_2 into well-dispersed slurries with minimal viscosity. For the sake of qualitative demonstration, three comparisons can be made in rapid succession as the experiment is repeated in lab, in the same manner as the demonstration produced for illustrative purposes in the video presentation: 0% vs. 2% dispersant slurries of micro TiO_2 , 2% dispersant in micro TiO_2 to 2% dispersant in nano TiO_2 , and 2% dispersant in micro TiO_2 to 9% dispersant in nano TiO_2 . The first will show the rapid reduction in viscosity of the micro TiO_2 slurry with addition of dispersant, from a viscous slurry with the consistency of mud, to a well-dispersed slurry with consistency near that of water. The second comparison will demonstrate the difference in surface area between micro and nano TiO_2 , by using equal amounts of dispersant. While the micro TiO_2 slurry will achieve a low viscosity (thin, runny liquid), the nano TiO_2 slurry will remain very viscous. The final comparison will show that it is possible to reduce the viscosity of the nano TiO_2 slurry to that of the 2% dispersant micro TiO_2 slurry, though it requires significantly more dispersant.

Figure 14: Comparison of slurries of micro and nanoTiO₂ with 2% dispersant.

Figure 15: Comparison of dispersant requirement for achieving minimal viscosity for micro vs. nano TiO₂.

These differences in viscosity as a function of dispersant concentration can be quantified by rheometry and presented to students in the form of graphical results illustrating the differences that result due to surface area. Dispersant demand curves, plotting dispersant concentration vs. the viscosity of the slurry, obtained at a constant shear rate, will show dramatic differences in the amount of dispersant required to produce minimum-viscosity slurries. These results are dramatic enough that no subtlety in

interpretation is required, and the presence of a significant difference will be apparent even to students not familiar with rheometry as an analytical technique.

Figure 16: Graphical representation of quantitative differences in viscosity profiles of micro and nano TiO₂ as a function of dispersant concentration.

3.4.3. Conclusions of Demonstration Design

The chosen demonstration satisfies 3 of the 4 design criteria extremely well, and satisfies the fourth to a good to excellent degree, depending on the scale of the demonstration and needs of the academic facilities performing it.

The demonstration is simple in required skills, both for preparing the sample and performing analysis. Sample preparation requires no skills more complex than pouring and mixing, while analysis via rheometry is a relatively simple technique for an undergraduate or graduate college student. In addition, simplicity of preparation leads directly to simplicity of understanding.

The qualitative demonstration is also not time-intensive, and execution of the entire demonstration, provided materials have already been collected, may take as little as two minutes, and additional time used to explain the significance of each procedural step

may not extend the demonstration to a total of more than 15 minutes. While quantitative analysis of each slurry is far more time intensive than the qualitative demonstration, it requires little time in comparison to many other analytical techniques typical of analytical chemistry, and the length of each period of data collection via rheometry may be used to prepare the next addition of dispersant for analysis. Potential mistakes made in sample preparation during steps of successive dispersant addition are easily rectified, as dispersant may simply be added up to the point prior to the procedural mistake.

Qualitative results are visually obvious, and hands-on experience by students will allow them to clearly see the differences between the two grades of TiO_2 . Nearly every procedural step involves some result related to the difference in surface area between the micro and nano materials. While the primary intention of the demonstration is to use dispersant concentration to probe surface area, differences in powder packing density and water absorption, which also result due to differences in surface area, offer additional opportunities to explore the properties of nanomaterials.

Quantitative results are also readily apparent when presented in graphical form. Depending on the experience level of the students with data analysis of rheometry, results may be presented in multiple ways to gain better understanding of the data. The simplest form of presentation is through the use of dispersant demand curves, plotting dispersant concentration vs. viscosity at a fixed shear rate. Data may also be presented as plots of shear rate vs. viscosity, with each different dispersant concentration tested represented by a different line on the graph.

Finally, the experiment is not an expensive method for demonstrating the properties of nanomaterials. TiO_2 is relatively inexpensive compared to many other

nanomaterials, which may cost ten times as much or more. In addition, the provided demonstration does not use expensive analytical techniques, or involve large amounts of expensive reagents. While chemical dispersion additives may be somewhat expensive, free samples may be available from distributors, particularly for institutions with healthy relationships with industrial partners. In the case that they are not available, the very small amount of dispersant required for this demonstration means supplies may be used conservatively.

3.5. Video Presentation Design Considerations

The learning module was designed to be primarily presented through the use of a video presentation. It was decided that the optimal form for the video was through the use of a narrated PowerPoint presentation with a video of the laboratory demonstration embedded within.

3.5.1. General Design Goals

The primary educational goal of the learning module was to teach students about the importance of the surface area of nanomaterials, and how differences in surface area affect fundamental properties. Because these fundamental differences affect the techniques necessary to manage waste streams involving nanomaterials, their understanding is critical to addressing the growing concern of nanowaste in the near future. It was decided that for educational purposes, the issue of surface area should be framed within the context of nanotechnology itself, using dispersed colloids of nanoparticles within slurries as a framework for understanding the issue.

The target audience for the learning module was selected to range from students with educational levels from the end of secondary education (high school seniors) to students in graduate programs with some involvement in the issues of nanomaterials. As a result, it was necessary to design the presentation in such a way that students at the ends of this range did not become alienated by material that was too complex or too simple. Due to the vast differences in educational levels of the potential target audiences, it was necessary to avoid focusing too much attention on either background material, or results of the demonstration

The length of the video presentation was designed to fall within a 15 to 30 minute time slot. This represented a length of time in which a significant amount of information could be related, without being intrusive to incorporate into the framework of existing academic programs. In addition, it provides plenty of opportunity for instructors to clarify material presented, such that it may be tailored to the educational needs or purposes of the program in which it is presented.

3.5.2. Design Challenges

The general design goals of the learning module directly resulted in a number of challenges to be addressed in the design of the presentation. The challenges related to conveying necessary information, maintaining appropriate information density, maintaining student interest, and using visuals to guide a viewer's attention were active considerations in the production of each level of the presentation, both during creation of individual slides, thematic sections within the presentation, and the presentation as a whole. The fifth listed challenge, the limited multimedia experience of the author, was a

limitation in human resources which determined available solutions to each of the other four.

