DIRECTED NANO-PATTERNING OF
POLYMER NANOCOMPOSITE THIN FILMS

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Thesis

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ABSTRACT

Polymer-nanoparticle (NP) composites have been studied extensively as a core material that exhibits advantageous optical, electrical and mechanical properties in nanotechnology. It has been well-established that a specific distribution state of nanoparticles in a polymer matrix is the key issue to optimize a desired polymer nanocomposite (PNC) property. However effective way of controlling the spatial distribution of nanoparticles is still a recurring challenge. Here we demonstrated facile processing approach to fabricate nanocomposite thin films with controlled nanoparticle dispersion state by exploiting the entropic interactions, thereby controlling the macroscopic performance of the material. The interactions of nanoparticles with polymers are mediated by the ligands attached to the nanoparticles. Location and dispersion of polystyrene grafted titanium dioxide (PS-g-TiO₂) and hydroxyl-functionalized polyhedral oligomeric silsesquioxanes (DPOSS) molecular nanoparticles in homopolymer matrices under various annealing conditions were investigated. PS-g-TiO₂ NP filled low molecular weight polystyrene thin films were thermally annealed under nanoscale pattern confinement, which was fabricated by imprinting digital recording media discs (DVD) pattern onto polydimethylsiloxane (PDMS). The NP dispersion changed from randomly distributed
to aggregating at the elevated regions of the imprinted films due to the entropic interaction caused by the size difference between the particles and the matrix chains.

DPOSS-PS is a type of giant shape amphiphiles which are built up by covalent bonding of molecular nanoparticles. When added to low molecular weight homopolymer matrices, DPOSS-PS nanoparticles exhibited better dispersion in PMMA than in PS matrix. Additionally, to understand the morphology transition and phase separation kinetics, various loading fraction of DPOSS-PS were incorporated into PMMA matrix. Phase separation at multiple length scales was observed when the composition of DPOSS-PS is in the range of 5% and 70%.
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CHAPTER I

INTRODUCTION

Polymer-nanoparticle (NP) composites are finding applicabilities in the field of photocatalysts, electronic devices, coating industry and environmental protection.\(^1\) As a key component in nanotechnology, polymer nanocomposites (PNCs) has been studied extensively. They offer a unique platform to modify macroscopic properties of materials by controlling the organization and dispersion of nanoparticles at nanoscale. In this thesis, we will be focusing on an alternative approach to modify the nanoparticle dispersion state in a homopolymer matrix.

1.1 Nanoparticles

Nanoparticle research has been an extremely interesting object in nanotechnology and materials science over the past few decades due to their enormous technological importance, such as their potential applications in optical, biomedical and electronic fields.\(^2\) Nanoparticles are typical particles between the size range of 1 and 100 nanometers. In nanotechnology, particles are defined as small objects that have the behavior as a whole integrity with respect to its transportation and properties.\(^3\) Nanoparticles can act like a bridge between the bulk materials and corresponding atomic or molecular structures. In a macroscopic view, the bulk material would have constant physical/chemical properties regardless of its
size. While for nanoparticles at nano-scale, their size-dependent properties are quite conspicuous. During the transition of materials changing from bulk to nano-size, the percentage of atoms placed at the surface of materials increasing dramatically. For instance, the number of atoms at the surface is quite neglectable compared to the total atom number in a bulk materials larger than one micron. However, the situation is contrary for nanoparticles. Thus, some interesting and unique properties of nanoparticles are due to their large specific surface area of the materials to a great extent. Nanoparticles can be classified into several categories based on substances, such as carbon-based nanostructures (fullerenes, carbon nanotubes), quantum dots (CdSe, CdSe-ZnS), metal oxide nanoparticles (ZnO, TiO2, Fe3O4), metallic nanoparticles (Ag, Au, Cu), organic polymer nanoparticles (Molecularly Imprinted Polymer) etc. Different types of nanoparticles have potential application in a variety of fields. Nanoparticles usually possess distinctive optical properties due to their small size to confine electrons and produce quantum effects. Absorption of solar radiation is also much higher and more efficient in materials which are composed of nanoparticles than those in regular thin films of continuous sheets. It is ideally in some cases to control the absorption of solar radiation by manipulation the size, shape and chemical structures of the nanoparticles. Meanwhile, the high ratio of surface area to volume of nanoparticles provides immense driving force for diffusion, especially at relatively high temperatures. Moreover, nanoparticles have been found to incorporated some extra properties into daily used products. For instance, the addition of titanium
dioxide nanoparticles provides the self-cleaning effect, and the particles are invisible to the naked eyes due to their nanoscale sizes.\textsuperscript{10} Zink oxide nanoparticles, as well as titanium dioxide, have been utilized extensively in the fabrication of sunscreen lotions and creams as physical sunblock components because they have been found to possess superior ultraviolet light blocking properties. Clay nanoparticle is another widely used materials when imparted into polymer matrices to improve mechanical properties as reinforcement agent.\textsuperscript{11} Nanoparticles composed of semiconducting materials, also known as quantum dots is they are in the size range of sub 10 nanometers where quantization of electronic energy levels dominates. Semiconductor nanoparticles exhibit great optical, electronic and mechanical properties and have attracted immense interest in the manufacturing of electronic circuits or photonic crystals, while they are also used in drug delivery, imaging agents and other biomedical applications. Another interesting type of nanoparticles is termed as Janus particle which contains one half hydrophilic part and the other half hydrophobic. Janus particles are specifically efficient in stabilizing emulsions since they can self-assemble at the interfaces of water-oil mixture as surfactants. Metal nanoparticles with tailored chemical and physical properties have the potential application in both catalysis and material science fields.\textsuperscript{12} In most of the cases, control the spatial dispersion of nanoparticles becomes extremely important. In the presented thesis, a novel way of capillary force lithography is used for controllably distributing polymer grafted nanoparticles in polymer matrices. Both
metal oxide nanoparticle Titanium Dioxide (TiO2) and molecular nanoparticle DPOSS will be studied to investigate their spatial distribution in polymer matrices.

1.1.1 Polystyrene Grafted Titanium Dioxide Nanoparticle

Over the past few decades, Titanium dioxide (TiO2) has been extensively used in pigment, UV-blocking, toothpaste and many other products since its commercialization in early twentieth century. Fujishima and Honda et al. discovered that under the UV light, the photocatalytic splitting of water would occur on a TiO2 electrode.\textsuperscript{13} Tremendous efforts have been devoted to the exploit of TiO2 material since then. It has been found that TiO2 can be used in many areas various from photovoltaics to electrochromics and sensors.\textsuperscript{14} However, many of these applications depend not only on the versatile properties of the TiO2 material, but also on the various modifications of TiO2.\textsuperscript{15,65} In this study, the use of polymer grafted TiO2 nanoparticles are introduced.

Polystyrene (PS), as an indispensable and commercially available material, plays an important role in the modern industry due to its low-cost and significant physical properties.\textsuperscript{16} PS grafted TiO2 was synthesized as a dispersing tool in this study and we prove that the dispersion of TiO2 nanoparticles was largely improved after functionalization of PS chains. The synthesis method of PS-g-TiO2 is shown below and the experimental process can be found in the experimental section.
1.1.2 Hydroxyl-functionalized Polyhedral Oligomeric Silsesquioxanes

Polyhedral oligomeric silsesquioxanes (POSS) is a kind of molecular nanoparticles (MNPs) with exquisitely defined chemical structures and surface functionalities. MNP can be seen as shape-persistent “nanoatoms” that can act as elemental building blocks for the synthesis of giant molecules through bottom-up approach. Typical MNP includes, but are not limited to fullerenes, polyoxometalates (POM), folded globular proteins and POSS. Among them, POSS is a type of unique inorganic compound that has precisely cage-like nanostructures. Polymer bonded POSS can be seen as a type of giant shape amphiphile, which are polymer tail-tethered molecular nanoparticles where the two components have enormous chemical differences to impart amphiphilicity. The resulting giant molecules can be seen as a size-amplified version but perfectly capture the functional structural features of their small molecule counterparts. As a result, giant surfactants bridge the gap between small molecules and block copolymers while possess a duality of both counterparts regarding of their self-assembly behaviors. Unconventional nanostructures of those MNPs can be obtained in precisely confined environments...
or via self-assembly. It is demonstrated that MNPs are a unique element in building engineering nanostructures.

