APPLICATION OF NANOPARTICLES IN POLYMERIC FOAMS

DISSERTATION

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ABSTRACT

With the increasing cost of and demand for energy, there is strong industrial interest to develop new lightweight materials that can provide high structural strength and better thermal insulation performance for general construction applications. Traditional plastic foams do represent such a group of lightweight materials. Their applications, however, are limited by poor mechanical strength, surface quality, and thermal stability. On the other hand, novel nanocomposite foams based on the combination of functional nanoparticles and supercritical fluid foaming technology may lead to a new class of materials that are lightweight, high-strength and multifunctional.

In this work, two types of nanoparticles, nanoclay and carbon nanofibers (CNFs), were used to synthesize polystyrene (PS) nanocomposite foams. Foams with different morphologies and densities were developed to address the needs of two different target markets, building construction and thermal insulation. The foaming agents used in this study were carbon dioxide (CO₂) and/or water, both selected with regard to their favorable environmental properties. More traditional hydrocarbon-based blowing agents are far less benign.

Foams with microcellular structure (cell size less than 10 μm and cell density higher than 10⁹ cells/cm³) have been reported to provide a high strength-to-weight ratio and excellent toughness as compared to solid polymers. The formation of microcellular
structure, however, requires stringent foaming conditions. In this study, the nucleation effect of CNFs and hence the facilitation of microcellular foam structure was demonstrated. PS-CNPs foams were synthesized using in-situ polymerization followed by a batch foaming process. CNFs exhibited outstanding nucleation effect on the PS foaming process. In the presence of only 1wt% CNFs, the cell size decreased from 20 (neat PS foam) to 2.6 µm, while the cell density increased by more than two orders of magnitude (from $8.23 \times 10^7$ to $2.78 \times 10^{10}$ cells/cm$^3$), yielding a perfect microcellular structure. The high nucleation efficiency of CNFs was quantitatively explained by the classical nucleation theory. The homogeneous fiber distribution, the favorable surface compatibility, and the desirable geometry of CNFs make them ideal nucleating agents for PS-CO$_2$ foaming process.

The reinforcement contribution of CNFs to PS foams was demonstrated by tensile and compressive properties. The inclusion of CNFs significantly improved the mechanical properties of the foams. For example, compared to neat PS foams, PS foams containing 1wt% CNFs exhibited an increase of 28% in tensile modulus and 45% in compressive modulus. Once the fiber loading level increased to 5wt%, the mechanical properties of PS foams reached a level even higher than those of the neat PS solid. At the same time, a comparative weight reduction of 50% was achieved. Obviously, the strength loss due to the existence of cells is compensated or surpassed by the reinforcement contribution of CNFs. These results demonstrate the feasibility of using nanocomposite foams as a new generation of lightweight high-strength structural materials.

In a particle-filled plastic system, the reinforcing efficiency essentially depends on the interactions between the particle and the polymer. Once the particle size is reduced
to the nanometer scale, these interfacial properties become extremely important due to the existence of a large interface area. In this study, a strong physical (non-bonding) interaction between the CNFs and the PS was first suggested by a PS sheathing phenomenon around the CNFs. The existence of strong interaction was further confirmed by the enhancement of solid surface-induced PS glass transition temperature ($T_g$). PS thin film (nanometer- or angstrom-scaled) spin-coated on the graphite substrate was used to resemble the interface between the PS and the carbon-based solids. Using a nanoparticle-embedding technique, $T_g$s of PS at different locations within the film were measured. A higher $T_g$ of PS compared to its bulk value (100°C), as well as a gradient of $T_g$ within the film with the higher value approaching the substrate, indicated a strong confinement (interaction) from the substrate. This confining effect and its impact on the $T_g$ of surrounding polymers became more pronounced with reduced film thickness. These results provide fundamental insights to the macroscopic reinforcement of carbon-based nanoparticles on the PS matrix. The methodology used in the work can be extended to other polymer nanocomposites systems.

To address the development of low-density polymeric foams for insulation applications, water expandable PS-clay nanocomposites (WEPSCN) was synthesized. A novel method, suspension polymerization of the water-in-oil inverse emulsion, was developed to produce WEPSCN beads containing myriads of water/clay droplets. Using this method, nanoclay can be incorporated into the beads and eventually the polymer systems without the use of a fire-hazard surfactant. Thus, the ultimate products may more easily comply with stringent industrial fire resistance requirements. Due to the hydrophillicity of nanoclay, more water can be trapped within the PS beads. This leads to
a higher expansion ratio upon heating. Further, once using CO₂ as the co-blowing agent to expand these beads, foams with ultra-low density (0.032 g/cc) and desirable cell structures (cell size of approximately 100 µm) for insulation were produced.
Dedicated to my parents
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CHAPTER 1

INTRODUCTION

1.1 Polymer nanocomposites

Polymer composites are widely used in the automotive, aerospace, construction and electronic industries. They provide superior mechanical properties and physical properties (e.g., stiffness, strength, appearance) than pure polymers. Traditionally, micron-sized particulates and long fibers are used as the inorganic component of the polymer composites. However, the application of nanoparticles in polymer composites has drawn a great deal of interest in recent years. Nanoparticles possess a high potential to achieve significant property improvement at a low-level particle loading. Thus, nanocomposites have become a new class of materials providing superior properties without sacrificing the lightweight property of a given polymer matrix.

The term ”nanocomposites” usually refers to a composite in which at least one phase (the filler phase) possesses particles with ultra fine dimensions (on the order of a
few nanometers). Basically, there are three types of nanoparticles, as shown in Figure 1.1. The first type of nanoparticles is characterized by a platelet-like structure. Material examples are nanoclay and layered nanographite. The thickness of these materials is usually a few nanometers and the lateral dimension ranges from several hundred nanometers to micrometers. The second type of nanoparticles possesses an elongated structure with two nano-scaled dimensions and one micro-scaled dimension, typically within the range of a few to hundreds of micrometers. Material examples are nanotubes and nanofibers. These two types of nanoparticles exhibit a high aspect ratio. The third type of nanoparticles, however, shows a spherical structure with three dimensions in the nanometer scale. Spherical silica particles, gold and other metal nanoparticles, and nanocrystals and block copolymers all belong to this type. A variant of the third type is nanoporous microparticles. While the diameter of the particle falls in the order of micrometers, the internal pore sizes are in the order of nanometers.

The first nanocomposite was developed by Toyota Motor Co. based on nylon 6 and montmorillonite (MMT) [1]. Since then, the technology of nanocomposite synthesis has been extended to other polymers and different nanoparticles. Compared to micro-sized fillers, nanoparticles generally offer superior reinforcing efficiencies. The extremely small size and large surface area facilitate the interactions with the polymer domain. Thus, the incorporation of a small amount of nanoparticles can lead to a significant enhancement of the composite properties. In addition, different nanoparticles exhibit certain advantages associated with their intrinsic physical properties. For instance, the layered structure of nanoclay has been reported to improve the barrier property and flame retardancy of polymer composites [2, 3]. The exceptional thermal and electrical
conductivity of carbon nanotubes (CNTs) can dramatically affect the transport properties of the host polymer by significantly lowering the percolation threshold. As a result, composites containing only a small amount of nanotubes (0.05-0.1 wt% for single wall carbon nanotube) can be applied to various applications such as electrostatic dissipation, transparent conductive coating and electromagnetic interference (EMI) shielding [4]. Therefore, the marriage between nanoparticles and polymers may result in an entire new class of multi-functional advanced materials.

1.2 Polymeric foams

Foams are widely used in a variety of applications such as absorbance, insulation, packaging and cushions [5]. In addition, foams of a high porosity with interconnected pores have also been used as tissue engineering scaffolds facilitating cell attachment and growth [6]. Various polymers have been used for foam applications, such as polyurethane (PU), polystyrene (PS), polyolefin (polyethylene (PE) and polypropylene (PP)), poly (vinyl chloride) (PVC), polycarbonate (PC). Table 1.1 [7] displays the market dissemination and growth rate for polymer foams in 2001 and 2006. As shown in this table, the US use of polymer foam products in 2001 was 7.42 billion pounds, translating into a market value of approximately $16.2 billion [8]. Among all the resin families, PU occupies the largest market share (53%) in terms of the amount consumed. PS is the second (26%).

A typical composition of a foaming system includes the polymer, foaming agent, nucleants and other additives (catalyst, fire retardancy agent, etc.). Generally, there are
two types of foaming agents: physical foaming agents and chemical foaming agents. For large-scale production, the direct utilization of physical foaming agents is the most commonly used method. Typical physical foaming agents are volatile chemicals such as chlorofluorocarbons (CFCs), hydrocarbons (HCs)/alcohols, and inert gases (CO₂, N₂, argon, water). CFCs have good solubility in the polymer matrix, low diffusivity and low thermal conductivity. These characteristics result in a foam product with good insulation and physical properties. Due to the depletion of the ozone layer, however, the use of CFCs or any of its derivatives, hydrochlorofluorocarbons (HCFCs), will be abandoned by the year 2010. Other alternatives such as hydrofluorocarbons (HFCs) and HCs, require strict regulation because they have negative impacts on global warming. They also can impose a severe fire hazard in closed-celled foams.

Among the rest, CO₂ is the most favorable choice. It is inexpensive, nontoxic, and environmentally benign (zero Ozone Depletion Potential, and 100 year Global Warming Potential compared to 1300 years for HFC-134a and 2000 years for HCFC-142b) [9]. However, the solubility limitation and the fast rate of gas escaping greatly limit the development of CO₂ as a foaming agent at an industrial scale. Further, CO₂ usually deteriorates the insulation value of foams due to its high thermal conductivity. Thus, a combination of CO₂ and HC (ethanol, 2-ethyl hexanol, etc.) is more feasible for those applications where the insulation property is critical [10, 11].

To obtain cells with controlled structure and uniform distribution, nucleating agents (nucleants) such as talc, silicon oxide, and titanium oxide are necessary additions to the foaming formulation [12]. Nucleants can serve as “hot spots” and substantially reduce the energy required for the formation of nucleation centers for a gaseous phase.
Although the mechanism of nucleation is still under debate, there is no doubt that the shape, size, surface chemistry, and the dispersion of particles will all affect their nucleation efficiencies.

With traditional macro-sized cells, the foam application is extremely limited by their inferior mechanical strength and low dimensional stability. In light of this, the concept of creating foams with microcellular structures to enhance their mechanical properties was first proposed in 1980s [13-15]. A typical microcellular structure can be characterized by cell sizes smaller than 10 µm and cell densities larger than $10^9$ cells/cm$^3$. With this particular cell morphology, foams can maintain essentially comparable mechanical properties as solids while greatly reducing the material weight. The use of microcellular foams can be extended to construction applications, an area that requires materials with specifically higher mechanical strengths.

Traditional methods for preparing microcellular foams are based on the thermally induced phase separation (TIPS) [16, 17]. In those methods, a polymer is dissolved in an appropriate hydrocarbon solvent and the temperature is quenched to induce a phase separation of the homogeneous solution composed of the polymer and the solvent. Subsequently, the solvent is removed by freeze-drying or supercritical extraction (SCE). However, complete solvent removal is difficult and may damage the final cellular structure.

An alternative “solvent free” technique was proposed by Nam Suh in the 1980s, whereby inert gases (blowing agent) such as CO$_2$ and N$_2$ are used for the generation of microcellular foams [18, 19]. The schematic illustration is shown in Figure 1.2. Typically, a polymer is saturated with the gas under a moderate pressure and temperature.
After a certain saturation time, the pressure is released and the polymer becomes supersaturated. The cell nucleation and growth take place when heating the sample to a temperature above the glass transition temperature ($T_g$). This method has been applied to a wide range of polymer materials, such as PS, PC, polyimide, and PVC. Obtained foams usually exhibit cell densities around $10^9$ cells/cm$^3$. However, gases near the edge are inclined to diffuse out of the sample rather than joining the bubble nuclei, thus forming a nonporous skin layer around the porous center.

More recently, gases in their supercritical state have been investigated as the blowing agents as well [20, 21] This method takes advantage of the great depression of $T_g$ of polymers in the presence of supercritical gases. Therefore, instead of heating the polymer-gas mixture, rapid depressurization at a constant temperature can drive the cell nucleation and growth as shown in Figure 1.3. The cells expand until vitrification occurs, freezing the final microcellular structure.

Two production of microcellular foams has been commercialized using a continuous extrusion process by MIT/Trexel [22] and Dow [23]. However, during microcellular foaming, a high thermal instability is generally required to drive the nucleation of a myriad of microcells. Therefore, stringent operation conditions such as high pressure, high pressure drop rate, and low foaming temperature are often required, creating a narrow operation window [24, 25].

In recent years, the integration of the nanocomposite technology and the traditional foaming process has led to novel cellular plastics, nanocomposite foams. The application of nanoparticles provides a freedom to design foams with various densities and properties for different applications. The largest advantage from nanoparticles is their
strong nucleation ability to create a large quantity of small bubbles, facilitating the formation of microcellular structures. The rationale for the superior nucleation effect of nanoparticles can be generalized as follows. First, the extremely fine dimensions and large surface area of nanoparticles provide much more intimate contact between the particles, polymer matrix, and gas. Secondly, a significantly higher effective particle concentration can be achieved at a low nominal particle concentration. Both could lead to improved nucleation efficiency.

Most earlier studies in this area were focused on nanoclay. The substantial nucleation effect of nanoclay has been reported for different polymer systems (e.g., PP-clay [26], PS-clay [24, 27, 28], Nylon-clay [29], PLA-clay [30, 31], PC-clay [32], PU-clay [33, 34] and PVC-clay [35]). A few studies addressed spherical nanoparticles such as nanosilica [36] and nano-sized block polymers [37, 38].

In addition to the nucleation effect, the nano-scaled size of nanoparticles makes them ideal reinforcement additives for polymeric foams. For most polymeric foams, the thickness of cell walls or cell struts falls into the regime of micrometer or sub-micrometer. Thus, traditional fillers (micro-scaled) are too large to effectively reinforce those regions. On the other hand, nanoparticles are especially beneficial for reinforcing those microstructures and thus improving the macroscopic mechanical strengths of the final products. The high aspect ratio and large surface area of nanoparticles offer the potential for high reinforcing efficiency and improved dimensional stability.

Another motivation for using nanoparticles is to comply with the use of CO$_2$. The surface of nanoparticles can be modified to change the intermolecular interactions with CO$_2$. Thus, the bubble nucleation as well as the final cell morphology can be
manipulated. The well-dispersed nanoparticles (especially plate-like particles) can also serve as a gas diffusion barrier, slowing down gas escape after processing. As discussed earlier for nanocomposites, the presence of nanoparticles can integrate multi-functionality (electric, dielectric, thermal properties) into polymeric foams. For example, char formation and reduced fire spreading have been demonstrated for PS and PVC nanocomposite foams [24, 35]. EMI shielding has been recently reported for PS foam containing carbon nanotubes/nanofibers [39, 40]. Therefore, nanocomposite foams based on the combination of functional nanoparticles and supercritical fluid (supercritical CO₂) foaming technology may lead to a new class of materials that bear desirable characteristics and minimize material environment impact.

1.3 Reinforcement at nanometer scale

Although macroscopic mechanical enhancement has been reported for various polymer-nanoparticle systems, the underlying principle of these nano-scaled reinforcements has not yet been elucidated. Compared to micro-sized fillers, a much lower particle loading is required to induce a remarkable change in bulk properties. While the high aspect ratio (e.g. 1000:1 for nanoclay) and large surface area of nanoparticles can certainly offer more reinforcing sites for improving mechanical properties, the interactions (physical and/or chemical) at the polymer-filler interface considerably influence the load transfer efficiency and the bulk mechanical responses.

Earlier studies proposed a second mechanism of reinforcement particularly for nano-filled polymers. It is assumed that there exists an interaction zone (interphase
region) around the particles, within which the dynamics and morphology of polymers are different from those in the bulk polymer [41-43]. Polymers in this region can undertake a higher level of external stress which would otherwise induce mechanical failure in the bulk. For micro-filled polymers, the fraction of this interaction zone within the whole domain may not be high enough to affect the overall polymer properties. In such case, load transfer, becomes the key issue. However, a large interfacial area, a result of the nano-scaled particle size, may lead to the interaction zones occupying a significant portion of the polymer domain for nano-filled polymers. Thus, any changes of polymer properties in this region (e.g., melting temperature for crystal polymers, $T_g$ for amorphous polymers) can be reflected in bulk. In summary, both interface and interphase regions play roles in determining the reinforcing efficiency for nanocomposites. While the interfacial shear strength between the nanoparticle and the polymer has been studied through both molecular simulation [44] and nano-pullout experiment [42, 45], little has been done on the investigation of polymer chain dynamics/mobility near the nanoparticles.

1.4 Scope and objectives of research

In this dissertation, PS nanocomposite foams were synthesized based on two types of nanoparticles: nanoclay and carbon nanofibers (CNFs). Foams with different morphologies and densities were designed specifically targeting two end markets: medium/high density PS-CNFs microcellular foams for structural applications and low/ultralow density PS-Clay macrocellular foams for thermal insulation. Supercritical
CO$_2$ (ScCO$_2$) was chosen as the foaming agent. In addition to the positive characteristics of its low cost and environmentally benign nature, ScCO$_2$ also exhibits relatively higher solubility in PS as compared to other inert gases (N$_2$, Argon, etc.). Moreover, CO$_2$ is well known to swell and plasticize many amorphous polymers, significantly reducing the polymer $T_g$ and benefiting the foaming process.

PS-CNFs nanocomposite foams were synthesized both batchwise and continuously. In the former case, nanocomposites were first synthesized via either in-situ polymerization or melt blending. Foams were prepared using a batch foaming process. In the latter case, foams were prepared using a continuous extrusion foaming process. Various factors affecting the dispersion of CNFs were investigated. The impact of CNFs on both foam morphologies (nucleation effect of CNFs) and foam properties (reinforcement of CNFs) were studied.

Using the thin film technology, the mechanism of nano-scaled reinforcement in PS-CNFs/CNTs was explored. The dynamics and chain mobility of PS in the vicinity of a solid substrate were evaluated using the film $T_g$ measurement. Highly Ordered Pyrolytic Graphite (HOPG) was selected as a carbon-based substrate with nanometer-scaled surface roughness. The film thickness was varied in the nanometer scale, thus any interactions (entropic and enthalpic) between the polymer and the substrate, or the confinement from the substrate, can be magnified and observed. Applying empirical models, the measured $T_g$ profiles were decoupled into two parts: the free surface induced-$T_g$ reduction and the substrate-induced $T_g$ enhancement. The results of this work were further correlated to the design of reinforcement in polymer nanocomposites.
Although a high $T_g$ is favorable for the ultimate applications of polymer composites, it poses practical difficulties for polymer processing. Our previous results suggested that once the content of exfoliated nanoclay increased to 10wt% in the composite, melt processing becomes a challenge [46]. In light of this, it is highly desirable to achieve an in-situ $T_g$ depression during polymer processing. For glassy polymers, the sorption of gas penetrates (e.g. CO$\text{}_2$) can generally reduce the bulk $T_g$. In the present work, CO$\text{}_2$-induced $T_g$ depression was demonstrated for the PS/HOPG thin film system as well. The competitive effect between the free surface (PS-CO$\text{}_2$) and the fixed surface (PS-HOPG) on the overall $T_g$ was discussed in detail.

The final part of this thesis is focused on the synthesis of fire hazard free polymer-clay nanocomposite foams for insulation applications. The targeted foams should have low/ultralow density (<0.1 g/cm$^3$) with improved thermal insulation performance. There are two challenges for this work. First, the clay surface is often modified by organic surfactants in order to improve the compatibility between the hydrophilic nanoclay and the hydrophobic polymers. However, these surfactants are considered fire hazards based on industry fire tests. Secondly, the incorporation of nanoclay in the polymer phase generally leads to foams with a bulk density much higher than the desired specification for insulation. While the nucleation effect favors the production of microcellular structural foams, it should be controlled for this particular study. To address these two issues, a novel process was developed to synthesize water expandable PS-clay nanocomposites (WEPSCN) beads. Water, in this case, serves as the foaming agent. Via heating above the $T_g$ of PS, the vaporization and expansion of the water phase leads to a cellular structure. Neat water expandable PS (WEPS) beads were
synthesized for comparison. Different methods were used to expand the WEPS/WEPSCN beads. The impact of the nanoclay on the water content and the expansion ratio of the beads were examined. The feasibility of using CO₂ as the co-blowing to expand these beads and generate a bi-modal foam structure was assessed using both a batch and a continuous extrusion foaming processes.

1.5 Outline

This dissertation consists of seven chapters. A general background and introduction of this work is provided in Chapter 1. Chapter 2 provides a literature review on polymer nanocomposites and polymeric foams. Specifically, it reviews the CO₂ foaming techniques and traditional methods to produce expandable PS (EPS). Earlier studies on the thin film $T_g$ measurement and the quantitative equivalence between the thin film $T_g$ and the reinforcement in nanocomposites are also introduced. Chapters 3 and 4 focus on the production of structural foams based on PS and CNFs. ScCO₂ is used as the foaming agent. Chapter 3 primarily addresses the morphology impacts (formation of microcellular structure) on the foams from CNFs. The nucleation efficiency of CNFs is evaluated and compared to that of other nanoparticles. Chapter 4 addresses the reinforcement of CNFs on foams. Tensile and compressive properties are examined in particular. In Chapter 5, nano-scaled reinforcement is explained by strong interactions between the PS and the solid carbon. The thin film $T_g$ of PS films supported on a graphite substrate is measured and interpreted as an indicator of the polymer chain mobility near the substrate. While the results in this chapter serves as a fundamental extension of
Chapter 4, its principle can be generalized for other polymer-nanoparticles systems. In Chapter 6, a novel technique to produce WEPSCN is presented in detail. Suspension polymerization of water-in-oil (w/o) inverse emulsion is applied to generate PS beads containing myriads of water/clay droplets inside. The effect of nanoclay on entrapped water in beads is discussed. The foams in this section are made using water and/or CO₂ as the blowing agent. Ultra-low density foams with reduced thermal conductivity are produced with success. The major conclusions of this work are summarized in Chapter 7. Several recommendations are made for future research in these areas.
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<tr>
<td>Total</td>
<td>7421</td>
<td>8529</td>
<td>2.8</td>
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Table 1.1: U.S. Markets for polymeric foam by resin family, through 2006 (Million Lbs)
Figure 1.1: Schematic of different nanoparticles
CO$_2$ or N$_2$

Room Temperature

Saturate

Vent

Supersaturated polymer

heat above T$_g$

Quench

microcellular structure nucleation and growth

Figure 1.2: Schematic illustration of the microcellular foaming procedure using inert gases as the foaming agent
Figure 1.3: Schematic illustration of the microcellular foaming procedure using supercritical CO$_2$ as the foaming agent
2.1 Polymer nanocomposites

Polymer nanocomposites have drawn a great deal of interest in recent years because these materials possess a high potential to achieve significant property improvement without sacrificing the lightweight of polymer matrices. The first nanocomposite was developed by Toyota R&D Labs based on nylon and layered silicate (nanoclay) [47]. Since then, active research has been carried out to synthesize polymer nanocomposites using a vast array of polymers and nanoclay combinations.

More recently, the discovery of carbon nanotubes (CNTs) [48] and vapor grown carbon nanofibers (CNFs) [49] brought up another revolutionary advancements in the field of nanocomposites. Unlike the platelet-like structure of nanoclays, CNTs/CNFs possess a tube-like structure with diameters in the nanometer scale and lengths up to tens of microns. Compared to traditional carbon fibers, CNFs/CNFs exhibit exceptionally higher mechanical strengths. For example, the elastic modulus of CNTs exceeds 1 TPa
The strength of CNTs is 50-100 GPa, 5-10 times stronger than steel at only a fraction of the comparative weight [50]. Therefore, there is a high expectation that CNTs/CNFs can serve as reinforcements for lightweight plastic materials. Further, the remarkable electrical and thermal conductivities of these carbon-based nanoparticles may also integrate multifunctionality into a completely new generation of composites.

In this study, both nanoclay and CNT/CNFs were used to produce polymer nanocomposites and foams. The following review is thus focused on these two nanoparticles. The structure of nanoparticles, the fabrication of nanocomposites, as well as the properties of nanocomposites are discussed in detail.

2.1.1 Polymer-clay nanocomposites

2.1.1.1 Introduction of layered silicates

Polymer - layered silicate (PLS) nanocomposites have been actively studied due to their high performance as compared to neat polymers or conventional filled composites. Since then, most of the work on PLS nanocomposites focus on using different methods to produce materials with specific morphologies and improved physical properties.

Layered silicate, commonly referred to as clay minerals, belongs to the structural family of phyllosilicates [1, 51-53]. There are two primary building blocks to the crystal lattice structure: a two-dimensional tetrahedral sheet of silicon-oxygen and a two-dimensional octahedral sheet of aluminum or magnesium. Depending on the ratio of the tetrahedral sheet to the octahedral one, layered silicate can be classified into two types:
1:1 and 2:1 silicate [51, 52]. The former consists a tetrahedral array linked with one octahedral sheet. Almost perfect 1:1 layer structure is realized in the kaolinite group. A schematic of this structure is shown in Figure 2.1 [51]. The latter (2:1) has crystal lattices consisting of one central octahedral sheet sandwiched between two tetrahedral sheets, as shown in Figure 2.2 [51]. Montmorillonite (MMT), hectorite, and saponite all belong to this group. Currently, the 2:1 type of silicates, MMT in particular, is most commonly used for the synthesis of polymer nanocomposite. The following discussion will focus on this group, and, henceforth, we will use the terms nanoclay, clay and MMT interchangeably.

The thickness of an individual clay layer is around 1 nm, and the lateral dimension of clay can vary from 300 Å to several microns. As a result, the aspect ratio (length to thickness, up to 1000) and the surface area (750 m²/g) of silicate are particularly high. These layers are self-organized into stacks with gaps in between. These gaps are also called the interlayers or the galleries. Isomorphic substitution within the layers, for example, Al³⁺ replaced by Mg²⁺ or Mg²⁺ replaced by Li⁺, generates a deficit of positive charges, or, in other words, an excess of negative charges which can be counterbalanced by alkali or alkaline cations situated in the interlayers.

The existence of ionic bonds and the ability to form hydrogen bonding with water make nanoclay highly hydrophilic and incompatible with most polymers. Therefore, ion exchange of the interlayer inorganic with other cationic surfactants is generally applied to render the clay surface hydrophobic [1]. The substitution of bulky organic cations (e.g. alkyammoniums) lowers the surface energy of nanoclay and increases the spacing between the layers, improving the compatibility between nanoclay and most polymers.
The capacity of ion exchange is directly related to the surface charge of the silicate layers. It is characterized by the cation exchange capacity (CEC) and expressed in meq/100g. In most cases, it varies from layer to layer and should be considered as an average value over the whole crystal. Besides the substitution of organic cations, silane-coupling agent can also be used to modify the clay surface [54-57].

Regardless of organic modified or not, nanoclay possesses three levels of morphologies: crystallite (tactoids), primary particle, and agglomerates [58]. Crystallites are located at the lowest level in this hierarchy. They are composed of as many as 100 individual layers. The general size of a crystallite is less than 0.5 μm. Via compact face-to-face stacking or low-angle intergrowth, crystallites form the second level of structure: primary particles (1-10 μm). These, in turn, weakly gather together to create agglomerates (100-1000 μm). In the synthesis of polymer-clay nanocomposites, it is imperative to disrupt all these three structures. In reality, a mixture of intercalated and exfoliated clay dispersions is usually observed.