Figure 17: Active design challenges related to creating the video presentation.

3.5.2a Conveying Necessary Information

Because the objective of a learning module is to actively transfer information to students, designing the module in a way to convey necessary information is the most important design consideration. The primary goal of this presentation was to educate students about the significance of surface area in the context of nanomaterials. Thus, it was necessary to reiterate the concept of geometric differences between the “micro” and “nano” regimes constantly throughout the presentation in order to ensure that students were constantly aware of its influence.

In addition to the necessary goal of communicating the importance of surface area, it was necessary to explain the science surrounding the events that occur in the laboratory demonstration, which exists at the heart of the presentation in the form of a one minute and thirty second video clip with narration. Thus, the presentation was designed around the demonstration, with preceding slides used to introduce concepts related to the use of dispersants as stabilizing agents for inorganic particle dispersions. Without this information, the demonstration would not make sense to students who are not familiar with dispersant chemistry. While surfactant chemistry is introduced to undergraduates and briefly to high school students, the mechanisms specific to stabilization of pigments and nanomaterials are not introduced until the graduate level. Even insofar as necessary background material is common knowledge, a brief mention of concepts, to remind students of what information is important, is useful for creating a thorough presentation of material.

3.5.2b Information Density

In order to deliver effective presentation of material, the information must be presented in a way such that it can be both absorbed and retained by students. The attention span of students is one of the most important issues for concerned educators seeking to maximize information retention of students. Failure to retain information may be related to lack of attention by students, either because too little or too much information is presented in a short period of time.

Because the learning module is designed to educate, it is important to present enough information in the available time. Thus, the information density must be high

enough to convey all the necessary information in as short a period time as is feasible while maintaining information retention. Long video presentations, especially when presented at a very basic level, are often perceived by students as an opportunity to stop paying attention. To keep video length as short as possible, the information density of the presentation must be high enough to convey all concepts in a short period of time. In addition, an overly simplistic explanation of basic concepts may bore students into lapsing in attention. Because the presentation must eventually transition into more complicated material, students may miss this transition point, causing them to fail to learn the most crucial material. This is compounded by the fact that because the presentation is pre-recorded, students cannot ask stop the instructor to ask questions.

If information density is too high, however, students will fail to retain information, whether due to intermittent attention, or simply due to mental overload. Attention span of students is a well-studied issue (though it is difficult to quantify), due to the direct implications in determining the optimal method of educating students. It has been shown that lapses in attention are surprisingly frequent, even if the actual lapse does not last for a significant amount of time (Bunce, 2010). If information density is too large in a video presentation, then these lapses might cause students to completely miss crucial concepts. Since students in a classroom setting cannot rewind the video each time attention lapses, they lose the opportunity to learn some piece of crucial information. If information density is very high, then there might simply be too much information for students to learn in a short period of time (Russel 1984). Each new piece of material will displace the material before it in students' minds, resulting in a confused student who understands the results of the demonstration, but not how or why they were obtained.

3.5.2c Maintaining Student Interest

Bored students are inattentive, and inattentive students do not learn material well. Because a video presentation is only likely to be played once for a group of students, interest must be maintained constantly through the first and only viewing. As mentioned previously, maintaining a proper level of information density is one of the keys to maintaining interest. In addition, appropriate use of visuals may help. Providing an appropriate visual aid reduces the amount of necessary text for conveying a given idea. Pictures are interesting to students, while text is not, so use of images to convey the main concepts, using text only as a supplemental aid, will help to maintain interest.

3.5.2d Visuals as Attention Guides

Certain concepts may be nearly impossible to explain to a broad audience reliably without images. Not only can use of visuals help to maintain interest by reducing necessary text and narration, but they can be used to guide attention through each concept in a logical manner, by providing a consistent reference point. For example, a description of the interactions between a pigment particle and dispersant molecule is significantly aided by a simple diagram. Use of visuals in this way is particularly necessary for complicated subjects such as chemistry, with many different interactions occurring between components of even relatively simple systems.

One of the fundamental differences between a narrated video and an in-person presentation is the lack of nonverbal communication cues when a narrator is not visible. Because a significant amount of human communication is nonverbal, this is a significant loss of an information transfer pathway that must be made up for through careful design

of visual aids. For example, academic or professional PowerPoint presentations often involve a large amount of information on a single slide, with the presenter guiding the audience through the material with the use of gestures, signaling, and pointing to relevant portions of the slide with the use of a laser pointer. Because none of these are present in a narrated presentation, visuals must be designed to guide the viewer's attention through subsequent ideas in a logical manner. In this presentation, each slide contains a group of related material, with both text and visual aids brought into view through fade-in animations, with the total amount of information per slide limited to prevent excessive clutter.

3.6. Presentation Structure and Slide Design

The PowerPoint presentation, for the purposes of discussion of design philosophy, may be broken into four sections, comprising a total of 19 content slides, not including the title and reference slides. These sections are: introduction, core educational, experimental and results, and conclusion. Each has different objectives and strategies for contributing to the conveying of the overall message, and different amounts of instructional content.

3.6.1. Introduction Slides

Comprising slides #2-6 and #9, this series of slides were developed to give a casual introduction to nanotechnology and nanoparticles, and introduce TiO_2 as a material of interest.

Figure 18: Introduction slides: presentation slide #2.

Slide number 2 is the first content slide that students see, so it was designed to generate interest by placing heavy emphasis on interesting visuals. The only instructional content on this slide is the definition of nanotechnology, presented both with simple text and visuals, to ease students into the presentation, rather than rapidly introducing concepts right from the start. The three images at the bottom of the slide were introduced as non-essential content, designed to generate student interest by associating the concept of nanotechnology with futuristic possibilities for which nanotechnology holds promise. In addition, because fundamental concepts are often difficult to present as important or interesting to students, use of these images creates a positive association with the idea of nanotechnology, before study of fundamental concepts is introduced.

Figure 19: Introduction slides: presentation slide #3

Designed to shift the focus of the presentation to nanomaterials, this slide begins with accessory information to transition the focus into the primary form of current nanotechnology: composite materials. This accessory information also provides a brief cognitive break, allowing a lapse of focused attention, before shifting focus to one of the most important core concepts of the learning module: the difference between micro and nanoparticles. It also provides an opportunity to introduce the concept of replacing microparticle additives with nanoparticle additives, using TiO_2 as a simple example.