There are many kinds of MNP-based giant surfactants according to their functional groups, such as hydroxyl-functionalized POSS (DPOSS), carboxylic acids-functionalized POSS (APOSS), perfluorinated-functionalized POSS (FPOSS), as is shown in the schematic below. They can self-assemble into a variety of nanostructures with sub-20 nanometer feature sizes among bulk, thin film and solution states. The polymer-tethered giant amphiphile was synthesized using sequential “click” approach, as described in the experimental section. In this study, the polymer tails chosen are hydrophobic polystyrene, in order to be chemically identical to the polymer matrix.

![Schematic of POSS-PS with different functional groups.](image)

**Figure 1-2. Schematic of POSS-PS with different functional groups.**

1.2 Polymer Nanocomposites

Nanocomposite is a type of multiphase solid material that one of the phases has the dimension of less than 100 nanometers. In the broad point of view,
nanocomposite can include colloids, gels, copolymers and porous media, but in most cases it refers to the solid combination of nanoscale phases and a bulk matrix which have differences in properties due to dissimilarities in chemistry and structure.

Nanocomposites can be classified into ceramic-matrix nanocomposites, metallic-matrix nanocomposites, and polymer-matrix nanocomposites. In this research, we will focus on the polymer nanocomposites (PNS) of nanoparticles filled polymer matrices. PNCs are composed of a polymer or copolymer with nanoparticles or nanofillers dispersed in the polymer matrices as various shapes (fibers, spheroids, platelets etc.). Inorganic-polymer nanocomposites are of immense interest for promising materials due to their largely improved and combinational properties. Incorporation of nanoparticles into a polymer matrix has been investigated as an efficient approach to improve the optical, mechanical, electrical and magnetic properties of hybrid materials with the combination of superior properties of nanoparticles and the stability and processability of polymer matrices. However, a continuous challenge in the current field of nanocomposites is to control the location and spatial dispersion of nanoparticles (NPs) in polymer matrices. This issue is getting increasing attention since it is well-established that the specific controllable dispersion of nanoparticles is critical to the optimization of desired properties of PNCs. The objective of this project is to establish effective method to arrange NP dispersion in polymeric thin films.
1.3 Capillary Force Lithography (CFL)

Photolithography has become the most useful way for the patterning of fabrication of electronic and optical devices. With the increasing demand for smaller feature sizes in electronic circuits, lithography is approaching its practical limit. Thus there need new technologies for patterning on much smaller scales.

Capillarity can be used in the patterning of polymeric films as a potential method, introduced by Kahp Y. Suh and co-workers.\textsuperscript{27} It has been investigated that CFL induced patterning can lead phase separation between PS/PVME blends.\textsuperscript{28} When a liquid material wets a capillary tube, the wetting phenomenon is likely to induce the capillary rise of the liquid in the tube, if the wetting leads to lowering the free energy of the system. Based on the capillary force, a cartoon illustrating the capillary force lithography technique is shown below. Polydimethylsiloxane (PDMS) is used as an elastomeric mold. The mixture of PDMS elastomer and curing agent were cured against a complementary stable structure (in this study we use DVD pattern) to fabricate a PDMS master which has a planar surface with protruding patterns. In this experiment, we use DVD as the template. After casting films onto a certain substrate, the PDMS would be placed on top of the film and then annealed at the temperature above the glass transition temperature $T_g$ of the polymer. Although the spontaneous wetting would occur under the PDMS mold, special care should be taken to avoid air bubbles or gaps between the interfaces of the mold and the polymer. During the annealing process, capillary force induces the polymer melt
to fill up the voids under the molds, thus obtaining the negative replica of the patterning mold after cooling and removing the mold.

Figure 1-3. Schematic of capillary force lithography technique.

During the fabrication of the PDMS master, the mold should be made pretty soft (curing agent ca. 6%) to avoid separation from the polymer surface under high annealing temperature due to the tremendous difference in the thermal expansion coefficient between the substrate and the mold ($\alpha_{\text{PDMS}} \gg \alpha_{\text{sub}}$). Therefore, there is no need to place weight or pressure on the mold to keep it contact with the substrates. The advantages of choosing PDMS as the mold are its low reactivity toward polymers and its sufficient elasticity to separate from the polymer film after annealing.
The driving force of the capillary force is that wetting of the PDMS channel tube by polymer melt lowers the free energy of the system. During the wetting of the mold, the capillary force is given as

\[ F_{\text{cap}} = \frac{2\gamma \cos \theta}{r} = \rho gh \]

Thus, the maximum height that the polymer melt can rise up to can be calculated by

\[ h_{\text{max}} = \frac{2\gamma_{\text{polymer/air}} \cos \theta}{\rho G L} \]

where \( L, h_{\text{max}}, \gamma_{\text{polymer/air}}, \theta, \rho \) and \( G \) represent the width of the channel, the maximum height, the surface tension at the interface of the polymer/air, the contact angle, the density of the polymer, and the gravitational constant, respectively. Also the polymer melt is considered liquid-like and the interaction at the interface should be negligible, thus it has become a competition between the gravitational force and the capillary wetting force.

Another important concept of the CFL is the time it takes to fill up the voids for the polymer melt. It can be estimated using

\[ t = \frac{2\eta z^2}{R \gamma_{\text{polymer/air}} \cos \theta} \]

where the effect of gravity is neglected, thus the flow rate of the polymer melt depends on the surface tension and the viscosity, as well as the size of the capillary tube. In the above equation, \( z, t, \eta \) and \( R \) represent the length of capillary, mold filling time, viscosity of the melt and the hydraulic radius (the ratio of the liquid...
volume in the capillary to the area of the interface between the solid and the surface, which is approximately equals to one half of the width L).\textsuperscript{27}

Nanoparticles provide an alternative route to modifying polymer thin film properties, however the control of morphology and dispersion of functionalized nanoparticle filled polymer films is quite difficult. Herein the method of capillary force driven soft-confinement pattern induced nanoparticle segregation (SCPINS) was introduced as a way of controlling the spatial distribution of nanoparticles in polymer matrices. The capillary force lithography can be a simple yet robust approach for nano-dimensional patterning and has the potential to become a strong candidate in the fabrication of electronic circuits as an alternative to photolithography.\textsuperscript{30}
CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

Polystyrene (PS) with a molecular weight of Mw=3kg/mol and a polydispersity of 1.09 was procured from Polymer Source Inc. (Sample# P8921-S). The glass transition temperature (Tg) of PS is 62°C. Poly(methyl methacrylate) (PMMA) with a molecular weight Mw=3.4kg/mol and a polydispersity of 1.09 was bought from Polymer Source Inc. (Sample# P9059-MMA). The Tg for PMMA is 105°C. Thermal analysis of the polymers was performed using a differential scanning calorimeter at a heating rate of 10°C/min. All polymers were used as obtained. The solvent used in this study is toluene, purchased originally from Fisher Scientific (Certified ACS; ≥ 99.5%; F.W. 92.14; CAS: 108-88-3; T24-20). The concentration of the toluene is above 99.5% and the density is 0.866g/cm³. Poly(4-styrenesulfonic acid), 18 wt% solution in water was purchased from Aldrich Chemistry (Batch #MKBC 5645) and dissolved in isopropyl alcohol (IPA), to make 1 wt% PSS solution for preparation of TEM samples.