2.1.1.2 Structure of polymer-clay nanocomposites

Once nanoclay (or layered silicate in general) is dispersed into a polymer matrix, three types of nanocomposites with different nanoclay dispersion can be formed, as illustrated in Figure 2.3 [1]. The specific formation of types largely depends on the compatibility between the polymer and the clay. In the case of completely incompatible polymer-clay combination, phase separation will occur, leading to composites filled with micro-sized clay agglomerates (Figure 2.3a). Once polymer chains penetrate into the
silicate layers, intercalated nanocomposites are obtained. These materials have well-ordered multi-layered morphologies composed of alternating polymer-clay layers (Figure 2.3b). When the polymers further diffuse into the interlayer and the silicates are completed delaminated within the polymer matrix, exfoliated nanocomposites are obtained (Figure 2.3c). Usually, exfoliated nanocomposites display maximum property enhancement.

The abovementioned structure can be characterized by either x-ray diffraction (XRD) or transmission electron microscopy (TEM). For intercalated clay dispersion, the repetitive layered structure is still preserved, and the interlayer spacing can be determined using the Bragg’s relation [1]

\[
\lambda = 2d \sin \theta \tag{2.1}
\]

where \( \lambda \) is the wavelength of the applied x-ray radiation, \( d \) is the interlayer spacing, and \( \theta \) is the diffraction angle. As shown in Figure 2.4 [53], the penetration of polymers usually increases the spacing and decreases the observed diffraction angle. Once the interlayer spacing exceeds the resolution limit of the Bragg-Brentano geometry (~ 8 nm) or the ordered structure is completely disrupted, no more peaks can be observed from the XRD patterns. In that case, TEM is needed to further reveal the spatial arrangement of clay layers. However, the information from the TEM is qualitative and highly localized. Other techniques such as neutron scattering and X-ray scatter have also been applied in this field.
2.1.2 Polymer – CNTs/CNFs nanocomposites

2.1.2.1 Introduction of CNTs/CNFs

Generally, there are two types of CNTs, single wall carbon nanotube (SWCNT) and multi wall carbon nanotube (MWCNT). The former is composed of a single graphene sheet rolled into a cylinder [59] (Fig. 2.5), showing an arm-chair or a zig-zag structure. The latter is usually consisted of multiple concentric graphene shells. The number of shells varies with a typical value of eight (Fig. 2.6 [60]). The diameter of a SWCNT is on the order of 1 nm, while that of a MWCNT ranges from a few to several tens of nanometers. CNFs, on the other hand, usually possess a larger diameter (50-200 nm), between that of conventional carbon fibers (5-10 µm) and CNTs (1-50 nm). The structure of CNFs is similar to that of MWCNT.

Development of the CNTs-based composites has been limited due to their high cost and inadequate availability. On the contrary, the cost of CNFs ($100/lb) is several orders of magnitude lower than that of SWCNT ($500/g) and it is available in large quantities. Therefore, CNFs are an ideal precursor system to studying the basic behaviors of SWCNT/MWCNT-polymer composites.

The primary synthesis methods for CNTs/CNFs include arc-discharge [61], laser ablation [62], and chemical vapor deposition (CVD) from hydrocarbons [63-65]. Both arc-discharge and laser ablation methods have limited productivities because of the limited size of the carbon source. Subsequent purification steps required in these techniques will further add to the production cost. In contrast, gas-phase processes, such
as CVD, offer the greatest potential for the scaled-up production. In a typical CVD process, CNTs or CNFs are formed by the decomposition of a carbon-containing gas in a tube furnace equipped with appropriate gas feed unit. The process can be operated in either a batch or a continuous mode. The obtained CNTs or CNFs have higher purity when compared to those synthesized by other methods.

In all systems with graphitic structures, the origin of the attractive force arises from the presence of extended $\pi$ electrons. Therefore, these systems are usually highly polarized and subject to strong intrinsic van der Waals forces. This in turn leads to a secondary bonding among graphitic layers [66-68]. In the case CNTs/CNTs, these forces are responsible for the aggregation of fibers. Most CNTs/CNTs are inclined to hold together as ropes with much larger diameters than in their original state, as shown in Figure 2.7 [69]. These ropes will further entangle with each other and form a spaghetti-like structure (Fig. 2.8) [59]. When incorporated into the polymer matrix, the attractive forces among the ropes will increase due to an entropic penalty induced by the confinement of the polymer configuration. Therefore, the dispersion of CNTs/CNFs becomes a major challenge in the study of the polymer-CNTs/CNFs nanocomposites.

2.1.2.2 Surface modification of CNTs/CNFs

The effective utilization of CNTs/CNFs in the composite applications requires homogeneous particle dispersion in the polymer matrix. Furthermore, a strong interfacial bonding is required to obtain an efficient load transfer across the polymer-particle interface. However, due to the intrinsic van de Waals attractions, CNTs/CNFs are tightly
entangled and the uniform dispersion is not easy to achieve. In addition, atomically smooth and non-reactive surface precludes the formation of interfacial bondings between the CNTs/CNFs and the polymer matrix. Under this circumstance, surface modification is widely applied to improve the mixing of CNTs/CNFs and the polymers.

Presently, there are two types of surface modification: surface coating [70] and surface functionalization [66, 70-75]. The former means physically coating the CNTs/CNFs by certain surfactants containing interaction-improving groups. The latter means the covalent attachment of certain functional groups onto the tube/fiber surfaces. The advantage of surface coating is that it can alter the nature of the fiber surface and make it compatible with the polymers. Meanwhile, the perfect structure of nanotubes and their essential mechanical properties can be preserved. The disadvantage of this method is that the forces between the coated surfactant and the nanotubes/fibers might be weak, causing a less efficient load transfer in the composites. Functionalization, on the contrary, can greatly improve the efficiency of load transfer due to the formation of covalent bondings. However, using this method, defects will form on the particle surfaces, lowering the strength of the reinforcing material itself.

2.1.3 Fabrication of polymer nanocomposites

Regardless of the type of nanoparticles, there are generally three methods to fabricate polymer nanocomposites: solution blending, melt blending, and in-situ polymerization.
2.1.3.1 Solution blending

In solution blending, the polymer is first dissolved in a common solvent or a solvent mixture. Subsequently, nanoparticles are mixed into the polymer solution, usually with the aid of ultrasonication. Depending on the interactions between the nanoparticles and the solvent, the van der Waals force among nanoparticles (stacks for nanoclay, ropes or bundles for CNTs/CNFs) could be reduced, thus facilitating the polymer chains to diffuse into the spaces among nanoparticles. The unique advantage of this method is that it is capable of dispersing nanoparticles in the polymer matrices while maintaining the large aspect ratio of the original nanoparticles. Moreover, with the aid of an electric or a magnetic field, solution blending can provide a novel way to orient those anisotropic nanoparticles (e.g. nanoclay and CNTs/CNFs). The major disadvantage of this method is the large amount of solvent needed, resulting in higher purification costs. In addition, its applicability will be greatly limited by the selection of proper solvents. Nevertheless, this method is especially attractive in preparing water soluble polymer-clay nanocomposites, e.g. polyvinyl alcohol (PVA) [76, 77], poly ethylene oxide (PEO) [76, 78-85], poly acrylic acid (PAA) [78]. Also, with the aid surfactant or surface modified nanoparticles, this method has been applied to produce CNTs/CNFs-filled polymers. Examples include PVA [86, 87], polystyrene (PS) [72, 88], poly(3-octylthiophene) (PSOT) [89], polyvinylidene fluoride (PVDF) [90], to name just a few.
2.1.3.2 Melt blending

Melt blending is the most widely used technique to synthesize polymer composites. Due to its compatibility to the current polymer extrusion process, melt blending offers a promising route to produce polymer composites on a large scale. In this process, the nanoparticles (nanoclay, CNTs/CNFs, etc.) are mixed directly with the molten polymers. Mixing may occur either statically or under high shear.

Twin-screw extrusion is the most common method to blend the polymers with the particles. It was found that both the screw design and the residence time affect the dispersion of nanoparticles. Generally, increasing the mean residence time and the use of back mixing will improve the particle dispersion. However, excessive shear intensity or back mixing will lead to a poor mixing. The reason for this phenomenon is yet not clear. Additionally, owing to the complexity of the process itself, the studies on how the process conditions affect the formation of nanocomposites is inadequate.

To date, a wide variety of nanocomposites has been prepared via melt blending. For nanoclay-filled systems, examples include nylon 6 [91-95], PS [96-99], polypropylene (PP) [100-107], PEO [80, 108], ethylene-vinyl acetate copolymer (EVA) [108]. For CNTs-filled systems, due to the high entanglement and strong affinity among tube ropes and bundles, melt blending is not feasible to uniformly disperse CNTs in the polymer domain. Instead, the combination of solution blending and melt blending offers a more powerful dispersion capability [109]. For CNFs-filled systems, on the other hand, melt blending offers a feasible and low-cost method to incorporate nanoparticles into
various polymers, e.g. PP [110-114], poly(ethylene terephthalate) (PET) [115], PC [116], etc.

Lattice-based mean field theory has been applied to explain the thermodynamics that driving the intercalation of polymers into the spacing among nanoparticles. Generally, a mixing process is controlled by both entropic and enthalpic factors. While an unfavorable entropy loss may occur during mixing, the enthalpy can be rendered favorable by maximizing the magnitude and number of polymer-particle interactions [1].

Although melt blending offers a simple way to synthesize nanocomposites, it is not a feasible method to achieve a nano-scaled particle dispersion for composite systems composed of a large volume of nanoelements and high molecular weight polymers. Moreover, in the case of CNTs/CNFs, a high temperature (to lower the melt viscosity) and a high shear force (for mixing) will result in the degradation of CNTs/CNFs.

2.1.3.3 In-situ polymerization

The idea of in-situ polymerization was first proposed in the 1960s and it has been widely applied to the polymer-clay systems. Recently, this method has been extended to the synthesis of polymer-CNTs/CNFs nanocomposites.

Unlike solution blending or melt blending where nanoparticles interact with the polymer molecules, in-situ polymerization offers a route where the dispersion of the nanoparticles takes place simultaneously with the growth of the polymer chains, from a low-molecular-weight monomers to high-molecular-weight polymers. In this method, the nanoparticle is first mixed with the monomer. Subsequently, polymerization takes place.
Due to the lower viscosity of the monomer (as compared to that of polymer melt or polymer solution), it is much easier to break the aggregated particles using either sonication or high shear mixing. In addition, once the monomer diffuses into the clay interlay or the CNTs/CNFs bundles, the interparticle space can be further expanded due to the growth of the polymer chains. Furthermore, combined with the use of surface modifications, this technique provides a practical way to grow the polymer chains directly from the particle surfaces. Therefore, both the particle dispersion and the interfacial bonding between the particles and the polymers can be significantly improved.

For thermosets, such as epoxy composites, in-situ polymerization is the only viable method to incorporate nanoparticles into the polymer domain [70, 117, 118]. For thermoplastics such as poly(methyl methacrylate) (PMMA) [119, 120], polyimide [121], PS [122, 123], in-situ polymerization also exhibits unique advantages to facilitate the particle dispersion and to improve the wettability between the particles and the polymers. Interestingly, it was found that during the in-situ polymerization of PMMA-CNTs, CNTs may participate in the PMMA polymerization with their opened π-bonds. The resultant composites possessed a strong interface across the CNTs and the PMMA matrix.

To summarize, in-situ polymerization can be used to produce polymer nanocomposites with molecular-level particle dispersion. In particular, functionalized nanoparticles become an integral, chemically bonded part of the polymer matrix, leading to a significant improvement in both mechanical and physical properties.
2.1.4 Properties of polymer nanocomposites

2.1.4.1 Properties of polymer-clay nanocomposites

Polymer-clay nanocomposites demonstrate significant improvements compared to neat polymers with a particle loading less than 10wt%. Mechanical reinforcement, thermal stability, char formation, and barrier properties are all improved and drawn great attention.

Mechanical properties refer to a wide range of material responses to external forces, such as tensile, compression, bending, fracture, and impact, to name a few. The following discussion is addressed on the tensile modulus (stiffness), strength (toughness), and elongation at break (elasticity). A remarkable increase in tensile modulus has been reported for various systems [124-129]. Further, the difference in the extent of dispersion strongly affects the measured tensile modulus. Compared to intercalated polymer-clay structure, the exfoliate dispersion leads to a higher modulus, thus a nonlinear evolution of modulus with the clay content is generally observed [124, 130]. Once tested in the rubbery state, the increase of modulus associated with the nanoclay is further enhanced [46].

The impact of nanoclay on the tensile strength, however, does not show a unanimously positive correlation. It greatly depends on the nature of interactions between the polymer matrix and the nanoclay [1]. For example, nylon-6 [124] and PMMA-clay [131] nanocomposites exhibit an increase in tensile strength, while PP-clay nanocomposites show no or very slightly strength improvement over the neat PP [103].
For PS-clay nanocomposites, the tensile strength even drops down as the clay content increases [132]. More interesting results are found for epoxy-based nanocomposites. While a reduced tensile strength is generally observed for high-glass transition temperature ($T_g$) epoxy systems [133], a considerable increase in the tensile strength is observed for elastomeric epoxy [134].

The elongation at break has not been widely reported for polymer-clay nanocomposites and the impact of nanoclay differs for different polymers. For thermoplastics, such as PS [132] and PMMA [131], the elongation at break is reduced. However, for elastomeric epoxy, the addition of nanoclay results in an increase in the elongation at break [134]. The elasticity also depends on the degree of particle dispersion. Compared to convention composites and nanocomposites with intercalated clay dispersion, exfoliated nanocomposites demonstrate a larger increase in elasticity.

The layered structure and high aspect ratio of nanoclay also lead to superior barrier properties against water or solvents [135-139]. Due to the tortuous pathway resulting from the insertion of nanoclay into the polymer matrix, reduced permeability and improved water and solvent resistance are observed for nanocomposites. For instance, the incorporation of 4wt% nanoclay in epoxy drops the rate of water vapor transmission by one order of magnitude. The addition of 5wt% nanoclay in PS foams slows down the CO$_2$ diffusion rate, with the exfoliated clay dispersion leading to the slowest diffusion [24]. The effective diffusion coefficient of polymer-clay nanocomposites has been modeled based on the particle shape, concentration, orientation and degree of delamination [138, 139].
Another highly important advantage of polymer-clay nanocomposites is their improved thermal stability and fire retardancy [140]. Using thermal gravimetric analysis (TGA), delayed thermal degradation, in terms of the reduced mass loss rate and the increased onset degradation temperature, was observed in various nanocomposite systems [141-143]. However, with the lack of the actual nature of thermal degradation, the mechanism of this clay-improved thermal stability remains unclear. Several origins of this phenomenon have been proposed including the char formation, the restricted thermal motion of the macromolecules within the silicate layers, and the hindered diffusion of the volatile decomposition products.

The flame retardant properties of nanocomposites have been studied in detail [2, 104]. Using a cone calorimeter, the responses (heat release rate, peak of heat release, time to ignition, mass loss rate, etc.) of a material on fire can be measured. Compared to traditional flame-retardants, such as aluminum trihydrate or halogen-containing compounds, a much lower particle loading is required for nanoclay to achieve a comparable improvement. For example, the incorporation of 3wt% organoclay into PS leads to a reduction of the heat release rate by 48%, a value which can only be achieved with the addition of 30wt% brominate flame retardant [140].

2.1.4.2 Properties of polymer-CNTs/CNFs nanocomposites

CNTs/CNFs have drawn enormous attention with the increasing demand for high performance and affordable polymeric composites. Their unique mechanical, electrical, and thermal properties make CNTs/CNFs ideal fillers for composites desired for specific
applications. However, for CNTs, either SWCNT or MWCNT, the current price is still too high to promote industrial-scaled usage. Instead, CNFs, offers a perfect balance between superior properties and low-cost fabrication. Thus, in this study, CNFs were selected. The following is a review of properties focused on polymer-CNFS nanocomposites.

CNFs have been observed to reinforce various polymers, ranging from thermoplastics (PP [111, 114, 144], PET [113], PMMA [145], PS [146], PC [147, 148], PE [149], etc.) to thermosets (epoxy [70], vinyl ester [150] etc.). For example, a 5wt% filler loading in PET leads to considerably higher compressive strength and tensional modulus [113]. PMMA containing 5wt% CNFs exhibits over 50% improvement in axial tensile modulus as compared to neat PMMA [145]. For PP-CNFS, inconsistent results were reported from different research groups. Finegan et al. found improved tensile strength and modulus in the presence of CNFs. While a moderate degree of oxidation further increased tensile strength, extensional oxidation impaired the composite properties [144]. However, in Lozano’s work, no real change in tensile strength was observed. The authors rationalized the absence of strengthening by the particle inference with the crystallization behavior of PP [111]. The mechanical reinforcement can be maximized by the fiber alignment and fiber surface treatment. Compared to PE containing randomly dispersed CNFs, PE containing aligned CNFs shows an further increase of 165% in tensile strength [149]. Via the surface modification of CNFs, the interaction between CNFs and epoxy was enhanced, leading to a comprehensive improvement in elastic modulus (~35%), tensile strength (~ 20%) and ultimate strain (~70%) [70].
The higher electric [151] and thermal conductivity [152] of CNF make it an ideal candidate to modify these transport properties of polymer matrixes [87, 90, 111, 112, 114, 116, 150, 153, 154]. For CNFs-filled polymers, the volume electrical property exhibited a characteristic percolation behavior [111, 150, 153, 154]. The percolation value depends on various parameters such as the dispersion of CNFs, the surface treatment, and the aspect ratio of CNFs. Polymers with highly dispersed CNFs are desirable for applications that require electrostatic discharge (ESD), electromagnetic interference (EMI) shielding or radio frequency interference (RFI) shielding. Unlike electrical properties, thermal conductivity of polymer-CNFs nanocomposites doesn’t exhibit a percolation behavior [155]. Experimental results indicated that the concentration dependence of thermal conductivity could be predicted by the effective medium theories [153].

In the presence of CNFs, polymers also possess improved thermal stability [145, 147, 156], reduced shrinkage [145], and exceptional high temperate ablation resistance [157].

2.2 Polymeric foams

2.2.1 Introduction of polymeric foams

Polymeric foams [5, 158-160], defined as materials consisting of gases voids surrounded by denser polymer matrix, have attracted enormous research attention due to their wide applications in insulation, cushion, absorbent, and weight-bearing structures.
More recently, foams with interconnected pore structures have been applied as the tissue engineering scaffolds for cell attachment and growth.

A variety of polymers has been used to synthesize polymeric foams. Based on different standards, there are several ways to classify polymeric foams. According to the original polymers, polymeric foams can be classified into two categories: reprocessable thermoplastic foams and un-reprocessable thermoset foams. The former includes but is not limited to such polymers as PS, PVC, polyester, polyolefins, polyacetal, acrylonitril-butadinen-stynene (ABS), and polyetherimide. The latter includes but is not limited to such polymers as polyurethane, polyisocyanurate, phenolics, epoxy and silicone. Based on the consumption amounts, PU has the largest market share in the United States, followed by PS and PVC.

Another standard is based on the size of foam cells. Polymeric foams can be classified as macrocellular foam (> 100 µm), microcellular foam (1-100 µm), ultra microcellular foam (0.1-1µm), or nanocellular foam (< 0.1 µm).

With respect to different material composition, foam morphology, physical properties and thermal characteristics, polymeric foams can also be classified into rigid or flexible foams. Rigid foams have a wide range of applications such as building and construction, transportation, floatation and cushion, packaging, molding and food/drink containers. On the other hand, flexible foams can be used for bedding, textile, shock and sound attenuation, gaskets, and sports applications.

Regarding different cell morphologies, polymeric foams can also be defined as either closed cell or open cell foams. By selecting foaming materials and foaming processes, the formation of open cells or closed cells can be controlled. In closed cell
foams, each cellular structure is surrounded by a complete cell wall and all cells are separated. In open cell foams, all cells are virtually connected to each other in the absence of the cell walls. Moreover, the foam structure is supported by the struts and ribs instead of the cell walls. Compared to closed cell foams, open cell foams usually exhibit higher absorptive capacity, higher permeability and better sound damping ability. However, the open-channel structure will lead to less efficient insulation behaviors.

Various techniques can be used to produce polymeric foams. For large-scaled production, the utilization of blowing agents is the most practical method. For thin film foams, other methods such as phase inversion, leaching [161], and thermal decomposition are commonly used [162].

A typical formulation of a foaming system is composed of the polymer (or polymer monomer), blowing agent, nucleating agent, and other necessary additives (fire retardant, surfactant, catalyst, etc.)

Generally, there are two types of blowing agents: physical blowing agents and chemical blowing agents. Chemical blowing agents are usually reactive species that can produce gases by certain chemical reactions or thermal decomposition. Physical blowing agents are typically volatile chemicals such as chlorofluorocarbons (CFCs), hydrocarbons/alcohols, and inert gases (CO₂, N₂, argon, water). Due to the depletion of ozone layer, the use of CFCs has been gradually abandoned. Instead, HCFCs/HFCs, chlorofluorocarbons, and inert gases are potential replacements. Of these, CO₂ is the most favorable choice due to its environmentally benign properties.

In order to produce polymeric foams with controlled cell structure and uniform cell size distribution, nucleating agents (nucleants) are usually added to reduce the
nucleation energy. Commonly used nucleating agents include talc [163-165], zinc stearate [18, 165-167], calcium carbonate [165, 168], and calcium stearate [164, 165, 169]. A fine dispersion of these nucleation agents can facilitate the formation of nucleation centers for a gaseous phase. Although the nucleation mechanism is still under investigation, it is generally known that the size, shape, and distribution of the particles, as well as the surface treatment, can all affect the nucleation efficiency. Nucleation in PS microcellular foaming using zinc stearate additives was investigated [170-172]. It was found that above the zinc stearate solubility limit, heterogeneous nucleation dominates and the nucleation rate increases with stearate concentration. The observations were not affected by the gas pressure. The presence of filler would also promote the accumulation of gas on the polymer-particle interface and creation of nucleation sites [173]. Furthermore, foams with finer particle-sized fillers show a higher cell density at a high saturation pressure. More recently, nanoparticles have been studied as the foaming nucleants as well. Detailed reviews on this field are presented in a separate session.

2.2.2. Fundamental in polymeric foaming

2.2.2.1 Cell nucleation

In polymer foaming, nucleation can be defined as a process in which a new gas phase is separated from the initial homogeneous polymer-gas solution. Generally, there are two types of nucleation: homogeneous nucleation and heterogeneous nucleation.
2.2.2.1 Homogeneous nucleation

In homogeneous nucleation, the nucleation rate is expressed as [18, 166, 167, 174-177]:

\[
N_{\text{hom}} = n_0 C_0 \exp(-\frac{\Delta G_{\text{hom}}^*}{k_B T})
\]  \hspace{1cm} (2.2)

where \( C_0 \) is the number of gas molecules dissolved per unit volume of the primary phase, \( k_B \) is the Boltzmann’s constant, \( T \) is the temperature, \( \Delta G_{\text{hom}}^* \) is the homogeneous critical nucleation energy required to form a nucleus with a critical size, and \( n_0 \) is a kinetic pre-exponential factor which is a function of both the surface tension and the mass of the gas molecule. The critical nucleation energy is expressed as:

\[
\Delta G_{\text{hom}}^* = \frac{16\pi \gamma_{lv}^3}{3\Delta P^2}
\]  \hspace{1cm} (2.3)

and the corresponding critical bubble size is:

\[
r^* = \frac{2\gamma_{lv}}{\Delta P}
\]  \hspace{1cm} (2.4)

Here, \( \gamma_{lv} \) is the liquid-gas surface tension, and \( \Delta P \) is the pressure difference between that inside the critical nuclei and that around the surrounding liquid. Assuming that the polymer is fully saturated at by the blowing agent and the partial molar volume of blowing agent in the polymer is zero, \( \Delta P \) can be taken as the saturation pressure [18, 158].
2.2.2.1.2 Heterogeneous nucleation

With the existence of impurities such as nucleating agents, additives, or initiator residues, heterogeneous nucleation will occur. Typically, the nucleation takes place at the particle surface due to a lowered activation energy.

The heterogeneous nucleation rate is expressed as follows [18, 166, 167]

\[ N_{het} = v_{het} C_{het} \exp(-\Delta G_{het}^*/kT) \]  \hspace{1cm} (2.5)

where \( v_{het} \) is the frequency factor. It is similar to \( v_0 \), which is a complex function of the vibration frequency of the atoms, the activation energy for diffusion, and the surface area of the critical nucleus. \( C_{het} \) is the concentration of heterogeneous nucleation sites, which can be related to the particle concentration. The critical Gibbs free energy \( (\Delta G_{het}^*) \) to form a critical embryo on the nucleating sites can be expressed as:

\[ \Delta G_{het}^* = \frac{\Delta G_{hom}^*}{2} f(\theta) \]  \hspace{1cm} (2.6)

\[ f(\theta) = \frac{1}{4} \left( 2 + \cos \theta \right) \left( 1 - \cos \theta \right)^2 \]  \hspace{1cm} (2.7)

here \( f(\theta) \) is energy reduction due to the presence of the particles, a function of the contact angle \( \theta \) formed on the particle-gas-polymer interface.

Considering the influence of the nucleant size [178], \( \Delta G_{het}^* \) can be expressed in another way, as shown in Equations (2.8) to (2.12).

\[ \Delta G_{het}^* = \frac{\Delta G_{hom}^*}{2} f(m, w) \]  \hspace{1cm} (2.8)
\[
f(m, w) = 1 + \left(1 - \frac{mw}{g}\right)^3 + w^3 \left[ 2 - 3 \left(\frac{w - m}{g}\right) + \left(\frac{w - m}{g}\right)^3 \right] + 3mw^2 \left(\frac{w - m}{g} - 1\right) \tag{2.9}
\]

\[
m = \cos \theta \tag{2.10}
\]

\[
w = R / r^* \tag{2.11}
\]

\[
g = \left(1 + w^2 - 2mw\right)^{\frac{1}{2}} \tag{2.12}
\]

here \(f(m, w)\) is the energy reduction affected by both the contact angle \(\theta\) and the curvature \((R)\) of the nucleant surface. Figure 2.9 [178] illustrates how the reduction of the critical energy is influenced by the nucleants in terms of the surface property (contact angle) and the particle geometry (nucleants curvature). Qualitatively, a small contact angle and a large surface curvature offer a higher reduction of critical energy, and, consequently, an increased nucleation rate.

### 2.2.2.1.3 Ideal nucleating agents (nucleants)

In heterogeneous nucleation, the choice of nucleants is of great importance. In order to obtain foams with controlled cell density as well as a narrow cell size distribution, it is desirable that all the nucleants are activated within a narrow time window and followed by the cell growth in a tandem mode.

Generally, there are three criteria for choosing suitable nucleants [18, 160, 166, 167]. First, cell nucleation should be thermodynamically favored on the surface of the nucleants. Secondly, the amount of nucleants should be sufficient to preclude the
homogenous nucleation, thus avoiding a skewed cell size distribution. Thirdly, all nucleants should have uniform particle size and surface properties.