What is titanium dioxide used for?

Paints & Coatings

- All colors

Cosmetics

- Sunscreen

Food

- Colorant

Case study for Micro vs. Nano:
Titanium dioxide in surface coatings and paints

4

Figure 20: Introduction slides: presentation slide #4

Titanium Dioxide

Chemical formula: TiO_2

Common, white pigment

- 4.6 million tons used per year
- Accounts for 70% of all pigments used

Useful properties:

- Very white
- Brightness
- Hiding power/opacity

Good hiding power

Poor hiding power

5

Figure 21: Introduction slides: presentation slide #5.

Figure 22: Introduction slides: presentation slide #6.

Slides 4-6 are used to introduce TiO₂ as an interesting and useful material, and establish its importance as a material worthy of being studied. Slide #4 is used to introduce non-critical information, and show students that TiO₂ is a material which is a key component of many common applications. This helps to establish TiO₂ as a familiar material, regardless of whether students are familiar with it or its properties. Slide #4 also introduces the idea of using TiO₂ in surface coatings as a framework for understanding the differences between micro and nano particles, allowing the rest of the presentation to use information and examples primarily related to the coatings industry, providing a more focused delivery of information.

Slide #5 contains entirely non-essential accessory information, and its primary purpose is to provide slightly more technical evidence of TiO₂'s usefulness. Its primary purpose is to stand in contrast to slide #6, both in terms of content and appearance. Slide

#6 is used to introduce the exotic and unusual properties of TiO_2 -infused materials, in a visually informative manner. These properties are more interesting than the relatively bland properties listed in slide #5, and the contrast in visual appearance helps the difference to appear more striking. This reinforces the establishment of TiO_2 as a material with interesting and unusual properties.

Dispersants

Chemical additive which aids in dispersion of insoluble matter

Used in a variety of industries:

Coatings

- Disperse inorganic pigments

Automotive

- Prevent residue buildup in engines

Oil drilling

- Used in drilling fluids to disperse solids and control foam

9

Figure 23: Introduction slides: presentation slide #9

Located in the midst of several educational slides, this slide is used to introduce chemical dispersants as common and useful substances in an identical manner to the way TiO_2 was first introduced in slide #4. It also reiterates the concept of focusing on the coatings industry as a case study for understanding the difference between micro and nano particles.

3.6.2. Core Educational Slides

While each slide in the presentation was designed with a purpose, the core educational slides contain the most important information that students are to learn and retain. While the introduction slides provide a framework for the rest of the presentation to reside on, the core educational slides use that framework to educate students about the surface area of nanomaterials. Information on the function of chemical dispersants in the stabilization of pigments and nanoparticles in aqueous media is also presented, as this information is crucial to understanding the laboratory demonstration, around which the rest of the presentation revolves.

Figure 24: Core educational slides: presentation slide #7.

Slide #7 is the most important slide in the presentation in terms of raw content. The difference in surface area between micro and nano sized materials is the most important fundamental concept to be understood by students studying nanotechnology or

nanowaste processing. This slide attempts to address the relationship between surface area and volume (and by extension, mass) of materials using geometric arguments, and uses visuals to aid in the understanding of the mathematical concepts. This is presented both graphically and numerically, so that students have a clear idea of what is meant when it is said that nanoparticles have very high surface area.

Nano TiO_2

Smaller particles than standard TiO_2

- Greater total surface area
- Enhanced surface properties

One small problem: TiO_2 is not soluble in water, or other common solvents

TiO_2 must be dispersed through careful formulation of the incorporating product

Going from micro to nano-sized particles requires additional formulation changes

Nano TiO_2 Micro TiO_2

Figure 25: Core educational slides: presentation slide #8

Slide #8 is designed to link the significance of surface area of nanomaterials to the differences between micro and nano TiO_2 , and the concept that differences between the materials exist at the fundamental level. This concept is then used to connect to the introduction of chemical dispersants as tools to control interparticle interactions in aqueous dispersions, by referencing the necessary changes to coatings formulations that are made necessary by the large difference in surface area between the micro and nano materials.

Dispersants for Aqueous Systems

Surfactants

- Head group interacts strongly with pigment
- Tail(s) solvated, extends outward

Purpose: stabilization of dispersions

- Charge stabilization
- **Steric Hindrance**

Hydrophobic head

Hydrophilic tail

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Figure 26: Core educational slides: presentation slide #10

Slide #10 introduces the theory behind the function of chemical dispersants on the molecular level. Dispersants are described as simple surfactant molecules, a necessary simplification to avoid the complicated discussion of different chemical structures of dispersants, a topic which would be far too technical for any non-graduate audience members. Steric hindrance is introduced as the most important stabilization mechanism for aqueous systems. This was done because the stabilization mechanism of the dispersant chosen for the laboratory demonstration, DISPERBYK-190, operates using this mechanism, and because the schematic representation of the mechanism on slide #11 allows for a very simple visual explanation of the underlying processes.

Figure 27: Core educational slides: presentation slide #11

A thorough discussion of interparticle interactions related to dispersion of particles in media (DVLO theory) was judged to be far too complex for inclusion in this video presentation. Instead, aggregation forces were alluded to as esoteric phenomena, with steric forces presented as the primary relevant antagonistic force. Dispersant tails are likened to “tiny springs” as a simple analogy to understand the mechanism of stabilization. This is reinforced using an interparticle interaction force diagram in which only steric forces are shown.

Figure 28: Core educational slides: presentation slide #12, before (left) and after (right) transition animation.

Slide #12 is an extremely important slide, as it visually demonstrates exactly how differences in surface area between equal masses of micro and nanoparticles can require significantly different amounts of dispersant. The animation here is used to prove that while the total mass of the particles on the left is equal to the mass of the particle on the right, the amount of dispersant required is much higher on the left. Text is kept to a bare minimum in this slide, used only to place emphasis on the concepts being described by the visual aid.

3.6.3. Experimental and Results Slides

These slides are the heart of the presentation, taking advantage of the laboratory demonstration described in section 3.4 to provide students with a clear demonstration of the differences between micro and nano particles. A very simple description of materials is provided, followed by short video clip of the highlights of the laboratory demonstration itself, and then quantitative results of the experiment.