Polystyrene grafted Titanium dioxide (PS-g-TiO2) was synthesized using “grafting to” approach. The core TiO2 nanoparticles were purchased from Sigma Aldrich Chemical Company, with an average diameter of ca. 23~25nm and surface
area of ca. 35~65m$^2$/g. Before synthesis, the nanoparticles were dried in the oven under vacuum at 110°C for 4 hours to remove moisture and other potential volatile organics. Silane coupling reagent (styryl ethyltrimethoxysilane) was used for the functionalization of TiO$_2$ nanoparticles, purchased from Gelest. Hydroxyl terminated polystyrene with molecular weight ca. 15kg/mol was used as the grafting chain via Williamson ether synthesis. The synthesized PS-g-TiO$_2$ was characterized using NMR, GPC, and TGA techniques. The grafting density of PS chain is ca. 47%, which is estimated through TGA weight loss during the process of decomposition of the grafting PS chains. The equation is shown as$^{32}$

$$
\sigma = \frac{wN_A}{M_n} = \frac{a \rho N_A}{4(3.14)a^2n} = a \rho N_A \times 10^{-21}/3(1 - z)M_n
$$

where $w$, $z$ and $M_n$ are the weight, weight loss and molecular weight of grafted chains(PS); $N_A$ is the Avogadro’s constant number; $a$, $\rho$ and $n$ are the radius, density and number of nanoparticles, respectively. More details can be found elsewhere.$^{33}$

Hydroxyl-functionalized polyhedral oligomeric silsesquioxanes(DPOSS) was synthesized using sequential “click” approach, which is a combination of both “grafting-to” and “post-functionalization” strategies. Copper-catalyzed Huisgen [3+2] cycloaddition (CuAAC) was used for POSS-polymer ligation and can save the purification process due to the stoichiometric bonding between polymers and POSS. The subsequent thiol-ene addition reaction is performed for POSS cage functionalization. The size of the DPOSS is ca. 2nm and the molecular weight of the
A grafted PS chain is 2.8kg/mol. More details can be referred to elsewhere. A schematic showing the chemical structure of DPOSS-PS can be viewed below in Figure 2-1. It basically consists of the POSS cage tethered to PS chain.

Figure 2-1. Schematic of DPOSS-PS chemical structure, made by the software Chembiodraw.

The substrates that were used in this project are N-type silicon wafers (orientation <100>), the size of which are 150mm and the thickness is 625µm, purchased from Quest International, Inc. Before depositing films, silicon substrates were rinsed with toluene and then put under ultraviolet-ozone (UVO) treatment for two hours. Digital UV Ozone system (Model #PSDP-UV12, 100 VAC, 50/60 Hz) was purchased from Novascan Technologies, Inc. UVO exposure can efficiently oxidize the substrate surfaces thus increase their hydrophilicity.
2.2 Sample Preparation

Here the preparation process of both soft elastomer PDMS mold and the deposition of nanoparticle filled polymer thin films were introduced. The synthetic process of both nanoparticles can be found elsewhere as introduced later.

2.2.1 DVD and Cross-Hatch Template Patterned PDMS

During the capillary force lithography process, the polydimethylsiloxane (PDMS) was cured by a mixture of curing agent/ PDMS uncured elastomer at a weight ratio of 1:20. The PDMS mold was then fabricated by casting PDMS onto the DVD exfoliated pattern surface. The surface morphology and sizes of the PDMS mold was obtained by AFM and is shown in the next chapter. The weight content of the curing agent is 4.76%, thus making the mold soft enough to prevent the mold from separating the substrate during annealing. The well mixed PDMS and curing agent were poured on top of DVD patterned templates followed by vacuum to remove air bubbles trapped in the mixture and oven curing under 120°C for 6 hours. The patterned PDMS mold was put in contact with the surface of the polymer thin film without any exotic load or pressure, followed by heating up to a certain temperature above the Tg of the polymer. After annealing and cooling to ambient temperature, the PDMS mold was removed from the film surface and the negative replica of the DVD channel pattern on the polymer was characterized by atomic force spectroscopy (AFM) and transmission electron microscopy (TEM). PDMS was then peeled off from the template to obtain approximately 1mm thick DVD patterned
mold. The DVD 100 pack spindle was purchased from Sony Corporation Taiwan Limited. Before being used as a nanoscale template, the polycarbonate surface layer of the DVD was peeled off to reveal the channel pattern. Scotch tapes were used to remove the aluminum layer off the pattern, followed by rinsing with methanol to remove colored dye before using. Scotch tapes were then used to cover the hole in the middle and enclose the edges of DVD. The maximum height difference of each nanoscale DVD channel is 120nm and the wavelength is 750nm.

The cross-hatch pattern was created basically using two orthogonal aligned channel patterns. Firstly two pieces of DVD-patterned PDMS were fully cured using the procedure described above. Liquid-like mixtures of PDMS and curing agent were then poured onto the precured PDMS surface, followed by heating at 120°C for 3~4 minutes until it’s solid enough to be peeled off from the bottom PDMS elastomer. This half-cured PDMS was kept on another piece of precured PDMS surface at a certain angle (usually 90° perpendicular to the original channel pattern direction) and heated for another half an hour at 120°C. A cross-hatch pattern was formed with two height differences 60nm at channels and 120nm at knots.

2.2.2 TiO2 Nanoparticle Filled Polymer Film Deposition

Different polymer brushes grafted TiO2 was synthesized by Praveen Prakash Pitliya from Prof. Dharmara Raghavan’s group at Howard University. The core size of TiO2 is between 23~25nm and was purchased from Sigma Aldrich Inc. The molecular weight of nanoparticle grafted Polystyrene is approximately 15kg/mol. The grafting
density is 47%, which was determined using TGA mass loss, which was attributed to the organic functionality attached to TiO2 core.

Solutions of 15% weight percent PS were made by dissolving Mn=2.8k PS in toluene, followed by vortexing for several hours. Similar procedures were used for making 15wt% PMMA solutions. PS grafted TiO2 nanoparticles were also dissolved in toluene, with the concentration being 2mg/ml, followed by sonication treatment for one hour. Solutions of PS and PS grafted TiO2 were admixed in an appropriate amount to form a final solution of composition ratio (TiO2 nanoparticle/ polymer matrix weight) 10% and 20%. Prior to flow coating thin films, all the polymer solutions were filtered using 0.2µm Millipore membrane filters. Since the system has identical polymer brush and polymer matrix, thus considering the entropy effect of the system: \( \chi = 0 \); under the condition of TiO2-g-PS in PVME system where \( \chi < 0 \) and TiO2-g-PS in PMMA system where \( \chi > 0 \) will be studied and discussed somewhere else. Thin films of PS-g-TiO2/PS nanocomposites were flow coated on top of UVO treated silicon substrates using the above mixture solutions. The flow coating conditions were varied to get different film thickness ranging from 50nm to 150nm. Film thicknesses were measured by interferometer and ellipsometer. Thermal-annealed samples were kept in ovens (Fisher Scientific Inc.) for a certain time period at predetermined temperatures under vacuum. DVD-patterned films were kept in ovens prior to placing PDMS molds on top of the films.
2.2.3 DPOSS-PS Nanoparticle Filled Polymer Film Deposition

The molecular weight of polystyrene grafted to DPOSS nanoparticle is approximately 2.8kg/mol. Polystyrene (Mn=2.8kg/mol), Poly(methyl methacrylate) (Mn=3.1kg/mol, 1.5kg/mol) were used as polymer matrix in this study. Same procedure was adopted for making solutions with different molecular nanoparticle versus polymer matrix weight ratio.

2.3 Instrumentation and Characterizations

AFM and TEM are main characterization methods used in this study. NMR spectroscopy was also used to characterize the composition of DPOSS-PS. The thicknesses of nanocomposite thin films were measured both Thin Film Interferometer and ellipsometer.