### 2.2.2.2 Cell growth

Cell growth is a process that involves mass, momentum and heat transportations of the fluid. Almost all the models describing the cell growth evolve from the “cell model”, a model used to describe the cell growth from a single bubble that is surrounded by an infinite sea of fluid with an infinite amount of available gas. Each cell is assumed to have equal and constant mass with a spherical structure. A schematic diagram of the bubble growth is shown in Figure 2.10 [179]. With several assumptions and simplifications, the equation of motion, the integral mass (gas) balance over the bubble, and the differential mass (dissolved gas) balance in the surrounding liquid phase take the following forms:

\[
\frac{dR_b}{dt} - \frac{(P_G - P_L)R_b}{4\eta} = \frac{\gamma_b}{2\eta} \quad (2.13)
\]

\[
\frac{d}{dt} \left( \frac{4\pi P_G R_b^3}{3RT} \right) = 4\pi R_b^2 D \frac{\partial c}{\partial r} \bigg|_{r=R} \quad (2.14)
\]

\[
\frac{\partial c}{\partial t} + \frac{\dot{R}_b}{r^2} \frac{\partial c}{\partial r} = D \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) \quad (2.15)
\]

where \( P_G \) and \( P_L \) are the pressure in the bubble and in the polymer melt, respectively. \( R_b \) is the radius of the bubble, \( \dot{R}_b \) is the rate of bubble growth, \( \eta \) is the Newtonian viscosity, \( \mathcal{R} \) is the gas constant, \( c \) is the gas concentration, and \( D \) is diffusivity.
2.2.2.3 Foam structure and foaming conditions

Foam structures can be characterized by cell density, cell size, and cell morphology. The relationship between the foam structures and the foaming conditions has attracted increasing attention in recent years. Several important foaming conditions, such as pressure, pressure drop rate, temperature, and gas concentration all play vital roles in determining the final cell structures.

In a batch foaming process, a higher saturation pressure can reduce the nucleation energy and thus increase the nucleation rate and the final cell density [20, 21, 180-183]. Moreover, since the pressure drop rate will affect the time length over which the cells can grow, a rapid pressure drop can effectively limit the bubble expansion. This results in a foam morphology with smaller cell sizes and higher cell densities.

In a continuous extrusion foaming process, the pressure drop rate influences the cell density in a different manner, as illustrated in Figure 2.11 [25]. The amount of gas dissolved in the system is indicated by the saturation pressure ($P_{sat}$). Above $P_{sat}$, the mixture is in a single phase. Two processes with the same pressure drop across the die are shown in this figure. Here we assume that for both cases, the pressure profile in the die is linear. It is clear that the pressure drop rate ($dP/dt$) of process 1 is higher than that of process 2, indicating that process 1 can create a higher thermal instability as well as a higher nucleation rate. Therefore, within the same nucleation time ($\Delta t_1 = \Delta t_2$), more bubbles will be generated by process 1. Macroscopically, the final foams synthesized by process 1 will have a higher cell density.
The temperature dependency of the foam structures is very complicated. Since physical properties such as the viscosity, surface tension, solubility, and diffusivity are all sensitive to temperature, the final change in the foam structures will be a result of comprehensive interactions of all these parameters. For example, an increase in the temperature usually causes a decrease in the surface tension of a polymer matrix. As a result, the nucleation energy barrier will be reduced and the nucleation rate and final cell density will be increased. However, considering that the surface tension of a polymer can also be reduced by the dissolved gas, a higher temperature will lead to a lower gas solubility, which in turn decreases the surface tension reduction. In that case, both the nucleation rate and the cell density will be decreased. Thus, there is no simple way to determine how temperature influences the final cell structure.

Generally, a higher gas concentration can be translated into a higher nucleation rate and much finer cell morphology [184]. However, it was found that the cell density would level off beyond certain value of the gas concentration, which is similar to the solubility limit.

2.2.2.4 Supercritical CO₂ (ScCO₂) in foaming

Recently, ScCO₂ has been extensively used in a variety of applications such as polymerization, polymer fractionation and extraction, impregnation, polymer foaming and blending, surface modification, coating and microlithography [185-188]. Supercritical fluid can be defined as a substance for which both the temperature and pressure are above the critical values. The critical point of CO₂ is relatively low, 31°C.
and 7.38 MPa, above which CO$_2$ exhibits a liquid-like density and a gas-like diffusivity. Compared to other volatile organic solvents, CO$_2$ is low cost, non-toxic, non-flammable, and environmentally benign. Furthermore, compared to other inert gases, ScCO$_2$ exhibits a relatively higher solubility. This leads to a higher nucleation ability. In addition, ScCO$_2$ is well known to swell and plasticize many amorphous polymers. It can significantly reduce the $T_g$ and the surface tension of the polymer matrix. All these advantages make ScCO$_2$ a promising blowing agent for polymeric foaming production. However, the high diffusivity of CO$_2$ may lead to a fast escape of the gas out of the foam and compromises the insulation properties. In order to obtain a clear understanding of the polymer foaming process utilizing ScCO$_2$, it is necessary to investigate the interactions between ScCO$_2$ and the polymers, in terms of its influence on the glass transition temperature, interfacial tension, and polymer viscosity.

### 2.2.2.4.1 Solubility

The solubility of CO$_2$ determines the upper limit of CO$_2$ that can be dissolved into the polymers. Owing to its influence on both the viscosity and the surface tension, solubility plays an important role during the foaming process.

Polymers with electron donor groups such as ether, fluro, and carbonyl groups, usually exhibit a higher solubility of CO$_2$. The interactions between these groups are based on a Lewis acid-base reaction. In this example, CO$_2$ is considered as a Lewis acid and the polymer with those functional groups as the Lewis base.
Wissinger et al [189, 190] and Zhang [191] found that in the PS-CO$_2$ system, there is a linear relationship between the solubility and the saturation pressure (Henry’s Law). Similar results were observed in the PP-CO$_2$ system. Handa et al [192] investigated the solubility of CO$_2$ in PMMA over a wide range of temperature (0-167°C) and pressure up to 61 atm. It was found that the linear relationship between the solubility and pressure only exists at high temperature regions. At low temperatures, the solubility was convex towards the pressure.

Techniques developed to measure the solubility include gravimetric, pressure decay, volumetric, and on-line visualization.

### 2.2.2.4.2 Glass transition temperature ($T_g$)

It is well known that CO$_2$ can effectively decrease $T_g$ of a polymer due to the plasticization effect. Chiou [193] found that at pressure of 20 atm, $T_g$ of PMMA and PS can be reduced by 45°C and 22°C, respectively. Hwang and Cha [194] found that the $T_g$ of PS can be reduced to room temperature at a high CO$_2$ solubility. Theoretical models of the $T_g$ depression have been developed considering the gas dilution, the polymer flexibility, and the equilibrium partitioning of the diluent [195].

### 2.2.2.4.3 Interfacial tension

The interfacial tension between the polymer and CO$_2$ can be significantly reduced with an increased pressure. The most commonly used technique to measure the interfacial
tension is Axisymmetric Drop Shape Analysis (ADSA). In the PS-CO\textsubscript{2} system, the interfacial tension was investigated over the pressure range of 1-140 atm [196]. At all three temperatures (210, 220, 230°C), the change of interfacial tension followed the same trend. It rapidly decreased as the pressure of CO\textsubscript{2} increased from 1 to 70.5 atm. Subsequently, it decreased at a much slower rate as the pressure further increased to 137.0 atm.

2.2.2.4 Viscosity reduction

For high-molecular-weight polymers, a high operation temperature is often required to decrease the viscosity and facilitate the polymer processing. However, the use of a high temperature may induce the polymer degradation and increase the processing cost. It has been found that once CO\textsubscript{2} is dissolved in the polymer melt, the viscosity can be efficiently reduced. This feature can be utilized in the polymer foaming process. For example, in a continuous extrusion foaming, high temperature is usually applied from the hopper to the gas injection point to ensure a complete melt of the polymer. Once the gas is injected, the barrel temperature can be decreased due to the reduction of the viscosity. This decreasing temperature profile will benefit both the processing cost and the final foam structures.
2.2.3 Microcellular foams

Microcellular foams are usually defined as plastic foams with cell sizes smaller than 10 µm and cell densities larger than $10^9$ cells/cm$^3$ [13, 14]. The idea of introducing small bubbles in solid polymers was first proposed by Nam Suh [13, 15]. The rationale is that if the bubbles are even smaller than the critical flaws in the polymer and can be introduced in a sufficient number, the material density could be reduced while maintaining the essential mechanical properties. Therefore, compared to conventional polymeric foams, microcellular foams offer higher impact strength, increased toughness and longer fatigue life [197-202]. In addition, small and uniform microvoids also make microcellular foams desirable for small-profile foaming parts for microelectronic applications [203].

Extensive researches have to been carried out in this area during the past several decades. Up to present, microcellular foams are made from a wide variety of polymers, e.g., PS [13, 14, 180, 181, 204], PC [182], PMMA [20, 205], polyimide and poly(lactic glycolic acid) (PLGA) [206].

2.2.3.1 Procedure to synthesize microcellular foams

Microcellular foams can be produced by a batch foaming, semi-continuous, continuous, or an injection molding process. In all these processes, there are three basic steps: mixing/saturation, cell nucleation and cell growth (Fig. 2.12) [207]. Good mixing is required to form a homogeneous solution of the polymer melt and the blowing agent.
Cell nucleation is usually induced by a thermodynamic instability such as a temperature increase and/or a pressure decrease. Subsequently, the cells will expand until vitrification occurs, thus freezing the final microcellular structure. Cell growth is a complex procedure controlled by the mass and heat transfer, the polymer rheology, and the fluid dynamics.

In a batch foaming process [182, 208, 209] (Fig. 2.13), polymer samples are placed in a pressurized autoclave and saturated with the blowing agent at certain saturation temperature and saturation pressure. Subsequently, the pressure is rapidly released, inducing supersaturation of the polymer with the blowing agent. If the saturation temperature is higher than the $T_g$ of the sample, the sample can be foamed under this temperature. Nucleation is driven by the pressure drop ($\Delta P$) and the pressure drop rate ($\Delta P/\Delta t$). If the saturation temperature is lower than $T_g$, expansion of the sample will be inhibited by the rigidity of its glassy structure. Therefore, the sample can be foamed only under a higher temperature ($>T_g$), denoted as the foaming temperature. In that case, nucleation is driven by the temperature increase ($\Delta T$) and the temperature increase rate ($\Delta T/\Delta t$). The latter method offers flexibility of manipulating the saturation conditions and the foaming conditions independently. Moreover, at lower saturation temperatures, the gas solubility is higher, which is beneficial for the bubble nucleation. However, during the transfer of a saturated sample to a higher temperature environment, diffusion is inevitable and will lead to thick skin regions. No matter which type of nucleation occurs, cell growth is stopped by quenching the sample at a temperature below the $T_g$ of the polymer. Due to the long saturation time (several hours to several days) required in this method, batch foaming has extremely limited productivity.
A semi-continuous foaming process was developed by Kumar et al. [210] to produce polymer sheets in a solid state. In this method, the polymer sheets are rolled with a gas channeling material (gas permeable materials) interleaved between the layered polymer sheets. The roll is then saturated with the blowing agent at room temperature. Finally, the pressure is released and the saturated polymer sheets are separated from the channeling material and then pulled through a heating station for bubble nucleation and growth.

A continuous extrusion foaming process was usually used for the mass production of foamed polymers due to its high productivity, easy control, and flexible product shaping [14, 25, 180]. Extrusion foaming can be performed on either a single-screw extruder or a twin-screw extruder. During the extrusion, it is desirable to reduce the temperature profile from the hopper to the die. The blowing agent is injected into the barrel and mixed with the polymer to form a homogeneous single-phase solution. Cell nucleation is induced by either a rapid, large pressure drop or a sudden temperature increase through the die. Cells will expand until the extrudate temperature is lower below the $T_g$ of the polymer. Usually, a shaping die is utilized to control the foam expansion and the foam shape. Compared to a batch foaming process, extrusion foaming has two distinctive characteristics. First, instead of a saturated amount of gas, a metered amount of gas is mixed with the polymer. Secondly, the driving force (pressure drop) for bubble nucleation is controlled by the flow instead of the saturation pressure.
2.2.3.2 Mechanical properties of microcellular foams

Although a wide range of polymers have been successfully synthesized into microcellular parts such as PS, PVC, PC, PP and PMMA, reports on their mechanical properties are still limited.

The status of previous research on the mechanical properties of microcellular foams can be summarized as follows. For most polymer systems, microcellular foams exhibited superior impact strength, toughness and fatigue life compared to their solid counterparts. However, the extent of improvement differs among different systems. Further, even for the same polymer-gas system, discrepancy in results were reported by different research groups. Finally, direct comparison of the mechanical properties between microcellular foams and their macrocellular counterparts with the same density is extremely limited. The following review is focused on the impact, tensile, compressive, and fatigue properties.

2.2.3.2.1 Impact properties

An improvement of impact strength was observed for PVC [199, 211, 212] and PC [213] microcellular foams. The notched Izod impact strength of microcellular PVC foams increased linearly with the relative foam density, defined as the foam density divided by the solid density. With a void fraction of 80%, the impact strength of PVC foams was four times as high as the PVC solid [199]. Very similar results have been reported in another work [211]. In Barlow et al.’s work, the Izod impact strength of PVC
foam was found to be a strong function of both the foam density and the cell size [212]. Impact strength of foamed PVC-cellulosic fiber composites was almost three times as high as that of the non-foam composites. The author attributed this strength enhancement to the energy absorption via the cell deformation and the cell wall buckling. Under a certain stress level, cell walls will yield, which leads to an irreversible deformation. This deformation, in turn, serves as an important source of the energy dissipation that results in the ultimate enhanced strength. The impact strength of PC foams has been examined as well [213]. All foams produced in that study had a narrow cell size distribution of 4-7 µm. For foams with a relative density of 0.6 or higher, the observed impacted strength was higher than that of the neat PC. At a relative density of 0.9, the highest impact strength (105 J/m) was achieved, which almost doubled from the value of the neat PC (55 J/m). Moreover, foams with a weight reduction of approximately 40% can be obtained while maintaining the essential impact strength of the solid PC. The affect of the cell size on the impact strength was also studied. It was found that with the increase of cell size, the impact strength increased. While most literature reported an enhanced impact strength of microcellular foams, Kumar et al. [214] found that the impact strength of foams does not universally increase upon the introduction of the microcellular structure. In their study, PVC microcellular foams exhibited a little lower impact strength compared to that of neat PVC. The reason is yet not clear.

The idea of using microvoids to enhance the toughness was originated from the rubber-roughened plastics. However, whether or not microbubbles can substitute the rubber particles and effectively toughen the plastics is still a matter of debate. Impact toughness of microcellular foams have been studied for PC, PS and SAN [197, 215].
Sharply and bluntly notched PC foams with microcellular structure were test using a charpy impact configuration \[215\]. Results suggested that, at a void of 28\%, microcellular PC foams increased the notched impact toughness dramatically over the PC solid. The author explained this result by the fact that the presence of small bubbles would relieve the triaxial stress at the crack tip, inducing a transition from brittle to ductile behavior. Impact toughness was also measured for PS and SAN microcellular foams \[197\]. Compared to PS solid, PS foams exhibited limited improvement in terms of the maximum load and the impact toughness. No obvious improvement was observed in case of SAN foams.

### 2.2.3.2.2 Tensile properties

Tensile strength and modulus of microcellular foams were studied for PC, ABS, PET and PVC \[199, 216-218\]. For these two properties, no improvement of microcellular foams over their bulk counterparts have ever been reported. However, the relative tensile strength of the microcellular foams appeared to be marginally higher than that of conventional foams. A linear (rather than a squared) relationship between the tensile strength and the foam density was found for all polymer systems examined. Tensile modulus of microcellular foams decreased as the void fraction increased (density decreased). The dependence of the modulus on the foam density can be described by the Mori-Tanaka model (Eqn. 2.16) over a wide range of relative densities \[216\].
\[
\frac{E_f}{E_m} = \left( \frac{\rho_f}{\rho_m} \right) + 2 \left( 1 - \frac{\rho_f}{\rho_m} \right)
\]

\(E_f\): modulus of foam  \(E_m\): modulus of foam
\(\rho_f\): density of the foam  \(\rho_m\): density of the matrix

Tensile toughness of the PS microcellular foams was studied by Waldman [216]. It was found that the toughness of PS foams increased nearly 400% compared to the solid because of the bubble-enhanced craze initiation. In addition, tensile toughness peaked at a relative foam density of 0.75. Collias and Baird repeated Waldman’s experiments and extended the research to SAN and PC foams [198]. The materials in their study were selected based on the rubber particle toughening mechanisms: crazing or shearing. Typical bubble sizes and void fractions obtained for all foams were 10 µm and 25%, respectively. The impact of microvoids on the tensile toughness was separated from those of the pressure and the thermal history of the samples. Compared to un-foamed solids, PS foams showed a limited improvement on the tensile toughness due to their coarse morphology, while SAN and PC foams showed a slight deterioration. The author explained these experimental results based on the rubber-toughening mechanism. For PS and SAN foams, even with a microcellular structure, the ligament thickness was still too larger to induce a complete transition from crazing to shear yielding.
2.2.3.2.3 Compressive properties

Systematic studies of the compressive behavior of microcellular PS foams was carried out by Arora [204]. An anisotropic model was proposed to describe the effect of the cell size and the cell shape on the compressive strength. The compressive strength of PS foams increases as the size of the cell increases. The phenomenon of heterogeneous, progressive buckling of the microcellular structures was correlated with the development of a stable neck in polymer subjected to a uniaxial tension. From an energy balance consideration, a model was established describing the densification process of microcellular foams under compression.

2.2.3.2.4 Fatigue life

Fatigue life characterizes how materials behavior under repeating external forces. Stemming from the original concept for developing microcellular foams, materials are expected to achieve a significant improvement in fatigue life with the inclusion of micro-scaled bubbles. PC foams with a relative foam density of 0.9 (10% of the weight reduction) showed the same fatigue life as that of the PC solid. Once the relative density increased to 0.97, foams exhibited a fatigue life one order of magnitude higher than that of solid [201, 202].
2.2.4 Polymer nanocomposite foams

Novel nanocomposite foams based on the combination of functional nanoparticles and polymeric foaming technology may lead to a new class of materials that are lightweight, high strength, and multifunctional. The following discussion is classified into two parts: impacts of nanoparticle on foam morphology and impacts of nanoparticles on foam properties.

2.2.4.1 Impacts of nanoparticles on foam morphology

Earlier studies in this area are mostly focused on the use of nanoclay [24, 26, 27, 30, 32, 34, 219-226], with a few on nanosilica [36] and nano-scaled block copolymer [37, 38]. The extremely fine dimension and large surface area of nanoparticles provide much more intimate contact between the particles, the polymer matrix, and the gas. Furthermore, a significantly higher effective particle concentration can be achieved at a low nominal particle concentration. Both these two considerations make nanoparticles potentially high-efficient nucleants for polymeric foaming. Compared to conventional micron-sized foaming nucleants, nanoclay exhibited superior nucleation effect in various systems, e.g. PP [26, 223, 224], PS [24, 27, 28], Nylon [29], PLA [30, 31], PC [32], PU [33, 34], and PVC [35], polyamide [225, 226]. The effect of particle concentration on the foam nucleation was also investigated [26, 31, 35, 227]. The cell density was found to increase linearly with the clay concentration at low clay concentrations, indicating the dominance of heterogeneous nucleation [31, 227].
The effect of particle dispersion and surface chemistry on the foam morphology were studied in detail [24, 27, 46]. It was found that, with exfoliated clay dispersion, the obtained PS-nanoclay foams exhibited the smallest cell size and the largest cell density. In addition, once the organoclay surface was grafted with PMMA, the strong affinity between CO\textsubscript{2} and the carbonyl groups in PMMA may reduce the interfacial tension and further promote bubble nucleation.

A similar effect of nanoclay on reducing the cell size and increasing the cell density has been observed in the thermoset (PU) nanocomposite foams at 5wt% clay content [34]. However, the efficiency of nanoclay on the size reduction in this system was not as strong as that in thermoplastic foams.

The effect of nanoparticles on bubble growth and ultimately the cell size were also examined. The presence of nanoparticles tends to reduce the cell size. As more bubbles start to nucleate concurrently, there is a less amount of gas available for the bubble growth, leading to a reduction of cell size. Moreover, the nanoparticles can significantly increase the melt viscosity. Strain induced hardening was observed under elongation, as a result of the nanoclay alignment [28, 220]. Both will hinder the cell growth and lead to a reduced cell size. Visual observation of CO\textsubscript{2} foaming of PP-Clay nanocomposites indicated a retarded bubble growth at the early stage of foaming [223, 224].
2.2.4.2 Impacts of nanoparticles on foam properties

The high aspect ratio and the large surface area of nanoparticles offer great potential to improve the comprehensive foam properties, including mechanical strengths, barrier performance, fire retardancy, dimensional and thermal stabilities, etc.

The nanometer dimension of nanoparticle is especially beneficial for reinforcing the foam materials, taking into consideration that the thickness of cell walls is in the micrometer or sub-micrometer regime. Compared to their neat polymer foam counterparts, polymer nanocomposite foams exhibit substantially improved properties. The tensile modulus of PS-clay nanocomposite foams was compared to those of neat PS foam and PS-talc microcomposite foams. With a similar bulk density, PS foams containing exfoliated nano clay possessed the highest modulus [24]. PVC foams containing 3wt% organoclay shows a 17.9% increase in the tensile strength, a 25.9% increase in the bending strength and a 250% increase in the elongation ratio over neat PVC foams [35]. The tensile strength and the impact strength of polyimide-clay nanocomposite foams have been studied systematically. In the presence of nanoclay, injection-molded polyimide foams exhibited microcellular structures, leading to an enhance impact strength when compared to the neat polyimide solid [225]. For polyamide-6-clay nanocomposite foams, the detrimental effect of cells on the tensile strength and the tensile modulus can be counterbalanced by the addition of nanoclay with a comparable magnitude [226].

The fire retardant properties of nanocomposite foams have been demonstrated for polymer-clay nanocomposite foams, e.g. PS [24], PE [228], and PVC [35]. After
burning, the nanocomposite foams formed char and maintained structural integrity, while the neat polymer foams quickly melted and dripped, causing the fire to spread. For foams applied in insulation and construction industries, this nanoclay-enabled char formation is of particular importance.

Nanoclay has also been demonstrated to improve the thermal insulation and aging properties of PU foam (indicated by k-factors in Btu.in/ft².h.F). PU foams with 10wt% nanoclay showed lower initial and aged k-factors, indicating better thermal insulation performance [229].

### 2.2.5 Expandable polystyrene

#### 2.2.5.1 Synthesis of expandable polystyrene

With an excellent balance between the cost and the thermal insulation properties, PS foams are highly competitive to other insulating materials, such as PU foams. Two most important processes for manufacturing PS foams are extrusion foaming and expansion of the expandable PS (EPS) beads. In this session, the production of EPS, especially the processes involved with the use of water as the blowing agent, is introduced in detail.

EPS beads are generally prepared via a modified route for the styrene suspension polymerization [230]. The route starts with the reaction of the styrene monomer dispersed in a water medium, containing suitable suspension agents and the blowing agent. Using
various heating medium (hot air, steam, etc.), these beads can be expanded to the desired densities.

The major concern of this process is the involvement of hydrocarbons. Due to their high inflammability and volatile nature, hydrocarbons are considered as fire hazards and ozone depleting agents (ODA). In light of this, the concept of producing water expandable PS (WEPS) was proposed. Instead of using hydrocarbons, water was used as the blowing agent. However, since the solubility of water in PS is very low, the abovementioned route to produce EPS is not feasible to synthesize WEPS. Therefore, alternative methods need to be sought.

The first method to produce WEPS was developed by Crevecoeur et al. [231]. Figure 2.14 ([231]) illustrates the main steps involved in their procedure. Instead of a process based on dissolution, water was emulsified in a pre-polymerized styrene/PS mixture with the aid of a suitable water-in-oil (w/o) surfactant (AOT). The viscosity of the oil phase should be sufficiently high to fixate the water droplets. Subsequently, the inverse emulsion was suspended in a water medium containing suitable suspension agents. Polymerization was continued until a complete conversion. The final products are spherical PS beads with entrapped micrometer-scaled water droplets. Instead of using commercial available surfactant, they further developed a new technique to synthesize in-situ amphiphilic block copolymer, a material with a better miscibility with water [232]. PS beads with very fine and homogeneous dispersion of water droplets were obtained. As a continuous effort, they also studied the expansion behavior of those WEPS beads. Different parameters, such as the temperature, the amount of water content, and the molar mass of PS matrix, were investigated to characterize the expansion performance [233].
Using a similar method, Snijders et al. synthesized WEPS with various molar masses [234]. A commercially available surfactant (SURF) was used to prepare WEPS. Compared to AOT, SURF resulted in a larger water droplet size but reduced suspension stability. To investigate the influence of the matrix melt strength on the expansion behavior (heating by silicon oil), WEPS beads with different mole masses were prepared. The expansion curve clearly suggested three pronounced stages: induction, expansion (processing window), and collapse. By introducing a melt strength “thickener”, end-capped poly(2,6-dimethyl-14-phenylene ether) (PPE), the processing window could be widened.

Pallay et al. presented a different method to prepare WPES [235]. Avoiding the use of w/o surfactant, starch was chosen as a water-swellable phase. As shown in Figure 2.15 ([235]), pre-polymerization of the styrene/starch mixture was first carried out to a conversion of approximately 30%. The viscous reaction phase was subsequently transferred to a water medium containing suitable suspension agents. In the last step, polymerization was completed and water was directly absorbed into the starch inclusions. It was found that the granule size distribution of starch would greatly affect the cell size in resulting foams.

In this thesis, the first route [231] to prepare WEPS is modified to produce water expandable PS-clay nanocomposites (WEPSCN). Traditional methods (melt blending, in-situ polymerization, solution blending) to produce PS-clay nanocomposites unavoidably involve the use of organoclay. Quaternary ammonium compounds (QAC), therefore, are generally used to render the clay surface hydrophobic and compatible with the PS phase. Although the presence of organoclay may improve the insulation performance of PS
foams, its inflammable surface (covered with QAC) will negatively impacts the material’s performance in industrial fire evaluations. Considering its hydrophillicity, raw-clay (Na\textsuperscript{+}-MMT) can be readily dispersed in water and then introduced into the PS beads.

### 2.2.5.2 Expansion of expandable polystyrene

A typical process of EPS manufacturing includes four stages: pre-expansion, drying, stabilization, and molding [236]. A schematic process is shown in Figure 2.16. In the first stage, the EPS beads are fed continuously or batch wise into a pre-expander. Steam and air are two additional feed streams. The final density of the products is determined in this stage. The minimum attainable density depends on various factors such as the initial size of the beads and the blowing agent content. Subsequently, the pre-expanded beads (prepuff) are dried in a fluid bed. Due to the development of vacuum in these newly created cellular structure, the pre-puff is very sensitive to the drying conditions. Thus a gentle drying procedure is generally required. The third step is the stabilization (i.e. maturing) of the prepuff. The vacuum developed in the cells is allowed to reach equilibrium with the ambient atmosphere. Caution must be taken during this stage. Condensation of the surrounding water vapor may occur and, the existence of water is harmful to the next molding stage. Therefore, sufficient time is required for this stage to fully eliminate the water and dissipate the residual blowing agent. In the last stage, the prepuff is fed into a closed mold in the presence of steam heat. At this point, prepuff will not expand further but fuses into a solid. The final shape of the foam product is defined by the mold.
2.3 Reinforcement in polymer nanocomposites

2.3.1 Correlation between nano-scaled reinforcement and $T_g$ behavior in thin films

The application of nanoparticles in polymer composites has been extensively investigated during the past decade. With the extremely small size and large surface area, those particles provide a superior opportunity for the reinforcement of polymer matrix. More recently, the application of nanoparticles has been extended to polymeric foams. Substantial mechanical enhancement has also been observed for these foam materials. However, all these macroscopic mechanical enhancements essentially result from the change of physical and chemical properties of polymers near the interface.