Materials

Ti-Pure® R706 (DuPont)

- Pigment grade micropowder
- Particle size- 360 nm

TTO-51(A) (ISK, LTD.)

- Nanoparticle powder
- Particle size- 10-30 nm

DISPERBYK-190 (BYK)

- Formulation/structure is proprietary knowledge
- Commonly used for pigment dispersion in aqueous systems

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Figure 29: Experimental and Results Slides: presentation slide #14.

Slide #14 is an extremely brief introduction to the materials used in the demonstration, designed to provide only the bare minimum of necessary information to convince students that this demonstration is of valid design for illustrating the desired concepts. While the particle size of the two TiO_2 grades is the most significant piece of information on this slide, even this information is not highly emphasized: hereafter, the two grades are referred to primarily as “micro” or “nano”, helping to generalize the results of the demonstration to nanomaterials as a whole. In addition, the trade names of the two TiO_2 grades are relatively complex, and requiring students to quickly memorize these names detracts from the overall experience.

The following slide, #15, is a placeholder slide where the laboratory demonstration itself is presented as a one minute and thirty second narrated video clip. The clip is designed to show each relevant step in the sample preparation procedure, and

highlight the three primary surface area dependent differences in behavior between the two grades of TiO_2 : packing density, water absorption, and dispersant requirement. The only text used in this clip was used to identify the contents of beakers containing slurries, as either “micro” or “nano”, and the concentration of TiO_2 or dispersant therein. The video clip only shows addition of 2% and 9% dispersant, to maximize the apparent difference in viscosity and appearance with dispersant addition. Quantitative data collection involved smaller, sequential additions of dispersant, but this would have needlessly complicated the video. Rheological analysis was not demonstrated in this clip, as it was judged that doing so would not positively enhance the viewing experience given the time required, and may detract by providing nonessential information.

Figure 30: Experimental and Results Slides: presentation slide #16

Slide #16 is the first of two quantitative results slides, showing the presented data as it was collected, with viscosity plotted as a function of shear rate at a variety of

different dispersant concentrations, with the top graph representing microparticles, and the bottom graph nanoparticles. Axes in both graphs are identical, and the dispersant concentration ranges were chosen so that the data series in each graph showed nearly identical values. The size of the legend in each graph was then made extremely large. Together, these allow a direct comparison of the amount of dispersant required for each grade of TiO_2 . The reason for these differences, the difference in surface area of the two materials, is reiterated for emphasis.

Figure 31: Experimental and Results slides: presentation slide #17

Slide #17 shows graphical results of plotting viscosity as a function of dispersant concentration for each of the two grades of TiO_2 . These results were presented after the results from slide #16 because they are derived from that data by analyzing viscosity values at a constant shear rate. In addition, while less information is presented than in slide #16, the information is clearer, and the final impression made to students regarding

quantitative data should be made by using the most easily interpreted data set. Because the data in this graph so clearly shows the difference between the two materials, the only supplemental text used is to clarify which data series belongs to which material.

3.6.4. Conclusion Slides

The final three slides in the presentation conclude the instructional content of the presentation, and are designed to link the fundamental concepts with the development of functional nanotechnology in the ensuing decades. In the same way that the first introduction slides introduced nanotechnology and narrowed the focus to a specific demonstration, the conclusion slides do the same in reverse.

Experimental Conclusions

Difference in surface area changes basic properties of nanoparticles

- Higher surface area results in more water absorbed, more dispersant required, and a fluffier powder
- Involving nanoparticles in a process may require a significant amount of redesign
- Fundamental understanding of processes at the nano-scale is necessary before new technology can be made**

	Micro	Nano
	2% dispersant	9% dispersant

Part A

Araldite® PZ 3961-1 US Epoxy Emulsion

Water

Total - Part A

Part B

Aradur® 3986 Waterborne Curing Agent

Disperbyk® 192 (Byk-Chemie, USA)

Byk® 024 (Byk-Chemie, USA)

Byk® 019 (Byk-Chemie, USA) (in DPGME)

Raybo® 60 (Raybo Chemical Co.)

Optiflow® H600 (Southern Clay Products)

Optiflow® L300 (Southern Clay Products)

Deionized Water

Minex® 7 (Unimin Corp.)

Tioxide® TR93 (Huntsman Corp.)

Cimbar XF (Cimbar)

Wollastcoat® 10 ES (R.T. Vanderbilt)

Vantatec® 6H (R.T. Vanderbilt)

Moku-White® C-100 (Moku-White Pigments)

18

Figure 32: Conclusion slides: presentation slide #18

Slide #18 is the primary conclusion slide, and contains the last bit of relevant instructional content. Due to the difficulty students often experience in connecting

fundamental concepts with useful applications, the direct results of the demonstration are reiterated only very briefly, and in only one bullet point. The other pieces of information provided describe the implications of the demonstration's results, in terms of how they might affect the design of a process or formulation involving nanomaterials. The final bullet point, in bold text, is intended to be motivational as well as informative, showing students why they should care about this type of material.

Figure 33: Conclusion slides: presentation slide #19

From Theory to Practice

There's a lot of research going on in the world of nanotechnology

Nanoelectronics:

- High efficiency solar cells
- Quantum computers

Structural materials:

- Body armor
- Space elevator

Nanomedicine:

- Artificial Muscles
- Targeted drug delivery

More research is needed:

- **Explore unique fundamental properties**
- **Turn properties into functional devices**

20

Figure 34: Conclusion slides: presentation slide #20

Slides #19 and #20 are designed as non-critical material to end the presentation. These slides expand on the “bigger picture” concept of slide #18, in terms of the academic and financial investment into nanotechnology, and the potential applications of nanotechnology which are currently being researched. While these slides present information that students may find interesting and motivational, they are designed to also provide an opportunity for students to lapse in paying close attention, as they absorb the more relevant technical information from earlier in the presentation. The final statements of the presentation are purely motivational, included as an attempt to frame the importance of work in the field of nanotechnology for both scientists and engineers.