2.3.1 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) or Scanning Force Microscopy (SFM) is a relatively high resolution type of scanning probe microscopy (with maximum lateral resolution: 10nm; vertical resolution: 0.1nm) widely used for the investigation of surface morphology of materials. A schematic illustrating basic principles of AFM is shown in Figure 2-2. The AFM consists of a cantilever with a sharp tip at the end which is used to scan the surfaces of samples. The materials of the cantilever are usually silicon or silicon nitride with a tip radius of curvature on the scale of nanometers. The AFM has several types of operating modes depending on the application required. Basically, static (contact) modes and dynamic (non-contact or
tapping modes, where the cantilever is oscillated or vibrated at a constant frequency just above the sample surfaces) modes are two general categories. In this study, under tapping mode, TM 200 Tapping Mode Tips (Probes, Tip Radius < 15nm, f: 145-230kHz, k: 25-95N/m, Sansa Probes, Santa Clara, CA) were used. During the engaging process, the tip is moving closer to the sample surface, the interaction forces between the tip and the sample lead to a deflection of the cantilever.\textsuperscript{35} A beam of the laser is generated at the tip end and is reflected to a position-sensitive photodetector. As the tip tracks down the surface topography of the sample, its oscillation frequency is determined by the surface features, recorded as phase contrast images. Along with the forces, additional properties such as adhesion, DMT modulus, deformation, and dissipation may simultaneously be recorded.

Compared with other characterization techniques such as optical microscopy and electron based microscopy, the main difference between them is that AFM does not rely on lenses or beam irradiation. Therefore, AFM owns the advantage that it does not need to create a vacuum space for beam guidance or special treatment on samples (such as staining), meaning that it does not have a limitation of space resolution. In this work, surface morphologies of the nanocomposite thin films were recorded on a Dimension Icon AFM (Bruker AXS Corporation, Camarillo, CA) under both Tapping Mode and Peak Force Quantitative Nanomechanical Property mapping mode. The controller used is Nanoscope V (Veeco Instrument Inc., Santa Barbara, CA).
2.3.2 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a widely used microscopy technique where a beam of electrons is transmitted through the specimen, usually less than 100nm ultra-thin. The resolution limit of TEM is approximately 0.1nm. The beam interacts with the specimens as it passes through them. An image is recorded based on the interactions which reflect directly the electron cloud density. The TEM setup consists of several components, including generally an illumination system and an imaging system. The schematic of TEM setup is shown in Figure 2-3. The illumination system is composed of a vacuum system where the electrons travel through, an electron emission source for generating electron stream, a series of electromagnetic lenses, as well as electrostatic plates. The electron gun is used to emit electrons via a heated tungsten filament and the electron density is controlled by the operating
voltage that applied on the filament. A grid cap allows generating a spot-shaped
focused electron beam. The lenses allow the operator to guide and manipulate the
electron beam as needed. Besides a specimen stage is used for the insertion, motion
and removal of specimens where the beam travels through. The imaging system is
composed of the objective lens, the projective lens, and the CCD sensors, which are
used for generation of images of the specimen. In the output images, the dark areas
correspond to strong scattering parts in the specimen.36

In this study, TEM images of both TiO2 and DPOSS-PS filled polymer matrix
were recorded on JEOL 1200 EX II with an accelerating voltage of 120 kV. Prior to
preparing TEM samples, 1 wt% PSS solution was used to coat films on UVO treated
silicon wafers. Those films were kept in an oven at 140°C for at least 6 hours to
remove excess solvent. Then PSS coated films were kept in UVO for ca. 7 minutes to
make the surfaces hydrophilic prior to flow coating polymer films on top of them.
Due to the water-soluble property of PSS, these double-layer thin films were
immersed at a certain angle into deionized water in the beaker, and PSS would
dissolve while the top polymer layer would float onto water thus can be transferred
onto TEM copper grids, which were purchased from TED Pella, Inc. After ca. 3
minutes, the excess solvent was wicked away by placing the copper grids onto a
piece of filter paper. The samples were then kept in the desiccator under vacuum to
allow drying. TEM images were taken on a digital CCD camera and processed using
the same accessory digital imaging system.
The molecular nanoparticle used in this study has similar electron cloud densities to the polymer matrix, thus it’s necessary to enhance the electron density between them under certain circumstances. Staining with heavy metal oxide is the most widely used treatment for TEM contrast enhancement. Ruthenium tetroxide (RuO₄) and osmium tetroxide (OsO₄) are the most commonly used staining agents. They can react with the aromatic and olefinic double bonds in the chemicals. Thin-film TEM samples were stained under the vapor of a 4.0 wt% OsO₄ aqueous solution in the hood for 1h to enhance the contrast between different blocks. All the TEM images were captured at several different spots (> 10) so as to be representative of the whole thin film sample.
2.3.3 Nuclear Magnetic Resonance Spectroscopy (NMR spectroscopy)

Nuclear Magnetic Resonance Spectroscopy (NMR) is a commonly used technique in determination the magnetic properties of certain atomic nuclei. NMR can provide information on the structure, dynamics, reaction state and chemical environment of sample molecules. It is unique and analytically tractable typically for small molecules, and can distinguish different functional groups, as well as identical functional groups in different chemical environment, thus is widely used to confirm the identity of substances. The NMR sample is prepared usually in a thin-walled glass tube, called an NMR tube. When placed in a magnetic field, the NMR active nuclei (\(^1H\) or \(^{13}C\)) would absorb electromagnetic radiation at a certain frequency characteristic of the isotope. Since the preparation of NMR sample requires dissolving in a solvent, the vast majority of nuclei in a solution which is reflected in the peak would belong to the solvent.\(^{37}\) In this study, the \(^1H\) NMR spectra were obtained in CDCl\(_3\) (Sigma-Aldrich, 99.8% D) at 30\(^\circ\)C using a Varian NMRS Mercury 300 or Varian 500 spectrometer, provided with an autosampler. For \(^1H\) NMR measurements, the concentration of the sample was ca. 10~20mg/ml. The \(^1H\) NMR spectra show the residual proton impurities in the CDCl\(_3\) at \(\delta\) 7.27ppm.\(^{34}\)

2.3.4 Film Thickness Measurement

Thicknesses of single-layer nanocomposite thin films were determined by a thin film Interferometer (F-20 UV Thin Film Analyzer, Filmetrics, Inc.), with the resolution of 1 nanometer. Thicknesses of multilayer (PSS precoated films) were
determined using an M-2000 spectroscopic ellipsometer (J.A. Woollam Co.). Ellipsometry is another widely used optical technique for investigating properties of thin films, including complex refractive index and dielectric function. It can be utilized in the characterization of composition, thermal expansion, roughness, electrical conductivity and thickness of materials. The sensor of an ellipsometer can detect the signal change in polarization, which is quantified by the amplitude ratio and the phase difference of the reflected waves, as the incident wave interacts with the specimen. Since the signal depends on the material properties and the thickness, ellipsometry is considered to be a universal technique for contact-free determination of thin film thickness. The basic structural design of an ellipsometer is shown below.

Figure 2-4. Schematic of basic structure of an ellipsometer.38
2.4 Image Analysis

AFM images were first analyzed using NanoScope Analysis (Bruker AXS). TEM images were digitized using image analysis software ImageJ (NIH) and the Fast Fourier Transform (FFT) algorithm was performed using Gwyddion. When calculating density ratio of the nanoparticles in the DVD imprinted films, both AFM and TEM images were converted to 8-bit black/white image type, followed by adjusting threshold function to fully reveal nanoparticle distribution in a particular area. Size distribution and other functions of nanoparticles can be determined further using ImageJ. Domain spacing can be determined using Gwyddion, TEM images were cropped appropriate sizes, followed by performing 2D FFT in the data process column. By fitting Gaussian function in the FFT image, the average magnitude \( r \) between peaks can be determined. The reciprocal of \( r \) is the domain spacing. An example of the Fast Fourier Transform process is shown below. Origin 8.5, Microsoft Office and SketchUp 2016 were used in this study to analyze data statistics and design schematics.