Polymer thin film/substrate configuration provides a well-defined system for studying the interfacial polymer dynamics. Previous research demonstrated that the properties of polymer thin films, such as $T_g$ [237, 238], structural relaxation [239], and polymer chain mobility [240], differ substantially from those in the bulk. However, most research in this field focused on the silicon-based substrate, which cannot chemically resemble the surface of CNFs (used in this study). In light of this, a carbon-based substrate with atomically smooth surface is highly desirable. PS films supported on these surfaces provide a relevant system for the study of polymer properties at the interface. Via evaluating the polymer mobility (such as $T_g$) within the film, any anchoring effect from the substrate as well as the level of interactions between the polymer and the substrate can be identified.
Bansal et al [241] addressed the apparent equivalent results between the polymer thin film $T_g$ and the thermomechanical responses of polymer nanocomposites. In their work, a direct analogy was drawn between the film thickness in thin films and the interparticle spacing in nanocomposites. It was demonstrated that for both non-wetting (e.g. SiO$_2$/PS) and wetting (e.g. SiO$_2$-grafted-PS/PS) polymer-particle systems, the $T_g$ of polymer nanocomposites with respect to the interparticle spacing fell on the same curve as that generated by corresponding thin film data. It was further concluded that the generic “two-layer” model [242] used to describe the reduction in $T_g$ of polymer thin film is not sufficient to capture the intrinsic physics. Instead, the distribution of altered polymer chain mobility, and hence the distribution of $T_g$ around nanoparticles, need to be considered [243].

2.3.2 Literature on $T_g$ measurement of supported thin films

Generally, there are two configurations of polymer thin films: supported polymer thin films and freestanding polymer thin films. For supported thin films, ellipsometry [237, 244, 245] is the most common technique to measure $T_g$. Other methods include but are not limited to X-ray reflectivity [246], positron annihilation lifetime spectroscopy [247], optical waveguide spectroscopy [248], and lateral force microscopy [249]. For freestanding thin films, there is only limited range of techniques that have been used to measure $T_g$. Brillouin light scattering [245, 250] can successfully measure the $T_g$ of freestanding films with a thickness down to 200 Å; however, this method is extremely time consuming. A single data point of $T_g$ can take as long as 20 hours. By comparison,
transmission ellipsometry [251] provides a rapid measurement, but it sacrifices the sensitivity to the sample defects. Among a wide range of polymers that exhibit glass-forming behavior, PS and PMMA are the most commonly used polymers for thin film $T_g$ investigation [237, 248, 252-255]. A few studies used tetramethyl bisphenol polycarbonate (TMPC) [256, 257], poly(vinyl pyridine) (PVP) [237], polysulfone [258], poly($\alpha$-methyl-styrene) [258] as well. For supported film system, silicone wafer, glass, and aluminum are the only three substrates reported to date.

It has been found that with the lack of strong polymer-substrate interactions, the thin film $T_g$ will be suppressed to a lower value compared to its bulk counterpart $T_g^b$. In addition, this effect ($T_g$ suppression) will be more pronounced as the film thickness $h$ decreases [237, 248]. The empirical correlation between $T_g$ and $h$ can be described by Equation (2.17), where $a$ and $\delta$ are fitting parameters ascribed to certain specific system.

$$T_g = T_g^b \left[ 1 - \left( \frac{a}{h} \right)^\delta \right] \quad (2.17)$$

In attempt to explore the nature of $T_g$ reduction in thin films, the notion of cooperation motion was introduced into this field. Incorporating this concept, a two-layer model was developed to predict the $T_g$ of thin films in a low $M_n$ limit where chain confinement is negligible [242]. In this model, the system is assumed composed of two regions: a surface layer with size $\xi(T)$ and surface $T_g$ ($T_g^{surf}$), and the reminder of the film with a bulk $T_g$ ($T_g^{bulk}$). $\xi(T)$ is size of the surface region and it is also regarded as the cooperative length scale. The average $T_g$ of the film with a thickness $h$ is thus

$$T_g = T_g^{bulk} + \frac{2\xi(T_g)(T_g^{surf} - T_g^{bulk})}{h} \quad (2.18)$$
Although this model was developed for freestanding films, it can also predict the $T_g$ reduction for supported films through a direct mapping between supported film with a thickness $h$ and freestanding film with a thickness $h/2$.

The importance of polymer-substrate interactions in supported thin films was not recognized until a contradicting result was reported by Wallace in 1995 [246]. For systems such as $PMMA/SiO_x/Si$ [240], $PVP/SiO_x/Si$ [237] and $TMPC/SiO_x/Si$ [256, 257], a qualitatively change in the thickness dependence of $T_g$ has been documented. The existence of the hydrogen bonding in these systems leads to an increase of $T_g$ above its bulk value for sufficient thin films. For PS-COOH films spin-cast on a Si wafer or grafted on $SiO_x$, an increase in $T_g$ was observed with a decreasing film thickness within the range of $h < 8$ nm [252]. By end-grafting PS chains (hydroxyl terminated PS) on the Si substrate, a brush polymer layer was formed [255]. The critical thickness for an elevation in $T_g$ (110 nm) doubled from that of the ungrafted films (55 nm). For films with a thickness of 43 nm, a $T_g$ elevation of $25^\circ C$ was observed. By side-grafting poly(4-hydroxystryren) (PHS) on the substrate, the critical thickness increased to almost 200 nm, resulting a $T_g$ elevation of more than $40^\circ C$ for films of 100 nm [255]. All these results suggested that, for supported films with strong polymer-substrate interactions, the suppressed mobility resulting from the substrate counteracts the enhanced mobility due to the free surface (polymer-air).

One should notice that Equations 2.17 and 2.18 can only describe a reduction in $T_g$ of polymer thin films. In that model, the dominant effect on $T_g$ is from the free surface. By considering both the surface and the substrate effects, a more general model was developed, as described in Equation 2.19 [259].
\[
\frac{T_g(z)}{T_g(\infty)} = \frac{1}{2} \left( \exp\left( -\frac{\alpha_1 - 1}{z \div z_0} \right) + \exp\left( -\frac{\alpha_2 - 1}{z \div z_0} \right) \right)
\] (2.19)

Here \( T_g(z) \) denotes the \( T_g \) of an amorphous polymer film with thickness \( z \). \( T_g(\infty) \) represents the bulk value. \( \alpha_1 \) and \( \alpha_2 \) is a measure of the effect from free surface effect and substrate, respectively. \( z_0 \) is a characteristic length. Depending on the relative contribution of the polymer-free surface and polymer-substrate effects, three typical cases of thickness-dependent \( T_g \) can be characterized. If the free surface effect dominates, a reduction in \( T_g(z) \) with respect to the film thickness is expected (case I in Fig. 2.17). If the polymer-substrate effect is sufficient strong to overcompensate the free surface effect, an apparent increase of \( T_g(z) \) with respect to a decreasing film thickness is expected (case II in Fig. 2.17). If the effects from the free surface and the substrate are comparable, the relative competition between these two effects depends on the film thickness. Thus, a minimum of \( T_g(z) \) will exist, as illustrated in case III (Fig. 2.17). Using this model, both the thickness-dependent reduction and enhancement of \( T_g \) of supported thin film can be predicted.

Despite the extensive observations of anomalous \( T_g \) behaviors in polymer thin films, the origin of this \( T_g \) shift is still unclear. The possible reasons proposed for the \( T_g \) shift can be classified into four categories: 1) decreased chain packing density in thin films, 2) decreased entanglement density at polymer-air free surface, 3) collective motions of chain “loops” near the surface, and 4) increased (enrichment) of chain ends near the surface. The simplest explanation of the \( T_g \) reduction in thin films is based on the
existence of a liquid-like surface layer that has an enhanced mobility relative to that of the bulk. Given this interpretation, eliminating the free surface must result in a lower mobility and thus a weak $T_g$ reduction. However, several studies aiming at identifying this enhanced surface dynamics revealed a striking discrepancy. For instance, the measured $T_g$ value of PS thin film supported on Si substrate (with only one free surface) was essentially the same as that of freestanding PS film (with two free surfaces) [245]. Other techniques have also been employed to ascertain the “mobile” surface layer, such as the nano-rheological tests (friction force measurement [260], the shear force modulation [261]), and the direct imaging of the surface perturbation [239, 262]). However, there is yet no consensus to date.

Nanoparticle embedding technique provides a direct verification of the existence of the mobile surface layer [253, 254, 263-265]. Spherical nanoparticles were placed on top of a supported polymer thin film. In the absence of enhanced surface dynamics, no embedding is expected to occur for $T < T_g^s$ (surface $T_g$). The embedding of nanoparticles only takes place at a temperature $T > T_g^s$. Using this method, the $T_g$ profile within the film can be directly measured and the enhanced (weak substrate confinement) or reduced (strong substrate confinement) polymer chain mobility can be identified. In addition, based on the concept that certain embedding thickness represents the lower bound of the liquid-like layer at certain temperature, this method provides an insight to the $T_g$ distribution in the near-surface regions of a supported thin film system.

With the rapid development and application of nanocomposites, the study of thin film $T_g$ has been extended to the nanocomposite systems [266]. $T_g$ of PS thin films containing functionalized SWCNT was found to decrease with $h$ when $h$ is less than 45
nm. However, compared to pure PS film with comparable thickness, the depression of $T_g$ ($\Delta T_g$) is less pronounced. Applying the rigidity percolation model derived by Long and Lequeux [267], the reduction of $\Delta T_g$ can be rationalized considering a higher fraction of slow domains (slow dynamics) in the PS-SWCNT thin film. This observation also suggested a competition between PS-SWCNT interactions and polymer-interface (free surface and substrate) interactions. However, the identification of the PS-SWCNT interactions was indirect and thus cannot be correlated with the macroscopic nanoparticle reinforcement. In addition, the segregation of nanoparticles near the substrate [268, 269], which has been reported for other similar systems, could induce more complexity in the understanding of the overall $T_g$.

Thin film $T_g$ subjected to a CO$_2$ environment was studied by Pham et al. [270, 271]. Thickness dependence of the CO$_2$-induced retrograde vitrification was observed for two systems: CO$_2$/PMMA/SiO$_x$/Si and CO$_2$/PS/SiO$_x$/Si. Provided sufficiently size constraints ($h < 50$ nm), the maximum pressure associated with the envelope shifts to a lower value compared to its bulk counterpart. A variable similar to $T_g$, devitrification pressure ($P_g$), was defined to characterize the pressure onset of devitrification. The thickness dependence of $P_g(h)$ was similar to that of $T_g(h)$. All these results suggested a magnified CO$_2$ plasticization in a confined polymer system. Further, for a given value of CO$_2$ activity, the depression of $T_g$ is much larger in thin films than that in the bulk. Another interesting result arises from comparing $\Delta T_g(T_g(T_g-h))$ of PMMA (film)/SiO$_x$/Si under ambient conditions versus that under certain CO$_2$ pressures. While $\Delta T_g$(ambient) is a positive value due to a strong polymer/substrate interaction, $\Delta T_g$(CO$_2$) turns to a
negative value under certain pressure. The formation of a CO$_2$ wetting layer on various hard and impenetrable surfaces may provide reasonable explanations for this examination [271-275].

Despite the qualitative agreement among a large number of studies on thin film $T_g$, scatter in data prevented the successful modeling of this behavior. For supported films or freestanding films with relative low $M_w$ ($\leq 350k$), there is no apparent $M_w$ dependence of $T_g$. Layer models [250] describing the dynamic heterogeneities of thin films has been shown to be applicable to this group of films. These models are based on the assumption that the segments near the free surface have a higher mobility (thus a lower $T_g$) due to the reduced steric constraints. $T_g$ near the top surface is the lowest and gradually increases while penetrating into the film towards the substrate. For freestanding films with higher $M_w$ ($\geq 500k$), however, a striking $M_w$ dependence of $T_g$ was observed, suggesting that the polymer chain confinement played an important role in these systems. A sliding model [276] considering the competition between the segmental mobility and the polymer chain sliding has been used to characterize the $T_g$ behavior of this group.
Figure 2.1: Schematic of 1:1 phyllosilicates [51]
Figure 2.2: Schematic of 2:1 phyllosilicates [51]
Figure 2.3 Schematic of polymer-layered silicates composites [1]
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CHAPTER 3

SYNTHESIS OF POLYSTYRENE-CARBON NANOFIBERS
NANOCOMPOSITE FOAMS

3.1 Introduction

Polymeric foams have been widely used in various applications such as cushioning, insulation, packaging and absorbency [5]. However, with the inclusion of voids into the polymer matrix, the foams usually exhibit low mechanical strength and poor dimensional stability. Recently, it has been found that microcellular foams with cell sizes less than 10 µm and cell densities larger than $10^9$ cells/cm$^3$ hold great promise as lightweight materials with excellent mechanical properties [13, 197-201]. Small and uniform microvoids also make microcellular foams desirable as small-profile foaming parts for microelectronic applications [203].

The production of microcellular foams usually requires a high pressure drop rate and a low foaming temperature, resulting in a very narrow operation window [24, 25].
this context, nucleating agents (nucleants) such as talc [163-165], zinc stearate [18, 165-167], calcium carbonate [165, 168], and calcium stearate [164, 165, 169] are used to produce microcellular foams with a high cell density and a uniform cell size distribution. More recently, nanoparticles have been studied as the foaming nucleants as well [24, 26, 27, 30, 32, 36, 219-221, 277]. Compared to conventional micro-sized nucleants, nanoparticles offer unique advantages for controlling both the foam structures and properties. Due to the extremely small particle size, it is possible to generate a large number of nucleants with a relatively low particle loading. Furthermore, the nano-scaled dimension, the high aspect ratio, and the large surface area make those particles desirable as reinforcing elements for the cell walls.

While spherical and plate-like nanoparticles have been used to synthesize nanocomposite foams, the use of cylindrical nanoparticles such as carbon nanofibers (CNFs) and single wall carbon nanotubes (SWCNTs) has not been reported. In this study, both CNFs and SWCNT were used to synthesize polystyrene (PS) nanocomposite foams. PS nanocomposites were first prepared by means of in-situ polymerization. The resulting composites were then foamed via a batch foaming process. Supercritical CO\textsubscript{2} (ScCO\textsubscript{2}) was chosen as the blowing agent due to its low cost, non-toxic, non-flammable and environmentally benign properties. The nucleation efficiencies of these nanoparticles are semi-qualitatively discussed using the classical nucleation theory, taking into consideration the nanoparticle dispersion, particle geometry and surface properties.
3.2 Experimental

3.2.1 Materials

Vapor grown carbon nanofibers (PR-24-PS, supplied by Applied Science Inc.) were pyrolytically stripped to remove the surface organic contamination. The average diameter of these CNFs was 100 nm and the original lengths ranged from 30 to 100 µm. SWCNTs (BuckyPearls™, Carbon Nanotechnologies Inc.) have an average tube diameter of 1 nm and tube length of 500 nm. Styrene and 2,2’-azobis (isobutyronitrile) (AIBN) were purchased from Aldrich and used as received.

3.2.2 In-situ polymerization

Due to the intrinsic van der Waals attractions, SWCNTs/CNFs are tightly entangled as bundles and ropes in their original state [66-68]. Once incorporated into the polymer matrix, these attractive forces will further increase due to an entropic penalty, which is induced by the confinement of the polymer chain configuration. Therefore, the dispersion of SWCNTs/CNFs becomes a major challenge in the synthesis of polymer-CNTs/CNFs composites. Strategies proposed to accomplish good dispersion include the use of ultrasonication, high shear mixing, surfactants, and functionalization of the carbon surface [66, 71, 72, 88, 117, 118]. In this work, we use high-shear mixing and ultrasonication to facilitate the dispersion of CNFs and SWCNTs.
Different amounts of CNFs/SWCNTs were added to the styrene monomer, together with AIBN as the initiator. The mixtures were then homogenized for 3 minutes and sonicated for 30 minutes. Polymerization was carried out isothermally at 60ºC for 20 hours and the composites were post-cured at 105ºC for 2 hours to complete the reaction.

3.2.3 Batch foaming

PS-CNFs nanocomposites were foamed with ScCO$_2$ as the blowing agent via a batch foaming process. Schematic of the foaming setup is shown in Figure 3.1. Samples were placed in a stainless steel vessel and CO$_2$ was delivered via a syringe pump. The system was allowed to equilibrate at 120ºC and 13.8 MPa for 24 hours. The pressure was rapidly released and the foam cells were fixed by cooling with a mixture of ice and water.

3.2.4 Characterization

The dispersion of nanoparticles in the polymer domain was characterized by transmission electron microscopy (TEM). Samples were microtomed at room temperature with a diamond knife and mounted on a 200-mesh copper grid. Images were obtained from a Phillips CM12 apparatus using an accelerating voltage of 80 kV. The foam morphology was characterized by scanning electron microscopy (SEM, Philips XL30). Samples were freeze-fractured in liquid nitrogen and the fracture surface was sputter-coated with gold. The resulting micrographs were analyzed by Scion Image software to determine the cell size and the cell density [24]. Typically, a micrograph showing more
than 50 bubbles is chosen. The number of bubbles ($n$) in this micrograph is determined by the software. If the area of a micrograph is $A$ cm$^2$ and the magnification factor is $M$, the cell density ($N_f$) can be estimated as

$$N_f = \left( \frac{nM^2}{A} \right) \frac{3}{2} \qquad (3.1)$$

3.3 Results and discussion

3.3.1 PS-CNFs nanocomposite foams

A series of PS-CNFs nanocomposites with CNFs content of 0.3, 1.0, and 1.5wt% were synthesized. These nanocomposites were subsequently foamed at 120°C and a CO$_2$ pressure of 13.8 MPa. The cell morphologies are depicted in Figures 3.2a-c. Pure PS foam [27] (Fig. 3.2f) synthesized at the same foaming conditions is shown for comparison. In the presence of only 0.3wt% CNFs, the cell density increased from 8.23×10$^7$ cells/cm$^3$ (pure PS foam) to 1.07×10$^9$ cells/cm$^3$, and the cell size decreased from 20 µm (pure PS foam) to 9.02 µm. By increasing the fiber content to 1wt%, the cell density increased to 2.61×10$^9$ cells/cm$^3$ and the cell size decreased to 6.2 µm. A further increase of the CNFs content to 1.5wt% yielded foams with the cell density of 4.59×10$^9$cells/cm$^3$ and the cell size of 4.82 µm. All PS-CNFs foams exhibit uniform cell size distribution. These results indicate that CNFs serve well as heterogeneous nucleating agents during the foaming process. Moreover, the monotonic increase of the cell density
with increasing fiber content indicates that bubble nucleation is dominated by the heterogeneous mechanism with the addition of CNFs [160].

To minimize cell interactions and cell coalescence, a sparse and stable nucleant distribution is preferred. However, we noticed that in the early stage of polymerization, the system viscosity was not high enough to achieve stable fiber separation. Thus, the CNFs were still inclined to attract each other, causing randomly distributed aggregates up to about 1 µm in the polymer matrix, as illustrated by the TEM result (Fig. 3.3a). Although these aggregates were observed in all the composites with fiber contents from 0.3 to 1.5wt%, only one representative TEM image (PS-1wt%CNFs) is shown here for illustration.

In order to improve the fiber dispersion, we added 10 wt% PS into the mixture of styrene-CNPs (1wt%) to achieve a higher initial viscosity. An extended settling time for CNFs in a more viscous medium was observed during the experiment. By increasing the AIBN content from 0.5 to 0.75wt%, a higher rate of viscosity increase was achieved due to the increased reaction rate. As a result, the resistance force opposed to the aggregation of fibers could be increased. The ultimate fiber dispersion in the polymer is shown in Figure 3.3b. In this case, most of the fibers have been completely separated and there are no obvious fiber aggregates, indicating a noticeable improvement of fiber dispersion. The composite was subsequently batch foamed and the foam morphology is shown in Figure 3.2d. Compared to its counterpart (Fig. 3.2b), the cell density was increased from \(2.61 \times 10^9\) cells/cm\(^3\) to \(2.78 \times 10^{10}\) cells/cm\(^3\), while the cell size decreased from 6.2 µm to 2.64 µm. Although the initiator concentration will influence the polymerization kinetics and eventually the molecular weight and polydispersity, a previous study showed that this
effect is insignificant on the cell densities and cell sizes [278]. Hence, this dramatic change of the cell structures primarily results from the improved fiber dispersion.

3.3.2 PS-SWCNTs nanocomposite foams

SWCNTs were used to synthesize PS nanocomposites and foams using in-situ polymerization and batch foaming processes as described previously. However, the dispersion of SWCNTs in the polymer domain is poor. From the fracture surfaces of both solid composites and foam struts, it is very difficult to observe any dispersed SWCNT. Instead, a large amount of ball-shaped aggregates with size up to a hundred nanometers form a bouquet-like pattern, which is similar to the fracture texture of the intercalated PS-nanoclay composite [279]. The formation of this structure could be caused by the penetration of polymer chains into the gallery of nanoparticle aggregates. For this reason, nanoparticles can be completely wrapped by the polymer, forming a large amount of ball-shaped polymer/particle agglomerates. A similar structure was observed in the intercalated PS-nanoclay composite [280]. However, even with such poor particle dispersion, the resultant PS foam with 0.1wt% SWCNTs still displays a much higher cell density and a much smaller cell size (Fig. 3.2e), compared to the pure PS foam. The average cell density is $1.44 \times 10^9$ cells/cm$^3$ and the average cell size is 7.11 µm.
3.3.3 Nucleation efficiencies of nanoparticles

Previously, a plate-like surface-modified nanoclay (MHABS) was also used to produce PS foams under the same foaming conditions [24, 27]. The acrylic groups attached to the clay surfaces can react with the styrene monomer, thus enabling the direct growth of polymer chains from the clay surface. Ultimately, an exfoliated dispersion of nanoclay was achieved [24]. The final PS nanocomposite foam with 5wt% MHABS exhibited a cell density of 4.02×10^8 cells/cm^3 and an average cell size of 10.8 µm [27]. However, despite an exfoliated dispersion and a higher nominal particle loading (5wt%), the cell density of PS-MHABS foam is still lower than any of the PS-CNFs foams attained in this study.

In heterogeneous nucleation, the highest nucleation efficiency can only be achieved when the nucleation on the nucleant surface is energetically favored (relative to its homogeneous counterpart) and the nucleant is uniformly dispersed in the polymer matrix. In most cases, the observed cell density is much lower than the potential nucleant density, implying that either the nucleants are not energetically effective, or their effects have been compromised due to poor dispersion. Here we compare the nucleation efficiencies of CNFs, SWCNTs and exfoliated nanoclay using a simple analysis.

The potential nucleant density in a heterogeneous nucleation system can be estimated by Equation. 3.2 [37]:

\[
\frac{\text{Nucleants}}{cm^3} = \frac{w \rho_{\text{blend}}}{\rho_p V_p}
\]  

(3.2)
where \( w \) is the weight fraction of the particle in the composite, \( \rho_p \) is the density of the particle, \( \rho_{blend} \) is the density of the polymer blend and \( V_p \) is the volume of the individual particle. In the case of CNFs, the potential nucleant density of the PS composite containing 1wt\% CNFs is \( 1.41 \times 10^{12} \) cells/cm\(^3\) according to Equation 3.2. Experimentally, the cell density of the foam with the same fiber content is \( 2.78 \times 10^{10} \) cells/cm\(^3\) (shown in Fig. 3.2d). The proximity of these two values indicates that most of the fibers served well as the nucleants in the PS foaming. The nucleation efficiency, defined by the ratio of the measured cell density to the potential nucleant density, is 1.97\% for CNFs. Similar calculation was conducted for PS-MHABS and PS-SWCNTs foams and the results are listed in Table 3.1. For both clay and SWCNTs systems, the potential nucleant densities are much higher than the final cell densities, ultimately leading to nucleation efficiencies that are orders of magnitude lower than that of CNFs.

Based on the classical nucleation theory \([18, 178]\), the heterogeneous nucleation rate is expressed as:

\[
N_{het} = v_{het} C_{het} \exp(-\Delta G_{het}^*/kT) \quad (3.3)
\]

where \( C_{het} \) is the concentration of heterogeneous nucleation sites, \( k \) is the Boltzmann constant, \( T \) is the temperature, \( v_{het} \) is the frequency factor of gas molecules merging with the nucleus, and \( \Delta G_{het}^* \) is the critical Gibbs free energy to form a critical embryo on the nucleating sites, i.e:

\[
\Delta G_{het}^* = \frac{\Delta G_{hom}^*}{2} f(m, w) \quad (3.4)
\]

\[
\Delta G_{hom}^* = \frac{16 \pi \gamma_{hc}}{3 \Delta P^2} \quad (3.5)
\]
\[ \gamma_r = \gamma_{r0} \left[ 1 - \frac{T}{T_c} \right]^{\frac{1}{\gamma_r}} \]  

\[ f(m, w) = 1 + \left( \frac{1 - mw}{g} \right)^3 + w^3 \left[ 2 - 3 \left( \frac{w - m}{g} \right) \right] + 3mw^2 \left( \frac{w - m}{g} - 1 \right) \]

(3.6)

(3.7)

(3.8)

(3.9)

(3.10)

(3.11)

where \( \Delta G_{\text{hom}} \) is the homogeneous Gibbs free energy, which is a function of the polymer-gas surface tension, \( \gamma_r \), and the pressure difference (\( \Delta P \)) between that inside the critical nuclei and that around the surrounding liquid. Assuming that the polymer is fully saturated with CO\(_2\) and the partial molar volume of CO\(_2\) in the polymer is zero, \( \Delta P \) can be taken as the difference between the saturation pressure and the atmospheric pressure [160, 166]. \( f \) represents the reduction factor of the critical energy due to the inclusion of nucleants, which is a function of the polymer-gas-particle contact angle \( \theta \) and the relative curvature \( w \) of the nucleant surface to the critical radius of the nucleated phase (Eqns. 3.7-3.11). \( r^* \) is the critical radius. Figure 3.4 illustrates how the reduction of critical energy is affected by the nucleants, in terms of the surface property (contact angle) and the particle geometry (nucleant curvature). Qualitatively, a small contact angle
and a large surface curvature offer a higher reduction of critical energy, and consequently an increased nucleation rate.

Under our foaming conditions (T=120°C, P=13.8 MPa), $\gamma_{lv}$ was calculated to be approximately 16.43 mJ/m$^2$ from Equation 3.6 and the known PS-CO$_2$ surface tension value from the literature [196, 281]. $r^*$ is 2.38 nm from Equation 3.10. Thus the relative radius $w$ is around 21 for individual CNF. With a typical contact angle of 20° [166], Equation 3.7 yields a reduction factor $f$ of 0.006 (also marked in Fig. 3.4), indicating that the energy required for the bubble nucleation ($\Delta G_{het}^*$) on the surfaces of CNFs is only 0.003 ($f/2$) of that in the homogeneous case ($\Delta G_{hom}^*$). In addition, since a complete dispersion of CNFs in the PS matrix was achieved, the actual nucleant density is close to the calculated one. The combination of a low energy barrier and a high nucleant density results in a high nucleation rate and ultimately a high cell density.