3.7. Final Project Details

The length of the final video presentation is just under 15 minutes, allowing it to fit neatly into any existing academic program to help teach students about issues related to nanotechnology and surface area. The design format of the video presentation, a narrated PowerPoint slideshow, allows easy modification of material in the event that changes are to be made to the content of the presentation. The greatest limitation to modifying presentation content is the need to re-record audio narration for the entire presentation in the event that the original voice actor is not available. However, as this is a relatively simple task compared to content design, it should not be a significant hurdle for a student adding a modification as part of a senior project or similar pursuit.

Informal response to the video has been overwhelmingly positive. While minor changes made to slide design might make certain slides more effective, response by students within the target audience has shown that the visual aids do a good job conveying concepts which might otherwise be difficult to explain. Response by academic instructors at the university level has been positive as well, praising the video as a presentation that can be readily incorporated into an academic program as a supplement. In addition, the design of the laboratory demonstration makes repeating it at the undergraduate or graduate level a simple task which may be useful for providing students with a chance to explore the differences between micro and nano materials via hands-on experience.

4. Self-Assembly in Liquid Crystalline Colloids

4.1. Background

4.1.1. Definition of Liquid Crystals

Liquid crystals (LCs) are an exotic state of matter existing between the conventional states of solid and liquid. They possess a degree of molecular ordering like solids, but are able to flow like liquids. As a result, they have a number of unique anisotropic properties, particularly optical, that make them interesting and useful materials (“History and Properties” 2003). Depending on conditions required to enter the liquid crystal phase, LCs may be divided into thermotropic, lyotropic, or metallotropic phases, and possibly further into one of many subphases. The morphologies of LC materials tend to be thin (high aspect ratio), linear, long, and fairly rigid. These properties produce structures that can be approximated as rigid cylinders, resulting in the observed anisotropic nature of the material (“Chemical Structure” 2007).

4.1.2. History of Liquid Crystals

While many modern LCs are synthetic, natural LCs are abundant in nature, where many biological structures exhibit liquid crystalline behaviors. This led to the accidental discovery of LCs as a unique state of matter by chemist Friedrich Reinitzer in 1888 while studying cholesterol derivatives (“History and Properties” 2003). While analyzing the solid material via melting point analysis to determine its purity, he observed two distinct melting points, the first turning the solid into a cloudy liquid, and a second in which the liquid became clear. Collaboration with German physicist Otto Lehmann bore the theory

that the cloudy liquid was a unique state of matter, termed a “liquid crystal” (“History and Properties” 2003).

Interest in these materials remained mostly a scientific novelty until the 1960s, when increased worldwide research efforts into fundamental studies as well as practical applications began to increase dramatically with better understanding of the properties of LCs. Understanding of the electro-optical properties of LCs, as well as development of techniques for preparing LC mixtures with room temperature nematic phases led to commercial application of these materials in liquid crystal displays (LCDs) (Castellano 2005). While early LCDs provided inferior image quality to other technologies used for television and computer displays, their low cost and weight allowed them to maintain a foothold in a niche market for portable displays, until large advancements in LC technology in the mid 2000’s propelled LCDs to be the new commercial standard for all electronic displays.

4.1.3. Liquid Crystal Phases

Liquid crystals may be divided into one of three general categories (thermotropic, lyotropic, or metallotropic), depending on the driving force for inducing molecular ordering. LCs in which the phase and ordering are controlled by temperature are called thermotropic liquid crystals (“Chemical Structure” 2007). At low temperatures, the material is present as a crystalline solid. Increasing the temperature past the material’s melting point causes the transition to the liquid crystal phase, where a large degree of molecular ordering is observed, but the material is able to flow. Further increase of temperature will cause the material to pass another transition temperature to form an

isotropic liquid. This occurs as a result of the change in the relative magnitude of the enthalpic and entropic forces controlling molecular ordering (Singh 2002). While it is enthalpically favorable for the molecules to align, it is more entropically favorable to form an isotropic liquid. Increasing temperature allows the entropic energy term to outweigh the enthalpic term in the Gibbs free energy equation, driving the transition into the isotropic phase. Many subphases of thermotropic liquid crystals exist, the most important being the nematic and smectic phases.

Figure 35: Phase transitions of a thermotropic liquid crystal.

The nematic phase occurs when the molecules maintain directional order, but have no positional order within the matrix (Poulin 1998). As a result, molecules are relatively free to flow, as no energy is required to break the positional ordering. Nematic liquid crystals may be easily aligned by external electrical or magnetic fields, and are thus extremely useful in LCDs.

Figure 36: Schematic representation of the nematic phase of a thermotropic liquid crystal.

Smectic phases are similar to the nematic phase, but generally occur at lower temperatures, and include a degree of positional order (“Introduction to Liquid Crystals” n.d.). Smectic phases possess the same long-distance directional ordering of the nematic phase, but are divided into sheets which are able to flow past each other. Ordering in the smectic phase may best be illustrated by two of the most common subphases: the smectic A phase, in which the director is perpendicular to the smectic plane, and the smectic C phase, in which the director is tilted compared to the smectic plane. In both subphases, molecules are separated into planar sheets, which may freely slide past each other (“Introduction to Liquid Crystals” n.d.). However, long-range directional order is preserved. Many other smectic subphases are possible, though less common, with subtle differences in molecular arrangement.

Figure 37: Smectic A (left) and C (right) phases of a thermotropic liquid crystal (“Introduction to Liquid Crystals” n.d.).

4.1.4. Molecular Anisotropy

Molecules in the liquid crystalline phase of a material have a high degree of molecular ordering, similar to the crystalline structure of solids. This results in a highly anisotropic substance, with molecules aligned along a common axis, known as the director (“Order and Disorder” 2007). The director is a unit vector, $\hat{n}$, which indicates the preferred orientation of molecules in the liquid crystal. The actual extent of ordering in a material is defined by an order parameter, S , which measures the average orientation of all molecules in the sample compared to the direction of the director.

Figure 38: Determination of order parameter for a liquid crystal (“Order and Disorder” 2007).

The value of the calculated order parameter varies from 0 for a perfectly isotropic liquid, to 1 for a perfect crystal. In practice, a liquid crystal may exhibit values from 0.3 to 0.9, depending on the specific conditions, such as temperature. Ordering in a liquid crystal may extend for only very short distances, or up to macroscopic length scales (“Order and Disorder” 2007). Because the director might change slightly throughout the LC matrix, the orientation of molecules may be described using a director field. This is essentially a vector field for the director at each point throughout the LC. Controlling the

orientation of the director field is important for optimal function of LCDs, as misaligned domains within the liquid crystal will result in improper function.