![Figure 2-5. Schematic of FFT on DPOSS-PS TEM image](image-url)
CHAPTER III

RESULTS AND DISCUSSIONS

3.1 PS Grated TiO2 Nanoparticles

Incorporation of nanoparticles into polymer matrices has been investigated extensively as an efficient way to improve the properties of materials, such as mechanical strength, electrical conductivity, and optical properties. However, the fabrication of novel functional materials, such as photocatalyst, photonic bandgap materials, nanostructured solar cells and high-density storage media, all requires well-controllable dispersion of nanoparticles. For the last past few decades, a variety of techniques have been developed to selectively control the arrangements of nanoparticles, including changing the surface chemistry of the nanoparticles by varying the composition of grafting ligands on nanoparticles in a block copolymer (BCP) matrix, introducing hydrophilic nanoparticles, tailoring the areal chain density of grafting ligands, and tuning the relative size magnitudes of nanoparticles and block copolymer microdomains. Not only did these methods prove effective on controlling the arrangements of nanoparticles in block copolymer matrices, but also the ordering of BCP matrices could be influenced by the addition of nanoparticles. Both the morphology and orientation of BCP microdomains can be
altered in these ways.\textsuperscript{44} Despite numerous methods have been developed towards the controlled distribution of NPs, the generation of long-range ordered NP arrays are still limited.

Herein we introduced nano-patterning confinement approach to establish an efficient processing technique for the fabrication of aligned nanoparticle embedded in polymeric films.

3.1.1 Oven Annealing of 20\% PS-g-TiO\textsubscript{2} in Low Mw PS Matrix

Oven annealing is capable of providing mobility between the corona polymer of the TiO\textsubscript{2} nanoparticle and the matrix when the heating temperature is above the glass transition temperature (T\textsubscript{g}) of the polymer. For PS (M\textsubscript{n}=2.8k), the glass transition temperature is 62\textdegree C. In this experiment, 47\% polystyrene grafted TiO\textsubscript{2} nanoparticles solution was added to the low molecular weight polystyrene homopolymer matrix. The core size of the titanium dioxide nanoparticle is ca. 23\textasciitilde 25nm, and the radius of gyration (R\textsubscript{g}) of the tethered chains, which is used to characterize polymer chain size, can be calculated based on equation\textsuperscript{45}

\[
Rg = b(N/6)^{1/2}
\]

where N is the degree of polymerization, and b is the segment size. For styrene, the segment size (b\textsubscript{St}) is 0.68nm.\textsuperscript{46} We then get R\textsubscript{g} of the tethered polystyrene chain is approximately 3.53nm after substitution N=27 and b into the equation above. The solution was made with 20wt\% PS-g-TiO\textsubscript{2} to the PS homopolymer in toluene. Flow-coated films with different film thicknesses were cast on Si wafers, followed by
annealing under various conditions, including oven annealed under vacuum with or without DVD-pattern confinement at different time nodes.
Figure 3-1. AFM images of surface morphologies of 20% PS-g-TiO2 in PS matrix thin films under different annealing conditions (upper) and corresponding height profiles (lower). The annealing temperature is 180°C. Annealing time was 0, 1h, 8h and 16h.
AFM scan sizes are shown above. Film thicknesses are inserted in the lower left corners of each graph.

AFM images of series oven annealed PS-g-TiO2 nanoparticles filled PS matrices are shown in Figure 3-1. According to the color range, brighter spots correspond to higher protrusions on the surface. Thus, we can conclude that Nanoparticle aggregation happened both in as-cast films and thermal annealed films. Red and blue lines correspond to AFM height profiles, where both the average heights and the highest part of the protrusions are collected in the lower figure.

AFM images demonstrate visualized surface morphologies of the thin films. Combined with height magnitudes, it is clear that for a certain film thickness, the average height of the nanoparticle aggregation increases with longer annealing time. However, for both 8h and 16h annealing films, the average height no longer changes, indicating that the films have reached a relative equilibrium state after 8 hours. While for the same annealing time, the average heights do not change much with various film thicknesses, but the heights of the brightest part of the film surface decrease with thicker films. This is due to the better swelling of large nanoparticle aggregations in thicker films. Still limited information can be achieved only from AFM topology images. Figure 10 below illustrates the TEM images of the same batch of above discussed films.
Figure 3-2. TEM images of 20% PS-g-TiO2 in PS matrix upon different thermal annealing time nodes. The annealing temperature is 180°C and annealing times are indicated in the right. Scale bar is 800nm.

According to the TEM images above, the dark agglomerations correspond to the aggregation of PS-g-TiO2 nanoparticles. No significant tendency is observed under different annealing time or film thicknesses. Large nanoparticle aggregation happens even in 16h oven annealed films. This is contrary to what we expected at first. Since the grafting PS chains and the polymer matrix is identical in this case, it is expected that with enough annealing time, the grafted TiO2 nanoparticles would homogeneously disperse in the polymer matrix. However, the reason of the aggregation is probably the low grafting density of the TiO2 nanoparticles. The grafting density of PS-g-TiO2 is calculated to be 0.01~0.02 polymer chains/nm². Thus,
large surface areas of the nanoparticles are actually exposed in the polymer matrix, causing the aggregation behavior to lower the surface energies. The well-dispersed nanoparticles in polymer matrix require relatively high polymer grafting density, but it is difficult to fulfill for TiO2 nanoparticles due to the limiting “grafting-to” synthesis approach.

3.1.2 DVD and Cross-Hatch Pattern Confinement

Oven annealed thin films without any confinement was prepared as a comparison to the DVD and cross-hatch pattern confinement. The procedures for making such soft confinement was discussed in the Experimental Section Chapter.

Figure 3-3. AFM image (A) and corresponding height profile (B) of the DVD-patterned PDMS.

The DVD-patterned PDMS top morphology is shown above. Well-aligned channels of the DVD pattern replica are produced. From the height profiles, we can see that the height difference of the channels is approximately 120nm, and the lateral
wavelength is approximately 375nm. The DVD-patterned cross-linked PDMS overlayer was capped on top of the nanocomposite thin films with 20% PS-g-TiO2 nanoparticles. The effect of the soft pattern on polymer thin films is shown below.

Figure 3-4. Schematic of the patterning process and the corresponding reorganization of film thickness under the PDMS confinement.

Since the height difference of the PDMS channel is 120nm, the patterned thin films would reorganize into repeated thick parts and thin parts. If the initial film thickness is \( h \) nm where \( h > 60 \), after patterning the thicknesses would become \( (h+60) \) nm and \( (h-60) \) nm for both parts of the film. Meanwhile, the thick parts would have a relatively high degree of mobility and the thin parts show lower mobility due to the stronger adhesion between thin films and the substrates. We proceeded to thermal anneal the same composition thin films at varying time nodes 1h, 8h and 16h under the PDMS pattern confinement. However, the 1h annealing films cannot be immersed in water, even with precoated PSS layer beneath. The same also problem happened in PS-g-TiO2/ PMMA nanocomposite films under 1h oven annealing. While PMMA is preferential wetting to the silicon substrate, the reason for PS films remained to be unexplained. The 8h and 16h annealed films are shown in Figure 3-5 below.
Figure 3-5. TEM images (no stain) of PS-g-TiO2 in PS matrix upon 8h thermal annealing under DVD-patterned PDMS confinement. The annealing temperature is 180°C. The scale bar is: (A) (B) 800nm; (C) (D) 200nm. Film thicknesses are (A) (C) 90nm; (B) (D) 110nm.

Together with the reorganization of the film thickness, the majority of TiO2 aggregations diffused into the higher parts, as illustrated in Figure 3-5 above. To better describe the nanoparticle distribution in the polymeric thin films, here we introduce the concept of Partition Coefficient. The Partition Coefficient, abbreviated $P$, or distribution coefficient ($D$) is defined as a particular ratio of the concentrations of a compound in a mixture of two immiscible phases at equilibrium in the physical science.\textsuperscript{47} Hence, the partition coefficients are an indicator of the difference in solubility of the compound (or solute in liquid science) in these two regions.\textsuperscript{48} In the chemical and pharmaceutical sciences, it is used to measure how hydrophobic or hydrophilic a chemical substance is by comparison the solute concentrations in

34
water or 1-octanol. In this thesis, the partition coefficient is modified as the density ratio of the nanoparticles in two different regions of the DVD-patterned thin films, namely the thin parts (base region) and the thick parts (elevated region). Thus $P$ shows the relative dispersion of the nanoparticles in the polymer matrix.