In the PS-SWCNTs system, if the SWCNTs are completely dispersed, then the relative radius $w$ is only 0.2 considering that the radius of an individual tube is 0.5 nm. In that case, $f$ is 1.8 and the nucleation energy on any single tube surface would approach the homogeneous limit (as shown in Fig. 3.4), completely diminishing the benefit of the heterogeneous nucleation. However, experimentally, most SWCNTs were observed as spherical agglomerates with an average radius of approximately several dozen nanometers. These agglomerates with much larger radii can serve as lower nucleation energy sites, but the actual nucleant density is much lower than the theoretical value owing to the poor dispersion, leading to the compromised nucleation efficiency.
In the PS-MHABS system, the relatively low nucleation efficiency can be explained first by an incomplete particle dispersion. Although exfoliated, stacks of multiple layers are still observable in the polymer domain [24]. A rough estimation from the TEM image of PS-5wt%MHABS indicates an average stack thickness on the order of tens of nanometers [24]. Therefore, the actual nucleant density in the PS-5wt%MHABS system would be reduced by one order from the value shown in Table 3.1, i.e., from $5.45 \times 10^{13}/\text{cm}^3$ to $5.45 \times 10^{12}/\text{cm}^3$. This value, however, is still much higher than the measured cell density ($4.02 \times 10^8/\text{cm}^3$), suggesting that there must be other reasons accounting for this relatively low nucleation efficiency. Here we seek to unveil this phenomenon based on the geometry of nanoclay and the compatibility between clay, PS and CO$_2$. On the clay surface, the nucleation energy should approach to the flat plate limit ($R \to \infty$) due to the layered structure of the nanoclay. The modified clay surface is more compatible with the PS matrix, and thus the interfacial tension between the PS melt and the clay is expected to be lower than that of PS and CNFs (carbon is well known for its non-wetting property to polymers and thus a high polymer-particle interfacial tension). Consequently, the contact angle $\theta$ would be higher. This would lead to a significant increase of $f$, or much less reduction in the nucleation free energy. Using equilibrium interfacial tension data from the literature, the lower limit of $\theta$ can be estimated as follows. We have known that $\gamma_{lv} = 16.43 \text{ mJ/m}^2$ and $\gamma_{sl} = 15 \text{ mJ/m}^2$ [282]. We need obtain $\gamma_{sv}$ in order to calculate $\theta$ from Young’s equation $\gamma_{sl} = \gamma_{lv} \cos \theta + \gamma_{sv}$. It is known that a decrease of $\gamma_{sv}$ will lead to a decrease of $\theta$. We thus estimate the lower limit of $\theta$ from the lower limit of $\gamma_{sv}$. The following three factors are considered in estimating the
lower limit of \( \gamma_{sv} \): 1) MHABS surface is covered by PS during nanocomposite synthesis [27]. 2) Inorganic solids have much higher \( \gamma_{sv} \) than organic solids like polymers. 3) For same substance, liquid has lower surface tension than that of solids [283]. It is therefore reasonable to use \( \gamma_{lv} \) to represent the lower limit of \( \gamma_{sv} \), which is 16.43 \( \text{mJ/m}^2 \). Using Young’s Equation, \( \theta \) is calculated to be 105.5°. Higher \( \gamma_{sv} \) would result in higher value of \( \theta \) and higher value of energy reduction \( f \).

With to a minimum reduction factor \( f \) of 1.4, a 30% reduction of the nucleation energy can be achieved, as illustrated in Figure 3.4. Therefore, although the PS-5wt%MHABS system has a much higher number of potential nucleants than both the PS-1wt%CNFs and the PS-0.1wt%SWCNTs systems, its nucleation efficiency is greatly compromised by the relative ineffectiveness of the energy reduction. This analysis is in favorable agreement with the previous findings that a weak polymer particle interface is advantageous for the bubble nucleation [18, 166, 167].

3.4 Conclusions

This study demonstrated the use of CNFs as the nucleating agents to form PS microcellular foams. It was found that the presence of a small amount of CNFs can significantly increase the cell densities and reduce the cell sizes. For comparison, SWCNTs and nanoclay were used to produce PS foams under the same foaming conditions. The nucleation efficiency, quantitatively defined as the ratio of the measured cell density to the potential nucleant density, is applied to compare the nucleation
effectiveness of different particles. Based on this parameter, CNFs exhibit an excellent nucleation effect on the PS–CO₂ foaming process. This may be due to its good dispersion in the polymer matrix, as well as the favorable wettability and surface curvature in this foaming system.

The classical nucleation theory was used to investigate the underlying mechanism for the difference in nucleation efficiencies among various particles. It was found that, with a complete dispersion and favorable particle size and surface properties, a 99.7% energy reduction in bubble nucleation is achieved on the surfaces of CNFs. In the case of SWCNTs, the existence of the agglomerates has a mixed effect on the bubble nucleation. While the large surface radii of these agglomerates are energetically favored for the nucleation, the actual nucleant density will be greatly reduced due to the poor particle dispersion. In the case of nanoclay, an incomplete separation of the clay layers as well as the high compatibility between the clay (MHABS) surfaces and the polymer (PS) matrix lead to a deteriorated nucleation efficiency.
<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>wt%</th>
<th>Dispersion</th>
<th>Potential Nucleant density $^{[b]}$ (#/cm$^3$)</th>
<th>Measured cell density (#/cm$^3$)</th>
<th>Efficiency (%)</th>
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</thead>
<tbody>
<tr>
<td>CNF</td>
<td>1</td>
<td>Complete</td>
<td>$1.41\times10^{12}$</td>
<td>$2.78\times10^{10}$</td>
<td>1.97</td>
</tr>
<tr>
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<td>$1.44\times10^{9}$</td>
<td>$9.06\times10^{-5}$</td>
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<tr>
<td>MHABS</td>
<td>5</td>
<td>Exfoliated</td>
<td>$5.45\times10^{13}$</td>
<td>$4.02\times10^{8}$</td>
<td>$7.37\times10^{-4}$</td>
</tr>
</tbody>
</table>

$^{[a]}$ actual particle dispersion observed by TEM images  
$^{[b]}$ calculated (Eqn. 3.2) with the assumption of complete particle dispersion

Table 3.1: Comparison of potential nucleant density and actual cell density
Figure 3.1: Schematic of the batch foaming setup
(a) cell size: 9.02 µm  
cell density: 1.07×10^9 cells/cm³

(b) cell size: 6.2 µm  
cell density: 2.61×10^9 cells/cm³

(c) cell size: 4.82 µm  
cell density: 4.59×10^9 cells/cm³

(d) cell size: 2.64 µm  
cell density: 2.78×10^10 cells/cm³

(e) cell size: 7.11 µm  
cell density: 1.44×10^9 cells/cm³

(f) cell size: 20 µm  
cell density: 8.23×10^7 cells/cm³

Figure 3.2 SEM images of foams (CO₂, 13.8 MPa, 120°C), (a-e) scale bar 20 µm (f) scale bar 50 µm (a) PS-0.3wt% CNFs, 0.5wt% AIBN (b) PS-1wt% CNFs, 0.5wt% AIBN (c) PS-1.5wt% CNFs, 0.5wt% AIBN (d) PS-1wt% CNFs, 0.75wt% AIBN, 10% PS (e) PS-0.1wt% SWCNT 0.75wt% AIBN, 10% PS (f) pure PS
Figure 3.3: TEM images of PS-CNFs nanocomposites, dark line: separated CNFs, circled particles: CNF agglomerates (a) PS-1wt% CNFs, 0.5wt% AIBN (b) PS-1wt% CNFs, 0.75wt% AIBN, 10wt% PS
Figure 3.4: Reduction of the critical nucleation energy by function $f(m,w)$

- Homogeneous Limit
- Flat Plate Limit
- SWCNT $f = 1.8$
- CNF $f = 0.006$
- MHABS $f_{\text{min.}} = 1.4$

\[ w \quad 0.0001 \quad 0.001 \quad 0.01 \quad 0.1 \quad 1 \quad 10 \quad 100 \]

\[ \theta = 180^\circ \quad \theta = 105.5^\circ \quad \theta = 60^\circ \quad \theta = 40^\circ \quad \theta = 30^\circ \quad \theta = 20^\circ \quad \theta = 10^\circ \quad \theta = 5^\circ \]
CHAPTER 4

PROPERTIES OF POLYSTYRENE-CARBON NANOFIBERS

NANOCOMPOSITE FOAMS

4.1 Introduction

With the increasing energy demand and cost, lightweight structural materials are highly desirable for automotive, aerospace and construction industries. Graphitic, ceramic and cellular metallic foams are emerging as novel and potential candidates for these applications. On the contrary, traditional thermoplastic foams, especially those generally considered as the insulation materials, are less attractive for these applications due to their inferior mechanical strength, poor surface quality, and low thermal and dimensional stability. In light of this, using nanoparticles to reinforce polymer foams has gained particular attention lately [24, 26-35, 219-221, 225, 284, 285]. The foam morphology and properties greatly depend on the inclusion of nanoparticles. It has been reported that nanoparticles exhibit improved nucleation efficiency in the polymeric foaming processes [24, 26-35, 219-221, 225, 284-286]. With a low particle loading, microcellular foams
with improved uniformity in foam morphology can be produced. Nanoparticles can also reinforce the micro-scaled cell walls/junctions, thus achieving macroscopic enhancement of the mechanical properties. Furthermore, the intrinsic physical properties (thermal, electrical) of nanoparticles can integrate multifunctionality into the foams, enabling nanocomposite foams as highly competitive lightweight structural materials.

In this work, carbon nanofibers (CNFs) were used as the nucleants and reinforcements for polystyrene (PS) foams. CNFs are a new class of tube-like nanoparticles, which are different from carbon nanotubes in the production method and the cost. As predicted by Applied Science Inc. (ASI), the price of CNFs can be reduced to $5/lb by the year of 2010, when the annual production reaches 10 millions pound. Thus CNFs satisfy the cost threshold for the automotive industry and many other filler-reinforcement applications. While the applications of CNFs in polymer composites have been extensively reported [70, 87, 111-113, 116, 150], limited research has been conducted on the application of CNFs in the polymeric foams [286, 287].

Due to the intrinsic van der Waals attractions, CNFs are highly aggregated in their original states, as shown in Figure 4.1. In order to fully realize their reinforcement and nucleation effects, uniform dispersion of CNFs in the polymer domain is required. Both mechanical forces (untrasonication, high shear mixing, etc.) and chemical treatments (surface coating, surface functionalization, etc.) can be used to facilitate the dispersion of CNFs. In this work, PS-CNFs composites were synthesized via the twin-screw extrusion process. Extensive shear was applied to disperse CNFs in the PS melt. The resultant composites were foamed using supercritical CO₂ (ScCO₂) as the blowing agent. Both continuous and batch foaming processes were used to generate foams with different
geometry requirements. Mechanical (tensile, compressive) and thermal (heat conductivity, infrared transmission) properties of PS-CNFs foams were measured and compared to those of neat PS foams.

The breakage of fibers during the twin-screw extrusion was observed and its impact on the final foam morphology was studied. Based on our observations, there may exist a threshold of the fiber length for the maximum nucleation efficiency in foaming.

4.2 Experimental

4.2.1 Materials

PS resin (CX5197) with a number average molecular weight of 86,000 was provided by Atofina. Vapor grown carbon nanofibers (PR-24-PS, supplied by ASI) are produced by decomposing organic vapors at elevated temperature in the presence of metal catalysts. They are pyrolytically stripped to remove any surface organic contamination. The average diameter of these CNFs is 100 nm and the lengths ranges from 30 to 100 µm. Tetrafuran (THF) was purchased from Aldrich and used as received.

4.2.2 Synthesis of nanocomposites

PS-CNFs nanocomposites were synthesized by either melt or solution blending. For melt blending, CNFs were pre-mixed with PS resin and then mechanically blended in a Leistritz ZSE-27 twin-screw extruder (L/D = 40, D = 27mm). The blending temperature
was 200 °C and the extruder was running in a co-rotating mode at a rotation speed of 250 rpm. For solution blending, appropriate quantities of PS resin and CNFs were dissolved in THF. The mixture of PS-CNFs/THF was ultrasonicated for 1 hour. The solution was dried extensively at room temperature and subsequently dried at 80°C in a vacuum oven for 24 hours to remove any residual solvent.

4.2.3 Synthesis of foams

Both continuous extrusion foaming and batch foaming were used to prepare PS-CNPs nanocomposite foams. ScCO$_2$ was used as the blowing agent. For extrusion foaming, a single screw extruder (HAAKE Rhomex 252P) was operated at a screw rotation speed of 15 rpm. A capillary die with a nozzle of 0.5mm (diameter) × 10mm (length) was custom-made to generate a rapid and high pressure drop. CO$_2$ was compressed to the required pressure at 40°C, reaching a supercritical state. While flowing through the static mixer, a homogeneous solution of polymer melt and CO$_2$ was formed. Due to a rapid pressure drop through the narrow capillary die, nucleation occurred and the foamed extrudate expanded until vitrified in the ambient air. For batch foaming, samples were placed in the high-pressure vessel and CO$_2$ was delivered via a syringe pump. The system was allowed to equilibrate at certain pressure and temperature for 24 hours. After that, the pressure was rapidly released and the cells were fixed by cooling with a mixture of ice and water.
4.2.4 Characterization

The dispersion of CNFs and fiber lengths were characterized by scanning electron microscopy (SEM, Philips XL30), transmission electron microscopy (TEM, Phillips CM12) and optical microscopy (Olympus, BH-2). For the SEM observation, samples were freeze-fractured in liquid nitrogen and the fracture surface was sputter-coated with gold. For the TEM observation, samples were microtomed at room temperature with a diamond knife and mounted on a 200-mesh copper grid. Images were obtained using an accelerating voltage of 80 kV. The foam structures were also examined by SEM. Foam samples was prepared using the same method as described above. The resulting micrographs were analyzed by Scion Image software to determine the cell size and cell density. Details of the image analysis was introduced in our previous report [24].

The tensile properties were measured by a rheometrics solids analyzer (RSA III). All the specimens were round rods with a length of 25 mm and a diameter ranging from 0.5 to 1.5 mm. The applied crosshead speed was 0.15 mm/sec. The compressive properties were measured using an INSTRON® 5848 Microtester. The specimens had the dimension of 10×10×3 mm³ and the crosshead speed of compression was set at 0.45 mm/min.

The thermal expansion coefficient (TEC) was determined using a thermomechanical analyzer (TMA 2940, TA Instruments), operated at a heating rate of 5°C/min with a 0.02 N preloaded force. The heat conductivity was measured using the heat flow meter (FOX 200, LaserComp). The temperature difference between the upper and lower plates was set at 30 °C. The Infrared (IR) transmission was measured by an
equipment composed of a diode laser fiber and an energy meter (Thermal SmartSensors™).

4.3 Results and discussion

4.3.1 Structure and properties of extruded foams

The nucleation effect of CNFs during the foaming process was demonstrated in this study. There are two major criteria for an ideal nucleant. First, the particles should be dispersible in the polymer matrix. Secondly, the nucleation of bubbles on the nucleant surface should be energetically favored [288]. Our previous work has reported that CNFs exhibit a high level of energy reduction for the CO₂ bubble nucleation in the PS melt [286]. Thus the dispersion of CNFs becomes the key issue in this study, which has a direct impact on the foam morphologies. CNFs at levels of 1 and 5wt% were shear mixed with PS via a twin-screw extruder. The dispersion of CNFs in the PS matrix was investigated by observing the fracture surface of the PS-CNFs composites, as shown in Figure 4.2. For both PS-1wt%CNFs (Fig. 4.2a) and PS-5wt%CNFs (Fig. 4.2b) composites, uniform dispersion of CNFs (white dots) in the PS matrix is evident, implying that the shear force generated by the twin-screw extruder is strong enough to break the agglomerates of CNFs. This uniform dispersion of CNFs was further verified by following TEM analysis. The composites were subsequently foamed by a single screw extruder and the foam structures are illustrated in Figure 4.3. The presence of CNFs effectively changes the foam morphology by increasing the cell density and decreasing
the cell size. For the neat PS foam (Fig. 4.3a) synthesized under the same foaming conditions, the cell size is 8.69 µm and the cell density is $2.29 \times 10^8$ cells/cm$^3$. With the incorporation of 1wt% CNFs, the cell density increased to $4.73 \times 10^8$ cells/cm$^3$, while the cell size decreased to 7.15 µm (Fig. 4.3b). Further increasing the content of CNFs to 5wt% yields foams with the microcellular cell structure with a cell density of $1.44 \times 10^9$ cells/cm$^3$ and a cell size of 4.1 µm (Fig. 4.3c).

The tensile properties of these extruded foams were studied and the results are shown in Figure 4.4a (tensile modulus) and Figure 4.4b (tensile strength). All the foams exhibit a similar foam density of 0.6 to 0.7g/cm$^3$, indicating a similar weight reduction compared to the bulk PS. For neat PS foam, the inclusion of cells in the polymer results in a weight reduction of 37%. However, it sacrifices the tensile modulus by 40% (1.26 to 0.74 GPa). In the presence of 1wt% CNFs, the tensile modulus increases by 28% (0.74 to 0.94 GPa), while achieving approximately the same weight reduction (34%). Once the fiber content is increased to 5wt%, the tensile modulus further increases to 1.07 GPa (a total 45% enhancement), which is even comparable to that of the bulk PS (1.26 GPa). In order to normalize the impact of the foam density on the mechanical properties, reduced modulus (modulus divided by the density) was used to compare these samples as well. Due to the relatively lower densities, the reduced modulus of PS-CNFs foams is much higher than that of the bulk PS. With the inclusion of 5wt% CNFs, the reduced modulus of PS foam (1.56 GPa/g/cm$^3$) is 25% higher than that of the bulk PS (1.25 GPa/g/cm$^3$).

Figure 4.4b shows the impact of CNFs on the tensile strength. Compared to the PS solid, the neat PS foam exhibits a lower tensile strength, but approximately the same
reduced value. However, once CNFs are added, the tensile strength of the PS foams is greatly decreased, indicating the inferior foam ductility.

4.3.2 Structure and properties of batch-foamed foams

Using the batch foaming process, neat PS and PS-CNFs foams were generated with suitable dimensions for the tests of compressive and thermal properties. By controlling the foaming conditions, two sets of foams were produced: low-density (≈0.2 g/cm³) foams and medium-density (≈0.5 g/cm³) foams.

Low-density PS-CNFs foams were produced under a saturation temperature of 100°C and a saturation pressure of 13.8 MPa. The depressurization time is approximately 20 seconds. Figure 4.5 shows the SEM images of freeze-fractured surface of these foams. The neat PS foam has fewer cells and larger cell size than the PS nanocomposite foams. However, all these foams have similar foam densities (≈0.2 g/cm³). The compressive properties of PS-CNFs foams are illustrated in Figure 4.6. As compared to the neat PS foams, PS nanocomposite foams exhibit an overall compressive enhancement. The addition of 1wt% CNFs results in a 45% increase in the compressive modulus and a 36% increase in the compressive strength. A higher fiber loading up to 5wt% yields foams with a 95% increase in the modulus and a 206% in the strength. Reduced modulus and strength illustrated here are defined in a similar way as mentioned above. The trend of the dependency of these reduced values on the fiber loading is the same as that of the absolute value.
Despite the improvement of PS-CNFS foams over neat PS foams, there is still a substantial reduction in the compressive properties when compared to the bulk PS (161.44 MPa). Thus a set of medium-density foams was produced under a lower saturation temperature (80ºC) and a faster depressurization (10 second). The saturation pressure was kept the same as 13.8 MPa. As shown in Figure 4.7, the resultant foams have much smaller cell sizes and higher cell densities compared to the low-density foams. The density of these foams falls in the range of 0.4~0.5 g/cm³. Figure 4.8 shows the compressive modulus (a) and compressive strength (b) for both bulk PS and PS-CNFS foams. Compared to the low-density foams, the weight reduction of these medium-density foams reduces from 80% to 50%, however, both modulus and strength considerably increase. In the presence of CNFs (both 1% and 5wt%), PS foams show even higher compressive modulus and strength than those of the bulk PS. For example, PS foam containing 5wt%CNFs exhibits a 12.4% increase in the modulus and 17.9% increase in the strength over the PS solid. This result indicates that the integration of CNFs into the PS foams have a great potential to bridge the gap between the lightweight and high strength requirements. On one hand, CNFs can effectively induce the nucleation of a large amount of bubbles, which ultimately provides a comparable weight reduction to the neat PS foams. On the other hand, the strength deterioration resulted from the inclusion of cells can be compensated by the reinforcement of cell walls/junctions by CNFs.

It has been reported that during the foaming process, nanoparticles (nanoclay) could be aligned along the cell walls due to the bi-axial forces, leading to improved mechanical properties [220]. In this work, a similar alignment was identified from the
SEM observations. Figure 4.9a shows the side view of the fracture surface of PS-CNFs foams resulted from the tensile breakage. CNFs, both exposed from the fracture surface and embedded in the cell wall (indicated by the small arrow), are uniformly aligned along the flow direction (the long arrow), leading to the direct strengthening of the cell wall. Figures 4.9b and c show the top view of the cell wall and the cell strut, respectively. Many CNFs (white dots and fibers) are well dispersed in these regions. All the fibers protrude out of the fracture plane, aligning along the cell wall and perpendicular to the fracture surface. To further verify the alignment of CNFs, another SEM sample was prepared to expose the surface parallel to the direction of the tensile stretching. Figure 9d confirms that the fibers laterally are orientated within the examined plane.

While the alignment of CNFs provides protective layers around the cell wall, the interfacial adhesion between the fibers and the polymer is another key issue for the effective reinforcement. Previous research on the carbon nanotube (CNT)-polymer composites revealed that strong interfacial strengths could be realized by either covalent bonding or polymer wrapping around the nanotubes (non-covalent bonding forces) [42, 45]. The polymer layers near the interface are different from those in the bulk, enabling a higher level of stress that would otherwise induce failures in the bulk polymer. Thus the sheathing polymer layer is a direct evidence of substantial nanotube-polymer interactions and would ultimately influence the load transfer. In this study, the existence of the polymer sheathing was identified by a series of SEM observations, and the results are consistent with previous reports based on CNTs [41, 289-292]. Figures 4.10a-c are high resolution images of CNFs exposed from the fracture surface. Compared to the original CNFs (insets #1and 2 in Fig. 4.10a), all these protruded structures exhibit much larger
diameters (136~195 nm vs. 100~105 nm), indicating absorbed PS layers along the fibers. Moreover, the outer surfaces of these protruded structures are not as smooth as those of original CNFs (shown in inset #2). Instead, they share a texture similar to that of PS. Coating the fracture surface of PS-CNFs foams with acetone further revealed CNF-polymer interactions. Figures 4.11a-d show the SEM images of those apparent CNFs (CNFs coated with PS) after the acetone treatment. It is clear that there exists a polymer outer layer (secondary absorbed layer) around the inner fiber, which would contract or ball up due to the dissolution of acetone. The inner polymer layer (primary absorbed layer), on the other hand, remains unaffected. Similar observations have been reported when energy was added to the CNF-polymer system via the disturbance caused by an AFM tip [41]. The above nanoscaled observations (increased fiber diameter, surface texture, multiple sheathing layers and balling-up effect) indicate that most CNFs in the PS-CNFs foams were wrapped with annular PS layers. The existence of the polymer sheathing, along with the alignment of fibers near the cell walls, reasonably explained the macroscopic strength enhancement of PS-CNFs foams.

4.3.3 Thermal properties of PS-CNFs foams

Thermal expansion coefficients (TECs) neat PS and PS-CNFs foams (medium-density) are shown in Figure 4.12. The slope of the linear expansion in a typical TMA curve (Fig. 4.12a) is defined as the TEC. As shown in Figure 4.12b, the addition of CNFs results in less thermal expansion, indicating the improved dimension stability. Compared to neat PS foam, PS foams containing 1 and 5wt% CNFs achieve a reduction
in TEC by 3.2% and 12.8%, respectively. This decreased thermal expansion of PS nanocomposite foams may result from the confinement of PS chains by the dispersed CNFs. The thermal conductivity (\(\lambda\)) of PS foams is shown in Figure 4.13 (group 1). For both neat PS and PS nanocomposite foams (medium-density), \(\lambda\) increases linearly with the temperature within the temperature range investigated in this study. The inclusion of 1wt% CNFs leads to an average of 6% increase in \(\lambda\), while 5wt% CNFs leads to a 30% increase in \(\lambda\). The effect of CNFs on \(\lambda\) actually results from two competing aspects.

The total thermal conductivity (\(\lambda\)) of foams is an integrated value of four components, as shown in Equation 4.1.

\[
\lambda = \lambda_g + \lambda_s + \lambda_r + \lambda_c
\]  

(4.1)

where \(\lambda_g\) is the conduction through the gas phase, \(\lambda_s\) is the conduction along the cell wall and the solid struts, \(\lambda_r\) is the thermal radiation and \(\lambda_c\) is the convection within cells.

For closed-cell foams, it is well accepted that \(\lambda_c\) plays a minor role in the heat transfer provided that the cells are less than 4 mm in diameter [293]. \(\lambda_g\) is determined by the gas volume faction and the thermal conductivity of the gas. Since the neat PS foams and PS-CNFS foams have similar densities, the contribution of \(\lambda_g\) is approximately the same. Therefore, the difference in \(\lambda\) essentially results from the combination of \(\lambda_s\) and \(\lambda_r\).

Since the CNFs used in this study have a high thermal conductivity of 1950 to 2000 W/m-K, it is evident that the inclusion of CNFs will greatly increases \(\lambda_s\), showing a positive effect on the overall \(\lambda\). This was confirmed by measuring the thermal conductivity of solid PS and PS-CNFS composites within the same temperature range, as
shown in Figure 4.13 (group 2). On the other hand, considering that carbon is an infrared (IR) absorber and reflector, the thermal radiation term will be reduced by the addition of CNFs. Our data shows that near-zero IR transmission of PS foams is achieved with only 1wt% of CNFs, while neat PS foams exhibit an 8% IR transmission. This CNFs-induced IR opacification will ultimately lead to a reduced $\lambda_s$ value. Therefore, the overall impact of CNFs on $\lambda_s$ is a mixed effect of the above two aspects.

4.3.4 Impacts of fiber length on foam structures

For fiber-reinforced composites, the aspect ratio of fibers can significantly affect the mechanical strength and the percolation threshold for other transport (electrical, thermal) properties [90, 294]. During the extrusion blending, an aggressive shear mixing is applied to disentangle the nanofiber bundles, however, it may break the fibers in length and reduce their aspect ratios. In this study, the attrition of CNFs and their impact on the foam structures were observed. Figure 4.14 shows a TEM image of the PS-CNFs composite with a fiber loading of 5wt%. As shown in this figure, nanofibers are evidently aligned along the flow direction, as indicated by the solid arrow. Therefore, if we section the TEM samples parallel to the extrusion direction, the fiber breakage during the sample preparation can be minimized and the fiber lengths can be reasonably determined. The longest fibers have a length of approximately 2 µm, which is much shorter than their original lengths (30–100 µm). The average fiber length is 0.28 µm as obtained by the image analysis. Moreover, a large amount of very small dark particles shown in this
figure indicates that a large amount of fibers essentially lost their original tube-like geometries due to the extensive shear mixing.