4.1.5. Optical Properties of Nematic Liquid Crystals

The most interesting and useful properties of liquid crystals are their optical properties. To understand the optical properties of liquid crystals, an understanding of light polarization is necessary. An individual light wave consists of a set of oscillating electrical and magnetic fields oriented at a 90° angle to each other. In ordinary, unpolarized light, these waves fluctuate at all angles in a circle around the propagation axis. However, light may be linearly polarized so that the waves only propagate in one specific plane, using a polarizer (or polarizing filter) (“Introduction to Liquid Crystals” n.d.). A polarizer will block all light except that occurring parallel to the optical axis of the device. If two polarizers are set up in succession, then the amount of light transmitted depends on the angle, from 0 to 90 degrees, between the optical axes of the two materials. At 0 degrees, the optical axes are parallel, and all the polarized light from the first polarizer is transmitted through the second. At 90 degrees, the optical axes are perpendicular, and no light is transmitted.

Figure 39: Propagation of linearly polarized light through parallel (top) and crossed (bottom) polarizers (“Light and Polarization” n. d.).

Linearly polarized light may be considered as the vector sum of two mutually perpendicular light waves. Stated another way, light linearly polarized at a 45° angle may be thought of consisting of vertical and horizontal components which sum to a single wave. If the two waves are in phase (0° between phases), then the vector sum results in a linearly polarized light wave, polarized at $+45^\circ$. If the waves are out of phase (180° between phases), the vector sum produces light linearly polarized at -45° . However, if light waves are between 0 and 180° , the vector sum of the two waves traces an ellipse as the wave propagates, rather than tracing a linear path.

Figure 40: Linearly polarized light produced by a) two in-phase propagating light waves, b) out of phase propagating light waves, c) circularly polarized light produced by 90° out of phase light waves (“Light and Polarization” n. d.).

Because liquid crystals are highly anisotropic, they exhibit birefringence, a property of materials where the speed of propagation of light (the refractive index) through the medium depends on the angle of the polarization of incident light relative to the optical axis of the medium (“Birefringence” n.d.). Light polarized parallel to the optical axis is refracted according to the standard law of refraction, while light perpendicular to the optical axis will be significantly slowed. As a result, different waves of light will pass through the birefringent material at different speeds, and the polarization state of the light will change depending on the birefringence and path length through the material. This mechanism can be visualized most easily using perpendicularly propagating light waves, as in figure 40. Passing these waves through a birefringent material alters the phase difference between the waves, changing the pattern traced by the vector sum of the waves.

Figure 41: Schematic representation of the differences in refractive index experienced by light parallel to the optical axis (o-ray) and perpendicular (e-ray.) (“Birefringence” n.d.).

Laboratory analysis of nematic liquid crystals takes advantage of the anisotropic alignment of the liquid crystal molecules to control how much light is able to pass through the material. Standard analysis of liquid crystals is performed using a polarizing light microscope (PLM) by placing a sample between crossed polarizers. Normally, when light is passed through two crossed polarizers, the net effect is blocking of all transmittance of light. However, presence of a LC sample may change the polarization state of the light, twisting the light and allowing transmittance. The first polarizer linearly polarizes the light, where it is then able to pass through the LC sample. Because the LC is birefringent, the polarization state of the light will then change as light passes through it, allowing transmission through the second of the two crossed polarizers (“Birefringence” n.d.). Aligning the LC director parallel or perpendicular to the optical axis of the crossed polarizers will minimize light transmitted, while aligning the director at a 45° angle will maximize the light transmitted.

4.1.6. Liquid Crystalline Colloids

Colloids dispersed in anisotropic media such as LCs are an unusual class of composite materials which experience interactions not present in isotropic dispersion media (Chandran 2011). The distortion in the local alignment of the director field caused by the interactions between particles and molecules of the liquid crystal costs elastic energy, which serves as a driving force for formation of anisotropic structures of colloidal particles (Poulin 1998). LC molecules interacting with the particle cause defects, which result in unfavorable interactions with the surrounding LC field. Loss of elastic energy may be minimized by further deformation of the LC in the vicinity of the defect, resulting

Figure 42: a) schematic representation of a hedgehog defect (Sethna 1992), b) strong homeotropic anchoring resulting in a hedgehog defect, c) hedgehog defect as seen under polarizing light microscopy (Chandran 2011).

in characteristic defect patterns depending on the type and strength of interactions. Linear alignment of particles in the LC may further minimize the loss in elastic energy, due to minimization of the total distortion of the director field. Minimization of loss of elastic energy (long range, inverse power law forces) is the driving force for this aggregation (Takahashi 2008). Particles will align near defects in a way analogous to allowing the particles to sit in “low pressure” areas formed by defect patterns of surrounding particles, resulting in linear arrangements. However, very short-range interactions at the defect itself are repulsive, providing a driving force against aggregation of particles. The type of interaction determines the aggregation behavior of colloidal particles, including the growth direction relative to the nematic vector.

Figure 43: Linear alignment of particles resulting from hedgehog defects (Chandran 2011).

Interactions between particle and liquid crystal in which interactions occur normal to the particle surface are called homeotropic anchoring. When homeotropic anchoring results in very strong interactions, dipolar hedgehog defects are formed near the particle. Hedgehogs are a general class of topological point defect not unique to LCs in which the crystal orientation faces outward in all directions from the point (figure 42a) (Sethna 1992). Because these defects change the orientation of LC molecules in the vicinity of the defect, the polarization state of light around the defect is different than in surrounding areas, allowing the defect to form a distinguishable pattern visible under PLM. Weak homeotropic interactions may be characterized by the formation of Saturn-ring defects. In these defects, a disclination loop surrounds the particle at the equator. When both hedgehog and Saturn ring defects are visible, the relative frequency of each can be used to further determine the strength of the homeotropic anchoring (Chandran 2011).

Figure 44: Saturn-ring defect (particle on the left) (Chandran 2011).