![TEM images (no stain) of PS-g-TiO2 in PS matrix upon 16h thermal annealing under DVD-patterned PDMS confinement. The annealing temperature is 180°C. The scale bar for the upper row is 800nm; for the lower row is 200nm. Film thicknesses are inserted in the lower left corner of the images.](image)

Figure 3-6. TEM images (no stain) of PS-g-TiO2 in PS matrix upon 16h thermal annealing under DVD-patterned PDMS confinement. The annealing temperature is 180°C. The scale bar for the upper row is 800nm; for the lower row is 200nm. Film thicknesses are inserted in the lower left corner of the images.

As demonstrated in Figure 3-6 above, we can see that the TiO2 nanoparticles have a higher concentration in the channels in thinner films like 90nm thickness. The partition coefficient $P$ for those films are shown below. The TEM images were firstly opened in ImageJ (NIH) and cropped into a proper size, followed by changing the image type to 8-bit. The next step is to adjust the threshold to make the pristine images turn digitized ones, and then analyze particles and calculate the total area of
the particles in the high regions \( S_{\text{high}} \). The similar procedure was conducted and \( S_{\text{low}} \) was obtained. Since the lateral total area of the high parts and low parts are approximately considered equal, the density of nanoparticles can, therefore, be considered as the total area of nanoparticles divided by the thickness of one region. Thus the partition coefficient can be calculated as

\[
P = \frac{S_{\text{low}}/h_{\text{low}}}{S_{\text{high}}/h_{\text{high}}}
\]

where \( h_{\text{high}} \) and \( h_{\text{low}} \) represent the thickness of the high part and low part, respectively. Here we calculated the partition coefficient transition with increasing initial film thicknesses of the 16h oven annealed 20% PS-g-TiO2 nanoparticles filled PS thin films and the curve graph is shown below.

![Partition Coefficient versus initial film thickness](image)

Figure 3-7. The plot of Partition Coefficient versus initial film thickness for the 16h oven annealed PS-g-TiO2 filled PS thin films.

From the curve we can see that the optimum thickness should be less than 100nm due to the lowest value of the peak point, indicating that most nanoparticles are dispersed in the elevated regions. This can be explained by the free energy change
of the systems. The phase behavior of multicomponent systems including nanoparticles can be determined by the free energy \(\Delta F_m\) \[\Delta F_m = \Delta H_m - T\Delta S_m\]

where \(T\), \(\Delta H_m\) and \(\Delta S_m\) are the temperature, changes in enthalpy and entropy of the mixing process respectively. It is essential to exploit both the entropic and enthalpic interactions to direct spatial nanoparticle distribution. For nanoparticle filled homopolymer athermal systems where the grafting chains of the nanoparticle is identical to the polymer matrix, the entropic interactions usually play a more significant role in the phase behavior.\(^5^1\) This entropic interaction is often referred to as “depletion force” or “depletion attraction”. Asakura-Oosawa and co-workers introduced a model describing interactions between particles suspended in solution of polymers in the 1950s as the pioneering study on depletion interaction.\(^5^2\) If the system contains two types of spheres with diameter \(D\) and \(d\) where \(D > d\) immersed in a certain solvent, there would be a region unavailable for small spheres (with diameter \(d\)) as big spheres (with diameter \(D\)) approach each other.\(^5^3\) Therefore, an osmotic pressure of the relatively small sphere solution is generated which has a tendency to push large spheres together resulting in the particle aggregation and compaction. Depletion attraction forces have been extensively exploited between colloids systems and polymeric solutions. By taking advantages of the depletion force in polymeric solutions, densely packed hexagonal nanorods arrays can be fabricated by the combination of external electric field and solvent annealing.\(^5^4\) This technique is expected to benefit inorganic-organic heterojunction photovoltaic
Another application involves nanoparticle filled polymer films coated on a surface containing a nanoscopic notch or crack, where the depletion attraction induced by the polymer melt drives the nanoparticles into the defect and the nanoparticles would migrate to and fill the cracks at elevated temperatures. This nanocomposite coatings can potentially generate defects-free surfaces with enhanced mechanical properties.

Figure 3-8. The composite morphology diagram. \( \alpha = N/P \) Different dispersion regions are described as well dispersed particles (WD), phase separated samples (PS), strings (S), connected sheets (CS) and small clusters (SC). The color-coded lines represent a first-order cut at classifying the data into well-defined regions in the schematic where different morphologies occur.

For nanoparticles embedded in homopolymer matrices, one of the possible situation is that the grafting ligands and the polymer matrix have the same chemical structures, as discussed in this part. The dispersion phenomenon of nanoparticles is primarily determined by the entropic effects since there are no competing enthalpic interactions. Recent studies of nanoparticle distribution in bulk polymer matrices
with varying P/N (P and N are respectively the degrees of polymerization of the matrix and ligands) and grafting density $\sigma$ have been summarized in Figure 3-8. It can be concluded that at high grafting densities where ($\sigma\sqrt{N} > 2$), there exist only two limits of phase separation (PS) or well dispersion (WD); while at low grafting densities, different structures can be formed including strings, sheets and spherical aggregates.\(^{26}\) In this study, the size of the nanoparticle is more than 25nm while the $R_g$ of the PS matrix is around 4nm. Thus the grafted TiO$_2$ nanoparticles also have the tendency to be pushed to the notches of the polymeric films due to the depletion attraction force induced by the low molecular weight PS matrix.

The 16h oven annealed films seem to have reached the equilibrium states. We calculated the mold filling time\(^{27}\) of the system and is determined to be less than 10 minutes. Thus we proceeded to thermal anneal those films with varying thicknesses at shorter time nodes. The results are demonstrated below.
Figure 3-9. (A) TEM images (no stain) of PS-g-TiO2 in PS matrix upon 10min thermal annealing under DVD-patterned PDMS confinement. The annealing temperature is 180°C. The scale bar is 800nm. Film thicknesses are inserted in the lower left corner of the images. The scale bar is 800nm. (B) The corresponding plot of partition coefficient versus initial film thicknesses.

From the partition coefficient plot, we can come to the conclusion that the bottom point of $P$ happens between 80nm and 100nm, near 90nm, which is in excellent accordance with the TEM images above, showing that most of the nanoparticles embedded in the elevated regions for the 90nm DVD-pattern confined films. Also, this result is similar to the 16h oven annealed films. Thus a novel way of producing well-aligned arrays of PS-g-TiO2 nanoparticles in a polymer matrix has been discussed. The produced nanocomposites have the potential application in the fabrication of electronic circuits using the intense pulsed light (IPL) sintering technique. The IPL sintering system usually contains a xenon flash lamp which can
emit an optical spectrum of light once triggered, an aluminum reflector, a power supply, capacitors for an arc plasma phenomenon, a simmer triggering pulse controller to form sparks, and a light filter. The IPL technique has been proved effectively to sinter copper nanoink printed on a low-temperature polymer matrix substrate at ambient temperature without damaging the polymer matrix in extremely a short time (approximately 2 ms). The IPL sintering technique can alleviate the shortcomings of the low conductivity and stability of inkjet printing and flexo-printing. The key issue in the printed electronic devices is the conducting lines and films. Herein by using the pattern confinement nanocomposite films we are able to produce well-aligned metallic nanoparticle arrays and thus have the potential to be applied in the roll-to-toll fabrication process. This is a universal method due to the versatility of the confinement, which can be circuit pattern as shown in Figure 3-10(B), sensor arrays, electronic speckle pattern, as well as the DVD nano-pattern.