To study the effect of fiber length on the cell structures, solution blending with the aid of ultrasonication was also used to synthesize PS-CNFs composite with a fiber content of 5wt%. Compared to melt compounding, this method can minimize the fiber breakage while moderately separate the fiber agglomerates into a loose fiber network. Since nanofibers are not aligned in the final composite, it is not feasible to prepare TEM samples without damaging the fibers in length. Optical microscopy was used instead to observe the fiber dispersion. As shown in Figure 4.15, uniform dispersion of CNFs is achieved in the solution-blended composite and the average fiber length is larger than 10 µm, as opposed to 0.28 µm in the melt-compounded composite. These two composites (PS-5%CNFs, melt compounded and solution blended) were batch foamed and the cell structures are illustrated in Figure 4.16. An apparent difference in cell structures exists between these two foams. The average cell density of the solution blended sample (5.70×10^8 cells/cm^3) is observably higher than that of the melt compounded one (1.85×10^8 cells/cm^3), while the average cell size is smaller (10.2 vs. 14.9 µm). Considering the same fiber content and foaming conditions used to prepare these two foams, this remarkable difference of the cell structures may result from the different fiber lengths in the polymer domain. Once the fibers have been shortened to very small particles with low aspect ratios, their nucleation effect seems to be substantially compromised. Therefore, the effective nucleant density is reduced, leading to a decreased cell density. Similar results have been reported in the rubber-high impact polystyrene (HIPS) system [295]. It has been found that the rubble particles less than 25 nm had little
effect on the bubble nucleation. On the contrary, particles large than 300 nm exhibited excellent nucleation ability. Future research needs to be carried out to determine the optimal fiber length for maximum bubble nucleation. With the knowledge of this value, a balance between the nucleant density (depending on the extent of the fiber attrition) and the practical nucleation effect of those shortened fibers can be achieved.

4.4 Conclusions

The nucleation and reinforcement effects of CNFs on PS foams are demonstrated in this study. It is found that CNFs can effectively change the foam morphology by increasing cell densities and decreasing cell sizes. With a fiber loading of 5wt%, the extruded PS foam shows a microcellular structure with a cell density of $1.44 \times 10^9$ cells/cm$^3$ and an average cell size of 4.1 µm. Compared to the neat PS foam, PS-CNFs foams exhibit significant enhancement of the mechanical prosperities (tensile, compressive). The addition of 5wt% CNFs yields foams with comparable (tensile modulus) or even higher (compressive modulus) stiffness than the bulk PS solid. Meanwhile, a 50% of weight reduction (compared to bulk PS) is obtained. Based on these results, PS-CNFs foams have a high potential to serve as a lightweight structural material.

High-resolution SEM observations revealed the alignment of CNFs along the cell walls and the existence of absorbed polymer layers around the fiber surface. These phenomena provide fundamental explanations of the reinforcement of CNFs on PS foams. A better understanding of the physical properties of polymers near the interface is essential to manipulate the nanoparticle-reinforced polymer systems. The inclusion of
CNFs results in a lower TEC. Compared to the neat PS foams, a reduction of 13% of TEC was observed for PS-5%CNF foams. The high thermal conductivity and IR absorbency of CNFs play a mixed effect on the overall heat conductivity of PS foams. A linear dependency of the heat conductivity on the temperature was observed for both neat PS and PS-CNFs foams.

The intensive shear mixing applied in twin-screw extrusion, although improved the fiber dispersion, resulted in a significant fiber breakage. On the contrary, solution blending with the aid of ultrasonication can preserve the fiber lengths to longer than 10 µm. The impact of the fiber length on the foam morphology is demonstrated in this study. Detailed mechanism on how the fiber lengths influence the bubble nucleation and growth needs further investigation. Considering that both the fiber dispersion and the fiber aspect ratio will affect the foam morphology and properties, a balance between these two aspects will be sought in future studies.
Figure 4.1: Entanglement of CNFs in their original states, scale bar 2 µm
Figure 4.2: Fracture surfaces of melt compounded composites, scale bar 10 µm (a) PS-CNFs (1wt%) (b) PS-CNFs (5wt%)
(a) cell size: 8.69 µm
cell density: $2.29 \times 10^8$ cells/cm$^3$

(b) cell size: 7.15 µm
cell density: $4.73 \times 10^8$ cells/cm$^3$

(c) cell size: 4.1 µm
cell density: $1.44 \times 10^9$ cells/cm$^3$

Figure 4.3: Cell structures of extruded foams, scale bar 50 µm
(a) PS (b) PS-CNFs (1 wt%) (c) PS-CNFs (5 wt%)
Figure 4.4: Tensile modulus (a) and tensile strength (b) of extruded foams
Figure 4.5: Cell structures of low-density foams, scale bar 200 µm (a) PS (0.176 g/cm³) (b) PS-CNFs (1wt%) (0.185 g/cm³) (c) PS-CNFs (5wt%) (0.229 g/cm³)
Figure 4.6: Compressive modulus (a) and strength (b) of low-density PS and PS-CNFs foams.
Figure 4.7: Cell structures of medium-density foams, scale bar 200 µm (a) PS (0.448 g/cm³) (b) PS-CNFs (1wt%) (0.459 g/cm³) (c) PS-CNFs (5wt%) (0.487 g/cm³)
Figure 4.8 Compressive modulus (a) and strength (b) of medium-density PS-CNFs foams
Figure 4.9: Alignment of CNFs along the cell wall
scale bar (a) 5 µm (b) 2.5 µm (c) 5 µm (d) 2 µm
Figure 4.10: Polymer sheathing around CNFs, scale bar (a) 200 nm (b) 200 nm (c) 100 nm insert #1 in figure a is TEM image of pure CNF (provided by ASI)
Figure 4.11: Contract and balling up of secondary PS layer around the CNFs
scale bar 200 nm
Figure 4.12: (a) A typical TMA curve of foams and (b) TEC of foams (medium-density)
Figure 4.13: Thermal conductivity of PS and PS-CNFs solids and foams (medium-density)
Figure 4.14: TEM micrograph of melt compounded PS-CNPs (5wt%)
Figure 4.15: Optical micrograph of solution blended PS-CNF (5wt%) composite
cell size: 14.9 µm
cell density: $1.85 \times 10^8$ cells/cm$^3$

cell size: 10.2 µm
cell density: $5.70 \times 10^8$ cells/cm$^3$

cell size: 25.8 µm
cell density: $3.25 \times 10^7$ cells/cm$^3$

Figure 4.16: SEM images of foams made by a batch foaming process, CO$_2$, 120°C, 13.8 MPa, scale bar 50 µm (a) PS - CNFs foam (5wt%), composite by melt compounded (b) PS - CNFs (5wt%) foam, composite by solution blended (c) neat PS foam
5.1 Introduction

5.1.1 Motivation

Polymer nanocomposites have generated a great deal of interest in recent years because these materials exhibit high potentials to achieve great property improvements through the addition of only a small amount of nanoparticles in the polymer matrices. Compared to traditional micro-sized reinforcing fillers, nanoparticles such as nanoclay and carbon nanotubes (CNT)/ carbon nanofibers (CNF) are lighter but possess higher inherent mechanical strengths. In addition, when incorporated into the polymer matrix, nanoparticles interact with the host polymer across a significantly larger interfacial area as compared to those micro-fillers at the same particle loading level. This immense
interfacial area allows the small addition of particles to significantly modify the performance of polymer composites. All these characteristics of nanoparticles make them ideal candidates as reinforcing agents for polymer composites.

For filler-reinforced composites, the realization of reinforcement depends highly on the interactions between the particles and the polymer regardless of the micro- or nano-scale of the filler component. A strong interaction generally leads to an efficient load transfer across the interface, resulting in macroscopic mechanical enhancement. The interaction, though, is not limited to the immediate interfacial area. The interactions can influence the properties of polymers in the vicinity of the particles as well. Earlier studies indicated that there might exist a definable interaction zone (interphase region) around the particles, within which the dynamics and morphology of polymers are different from those in the bulk polymer [41, 43]. Polymers in this region can undertake a high level of external stress that would otherwise lead to a mechanical failure in the bulk. For the filler-polymer system, both the interface and interphase regions play roles in maximizing the reinforcing efficiency. Once the dimension of the particles decreases to the nanometer scale and the fraction of interfacial areas reaches a sufficient high level, the interfacial properties become dominating the overall composite behaviors.

In this work, we seek to reveal the mechanism of the reinforcement in polymer nanocomposites using a simplified polymer-particle configuration. Polystyrene (PS) films supported on a carbon-based substrate, highly ordered pyrolytic graphite (HOPG), were chosen to mimic the structural element of PS-CNTs/CNFs nanocomposites. Glass transition temperature ($T_g$) of both the bulk composite and thin films were measured and interpreted as a reflector of the strength of the polymer-particle interactions. A
quantitative agreement was observed between the filler-induced change of bulk $T_g$ in composites and the substrate-induced change of $T_g$ profile in thin films.

5.1.2 Evidence of strong interactions between PS and CNTs/CNFs

Earlier studies on PS-carbon based nanoparticles (CBN) nanocomposites revealed strong interactions between the particles and the polymer. Even in the absence of covalent bonding, macroscopic improvements in the mechanical properties, such as tensile, compressive, flexural, have been widely reported for different carbon-based nanoparticles [68, 296]. Direct transmission electron microscopy (TEM) and scanning electron microscopy (SEM) observations of polymer wrapping around the particles further indicate a strong physical adhesion between PS and CBN at the nanometer scale [41, 42, 297, 298]. Through both experiments and simulation, the origin of the intrinsic interactions between CBN and PS has been explored. Liao and Wong carried out molecule mechanics simulation and elasticity calculations to quantify the interfacial characteristics that critically control the performance of PS-CNT composite [44, 67]. Their results indicated that both electrostatic and van der Waals forces play roles in determining these interfacial properties. In addition, a high interfacial shear stress (186 MPa for PS-CNT) was estimated for nano-filled composites. Using first principle calculations, Zhao et al. studied the non-covalent interactions between carbon nanotubes and aromatic organic compounds (including benzene) [299]. The $\pi$-electron coupling between the nanotube and the organic molecules was investigated using the electron density analysis. They claimed that the delocalization and hybridization of $\pi$ conduction
electrons result in the strong interactions. This is a common feature of all aromatic molecules absorbed onto the nanotubes. Through fourier transfer infrared (FTIR) and Raman spectra, Baskaran et al. [41, 292, 296, 300] identified non-covalent and nonspecific CH-π intermolecular interactions between multiwall carbon nanotube (MWCNT) and PS. Their result rationalizes the general coating or wrapping phenomena observed in various polymer-CNT systems. A recent work by Zhang et al. [298] indicated that the nonbonding interactions between MWCNT and PS would be further enhanced during the melt mixing process. The mechanism for this enhancement can be attributed to the grafting PS chains on the MWCNT surface. During melt mixing, thermal degradation of polymers (such as PS) readily occurs, forming many radicals [301]. At the same time, CNTs with fullerene structures serve as a good radical acceptor [302, 303]. Even for other solids such as graphite or carbon black, the mechanochemical dispersion mixing will induce the rupture of chemical bonding, facilitating the formation of free radicals or ion-type reactive sites on the fresh surface. Chemical grafting, consequently, can occur between macromolecular radicals and reactive particles [304].

5.1.3 Thin film \(T_g\) and its correlation to polymer nanocomposites

\(T_g\) of supported polymer thin films has been studied for more than a decade. In this nano-confined configuration, the mobility of polymer chain can be substantially affected by the enthalpic and entropic effects arising from the polymer-air and polymer-substrate interfaces. While the former generally enhances the chain mobility by increasing the free volume, the latter will reduce the chain mobility via the substrate

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confinement. The overall $T_g$ of the film is thus determined by these two competing contributions. It has been reported that the $T_g$ of the thin film will be suppressed to a lower value compared to its bulk counterpart $T_g^b$ for systems with weak polymer-substrate interactions (e.g. $PS/SiO_x/Si$) [237]. However, the existence of strong interactions (hydrogen bonding) between the polymer and the substrate for systems such as $Poly(methyl methacrylate)(PMMA)/SiO_x/Si$ [240], $poly(vinylyl pyridine)(PVP)/SiO_x/Si$ [237] and $tetramethyl bisphenol polycarbonate(TMPC)/SiO_x/Si$ [256, 257] will lead to an increase in $T_g$.

The similarity between the polymer thin film $T_g$ response and the thermomechanical responses of polymer nanocomposites was first addressed by Bansal et al [241]. In their work, a direct analogy was drawn between the film thickness in thin films and the interparticle spacing in nanocomposites. It was demonstrated that $T_g$ of polymer nanocomposites with respect to the interparticle spacing falls on the same curve as corresponding thin film data for both non-wetting (e.g. $PS/SiO_2$) and wetting (e.g. $PS/PS$-grafted-$SiO_2$) polymer-particle systems. It was further concluded that the generic “two-layer” model [242] used to describe the reduction in $T_g$ for polymer thin films is not sufficient to capture the intrinsic physics. Instead, the distribution of altered polymer chain mobility, and hence the distribution of $T_g$ around the nanoparticles, needs to be considered [243].

In this study, we examined the $T_g$ distribution rather than a single integrated $T_g$ for PS films supported on highly ordered pyrolytic graphite (HOPG). Atomic force microscopy (AFM) with nanoparticles as the probe, generally referred as the nanoparticle embedding technique [253, 254, 263-265], was used to determine the $T_g$ profile within
the thin film. Spherical nanoparticles were placed on top of a supported polymer thin film. The embedding kinetics of the nanoparticles can be determined by measuring the apparent height of the nanoparticles as a function of the annealing time. Using this method, a mobile surface region \((T_g < T_g^b)\) of a supported PS film on the order of 3-4 nm thick was identified [253, 264]. Furthermore, by applying a series of annealing temperatures, the near-surface distribution of \(T_g\) in a polymer thin film was determined [265]. By revealing the \(T_g\) gradient of a supported polymer thin film, the level of the substrate confinement (strong or weak) and its impact on the polymer chain mobility can be identified.

Although a high \(T_g\) is favorable for the ultimate applications of polymer composites, it poses practical difficulties for polymer processing. In light of this, it is highly desirable to achieve an in-situ depression of \(T_g\) during material processing. The sorption of gas penetrates (e.g. CO\(_2\)) can generally reduce the \(T_g\) of glassy polymers. Moreover, the difference between the normal \(T_g\) and \(T_g\) in the presence of CO\(_2\) is much larger in thin films than in the bulk for a given value of CO\(_2\) activity [270]. In the present work, we demonstrated the CO\(_2\)-induced \(T_g\) depression in the PS/HOPG thin film system. In the presence of CO\(_2\), the confining effect from the substrate (restricted chain mobility) can be counteracted or even surpassed due to the CO\(_2\) plasticization effect. As a result, \(T_g\) profiles were shifted to a lower level for films with all thicknesses investigated in this study.
5.2 Experimental

5.2.1 Materials

Solutions of PS ($M_n=214,000$, $M_w/M_n = 1.03$, $T_g = 100.2^\circ C$, Polymer Source Inc.) were prepared by dissolving the polymer in toluene. HOPG was supplied by Mikromasch. An unconjugated gold colloid with a particle size of 20.4±8% nm was supplied by Ted Pella, Inc. The colloid was diluted 50-fold with 18 MΩ•cm water. Carbon dioxide (99.99%) was supplied by Praxair. CNFs (PR-24-PS) were donated by Applied Science Inc. PS used for the synthesis of bulk composites was from Arkema (formerly Atofina) with a number average molecular weight of 86,000.

The size of gold nanoparticles was calibrated using TEM. One drop of the gold colloid was placed onto a carbon-coated copper grid. Images were taken after evaporation of the water. Figure 5.1a shows the TEM micrograph of the gold nanoparticles. Image analysis (Scion Image) indicates an average particle size of 19.8 nm with a standard deviation of 1.6 nm (Figure 5.1b). This result agrees well with the specification from the manufacturer.

The surface roughness of fresh-cleaved HOPG was examined using AFM (NanoScope IIIa, Digital Instruments). As shown in Figure 5.2, the bare HOPG is extremely smooth with a surface roughness (RMS) of 0.188 nm.
5.2.2 Bulk $T_g$ measurement

PS-CNFs nanocomposites with a particle loading up to 10wt% were synthesized using a DACA micro-compounder. The blending temperature, blending time, and screw rotation speed were set at 200°C, 5 minutes, and 250 rpm, respectively. Bulk $T_g$s of the neat PS and PS-CNFs nanocomposites were measured using a differential scanning calorimeter (DSC, TA 2920). A typical samples size was approximately 10 mg. To eliminate the thermal history, samples were initially annealed at 180 °C for 30 min under nitrogen protection. Subsequently, samples were cooled down to 30°C and held at that temperature for 10 min. The second scanning was conducted at a heating rate of 10 °C/min and the DSC trace was recorded. The value of $T_g$ was taken at the onset point of the DSC trace.

5.2.3 Preparation of supported PS Films

The PS-toluene solution was filtered through an inorganic membrane with a pore size of 0.1 µm (Whatman, Anotop 25). The PS film was prepared by spin-coating the PS-toluene solution onto a fresh-cleaved HOPG substrate. The film thickness was controlled by the solution concentration and the spinning speed. Films were dried at ambient temperature for 48 hours and then annealed at 120°C for 12 hours under vacuum. This step is required to remove the solvent and to relieve any residual stresses built into the film during spin coating. After annealing, films were cooled to room temperature under vacuum.
A drop of diluted gold colloid was placed on top of each PS film and then allowed to dry at room temperature. Samples were annealed at pre-specified temperatures under vacuum or in the CO\textsubscript{2} environment. After reaching an equilibrium state, the system was quenched with ice and then taken out for the AFM measurement.

### 5.2.4 Nanoparticle embedding technique

The logic of using a nanoparticle-embedding technique to determine the surface \( T_g \) is illustrated in Figure 5.3. The diameter of these spherical nanoparticles is denoted as \( 2R \). After the system reaches the equilibrium state at a temperature \( T \), the embedding depth of the particles (distance beneath the polymer-air interface, i.e. the free surface), \( \delta \), can be calculated from the particle size and the apparent height of nanoparticle (\( h_a \)). It is equal to \( 2R-h_a \). The annealing temperature \( T \) is thus defined as the \( T_g \) of the polymer layer at the depth \( \delta \).

Topological imaging of the embedded nanoparticles on the PS film was obtained via AFM in the tapping mode. The scanning size was kept as 5 \( \mu \text{m} \times 5 \mu \text{m} \). Since the out-of-plan features are insensitive to the shape of the AFM tip, the distance between the top of the nanoparticle and the PS surface (\( h_a \)) can be accurately determined \cite{254}. For each sample, over 200 nanoparticles were examined to provide statistically meaningful results.
5.3 Results

5.3.1 Bulk $T_g$ of PS-CNFs nanocomposites

Bulk $T_g$s of PS-CNFs nanocomposites were measured using DSC and the results are presented in Figure 5.4 (squares). Within our investigation range, $T_g$ shows a positive dependence on the fiber content. Compared to the neat PS, PS containing 10wt% CNFs shows a 6.5°C increase in $T_g$. Similar observations have been reported in earlier studies investigating PS-single wall carbon nanotubes (SWCNTs) [266] and PS-multiwall carbon nanotubes (MWCNTs) [305]. The literature data for these two systems were reproduced in Figure 5.4, marked as triangles and circles, respectively. In all these three systems (PS-CNPs, PS-SWCNTs and PS-MWCNTs), there is no chemical bondings between the PS and the nanoparticles, thus the observed $T_g$ enhancement may serve as an evidence of positive physical interactions at the PS-carbon interface.

5.3.2 $T_g$ profile of PS films supported on HOPG

The PS used for the thin film preparation has a radius of gyration ($R_g$) of 13.0 nm. We prepared PS films with three thicknesses: 13.1 nm (thin), 53.7 nm (medium), and 2 um (thick).

Since all the data collected from the AFM images were based on the height difference, it is necessary to obtain a bare polymer film with a nano-scaled surface roughness. Using the AFM measurement, we verified that all PS films prepared in this
work have a roughness (RMS) of less than 1 nm, as demonstrated in Figure 5.5. Once nanoparticles have been placed on top of these films, a series of annealing temperatures were applied to investigate the dependence of the embedding thickness on temperature. Figure 5.6 shows two representative AFM images. We use the results of thick (2 μm) PS films as an example to demonstrate the method to interpret the AFM data. Four annealing temperatures ranging from 60°C to 90°C were studied. Here we just illustrate two images associated with 60°C and 90°C. As shown in this figure, the apparent height $h_a$ of the gold particles decreased as the temperature increased. $h_a$ is 19.5 nm at 60°C (Fig. 5.6a) and 7.0 nm at 90°C (Fig. 5.6b). Considering that the average particle diameter is 19.8 nm, the $h_a$ listed above can be translated into an embedding thickness of 0.3 nm and 12.8 nm, respectively. Since both the gravitational force exerted on the gold particle (8×10^{-19} N) and the non-linear viscoelastic effect of PS can be neglected [254], this embedding phenomenon results mainly from the existence of mobile PS layers, within which the $T_g$ is lower than the annealing temperature. The lower end of the embedded particle is the lower bound of this mobile region, at which the equivalent $T_g$ equals to the annealing temperature. Based on this analysis, $T_g$ of the polymer layer located at a depth of 0.3 nm below the free surface is 60°C for the thick (2 μm) PS film. By comparison, the $T_g$ of the polymer layer located at a depth of 12.8 nm below the free surface is 90°C. The completely mobile region ($T_g < T_g^b$) has a thickness of larger than 12.8 nm. This result agrees well with the literature report that any confinement effect from the substrate can be neglected and the length scale associated with the enhanced mobility due to the free
surface ($\lambda_{fs}$) is approximately 10 nm [238]. However, with this film thickness, any confinement from the substrate cannot be reflected.

To reveal the level of the substrate confinement, PS films with reduced thickness were studied as well. The same embedding test and data analysis were performed for films with medium (53.7 nm) and thin (13.1 nm) thicknesses. Near-surface $T_g$ profiles for all three sets of films are plotted in Figure 5.7. Here the x-axis (depth) is defined as the distance from the free surface. For all these films, $T_g$ near the free surface was lower than $T_g^b$ and gradually increased as approaching the substrate (increasing depth). With a decreased film thickness, the $T_g$ profile shifted to a high level and the mobile region became smaller. Furthermore, a higher $T_g$ compared to its bulk counterpart is observed for films with medium and thin thicknesses. For films of 53.7 nm, $T_g$ of the PS layer 8.9 nm underneath the free surface was 100°C. Once the depth increased to 13.5 nm, $T_g$ became 10°C higher than $T_g^b$. For films of 13.1 nm, the increase of $T_g$ compared to $T_g^b$ was more pronounced. A 30°C increase in $T_g$ was observed for a PS layer 5.7 nm underneath the free surface. These results clearly suggest a strong polymer chain confinement due to the substrate. In other words, the interactions between the PS and the HOPG substrate significantly impede the segmental movement of the polymer chains, negating the enhanced mobility from the free surface and ultimately results in a higher $T_g$.

To relate this thin film study to the macroscopic reinforcement in nanocomposites, the above results are interpreted in a different way. We define another length scale, $\lambda_{sub}$, which is associated with the reduced chain mobility due to the substrate confinement. For systems with weak polymer-substrate interactions, $\lambda_{sub}$ is 2~3 nm,
indicating that any influence from the substrate can just penetrate into the film 2~3 nm above the substrate [250]. However, we observed a much wider range in this study, over which the confinement from the substrate exists. For example, for the 13.1 nm film, the $T_g$ profile crosses the bulk value at a depth of 3 nm, $T_g$ is higher than $T_g^b$ beyond that point. Even in the presence of the free surface effect, an influenced region can still extend up to 10 nm away from the substrate.

**5.3.3 Subtract the impact on the $T_g$ profile from the free surface**

Unlike polymer thin films, polymer-air free surfaces do not exist in real polymer composites. Thus, it is desirable to obtain a $T_g$ profile of polymers in the absence of the free surface. Here we analyze the experimentally measured $T_g$ profiles for thin films to subtract the free surface effect.

For a film with a limited thickness, the deviation of the measured $T_g$ from its bulk counterpart originates from two aspects: the free-surface induced $T_g$ depression and the substrate induced $T_g$ enhancement (assume strong polymer-substrate interactions such as PS/HOPG in this study). Thus, the measured $T_g$ at any location within the film reflects an addition of these two effects. As shown in Figure 5.8, the ultimate $T_g$ profile (Fig. 5.8b, curve c) results from a superimposition of the $T_g$ gradient resulted from the free surface (Fig. 5.8a, curve a) and the substrate (Fig. 5.8a, curve b). The levels of the impacts from these two aspects are associated with the distance from the two interfaces, the polymer-air interface and the polymer-substrate interface, respectively. We seek to describe the experimental data using an empirical relation (Eqn. 5.1)
\[ T_g = T_{g0} \left[ 1 - \left( \frac{A_1}{h} \right)^{\alpha_1} + \left( \frac{A_2}{H - h} \right)^{\alpha_2} \right] \]  \hspace{1cm} (5.1)

Here \( T_{g0} \) is the bulk \( T_g \) of PS (100.2 °C for this study), \( H \) is the film thickness, and \( h \) is the distance from the free surface. \( A_1 \) and \( \alpha_1 \) are fitting parameters associated with the free surface effect, and \( A_2 \) and \( \alpha_2 \) are fitting parameters associated with the substrate effect. The difference between the observed thin film \( T_g \) and the bulk \( T_g \) arises from the addition of two parts, \( \Delta T_{g1} \) (free surface) and \( \Delta T_{g2} \) (substrate), as shown in Equations 5.2 and 5.3.

\[ \Delta T_{g1} = T_{g0} \left[ -\left( \frac{A_1}{h} \right)^{\alpha_1} \right] \]  \hspace{1cm} (5.2)

\[ \Delta T_{g2} = T_{g0} \left[ \left( \frac{A_2}{H - h} \right)^{\alpha_2} \right] \]  \hspace{1cm} (5.3)

For a film with a thickness of 2 \( \mu \)m, it is assumed the measured \( T_g \) profile only reflects the impact from the free surface. Thus, we fit the \( T_g \) profile (denoted as \( T_{g,\text{free}} \)) using Equation 5.4.

\[ T_{g,\text{free}} = T_{g0} \left[ 1 - \left( \frac{A_1}{h} \right)^{\alpha_1} \right] \]  \hspace{1cm} (5.4)

The best fit (shown in Fig. 5.9, brown line) is satisfied when \( A_1 \) is 0.015 nm and \( \alpha_1 \) is 0.28.

Combining the above two parameters with the experimental \( T_g \) data for both 13.1 nm (Fig. 5.10, red solid circles) and 53.7 nm (Fig. 5.10, blue solid circles) PS films,
$A_2$ and $\alpha_2$ can be subsequently determined as 5.34 nm and 2.35, respectively. The fitted curves are displayed in Figure 5.10 as red (13.1 nm) and blue (53.7 nm) lines.