The other interaction mode occurs when interactions occur tangential to the particle surface, resulting in homogeneous planar anchoring. The sides, rather than ends, of the liquid crystalline molecules interact with the surface of the colloidal particle. These produce characteristic boojum defects, with small distortions occurring where the director

field merely bends around the particle (figure 45a). Because LC molecules interact in a planar fashion, defects do not appear at the sides, top, or bottom of the particle, resulting in a quadrupolar symmetry. Homeotropic anchoring promotes alignment of particles parallel to the nematic director, while homogeneous anchoring results in alignment of particles offset at a small angle (Chandran 2011).

Figure 45: a) schematic of a quadrupolar boojum defect, b) boojum defect seen under PLM (Chandran 2011).

Figure 46: Linear alignment of particles as a result of a) homeotropic anchoring (Chandran 2011), b) homogeneous planar anchoring (Martinez 2011).

4.2. Self-Assembly of Functionalized Silica Microspheres in a Nematic Liquid Crystal

4.2.1. Preparation of Colloidal Dispersions of Silica Microspheres in 5CB

10mg silica microspheres (5 μ m, Polysciences, Inc.) were obtained as a dry powder, and added to a 5 wt.% solution of Dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride (DMOAP) (Sigma-Aldrich) in water, at 20 wt.% relative to DMOAP. The mixture was shaken via vortexer for 30 minutes, and then sonicated for 1.5 hrs. The mixture was microfuged (18-Centrifuge Biotechnical Services Inc.) for 5 minutes at 14,000 RPM, and supernatant removed. The functionalized spheres were resuspended in water, and the process of resuspension, vortexing, sonication, and microfugation was repeated for a total of 5 iterations. After the final microfugation, spheres were suspended in ethanol, and then dried at 85°C to remove any residual water via azeotrope. Spheres were resuspended in ethanol, and several drops of this solution were added to the liquid crystal 4-cyano-4'-pentylbiphenyl (5CB, nematic to isotropic transition at 35°C, TCI Chemicals) (~1 drop silica microsphere solution per 5 drops LC). LC solution was sonicated continuously at a solution temperature of 50°C.

Figure 47: Chemical structures of a) DMOAP, b) 5CB.

4.2.2. Preparation of PVA Spin-Coated Glass Cells

3.0g of polyvinyl alcohol (Sigma-Aldrich, MW 30-50 KDa) was dissolved in 100g of water and stirred gently with moderate heating for several days until dissolved. Clean glass microscope and cover slides were washed with acetone to remove any traces of dirt or other contaminants. Slides were spin-coated with an excess of PVA (9s 400 rpm, 30s 1500 rpm). Cover slides were spun such that the entire mass of the slide sat on one side of the center of revolution, to ensure that PVA was spread unidirectionally across the surface.

Figure 48: Spin coating apparatus used for coating glass cover slides, with two cover slides sitting on the ends of a microscope slide laid across the spin chuck.

Residual water was removed by heating the slides at 85°C for 10 hours. Prior to the construction of glass cells, slides and cover slides were rubbed unidirectionally with a piece of cloth. Microscope slides were rubbed lengthwise, while cover slides were rubbed in the same direction in which PVA was spread during the spin coating process. Cells were constructed using transparent adhesive tape (58µm) as a spacer on the top and bottom of each microscope slide. Cover slides were added and held in place by a second layer of tape placed over the top. Rubbing directions of cover slides and microscope slides were matched. Prior to loading LC, it was allowed to cool into the nematic phase, indicated by a transition from a clear liquid to an opaque liquid. Loading was done by capillary force, such that the flow of the liquid occurred in the direction of the rubbed polymer. Samples were allowed to sit at room temperature (in the nematic phase) for 30

minutes prior to analysis. All analysis was performed on a Leica DM 2500 P polarizing light microscope using 20x or 40x magnification. Images were processed in the Leica Application Suite™ V4.0.

4.2.3. Results

Interactions between functionalized silica microspheres and the nematic phase of the liquid crystal show clear formation of hedgehog defects, indicating strong homeotropic interactions occurring normal to the particle surface. These interactions

Figure 49: Formation of strong homeotropic interaction results in hedgehog defects. These defects drive the formation of linear chains of particles. A very small Saturn-ring defect is visible in the particle on the far right.

drive the formation of linear chains of particles. Particle aggregates ranging from isolated pairs to strings of over a dozen particles were observed, occurring predominantly in the direction of the nematic vector. Perfect alignment is not always observed, as the driving force for forming interactions (minimization of loss of elastic energy) is not sufficient to

Figure 50: Strings of particles form in the direction of the nematic director. Alignment of particles in a linear manner is clearly predominant over random aggregation.

Figure 51: Time dependent aggregation of a linear string of four particles into a larger aggregate a) before aggregation b) after incubation at room temperature for 24 hours.

drive the particles into perfectly linear formations. Minimal formation of Saturn-ring defects is also observed.

Ordering of particles via long-range elastic forces is a dynamic process that may occur over significant (hours to days) periods of time. Our results show limited evidence of this behavior occurring over timescales from 12-24 hours under the preparation conditions used. Further optimization of experimental parameters, such as incubating samples at specific temperatures near the nematic-isotropic transition temperature may result in further evidence of time-dependent aggregation of particles into linear structures. Under the current conditions, aggregation did not occur in linear fashions. The likeliest reason for observation of large formations of linear structures, but no further time-dependent formation, is due to rapid formation of structures near the nematic-isotropic transition temperature during initial loading, followed by cooling of the sample, decreasing the mobility of the silica particles within the LC.

Figure 52: Particle aggregation along grain boundaries of polydomains within the liquid crystal.

Previously unreported in nematic colloidal systems, formation of particle strings were observed along what appear to be grain boundaries of nematic polydomains. These grain boundaries arise from differences in the local nematic director, where intersection

of differing director orientations occurs. Previous research has shown that the free energy per unit surface area at unfavorable grain boundaries may be lowered in block copolymer microstructures by blending the copolymer with a homopolymer that is chemically similar to one of the copolymers (Duque 2002). Further research revealed that the same phenomenon could be used with nanoparticles in copolymer/nanoparticle blends (Listak 2006). Here, the phenomenon is observed to occur in a nematic liquid crystal, where nanoparticles stabilize high energy boundary structures. While this result is preliminary, it was observed to occur with relative frequency in various different samples. Further research will be done to explore this phenomenon.