Figure 3-10. (A) Schematic of Intense Pulsed Light reactive sintering process in the fabrication of conductive pure copper film: (a) the PVP-coated copper NPs; (b) IPL
generator xenon flash lamp; (c) reactively sintered pure copper film.\textsuperscript{57} (B) Image of a circuit pattern.

Besides DVD-pattern, we also conducted cross-hatch pattern confinement and study its effect on nanoparticle filled polymer thin films. The fabrication of the cross-hatch pattern was discussed in the Experimental Section. Relaxation of polymer nanostructures and decay of the nano-pattern after the release of spatial confinement\textsuperscript{59} were studied. The annealing temperature is chosen to be 180°C higher than the glass transition temperature of polystyrene. The pattern and height decay results were characterized by TEM. For simple Newtonian fluids and $H$ represents the channel height or twice the pattern amplitude, $H$ is expected to follow a simple exponential decay along with time constant\textsuperscript{60}

$$\tau \approx \frac{\eta_{eff} \Lambda}{\pi \gamma}$$

where $\eta_{eff}$, $\gamma$ and $\Lambda$ represent effective viscosity, surface tension and local curvature.

The cross-hatch pattern confinement nanoparticle filled polymer thin films are shown below. In such cross-hatch lattice pattern, three thickness gradient were generated.
Figure 3-11. TEM images of 10min oven annealed 20% PS-g-TiO2 in PS (Mn=3kg/mol) under cross-hatch pattern confinement. The annealing temperature is 180°C and (insert) initial film thicknesses.

Three different film thicknesses were generated in the cross-hatch hierarchical patterns. If the initial film thickness is \( h \) nm \((h > 60)\), after cross-hatch patterning, the thicknesses of each region would become: \((h-60)\) nm for the plain lower area (most bright area in the TEM images), still \( h \) nm for the channel area (grey area) and \((h+60)\) nm for the knots (dark squares). The knots are an addition effect of two vertical aligned channels thus have the largest magnitude in height. We can tell from the TEM images that for the 80nm and 100nm films, most nanoparticle aggregations happened in the knots, while others are placed in the channels. Few nanoparticles were dispersed in the base region. However when film thickness increased to 140nm, nanoparticles seemed to have a more homogeneous distribution of the film. The depletion attraction force was no longer effective with thicker films. The pristine cross-hatch patterned films and their homogeneity recovery behavior are investigated and shown below.
3.1.3 Homogeneity Recovery Behavior of PS-g-TiO2 Filled Polymer Films

Figure 3-12. TEM images of cross-hatch pattern confined 10min oven annealed 20% PS-g-TiO2 in PS (Mn=3kg/mol) and their homogeneity recovery behavior after 4h (upper) and 24h (lower) slumping process. The annealing temperature is 180°C and inserted are initial film thicknesses. The scale bar is 800nm.

The homogeneity recovery process (“slumping”) was carried out by oven annealing the nano-patterned films under 180°C after the release of confinement.
The slumping behavior is time dependent and induced by the effective viscosity of the polymer. Different timescale slumping was investigated. For the 4h slumping images, it is clear that the single line pattern (DVD-pattern) fully and isotropically decayed. While for the two direction pattern (cross-hatch pattern), the dissipation happened not as fast. There are still line pattern trace existed as indicated by the red arrow on the image. For the 24h slumping images, the pattern fully disappeared after recovery both in the DVD or cross-hatch pattern even the nanoparticle aggregation still existed. Thus, it can be concluded that the fully homogeneity recovery of the nano-pattern films happens between 4h and 24h of slumping. However, more experiments need to be conducted to fully study the recovery behavior and effect of the addition of nanoparticles to the polymeric films.

3.1.4 Oven Annealing of 10% PS-g-TiO2 in Low Mw PS Matrix

What has been discussed extensively is the 20 wt% PS-g-TiO2 in low molecular weight PS matrix, another weight fraction of 10 wt% nanoparticle loading is also tested here.
Figure 3-13. TEM images of 10 wt% PS-g-TiO2 filled PS matrix thin films of as cast, oven annealed with and without DVD-pattern confinement. The annealing temperature is 180°C and inserted are film thicknesses. The scale bar is 800nm.

Compared to the 20 wt% loading of the nanoparticles, the as cast films have lesser aggregation. After one hour of thermal annealing, larger aggregation of the nanoparticles has formed. For the DVD-patterned films, the one with 90nm has more nanoparticles aggregated in the mesa, in comparison to the 120nm films. All those results are in good accordance with the 20 wt% loading nanoparticle filled polymeric thin films. Nevertheless, the films showed some dewetting behavior on silicon substrates due to the low nanoparticle loading percentage as shown below.
Figure 3-14. Optical Microscope images of 10% PS-g-TiO2 nanoparticles filled PS matrix dewetted on silicon substrates. The scale bar is 50μm. Film thicknesses are inserted.

From the optical microscope (OM) images, we can clearly observe the dewetting of the thin films on substrates. Such phenomenon did not occur in the 20 wt% loading PS-g-TiO2 nanoparticle thin films. Therefore, it is believed that the addition of nanoparticles has a suppression effect on the dewetting of thin films on substrates.61

3.2 PS Bonding DPOSS Molecular Nanoparticles

In this thesis, polymer grafted TiO2 nanoparticles was chosen as a representative of the metal oxide NP. Another kind of NP hydroxyl-functionalized polyhedral oligomeric silsesquioxanes (DPOSS) was studied as a representative of the molecular nanoparticle. The $^1$H NMR spectra of DPOSS-PS (2.8k) is shown below, along with the chemical structure. The peaks of the chemical shift and the corresponding chemical groups are indicated.
3.2.1 5% DPOSS-PS in Low Mw PS/PMMA Matrix

For the PS bonding DPOSS nanoparticle, the DPOSS tail is approximately 2nm and the Rg of PS (Mn=2.8k) is estimated to be 3.6nm. Thus the size of the bonded molecular nanoparticle is quite small. DPOSS-PS bulk was firstly dissolved in toluene
at a concentration of 0.02g/ml. Then different loading of nanoparticles was admixed with different molecular weight PS/PMMA polymer matrices.

Figure 3-16. TEM images (no stain) of 5 wt% DPOSS-PS in PS (2.8k) matrix under different conditions: as cast, 1h oven annealing; 1h oven annealing with DVD-pattern confinement. The annealing temperature is 160°C. Film thicknesses are inserted in the lower left corners. The scale bar is 200nm for both as cast and 1h oven annealed films, and 600nm for DVD-patterned films.

The as-cast films show that DPOSS-PS nanoparticles are well dispersed in the polymer matrix. After oven annealing for 1 hour at 160°C, obvious large aggregation is formed. The DPOSS cages have two hydroxyl groups at each end of the polyhedron, making the cages quite hydrophilic to have relatively strong competing interactions with polystyrene, driving the formation of aggregated self-assembled structures. However for the DVD-patterned thin films, the aggregation seems not so clear and the dispersion of the rounded clusters seems pretty random. Due to the
limitation of TEM technique, the contrast is not as good without any staining, especially with the existence of the nano-patterns. More control experiments need to be done to exploit the real morphology under confinement.

Figure 3-17. TEM images (no stain) of 5 wt% DPOSS-PS in PMMA (3.1k) matrix under different conditions: as cast, 1h oven annealing; 1h oven annealing with DVD-pattern confinement. The annealing temperature is 160°C. Film thicknesses are inserted in the lower left corners. The scale bar is 200nm for both as cast and 1h oven annealed films, and 100nm for DVD-patterned films.

When the polymer matrix changes to PMMA, the as-cast films does not vary too much. While weak phase separation happens after 1h oven annealing under 160°C. A still further investigation like AFM topology needs to be done to study the nano-patterned film morphologies.
Figure 3-18. AFM images of 5 wt% DPOSS-PS in PMMA (3.1k) matrix under 1h oven annealing with DVD-pattern confinement. (A)(B): 3D images showing the surface nanoparticle dispersion; (C) AFM height image; (D) The height profiles corresponding to the lines in the height image. The films thickness is 80nm and scan size is 10μm.