Subtracting the free surface effect, the $T_g$ profile of a supported PS film that only reflects the substrate effect (denoted as $T_{g,\text{sub}}$) is described in Equation 5.5.

$$T_{g,\text{sub}} = T_{g,0} \left[ 1 + \left( \frac{A_2}{H - h} \right)^{\alpha_2} \right]$$  \hfill (5.5)

Applying this equation, the corrected $T_g$ ($T_{g,\text{sub}}$) profiles eliminating the free surface effect are shown as dash lines in Figure 5.11. For these two $T_{g,\text{sub}}$ profiles, the x-axis refers to distance from the top of the PS film. The $T_{g,\text{sub}}$ values at four locations corresponding to the previous four distances are evaluated and marked as the open circles (13.1 nm) and triangles (53.7 nm) in this figure. Regardless of the film thickness, the $T_{g,\text{sub}}$ profiles shift to a higher level as compared to the original ones. For the 13.1 nm film, the original $T_g$ profile (red solid line) surpasses the bulk value (100.2°C) at distance of 3 nm. However, once subtracted the free surface influence, the entire $T_g$ profile (red dash line) is located above the bulk value. For the 53.7 nm film, the change of $T_{g,\text{sub}}$ is unobvious within the distance scale in Figure 5.11. However, if we investigate the $T_{g,\text{sub}}$ profile for the entire film thickness, a distance dependency becomes more evident. As shown in Figure 5.12, $T_{g,\text{sub}}$ increases dramatically as approaching the substrate, with a turning point at approximately 45 nm. A slight increase in $T_{g,\text{sub}}$ within the regions of 10 nm below the top surface is demonstrated in the inset of this figure.
In Figure 5.13, the correlation between the $T_{g,sub}$ and the distance from the substrate (denoted as $\delta$) is revealed. Substituting $(H-h)$ in Equation 5.5 with $\delta$, Equation 5.6 can be applied to generate the fitted curve in Figure 5.13.

$$T_{g,sub} = T_{g0} \left[ 1 + \left( \frac{A_2}{\delta} \right)^\alpha_2 \right]$$

(5.6)

$T_{g,sub}$ shows higher values near the substrate and levels off to the bulk $T_g$ (100.2 °C, black dash line) at distance of approximately 40 nm. In other words, the impact on $T_g$ from the substrate can penetrate into a location of 40 nm away. The evaluated data points for both 13.1 and 53.7 nm films are displayed as open circles in the same figure. Due to the elimination of the free surface influences, all these data fall onto the same curve.

In real composites, the polymer chains are confined between fillers. A simplified one-dimension configuration for real composites is a three-layer structure (i.e. a polymer film sandwiched between two solid surfaces). In this configuration, the film thickness can be directly related to the interparticle spacing in nanocomposites.

Considering two identical substrates, the $T_g$ profile of a sandwiched polymer film is expected to be symmetric along the centerline. A typical $T_g$ profile for a solid/polymer/solid system with strong positive interfacial interactions is illustrated in Figure 5.14a. There are three zones with different $T_g$ behaviors: (1) two confined zones (length scale: $\lambda_c$) within which the local $T_g$ decreases from the highest value at the interface to the bulk $T_g(T_g^b)$, (2) one bulk zone (length scale: $\lambda_b$) within which the $T_g$ of the polymers remains the same as $T_g^b$. By increasing the interaction strength and/or decreasing the film thickness (particle interspacing in composites), a $T_g$ profile with a
reduced bulk zone (Fig. 5.14b, curves 1&2) or even without the bulk zone (Fig. 5.14c, curve 3) can be obtained. A similar concept can be applied to interpret the $T_g$ behavior of polymer nanocomposites. If the confined region dominates the entire composite domain, an overall $T_g$ enhancement in the presence of nanoparticles will be observed.

We further attempt to predict the $T_g$ profile of a PS film sandwiched between two HOPG substrates using Equation 5.7

$$T_{g,2\text{sub}} = T_g^0 + \left[ \frac{A_1}{\delta_1} + \frac{A_2}{\delta_2} \right]^\alpha$$

(5.7)

Here, $\delta_1$ is the distance from substrate 1 and $\delta_2$ is the distance from substrate 2. The summation of $\delta_1$ and $\delta_2$ equals to the film thickness, $H$.

However, the current model led to an over-estimation of the $T_g$ values at the extreme regions (either $\delta_1 \to 0$ or $\delta_2 \to 0$). Thus, neither the $T_g$ values near substrate or the $T_g$ profile of a sandwiched polymer film can be predicted. Sophisticated mathematical method dealing with the extreme problems needs to be applied in the future research.

5.3.4 CO$_2$-induced $T_g$ depression

CO$_2$-induced $T_g$ depression is a well-known phenomenon for bulk polymers. The absorption of CO$_2$ is believed to increase the free volume within the polymer matrix, thus enhancing the polymer chain mobility. As a result, a decreased $T_g$ is generally observed. In this study, we focused on the impact of CO$_2$ on the $T_g$ profile in the PS/HOPG systems.
In particular, we expect to observe lowered $T_g$ profiles for medium and thin PS films under a CO$_2$ environment.

The $T_g$ profiles of films annealed under a CO$_2$ pressure of 200 psi are illustrated as open symbols in Figure 5.7. For both thick and medium films, the absorption of CO$_2$ led to significant $T_g$ suppression. The lower bound of the mobile region extended further towards the substrate. Most importantly, all the $T_g$s within the investigated depth were lower than $T_g^b$ for the medium-thickness film (53.7 nm), indicating that the confinement from the HOPG substrate was mitigated by the plasticization effect of CO$_2$. These results further suggest that for systems with strong polymer-particle interactions (such as PS-HOPG), while a higher local $T_g(>T_g^b)$ near the solid surface can be expected, a lower in-situ $T_g(<T_g^b)$ can also be obtained with the assistance of CO$_2$. Therefore, with a proper material and processing design, we can achieve both the improved ultimate properties and easier processing of polymer nanocomposites.

It is worthwhile to point out that detrimental dewetting occurred for PS thin films (13.1 nm) annealed under a CO$_2$ environment. Stabilizing of polymer thin films against dewetting is a technological important and complicated topic. Various strategies have been applied to inhibit the thin film dewetting such as grafting of polymer layers onto the solid surface [306], metal complexation and sulfonation of the polymer [307], and the introduction of the nanoparticles into the polymer thin films [268, 269, 308, 309]. Although the theory of dewetting has not been well understood, it is well accepted that a combination of the polymer-solid interaction (equilibrium) and the changes in $T_g$ (kinetic effects) are both involved. The dewetting kinetics can be expedited by either the thermal-enhanced or the gas penetrate-enhanced polymer chain mobility. Although we cannot
obtain any $T_g$ result for a PS film with this thickness, the observed dewetting phenomenon still provided an indirect support of the CO$_2$-enhanced polymer chain mobility.

5.5 Discussion

In this work, we used the atomic force microscope to study the embedding of gold nanoparticles into the surface region of a PS thin film. However, the validity of this method and the way to interpret the experimental data are still under debate. While it is agreed that the gravitational and buoyant forces are negligible in a PS-gold nanosphere system [254, 310], there is disagreement on the contribution of the non-linear viscoelasticity of the PS on the observed embedding behaviors. Hutcheson et al. [310, 311] used a viscoelastic contact mechanics model to calculate the embedding profile of gold particles on a PS film. The quantitative agreement between their modeled data and other group’s experimental data [310] suggested that the embedding of the nanoparticle may merely result from the surface interactions between the PS and the gold, without involving a depression in the $T_g$ or a liquid-like layer at the PS surface. On the contrary, Sharp et al.’s [312] claimed that the non-linear viscoelastic effects of the PS will not play a significant role in determining the embedding behavior of the gold particles. Once the nanoparticles have embedded by more than 0.2 nm, the stress exerted on the gold particles is smaller than the yield stress of the PS. Therefore, it is unlikely that the embedding (3-4 nm) is simply caused by the surface interactions. In addition, the higher viscosity of a gold-filled polymer compared to that of the neat polymer and the slowed
polymer chain motion near the gold surfaces [313] indicated that it was unlikely that the
gold surface leads to the plasticization of a PS film.

Another issue of using this method arises from the under-estimation of the
embedding thickness when the net force exerted on the gold particle becomes negative
(opposite to the embedding direction). Earlier studies [254] showed that the net force
takes the functional form as described in Equation 5.8

\[ F_{\text{net}} = 2\pi R\gamma \sin \phi \sin(\theta + \phi) \]  

(5.8)

where \( R \) is the radius of the gold particles, \( \gamma \) is the PS surface tension, \( \theta \) is the
equilibrium PS-gold sphere contact angle, and \( \phi \) is the angle between the centre of the
sphere and the PS/gold contact line. A schematic force balance is shown in Figure 5.15.

With a fixed equilibrium contact angle \( \theta \), \( F_{\text{net}} \) first increases as the embedding thickness
increases (\( \phi \) increases). After reaching a maximum at \( \phi + \theta = 90^\circ \), it gradually decreases
to zero (\( \phi + \theta = 180^\circ \)) and then becomes negative. Provided that \( F_{\text{net}} \) is positive, the
particle will continue embedding until it reaches the glassy region. In that case, we can
define the \( T_g \) at the lower bound of the embedding as the applied annealing temperature.
However, if \( F_{\text{net}} \) becomes zero, the embedding will terminate regardless of reaching the
glassy region or not. In other words, the particles may keep suspended within a rubbery
region in the PS film. Thus, the measured embedding thickness will be under-estimated.

The above considerations cast doubt on the validity of one data point obtained in
this study: an embedding thickness 13.49 nm for the 53.7 nm PS film annealed at 110°C.
The equilibrium contact angle of PS on the 20 nm gold sphere is 59° (at 105°C) [254].
Assuming this value doesn’t change significantly from 105°C to 110°C, \( F_{\text{net}} \) becomes zero when \( \phi \) is 119° (180°-59°) as illustrated in Figure 5.16. Applying the relation of \( \cos \phi = \frac{h - R}{R} \), the corresponding maximum embedding thickness is 14.9 nm. The approximation between this value and the above measured thicknesses (13.49 nm) make this data questionable and need further confirmation.

Considering the complexity of the viscoelastic responses of a PS film in this nano-scale spherical geometry, care needs to be taken when interpreting the data. At any annealing temperature, the embedding behavior of gold particles will be influenced by the force balance at this temperature, which further depends on the temperature-dependent viscoelasticity of the polymer (e.g. creep compliance, Poisson’s ratio). Therefore, the local \( T_g \) defined in this study can only represents an apparent value (\( T_g^{'} \)). Nevertheless, we expect that our measured \( T_g \) profiles can still reflect the trend of the intrinsic change in the interface-induced polymer chain mobility. Future study will be addressed on the calculation of the true \( T_g \) profile of a supported polymer (PS) film using molecular dynamic simulation.

### 5.4 Conclusions

In this study, a polymer thin film/substrate configuration was used to study the impact of substrate confinement on the polymer property. Specifically, \( T_g \) (the apparent \( T_g \)) was measured and interpreted as the changed polymer mobility near the substrate. PS films supported on a graphite surface were chosen as a model system to resemble the
structural element of PS-CBN nanocomposites. Using films with different thicknesses, 
the competition between the free surface-induced $T_g$ depression and the substrate-induced
$T_g$ increase was observed. For films with a sufficiently thin thickness, a higher $T_g$
compared to its bulk counterpart was observed. Strong interactions between PS and
carbon-based solids were successfully identified using the thin film study.

Subtracted the free surface impact, the $T_g$ profiles of a supported PS film shifted to 
a higher level regardless of the of original film thickness. A direct correlation between
the $T_g$ value and the distance from the substrate was revealed in this study. It suggested
that the impact on the polymer $T_g$ from the substrate will diminish at location of 40 nm
away from the solid surface for the PS/HOPG system.

While a higher $T_g$ benefits the ultimate applications of polymer composites, a
lower $T_g$ is highly desirable for polymer processing. CO$_2$-induced $T_g$ depression was
observed for this PS/HOPG thin film system. In the presence of CO$_2$, the $T_g$ profiles were
suppressed to a lower level ($<T_g^b$) even at a low pressure, while the mobile surface region
broadened towards the substrate.

The focus of this chapter is the PS-CBN nanocomposites and thus most effort was
addressed on the thin film $T_g$ of a PS film supported on HOPG. To relate this thin film $T_g$
study to the reinforcement in the PS-nanoclay nanocomposites, the $T_g$ profile of a PS film
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<tr>
<td>Mean roughness (Ra)</td>
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Figure 5.6: $T_g$ of PS-CNFs/CNTs nanocomposites
Figure 5.7: $T_g$ profiles of PS films supported on HOPG. The dash line represents $T_g^b$. Circles, diamonds, and squares represent the $T_g$ profiles of thin, medium and thick films, respectively. Solid symbols: films annealed under vacuum, open symbols: films annealed under CO$_2$ (200 psi)
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Figure 5.16: Dependence of the reduced net force on $\phi$ as the gold sphere embeds into the film ($\theta = 59^\circ$)
6.1 Introduction

Polymer-clay nanocomposites have been widely investigated because they exhibit superior properties when compared to neat polymers or microparticle-filled composites. Earlier studies have shown that incorporation of nanoclay into the polymer domain leads to enhanced mechanical properties, higher heat deflection temperature, reduced gas permeability, and improved dimensional stability [1, 2, 24, 124, 136, 138, 140, 314, 315]. Recently, considerable efforts have also been devoted to another related research area: polymer-clay nanocomposite foams [26, 27, 30, 219-221, 277]. The presence of nanoclay may enhance cell nucleation, provide foam reinforcement, lower gas escape rate, and result in char formation when foam is under fire. This makes polymer-clay nanocomposite foam an excellent choice for applications requiring high strength, lightweight, and better fire resistance. With an annual consumption of 1.9 billion pounds
in 2001, polystyrene (PS) foams (both extruded and expanded) occupy the second largest market share in the US foam portfolio [316]. In this study, expandable PS (EPS) containing nanoclay is our focus.

Morphology control and property enhancement for both nanocomposites and nanocomposite foams depend on good dispersion of nanoclay in the polymer domain. In order to improve the compatibility between the hydrophilic nanoclay and the hydrophobic polymers, the clay surface is usually modified by organic surfactants, often quaternary ammonium compounds. The presence of these low molecular weight hydrocarbons, however, results in negative impacts on the material’s fire resistance performance, as evidenced in such industrial fire evaluations as the Oxygen Index Test and the Flame Spread Test. Therefore, it is highly desirable to develop a method to incorporate nanoclay into polymers with uniform clay dispersion, but without the use of fire hazardous surfactants.

EPS are generally prepared via a modified route for styrene suspension polymerization [230]. The route starts with the reaction of styrene monomer dispersed in the water medium, containing suitable suspension agents and organic blowing agent such as pentane. To avoid the use of flammable blowing agents, the concept of WEPS was proposed. Since the solubility of water in PS is very low, the abovementioned route to produce EPS is not feasible for WEPS. Two alternative methods have been reported to date.

The first method to produce WEPS was developed by Crevecoeur et al. [231]. In that method, water was emulsified in a pre-polymerized styrene/PS mixture in the presence of emulsifiers. Subsequently, the inverse emulsion was suspended in a water
medium containing suspension agents. Polymerization was continued until a complete conversion. The final products are spherical PS beads with entrapped micrometer-scaled water droplets. The second method was developed by Pallay et al. [235]. Instead of using emulsifiers, starch was used as a water-swellable phase. Pre-polymerization of the styrene/starch mixture was carried out to a conversion of approximately 30%. The viscous reaction phase was subsequently transferred to a water medium containing suitable suspension agents. In the last step, polymerization was completed and water was directly absorbed into the starch inclusions.

To address the demand for surfactant free expandable PS-clay nanocomposites, the first method (developed by Crevecoeur) was modified and applied in this work. Instead of emulsifying pure water, a mixture of water and a raw clay, sodium montmorillonite (Na⁺-MMT), was emulsified in the organic styrene/PS phase. Due to the hydrophilicity of the raw clay surface, a uniform and stable dispersion of clay in water is achieved. Therefore, using water as the carrier, nanoclay can be incorporated into the polymer system.

The selection of emulsifier for w/o inverse emulsion is of essential importance to achieve a stable reaction system and uniform water dispersion. Two criteria are used in this study: 1) the hydrophilic-lipophilic balance (HLB) value falls in the range of 3~6 [317, 318] and 2) no reactive group (unsaturated carbon-carbon double bond) in the surfactant molecules. It has been demonstrated that sodium bis(2-ethylhexyl)sulfosuccinate (AOT) is highly efficient to stabilize the water-in-styrene inverse emulsion [231]. According to HMIS (Hazardous Materials Identification System) and NFPA (National Fire Protection
Association) ratings, AOT is non-flammable. These aspects match well with our desire to produce fire-hazard free nanocomposites. Thus, we chose AOT for our system.

6.2 Experimental

6.2.1 Materials

The styrene monomer was purchased from Aldrich and used without distillation. The initiators, 2,2’-azobis (isobutyronitrile) (AIBN) and dibenzoyl peroxide (BPO) with a halflife ($t_{1/2}$) at 90°C of 25 min and 145 min, respectively, were purchased from Aldrich. AOT was supplied by Fluka and used as received. The suspension stabilizers, hydroxyethyl (HEC, $M_w = 250,000$) and polyvinyl alcohol (PVA) were supplied by Aldrich and used as received. Nanoclay (Na⁺-MMT) was donated by Southern Clay Products.

6.2.2 Preparation of water/clay mixture

Nanoclay (5wt% based on emulsified water) was dispersed in emulsified water with the aid of sonication. The sonication time was controlled until the formation of uniform and stable water/clay mixture. Subsequently, 0.5wt% NaCl (based on emulsified water) was added into the mixture. The salt would facilitate the emulsification of water droplets in the later stage of the process [231]. The concentration and the addition sequence of NaCl need to be taken with care. Details are discussed later.
6.2.3 Preparation of inverse emulsion

AIBN (0.25wt% based on styrene), BPO (0.25wt% based on styrene) and AOT (10wt% based on emulsified water) were dissolved in styrene. The mixture was heated to 90°C under the protection of nitrogen and a stirring rate of 350 rpm. The reaction was performed in the bulk phase to a conversion of approximately 60% (determined by offline differential scanning calorimetry (DSC), at which point, the viscosity of the continuous phase is sufficient high to fixate the water droplets. At a higher stirring rate (700 rpm), water/NaCl or water/NaCl/clay was added into the styrene/PS mixture to form a water-in-oil-in-water (w/o/w) reaction medium. Polymerization was continued for another 10 min. A schematic of the emulsion system is shown in Figure 6.1a.

6.2.4 Suspension polymerization

The viscous inverse emulsion (100g) was suspended in water (suspension water, 300 g), with the aid of suspension stabilizers HEC (0.6wt% based on suspension water) and PVA (0.005wt% based on suspension water). Polymerization was continued under the nitrogen atmosphere. The stirring rate and temperature were kept at 350 rpm and 90°C, respectively. Finally, the suspension was cooled to room temperature and the spherical products were recovered by filtration. A schematic of the suspension system is shown in Figure 6.1b.
6.2.5 Expansion of compacted beads

The recovered beads were expanded via two different heating media: hot air and oil bath. The heating temperature was set at 135°C in both cases. After exposure to the hot medium for 1 minute, the expanded beads were quenched by either compressed cold air (the hot air method) or an ice-water mixture (the oil bath method).

6.2.6 Batch foaming of WEPS/WEPSCN using carbon dioxide (CO₂)

(a) a two-step batch foaming process: WEPS/WEPSCN beads were saturated with CO₂ at 25°C under a pressure of 13.8 MPa. After reaching an equilibrium state, the pressure was quickly released and the beads were taken out of the high-pressure vessel. Subsequently, the beads were immersed into a pre-heated oil bath (135°C). The total transition time between the end of the pressure release and heating in the oil bath was approximately 1 min. Foaming took place due to the expansion of water droplets and the bubble growth of CO₂ in the PS matrix. The foaming time was set at 1 minute, after which, the foamed samples were quenched with a mixture of ice and water. (b) a one-step batch foaming process: WEPS/WEPSCN were saturated with CO₂ in a high pressure vessel. The system was allowed to equilibrate at 120°C and 13.8 MPa for 24 hours. At these conditions, CO₂ is in the supercritical state. After equilibrium, the pressure was rapidly released, leading to simultaneous bubble nucleation and growth. The foam structure was fixed by immediate cooling with a mixture of ice and water.
6.2.7 Continuous foaming of WEPS/WEPSCN using CO$_2$

A two-stage single screw extruder (HAAKE Rhomex 252P) was utilized at a screw rotation speed of 10 rpm. A static mixer (Omega, FMX8441S) was attached to the end of the extruder to provide extra distributive mixing. A capillary die with a nozzle of 0.5mm (diameter) and 10mm (length) was custom-made to generate a rapid and high pressure drop during the extrusion. CO$_2$ was compressed to approximately 1000 psi at 4°C. The CO$_2$ pressure and volumetric flow rate was controlled precisely by the pump controller. Upon injected into the barrel, CO$_2$ was mixed with the polymer melt by the screw rotation. A homogeneous solution of WEPS melt and CO$_2$ was formed when the mixture flowed through the static mixer. Due to a rapid pressure drop through the narrow capillary die, nucleation occurred and the foamed extrudate flowed out of the nozzle and expanded until vitrified in the ambient air.

6.2.8 Characterization

The morphology of both compact (before expansion) and expanded beads was examined by a scanning electron microscope (SEM, HITATCHI S-4300). Samples were freeze-fractured in liquid nitrogen, and the fracture surface was sputter-coated with gold. The ultimate water content in the beads was determined by thermogravimetric analysis (TGA, Perkin-Elmer TGA 7) operated under a nitrogen atmosphere. The sample was heated from room temperature to 140°C at 10°C/min followed by an isothermal heating period of 60 min. The location of nanoclay in expanded beads was examined by a
transmission electron microscopy (TEM, Phillip CM12), performed using an accelerating voltage of 80 kV. The nanocomposite foams were sectioned into ultra-thin slices (<100 nm) at room temperature using a microtome and then mounted on 200 mesh copper grids. The heat conductivity of foams was measured using a heat flow meter (FOX 200, LaserComp). The temperature difference of the upper and lower plates was set at 40°C.

6.3 Results and discussion

The application of EPS is determined by the diameter of the beads and the content of the blowing agent [319]. Foams expanded from large EPS beads (diameter of 800 to 2000 µm) are generally used for insulation and building panels, while foams expanded from small beads (300 to 800 µm) are generally used for thin-walled containers. The ultimate bead size is mainly determined during suspension polymerization. It can be controlled by a number of means including mixing speed and the type and content of stabilizers. For WEPS and WEPSCN synthesized in this study, the bead size fell in the range of the large group. The incorporation of 0.5wt% nanoclay didn’t exhibit any strong impact on the bead size and size distribution.

In order to achieve foam products with desirable structure and properties, it is important to acquire a uniform distribution of water droplets in the water-in-styrene emulsion. AOT combined with a low concentration of NaCl was reported to be an effective emulsifying system for the preparation of WEPS [231, 234]. The basic concept is that the existence of an electrolyte will decrease the repulsion force between ionic head groups of AOT, thus permitting a closer and more compact arrangement of AOT around
the water drop. In Crevecoeur’s study [231-233], 0.9wt% (based on emulsified water) NaCl was used to improve the stability of the emulsion. In Snijders’s study [234], an optimal concentration of NaCl (0.1wt%) was reported to achieve a homogenous and stable dispersion of water droplets. However, the existence of an electrolyte (e.g. NaCl) can also interfere with the flocculation of clay in water. Thus, the electrolyte should be selected with care [320]. While a low concentration of electrolyte can prevent particle aggregation due to the osmotic repulsion, a high concatenation will lead to the compression of double layers at both the planer and edge surfaces. As the concentration of electrolyte increases to the critical flocculation concentration (CFC), all three modes (face-to-face, face-to-edge, edge-to-edge) of clay aggregation will occur. For Na⁺-MMT used in this study, the highest NaCl concentration we can use while still maintaining a stable water-clay suspension was 0.5wt%. We found that the time to add NaCl is another factor that affects the stability of the water-clay suspension. If we added both nanoclay and NaCl into the emulsified water simultaneously (sequence I), the exfoliation of clay became more difficult. However, once the clay has been exfoliated in water, the addition of NaCl (sequence II) merely reduced the stability of this suspension.

The distribution of water droplets in compact beads is illustration in Figure 6.2. With a constant AOT to water (emulsified) ratio (1:10) and the same NaCl concentration, a similar domain size and size distribution of water droplets were obtained for both WEPS and WEPSCN. Most water droplets exhibited a size of 5 µm, with several larger droplets of approximately 10 µm. The ultimate clay content in beads was measured using TGA, and the result is illustrated in Figure 6.3. With a designed water content of 10wt%, the final incorporated water in PS beads was 7.6wt%, while that in PS containing 0.5wt%
nanoclay was 9.2wt%. This difference can be attributed to the hydrophillicity of nanoclay, which holds more water into the polymer during synthesis. This water-phillic property of nanoclay also facilitates the fixation of water within the beads during storage. We measured the water content of beads three months after synthesis. For WEPSCN (the original water content of 9.2wt%), the residual water was 2.5wt%, while for WEPS (the original water content of 7.6wt%), the residual water was only 0.2wt%.

Two heating media were used to expand compacted beads in this study: hot air and an oil bath. The expansion temperature was 135°C. The foam structures of WEPS and WEPSCN are illustrated in Figure 6.4. Comparing foams expanded by these two methods, it is obvious that a higher expansion ratio could be achieved by hot air (Figs. 6.4a and 4c) than by oil bath (Figs. 6.4b and 4d), as summarized in Table 6.1. For WEPS, the average expansion ratio was 2.2 if using the air gun, as opposed to 2.95 using the oil bath. For WEPSCN, the compacted beads expanded nearly 90% more in oil bath (6.1) than by the hot air (3.2). The different performance of these two media can be rationalized as follows. During the expansion, a substantial faction of water would diffuse out of the beads rather than participating in expansion [233]. If the surrounding medium is hot air, this diffusion would be expedited. However, if the surrounding medium is hot oil, more water can be trapped within the beads and is utilized as the blowing agent. Therefore, a higher expansion ratio can be obtained.

The effect of nanoclay on the expansion, as well as the final foam structures, is illustrated in Figure 6.4. Regardless of the heating method applied, compacted beads with nanoclay exhibited much higher expansion ratios, as indicated in Table 6.1. If heated via hot air, the incorporation of 0.5wt% nanoclay led to an increase of the expansion ratio
from 2.2 to 3.2. If heated via the oil bath, the increase of the expansion ratio due to the presence of nanoclay was more than 100% (2.95 vs. 6.1). While higher water contents may lead to a higher expansion ratio, the enhanced barrier property resulting from the nanoclay may also play an important role. Before expansion, nanoclay was dispersed in the water droplets. During expansion, the clay particles were pushed against the cell wall and formed a barrier layer around the cell, as illustrated in Figure 6.5. The existence of the clay barrier layer can obviously reduce the loss of water and increase the expansion ratio. Another interesting observation is that a bi-modal foam morphology (Figs. 6.4c and 4d) was achieved with the addition of nanoclay. Since water is the only blowing agent, this observation suggests a heterogeneous nucleation due to the presence of nanoclay. A reasonable postulation is that those big bubbles were originated from existing water droplets, while those surrounding small bubbles were formed from the nucleation of water vapor on the clay surface.

In an attempt to produce foams with higher expansion ratio and lower density, CO$_2$ was applied as the co-blowing agent to foam WEPS/WEPSCN beads. In the presence of two blowing agents, water and CO$_2$, foams with a bi-modal structure (also for beads without clay) are expected. To avoid the water loss during the CO$_2$ saturation, a two-step batch foaming process was applied, as described in experimental. The water content was measured immediately before the CO$_2$ co-foaming. WEPS and WEPSCN beads contained 7.7wt% and 8.6wt% H$_2$O, respectively.