4.2.4. Conclusions

Surface functionalized silica microspheres were dispersed in the nematic phase of a thermotropic liquid crystal, and loaded onto rubbed PVA-coated glass slides. Formation of strong homeotropic (normal) interactions was observed, indicated by the formation of hedgehog defects around particles. The loss of long-range elastic energy caused by these defects was observed to act as a driving force for linear alignment of particles. This linear alignment acted to minimize the elastic energy lost. Time-dependent aggregation of particles is also observed, with limited observation of time-dependent aggregation oriented in an anisotropic fashion. Finally, stabilization of grain boundaries in the nematic phase, a phenomenon not previously reported for nematic polydomains, was observed. Future work will focus on exploring this phenomenon, and the implications for nematic liquid crystalline colloids.

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6. Appendix A – List of Learning Module PowerPoint Slides

Nanoparticle Dispersions: Simple Access to Modern Nanotechnology

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Nanotechnology

Definition:

- Manipulation of devices and materials on nanometer scale

The Future of Technology

Nanomaterials

Modern commercial nanotechnology:

- ~1500 products on the market
- Surface coatings, cosmetics, electronics

Most applications: combine nanoparticles with existing technology (composites)

Nanoparticle vs. Microparticle

Simple example: Replace titanium dioxide microparticles with nanoparticles

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What is titanium dioxide used for?

Paints & Coatings

- All colors

Cosmetics

- Sunscreen

Food

- Colorant

Case study for Micro vs. Nano:
Titanium dioxide in surface coatings and paints

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Titanium Dioxide

Chemical formula: TiO_2

Common, white pigment

- 4.6 million tons used per year
- Accounts for 70% of all pigments used

Useful properties:

- Very white
- Brightness
- Hiding power/opacity

Good hiding power

Poor hiding power

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Exotic Properties in TiO_2 -Infused Coatings

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Nanoparticles and Surface Area

Surface area of spherical particle: $4\pi r^2$

Volume of spherical particle: $\frac{4}{3}\pi r^3$

Ratio of surface area to volume: $\frac{3}{r}$

Two smaller particles have more surface area than a single, large particle of equivalent volume

For 1cm^3 of equally sized spheres:

Particle Radius (nm)	Total Surface area (m^2)
10000	0.3
1000	3
100	30
10	300

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Nano TiO_2

Smaller particles than standard TiO_2

- Greater total surface area
- Enhanced surface properties

One small problem: TiO_2 is not soluble in water, or other common solvents

TiO_2 must be dispersed through careful formulation of the incorporating product

Going from micro to nano-sized particles requires additional formulation changes

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Dispersants

Chemical additive which aids in dispersion of insoluble matter

Used in a variety of industries:

Coatings

- Disperse inorganic pigments

Automotive

- Prevent residue buildup in engines

Oil drilling

- Used in drilling fluids to disperse solids and control foam

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Dispersants for Aqueous Systems

Surfactants

- Head group interacts strongly with pigment
- Tail(s) solvated, extends outward

Purpose: stabilization of dispersions

- Charge stabilization
- Steric Hindrance

BYK

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Inter-particle interactions

Steric forces

- Not enough room to fit together
- Dispersants-"tiny springs"

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Particle Size and Dispersants

Smaller particles sizes:

- Much greater interfacial area
- More dispersant required to fully cover the surface

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Experimental Objective

Demonstrate the effects of two variables:

- Size of TiO_2 particles
- Concentration of dispersant (relative to TiO_2)

Dispersion of particles in an aqueous slurry
(mixture of particles and water)

Measure viscosity to evaluate degree of dispersion

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Materials

Ti-Pure® R706 (DuPont)

- Pigment grade micropowder
- Particle size- 360 nm

TTO-51(A) (ISK, LTD.)

- Nanoparticle powder
- Particle size- 10-30 nm

DISPERBYK-190 (BYK)

- Formulation/structure is proprietary knowledge
- Commonly used for pigment dispersion in aqueous systems

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Results

Viscosity- "thickness" of fluid
Shear rate- how quickly the fluid is disturbed

Nano requires more dispersant
- 5-10 times more than micro

Due to difference in surface area
- Nano has 10-20x surface area
- More molecules required to cover each particle

Dispersant Demand

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Experimental Conclusions

Difference in surface area changes basic properties of nanoparticles

- Higher surface area results in more water absorbed, more dispersant required, and a fluffier powder
- Involving nanoparticles in a process may require a significant amount of redesign
- Fundamental understanding of processes at the nano-scale is necessary before new technology can be made

Micro	Nano
2% dispersant	9% dispersant
Part A	
Araldite® F2 3965-1 US Epoxy Emulsion	
Water	
Total - Part A	
Part B	
Araldite® 3988 Waterborne Curing Agent	
Disperbyk® 332 (Byk-Chemie, USA)	
Byk® 624 (Byk-Chemie, USA)	
Byk® 623 (Byk-Chemie, USA) (in DPGME)	
Raybo® 60 (Raybo Chemical Co.)	
Optiflow® 4600 (Southern Clay Products)	
Optiflow® 1100 (Southern Clay Products)	
Deionized Water	
Minex® 2 (Union Corp.)	
Tender® 1853 (Huntsman Corp.)	
Combar® KF (Combar)	
Wollastocast® 30 ES (R.T. Vanderbilt)	
Vantab® 6H (R.T. Vanderbilt)	
Moly White® C-100 (Moly White Nanotech)	

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Follow the Money

Two minutes and \$10 in materials to show how the simplest nanotechnology is nontrivial to use

- What about worldwide figures?

Source: nanowerk.com

Tens of thousands of publications annually

- 1000's of man-hours per publication

Source: nanotechweb.org

2013 Nanotechnology Investments:

- Total (public and private): **\$14 billion**

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From Theory to Practice

There's a lot of research going on in the world of nanotechnology

Nanoelectronics:

- High efficiency solar cells
- Quantum computers

Structural materials:

- Body armor
- Space elevator

Nanomedicine:

- Artificial Muscles
- Targeted drug delivery

More research is needed:

- Explore unique fundamental properties
- Turn properties into functional devices