AFM images provide a better view of the surface morphology of the DVD-patterned thin films. From the three-dimensional images, it is clear that nanoparticles aggregate in the mesa region of the pattern, thus providing similar results as grafted TiO2 in polymeric thin films.
Figure 3-19. TEM images (no stain) of 5 wt% DPOSS-PS in PMMA (1.5k) matrix under different conditions: as cast, 1h oven annealing; 10min oven annealing with DVD-pattern confinement. The annealing temperature is 160°C. The film thickness is 90nm. The scale bar is 100nm for both as cast and 1h oven annealed films, and 400nm for DVD-patterned films.

We proceeded to investigate other molecular weight of the PMMA polymer matrix by changing to a lower 1.5kg/mol PMMA and the results are shown above. It can be observed that in the 1h oven annealed films, worm-like cylinders are formed during phase separation.

3.2.2 70%DPOSS+30%PS/PMMA

Previously 5% weight percent DPOSS-PS in polymer matrices studied. Herein other compositions of DPOSS-PS nanoparticle versus low molecular weight polymer matrices are investigated to understand the effect of loading fraction of DPOSS-PS nanoparticles on the nanocomposite films. The loading fraction of DPOSS-PS increased from 5% to 70%. The polymer matrices are PS (Mn=2.8kg/mol) and PMMA (Mn=3.1k).
Figure 3-20. TEM images (no stain) of 70 wt% DPOSS-PS in PS (2.8k) matrix under different conditions: as cast, 1h oven annealing; 10min oven annealing with DVD-pattern confinement. The annealing temperature is 160°C. Film thicknesses are inserted in the lower left corners. The scale bar is 800nm.

By increasing the content of DPOSS-PS in the system, the as-cast films illustrate more nanoparticle aggregation and is increasing with thicker films. While for the oven annealed films, with or without patterning, there forms nucleation crystallization. It is notable that for the oven annealed films, phase separation seems to occur at a smaller scale. This can also be explained by the hydrophilic DPOSS cages and the strong competing interactions with polystyrene, driving the formation of such self-assembled structures. Compared with lower loading fraction of DPOSS-PS in the system (5%), increasing the relative content of DPOSS makes it possible for phase separation to occur.
Figure 3-21. TEM images (no stain) of 70 wt% DPOSS-PS in PMMA (3.1k) matrix under different conditions: 1h oven annealing; 10min oven annealing with DVD-pattern confinement. The annealing temperature is 160°C. The film thickness is 110nm. The scale bar is 100nm for 1h oven annealed film and 500nm for the DVD-patterned film.

Figure 3-21 shows 70% DPOSS-PS in low molecular weight PMMA matrix. The 1h oven annealed TEM images were recorded at a quite high magnification, thus nanoscale phase separation can be observed. In this system, since the weight fraction of DPOSS-PS is 70%, the films can be considered to contain 35% DPOSS, 35% PS and 30% PMMA. For low molecular weight PS and PMMA, the Flory-Huggins interaction parameter $\chi$ and the degree of polymerization $N$ were determined. The parameter $\chi$ of PS and PMMA blend system as a function of absolute temperature $T$ can be calculated using empirical equation\textsuperscript{62}

$$\chi = (0.028 \pm 0.002) \frac{(3.9 \pm 0.6)}{T}$$
The product of $\chi N$ is representative of the segregation strength, which indicates the entropic and enthalpic contribution. When the product of $\chi N$ is below a certain value at a composition (defined by the volume fraction of one blend phase), chains are intermixed in the system. For block copolymers, the critical value of the product of $\chi N$ is 10.5. While in this case for PS/PMMA blend system, the critical value is 2. The calculation of $\chi N$ yields 1.11 and is less than 2, meaning low molecular PS and PMMA in the system are miscible. However TEM images demonstrate that phase separation occurs in the blend system. One possible explanation is that PS is grafted to DPOSS cages, causing less mobility of PS chains, thus would increase the actual value of $\chi$. It is also noted that the images of TEM display in 2D but are actually a reflected combination of the 3D morphology. The limitation of the technique is another problem need to be solved in further study.

3.2.3 Kinetic Study of Morphology Evolution

The nanoscale phase separation of 70% DPOSS-PS in PMMA polymer matrix caught our attention. Further experiments were conducted to investigate the kinetics of the morphology evolution. Same batch of thin films with thicknesses of 100nm were thermal annealed at 160°C for various time nodes. Starting from 15 minutes to 6 hours and the results are shown below.
Figure 3-22. Kinetic study of morphology revolution on 70 wt% DPOSS-PS in PMMA (3.1k) matrix. The annealing temperature is 160°C. The film thickness is 100nm and annealing time are indicated along the arrow. The scale bar is 100nm. Inserted is FFT image of 1h oven annealed film.

The morphology of the thin films does not change much with the increase of annealing time from 15 minutes to 6 hours. The inserted Fast Fourier Transform image indicates the domain spacing of the film is approximately 10.11nm, which is in good accordance with a reality check. We can conclude that the phase separation reaches an equilibrium state in just several minutes, as is expected.

3.3.3 Morphology Transition with Increasing DPOSS-PS Composition

Comparing the film morphology for DPOSS-PS nanoparticles in low molecular weight PMMA matrices of different composition, it can be observed that the domain spacing of phase separation changes significantly. In this part, different weight fraction of POSS-PS versus PMMA thin films was annealed under the same condition. For the morphology transition study, pure DPOSS-PS weight ratio was increased from 0 to 100%, under the same annealing conditions.
Figure 3-23. Morphology transition study on increasing DPOSS-PS nanoparticle weight fraction in PMMA (3.1k) matrix thin films. The annealing temperature is 160°C. Film thickness is 100nm and compositions of DPOSS-PS are indicated along the arrow. Scale bars are inserted in lower right corners. The DPOSS domain appears darker than PS domain.

Noted that relatively large scale phase separation occurs in the 5% DPOSS-PS in PMMA thin films. When the loading fraction increased to 50%, phase separation happens at a much smaller scale. For the 30% loading of DPOSS-PS, the films demonstrate both large and small scale phase separation. When the composition of DPOSS-PS increases to 90%, TEM images display basically nothing. The possible reason is that for pure DPOSS-PS thin film where the molecular weight of PS is 2.8kg/mol, the volume fraction of PS in the system is between the region (0.64 < f < 0.76) where morphology is in lamella phase and is hard to observe under TEM. Grazing Incident Small-Angle X-ray Scattering (GISAXS) and cross-
sectional TEM would be alternative techniques to further investigate the interior morphologies of those thin films.
CHAPTER IV

CONCLUSION

In the present work, PS grafted TiO2 nanoparticles and DPOSS-PS molecular nanoparticles were incorporated into various homopolymer matrices involving PS, PMMA to fabricate nanocomposite thin films. The location and distribution of nanoparticles in polymeric films under different annealing conditions, as well as the effect of PDMS soft nano-patterning on nanocomposite films were investigated. We present a novel way of controlling the dispersion of PS-g-TiO2 nanoparticles by nano-pattern confinement imprinting, which is of great significance since the specific dispersion of nanoparticles is critical to optimize a required property of polymer nanocomposites. When thermal annealed under DVD-pattern confinement, grafted TiO2 nanoparticles dispersion changes from randomly distributed to aggregating at the elevated regions of the imprinted films. This phenomenon can be explained via the depletion force caused by the size difference between the particles and the matrix chains, thus providing an effective way to adjust macroscopic properties by controlling the distribution of nanoparticles. DPOSS-PS molecular nanoparticle, also known as shape amphiphile, shows better dispersion in low molecular PMMA than in PS matrix. To understand the morphology transition of the nanocomposite film, various loading fraction of DPOSS-PS was incorporated in low Mw PMMA matrix,
leading to phase separation at different length scales when the loading fraction of DPOSS-PS is between 5% and 70%.
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