Our postulation on the cell morphology was verified. As illustrated in Figure 6.6, foams exhibited an obvious bi-modal cell structure even without nanoclay. A similar cell structure forms for WEPSCN beads. However, instead of possessing a higher expansion
ratio, foams prepared using this method showed thick (~ 0.5 mm) un-foamed skin region, and consequently, a very high bulk density (0.6~0.7 g/cm³). Various foaming temperatures and foaming times were tried in this study. However, all the foams exhibited similar structures and densities. We believe that the technical barrier for achieving an efficient expansion originates from the lack of a suitable foaming temperature for both water and CO₂. For PS synthesized in this study (\(M_w = 237\) kg/mol), a temperature lower than 120°C appears to be insufficient to generate a high water vapor pressure to expand the viscous PS matrix. On the other hand, a high temperature suitable for water expansion (e.g. 135°C in this study) may lead to fast escape of CO₂ out of the beads and ultimately a thick surface skin.

The feasibility of using CO₂ extrusion foaming to expand the WEPS beads was tested using a single screw extruder. Considering the high pressure generated within the extruder and the confinement of the polymer melt by the screw and the extruder barrel, water is expected to be held within the polymer phase during extrusion. This can be verified by the existence of a bi-modal foam structure and a higher expansion ratio compared to the foam generated from the neat PS. Figure 6.7a shows the morphology of an extruded PS foam made from the neat PS. In this case, CO₂ was the only blowing agent. Figure 6.7b shows the morphology of an extruded PS foam made from WEPS beads containing 7.7wt% water. In this case, both water and CO₂ served as the dual blowing agent. Comparing these two samples, it is obvious that the existence of water enhances the expansion of PS. The WEPS foam (Fig. 6.7b) shows much larger cell sizes and a lower cell density than the PS foam (Fig. 6.7 a) under the same foaming conditions, leading to a much lower bulk density (0.17g/cm³ vs. 0.5 g/cm³, foam b vs. foam a).
Furthermore, the WEPS foam possesses a bi-modal cell morphology due to the existence of two blowing agents, which is demonstrated more clearly in a lower magnification image (Fig. 6.7c). The extrusion of WEPS beads results in a similar foam structure as the oil bath-based batch foaming of the same material. In addition, no obvious skin region was observed using this foaming route. It is worthwhile to point out that the current extruder was equipped with a capillary die, which is designed to generate a high-pressure drop and facilitate the formation of microcellular suture. In order to produce low-density foams for insulation applications, an extruder with a wide slit die is desirable. Nevertheless, this work demonstrated the feasibility to produce extruded PS foams with a lower bulk density using WEPS beads.

All the foams discussed above were expanded using freshly prepared beads, which retained most of the water as synthesized. Since the water loss during storage is inevitable, it is desirable to investigate alternative methods to expand beads with dried beads. WEPS and WEPSCN beads were intentionally dried before foaming. Since styrene/PS has approximately the same density as water, the volume percentage of the cavities in the beads is similar as the weight percentage of water inside the beads. For comparison, we synthesized PS and PS-clay nanocomposite using a similar polymerization procedure, but without entrapping any water droplets, in other words, no cavities. CO₂ foaming via a one-step batch process (introduced in experimental) was applied here. Four samples were foamed under the same foaming conditions: (a) PS (w/o water cavity) (b) dried WEPS (w/ 7.6vol% water cavity), (c) PS (w/0.5wt% clay, w/o water cavity), (d) dried WEPSCN (w/ 0.5wt% clay, w/ 9.2vol% water cavity). The resultant foam morphologies are show in Figure 6.8. By comparing Figures 6.8a and 8b,
it is clear that the existence of water cavities helps enlarge the cell size and reduce the foam density. With the inclusion of 7.6vol% cavity, the foam density can be reduced from 0.7 g/cc to 0.035g/cc.

The addition of nanoclay in the foam formulation has a mixed effect on the foam morphology and insulation performance. While the barrier resistance and flame retardancy of nanoclay benefits the insulation applications, its nucleation effect often leads to foams with unfavorable morphology (i.e. cell size too small) and density (bulk density too high). However, the nucleation effect of nanoclay can be balanced by the cell enlargement effect caused by the presence of water cavity in WEPSCN. Figure 6.8c illustrates PS foams produced from beads containing 0.5wt% nanoclay. Comparing to neat PS foam (Fig. 6.8a), the nucleation effect of nanoclay significantly reduced the cell size and increased the cell density. Using the same foaming set-up and conditions, this sample could not be expanded to fill the entire mold in batch foaming, leading to a corrugated foam surface. The foam density is 0.181 g/cc, which is too high for insulation applications. However, the presence of 9.2vol% water cavity (sample d, Fig. 6.8d) enlarged the cell size in a similar manner as in the neat PS case. While more cells were created compared to the neat PS foam (Fig. 6.8a vs. 8d), the bubble size was remained around 100 µm. The bulk foam density is 0.032 g/cc, which is even lower than its non-clay counterpart (sample b, Fig. 6.8b).

The thermal conductivity of the abovementioned foams was measured at 40°C and the results are shown in Figure 6.9. An extruded PS foam with a bulk density of 0.098g/cc shows a thermal conductivity of 32.61 mW/m/K. Batch foaming of WEPSCN produced foams with a very low density (0.032g/cc) and correspondingly, very a low
thermal conductivity (20.18 mW/m/K). For all the samples investigated in this work, the conductivity data shows a monotonic dependence on the bulk density. At the ultra-low density range, the conductivity is very sensitive to the bulk density. Our data indicate that a lower bulk density provides a better thermal insulation value. To achieve ultra-low-density foams (<0.05g/cc) in traditional manufacturing processes, an expensive vacuum system is often required. Thus, our materials and approach may eliminate the need of this multi-million dollar capital investment in the industrial foam line. Furthermore, using this method, traditional industrial blowing agents such as CFC (chloro fluoro carbon) and HCFC (hydro chloro fluoro carbon) can be completely replaced with inexpensive and environmentally benign CO$_2$.

6.4 Conclusion

Water expandable PS-clay nanocomposites were successfully synthesized via the suspension polymerization of water-in-oil inverse emulsion. Using water as the carrier, surfactant-free nanoclay can be incorporated into the polymer beads. The addition of nanoclay can trap more water in the beads during synthesis and reduce the water loss during storage.

CO$_2$ foaming of compacted beads offers an alternative method to utilize in-stock WEPS/WEPSCN products with reduced water content. The presence of water cavities significantly enlarges the cell size and leads to foam with ultra-low density and lower thermal conductivity. More significantly, PS-clay nanocomposite foams with
considerable large cell size (~ 100 µm) and low foam density (< 0.05g/cc) can be produced using this approach.

Future research will be addressed on the following two aspects. First, new formulations (e.g. emulsifiers, suspension agents) will be developed to stabilize the reaction system with higher clay content. The present work demonstrated the feasibility to produce WEPSCN. However, in order to achieve noticeable advantages from nanoclays, such as mechanical enhancement and the char formation, higher clay content is required. Second, CO₂ co-foaming of “wet” WEPS/WEPSCN beads containing water inside will be developed. The key issue is to avoid the water loss during the foaming process. The success of this work may lead to foams with even lower foam density and better insulation performance. With the thinning of the cell wall, it is also possible to achieve an open cell structure. Therefore, by controlling the water content, foams with a wide range of densities and applications (insulation, filtration, sound dampening, etc) can be produced.
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<th>WEPCN W/ 0.5% clay 9.2wt% H₂O</th>
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<td>2.2</td>
<td>3.2</td>
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<tr>
<td>Oil Bath (135°C, 1min)</td>
<td>2.95</td>
<td>6.1</td>
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Table 6.1: Expansion ratios of WEPS and WEPCN (Designed water content 10wt%)
Figure 6.1: Schematic representation of the preparation process of WEPS-CN (a) emulsification of water/clay mixture in pre-polymerized styrene/PS (b) suspension polymerization of styrene/PS droplets containing emulsified water/clay droplets.
Figure 6.2: Dispersion of water droplets in compacted beads, scale bar 200 µm (a) WEPS, designed H₂O 10wt%, actual H₂O 7.6wt% (b) WEPSCN (0.5wt% nanoclay), designed H₂O 10wt%, actual H₂O 9.2wt%
Figure 6.3: Water content in beads determined using TGA
Figure 6.4: SEM micrographs of foam morphology of expanded WEPS or WEPSCN beads at 135°C for 1min, all beads have designed H₂O 10wt%, scale bar 200 µm (a) WEPS (7.6wt% H₂O), air gun (b) WEPS (7.6wt% H₂O), oil bath (c) WEPSCN (0.5wt% nanoclay, 9.2wt% H₂O), air gun (d) WEPSCN (0.5wt% nanoclay, 9.2wt% H₂O), oil bath
Figure 6.5: TEM micrograph showing nanoclay around the cell wall
(a) nanoclay forming layers (dark lines) around the cell wall (b) layered-structure of nanoclay under high magnification
Figure 6.6: SEM micrograph of PS foam, WEPS (7.6wt% H$_2$O), CO$_2$ co-blowing, saturation pressure 13.8 MPa, saturation temperature 25°C, foaming temperature 135 °C (oil bath), foaming time 1 minute, scale bar 100 µm
Figure 6.7: SEM micrographs of foams prepared using a single screw extruder, CO$_2$ is the blowing agent (a) foam made from neat PS, scale bar 200 µm, $\rho = 0.50$ g/cc (b) foam made from WEPS beads, water is the co-blowing agent, scale bar 200 µm, $\rho = 0.17$ g/cc (c) lower magnification of foam (b), scale bar 100 µm
Figure 6.8: SEM micrographs of PS foams, batch foaming, CO₂, 13.8 MPa, 120 °C, scale bar 500 µm (a) PS (no cavity), ρ = 0.07 g/cc (b) WEPS (7.6wt% cavity), ρ = 0.035 g/cc (c) PS/0.5wt% nanoclay (no cavity), ρ = 0.181 g/cc (d) WEPSCN (0.5wt% nanoclay, 9.2wt% cavity), ρ = 0.032 g/cc
Figure 6.9: Thermal conductivity of foams (40 °C)
CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

With the soaring cost of energy, it is essential to develop new lightweight materials that can provide high structural strength for automotive and aerospace applications, and better thermal insulation performance in housing and construction industries. Although traditional polymeric foams are widely used, their applications are limited by poor mechanical strength, surface quality, thermal stability and fire retardancy. Furthermore, traditional blowing agents (CFC and HCFC, etc.) cause ozone depletion and will be banned by 2010 according to the Montreal Protocol. To address these weaknesses, novel nanocomposite foams based on the combination of functional nanoparticles and Supercritical CO$_2$ (ScCO$_2$) foaming technology were developed in this work. By designing the foaming formulations and controlling the foaming processes, nanocomposite foams with different structures and properties were developed for various applications. While the medium-density (~ 0.5 g/cm$^3$) nanocomposite foams with a similar mechanical strength as solid polymers are for structural applications, the ultra
low-density (< 0.1 g/cm³) foams with better fire resistance and reduced thermal conductivity are for heat insulation applications.

The structural foams were prepared based on polystyrene (PS) and carbon nanofibers (CNFs). ScCO₂ was applied as the blowing agent. The impact of CNFs on the foam morphologies was explored. It was found that the presence of CNFs greatly facilitated the formation of microcellular structure, which is characterized by the cell sizes less than 10 µm and the cell densities larger than 10⁹ cells/cm³. For example, with the addition of only 1wt% CNFs, the cell size decreased from 20 (neat PS foam) to 2.6 µm, while the cell density increased by more than two orders of magnitude (from 8.23x10⁷ to 2.78x10¹⁰ cells/cm³). The monotonic increase of the cell density with an increasing fiber content indicated the predominance of heterogeneous nucleation in the presence of CNFs. Compared to nanoclay, CNFs exhibited substantially higher nucleation efficiency, which was semi-quantitatively explained using the classical nucleation theory. The uniform fiber distribution and the favorable surface and geometrical characteristics of CNFs make them ideal nucleating agents in the PS-CO₂ foaming process.

The properties of PS-CNPs foams, particularly the short-term mechanical responses such as modulus and strength, were investigated. The inclusion of CNFs dramatically improved the mechanical strengths of PS foams. Compared to neat PS foams, 1wt% CNFs leads to an increase of 27% in the tensile modulus and 45% in the compressive modulus. At a fiber loading of 5wt%, the mechanical properties of PS foams reach a level comparative to (tensile modulus) or even higher (compressive modulus and strength) than the PS solid. Meanwhile, a 50% weight reduction (compared to PS solid)
is obtained. These results demonstrate the concept of using nanoparticles (CNFs in this work) to compensate for the strength loss in cellular plastics, thus achieving both lightweight and high strength. Nanoparticle-enabled microcellular structure, plus the nano-scaled reinforcement on the polymer phase, makes nanocomposite foams highly desirable as a new generation of lightweight structural materials.

The mechanism of nano-scaled reinforcement in carbon-based nanoparticle (CBN)-PS systems was studied. As well established, the reinforcing efficiency largely depends on the interactions between the particle and the polymer for particle-reinforced composites. These interactions, in turn, can be reflected on the mobility of the polymer chains near the interface. Once the dimension of the particles decreases to the nanometer scale, these interfacial properties become more pronounced. In this study, the interactions between CBN and PS and its influence on the PS chain mobility were examined using the supported thin film glass transition temperature ($T_g$) measurement. A model system, a PS film coated on HOPG (highly ordered pyrolytic graphite), was selected. The nanoparticle-embedding technique was applied to measure the $T_g$ profile within the PS film. A strong interaction between PS and HOPG was reflected by a substantial increase in the measured $T_g$ value. This substrate-induced $T_g$ enhancement became more pronounced as the film thickness decreased. For films with a thickness of 13.1 nm, a $30^\circ$C increase in $T_g$ above its bulk value ($100^\circ$C) was observed. With the knowledge that $T_g$ is a critical parameter determining the mechanical strength for polymers (e.g. Young’s modulus changes 3 orders around $T_g$), these observations provide some fundamental insight to the reinforcement in CBN-PS systems. While a higher $T_g$ benefits the ultimate applications of polymer composites, a lower $T_g$ is highly desirable for polymer
processing. The CO$_2$-induced $T_g$ depression was also demonstrated using this PS/HOPG thin film configuration.

Aiming at another application, thermal insulation, ultra-low density polymer nanocomposite foams with improved fire resistance and reduced thermal conductivity were developed. PS and nanoclay were used as the base materials. Surfactant-free water expandable polystyrene-clay nanocomposite (WEPSCN) was successfully synthesized via the suspension polymerization of the water-in-styrene inverse emulsion. This method provides a new technique to incorporate nanoclay into the polymer phase without the aid of fire hazardous surfactants. The presence of nanoclay demonstrated several advantages including, but not limited to a higher expansion ratio of the compacted beads, and a reduced water loss during storage. Expanding WEPSCN beads using CO$_2$ as the co-blowing agent led to ultra-low density PS-nanoclay foams (0.032g/cm$^3$) with a reduced thermal conductivity. There foams also show a desirable low density and bi-modal cell structure for insulation. Conventional foaming techniques, such as extrusion foaming, face tremendous technical challenges to obtain foams with the similar morphologies and properties.

7.2 Recommendations

7.2.1 PS-CNFS nanocomposite foams

7.2.1.1 Impact of fiber lengths on the nucleation and reinforcing effect

In this study, twin-screw extrusion was used to prepare PS-CNFS nanocomposites at a large scale. While an aggressive shear mixing can effectively disentangle the CNFs
bundles, it can also break the fibers in length and significantly reduce their aspect ratios. For polymer composites, it is well known that the aspect ratio of particles can affect their reinforcing efficiency on mechanical properties. For CNFs-filled polymers, other transport properties (electrical, thermal) also depend on the retained fiber length. Our experimental results further suggest that the length of CNFs would affect their nucleation efficiency as well. Compared to CNFs with longer fiber lengths (several dozens of microns), the ground CNFs exhibited deteriorated nucleation efficiency. Therefore, it is highly desirable to develop a method, which is capable of dispersing CNFs uniformly in the polymer matrix while maintaining the high fiber aspect ratio. Also, it is desirable to generate a serial of PS-CNFs composites with different fiber lengths and correlate the fiber length with its nucleation and reinforcing performances.

Compared to melt blending, in-situ polymerization and solution blending are more promising to achieve a balance between the level of fiber mixing and the fiber breakage. However, those two methods will induce higher costs and greater environmental impacts for large-scale production. Thus melt blending is still recommended. Another advantage of using melt blending is the ability to easily adapt to the extrusion foaming or injection foaming processes. An optimization of the screw design, therefore, needs to be studied in the future.

For a twin-screw extruder, the selection of different screw elements and their combination offer a lot of design freedom for various applications. Typically, there are three kinds of screw elements (Figure 7.1) with different mixing styles. The combining elements mainly work as the distributive units, enabling the homogenization of a secondary phase (e.g. CNFs) within the matrix (e.g. PS). The kneading elements mainly
work as the dispersive mixing units, breaking down the secondary phase into smaller pieces. The conveying elements, in general, provide very limited mixing power.

Two strategies are proposed here to control the fiber length and uniformity in the polymer matrix. First, if we need to generate CNFs-polymer nanocomposites with different fiber lengths, controlling the amount of kneading elements will be more effective. For example, we can change the amount of kneading blocks with the same operation conditions and other screw configurations. Composites containing CNFs with different lengths can thus be obtained. In addition, different mixing speed and/or temperature may also lead to different fiber lengths under a fixed screw design (with kneading blocks). Keeping some of the kneading elements is essentially important to comply with the extrusion foaming process, since these units also act as the gas sealing elements.

Secondly, if we need to prepare CNFs-filled nanocomposites with the maximum fiber lengths, a screw design without any kneading elements is preferred. However, a pre-dispersion of CNFs into the polymer is required since the combining elements can barely break up the fiber agglomerates into individual fibers. Either in-situ polymerization or solution blending can be used to generate a master batch of CNFs-polymer composites containing relatively long fibers. These composites, subsequently, can be diluted into different filler concentrations using the twin-screw extruder. More combining elements may need to be added to improve the uniformity of the secondary phase, pre-formed CNFs-polymer composites, into the neat polymer.
In the present study, the mechanical enhancement of CNFs on PS foams was demonstrated. However, attention was focused on the moderate-term mechanical responses, such as modulus and strength. Further, all the testing were conducted at ambient temperature. The following three aspects are recommended as future work to obtain a comprehensive characterization of PS-CNFs foams.

First, long-term (fatigue and creep) and short-term (impact resistance) responses of PS-CNFs foams need to be investigated. It was demonstrated that the nucleation effect of CNFs would facilitate the formation of microcellular structures. We also know that the rationale for developing microcellular foams stems from the hypothesis that those microbubbles can act as the toughening elements. Therefore, it is highly possible to observe more mechanical improvements such as toughness and fatigue life with the addition of CNFs into the foam formulation. The completion of this work will explore more applications of PS-CNFs foams.

Second, it is suggested to investigate the mechanical properties of PS-CNFs foams under elevated temperatures. Our previous study showed that the incorporation of nanoparticles can improve the dimensional stability of polymers at elevated temperatures [123]. In addition, the mechanical properties of nanocomposites, tensile modulus, tensile strength and elongation in particular, exhibit more striking improvements over neat polymers once heated above $T_g$ [321, 322]. The completion of this study will provide guidance for material selection for high-temperature structural applications.
Finally, it is highly worthwhile to examine the electrical properties of PS-CNFs foams. One remarkable advantage of integrating CNFs into a polymer system is to improve the electrical conductivity of the plastics. It has been reported that the electrical conductivity of polymer matrix can be increased by several orders of magnitude in the presence of CNFs [112]. Composites with Electron Static Discharge (ESD) or Electron Magnetic Interference (EMI) shielding can thus be fabricated. With the knowledge that the electrical percolation occurs due to the tunneling or hopping of electrons between the conductive elements (e.g. individual nanotube or fiber), it is possible to obtain similar electrical properties in cellular CNFs-filled polymers as well. However, either a higher percolation level or fiber alignment may be required to obtain significant electrical improvements with the inclusion of bubbles. The completion of this work will promote the development of novel polymeric foams covering a broad spectrum of potential applications from high performance materials (high modulus/strength) to electronic materials (electrostatic discharge or electromagnetic interference).

### 7.2.2 Water expandable PS-nanoclay nanocomposites

In this work, the feasibility of synthesizing surfactant-free WEPSCN via suspension polymerization of inverse water/styrene emulsion was demonstrated. Continuing efforts on this project are recommended as follows.
7.2.2.1 Increase of the clay content

The clay content in the final product is determined by both the initial clay content in the emulsified water and the water content in the inverse emulsion. Although an improved thermal insulation property (lower thermal conductivity) was observed with the existence of only 0.5wt% of nanoclay, a higher clay content is desirable to achieve other advantages such as mechanical enhancement and the char formation. The technical barrier to increase the clay content arises from three factors. First, it is difficult to increase the nanoclay content in the emulsified water. Once it reaches to 10wt%, the suspension of nanoclay/water forms a thick paste, making it difficult to add more nanoclay into the styrene/polystyrene mixture. Secondly, the water content in the inverse emulsion highly depends on the selection of emulsifiers. AOT was used in this study, however, a more efficient emulsifier or emulsifier combination should be designed in order to achieve higher water content. Thirdly, it was found that the existence of nanoclay would interfere with the stability of the oil-in-water suspension. Compared to the synthesis of WEPS, the incorporation of nanoclay requires a higher dosage of suspension agents. A clear understanding of this interference is also recommended in future study.

7.2.2.2 Selection of expansion method and optimization the expansion conditions

In this study, both an oil bath and hot air were applied as the heating medium to expand WEPSCN beads. Although the use of an oil bath may reduce the diffusion of water out of the beads, the ultimate expansion ratio is still lower compared to the
theoretical value, indicating a significant loss of water during the expansion. While the increase of the clay content will improve this situation, the selection of a more efficient heating medium is also important. Several alternatives are recommended for future studies (i.e. hot steam, electromagnetic field [235]).

The expansion behavior also depends on the heating conditions, such as the heating temperature and the heating time [233]. At low temperatures, the vapor pressure of water is not sufficient to expand the viscous polymer domain, leading to the loss of water via diffusion. At high temperatures, the failure of cell wall will also lead to the escape of water through the beads. Due to these two opposing effects, there must exist an optimum temperature corresponding to a maximum expansion ratio. The expansion profile and the expansion window thus require further investigation.

### 7.2.3 Nanocomposite foams based on other polymers and nanoparticles

The work presented here mainly focused on the PS foams. However, the market of polymeric foams is highly fragmented. Other foams, such as polyolefin (polypropylene (PP), polyethylene (PE)), polyvinyl chloride (PVC), and polyurethane (PU) foams, also occupy high market shares. Thus, it is highly recommended to extend our current experience on polymer nanocomposite foams to those systems as well. While we expect to achieve similar advantages (e.g. enhanced nucleation, improved mechanical strengths, barrier properties, etc) for other polymer nanocomposite foams, technical challenges may exist for each particular system. For example, PP foam has become more attractive due to the unique properties of the polymer matrix, such as the high stiffness, flexural modulus,
impact resistance, chemical and abrasion resistance. However, the weak melt strength and weak extensibility greatly limit the production of PP foams. While nanoclay can increase the extensional viscosity and improve the foamability of PP, it may affect the crystal formation and thus the bubble growth as well [219, 220]. How these two processes (bubble nucleation and crystal nucleation) interfere with each other what are the ultimate impacts from the nanoparticles remain unclear.

In the present work, only two kinds of nanoparticles were addressed. There are many other types of nanoparticles and their potential to be used in producing nanocomposite foams remains unknown. Each nanoparticle may have its own advantages depending on applications. For geometrically anisotropic nanoparticles, such as carbon nanotubes, the orientation of particles in the polymer domain may also influence the foam morphologies and properties. Thus it is possible to explore more advantages of nanocomposite foams by tuning the particle dispersion and orientation.

### 7.2.4 Model system for the investigation of polymer-particle-gas interactions

Once nanoparticles are applied as the foaming nucleants, their nucleation efficiencies greatly depend on the interactions among the polymer, particle and gas. As indicated in Chapter 3, the contact angle (θ) formed between three interface tensions (γ_{sl}, γ_{sv}, γ_{lv}) significantly changes the energy barrier for nucleation. Thus, it is highly desirable to develop a method to directly investigate the polymer-gas-particle interactions and its dependence on the gas pressure and temperature.
In order to mimic nanoparticles, model solid surfaces need to be constructed. Generally, carbon-based surface such as HOPG can be used to resemble CNTs/CNFs and Silicon-based surface can be used to resemble nanoclay. Relating to our previous work on polymer nanocomposite foams, bare HOPG and silicon surface grafted with polymer (e.g. PS, PMMA) are two most relevant substrates. Our studies used an organoclay, MHABS, as the foaming nucleant. The clay surface is covered with acrylic groups, which can further react with monomers containing unsaturated carbon-carbon double bond. It is suggested that the immobilization of a more CO$_2$-phillic polymer (e.g. PMMA) on the clay surface leads to a substantial improvement in the nucleation efficiency. In order to achieve a better understanding of the interactions between the polymer, CO$_2$ and the solid surface, fundamental studies such as the contact angle measurement are needed. Zeng [46] has demonstrated the feasibility to prepare a surface on which the polymer is immobilized. In his method, a negatively charged silicon wafer was directly immersed into a reactive surfactant, MHAB. However, it is difficult to form a uniform surface coverage using this method. Two approaches are recommended to improve the uniformity of the surfactant coverage. First, a monolayer of amphiphilic molecules can be formed on a solid surface using the Langmuir-Blodgett film technique. The selection of the subphase and the solvent will determine the quality and stability of the film in this case. Another approach is the self-assembly monolayer (SAM) technique. SAM has been widely used to graft polymers on solids. To mimic the MHABS surface, assemblers possessing reactive carbon-carbon double bond (e.g. 3-trimethoxysilyl propyl methacrylate) need to be selected. Once a stable SAM is formed, the subsequent polymerization with monomer (e.g. styrene, MMA) will generate a solid surface similar
to nanoclay covered with PS or PMMA. The obtained model surface can be applied for various fundamental studies. For example, it offers the possibility to directly measure the contact angle of polymers formed on such surfaces under a CO$_2$ environment. With the aid of advanced characterization methods such as light scattering, bubble nucleation on these solid surfaces may be observed.

7.2.5 Thin film $T_g$ evaluation and reinforcement in polymer nanocomposites

In this study, polymer thin film $T_g$ measurement was applied to investigate the polymer chain dynamics in the presence of certain polymer-substrate interactions. In particular, a model system, the PS film supported on HOPG, was used to correlate with the macroscopic reinforcement in CBN-PS nanocomposites. The observed $T_g$ increase in the PS/HOPG configuration indicated a strong interaction between the PS and the carbon substrate. This further provides rationale for maximizing the reinforcing efficiency by tuning the polymer-substrate interactions.

In order to relate this work to the design of polymer nanocomposites, the nanoparticle-embedding technique used in this work needs to be improved and integrated with the molecular dynamics simulation.

First, the measurement depth of $T_g$ using a nanoparticle embedding technique is limited by the size of gold spheres. For instance, if we use gold spheres with a diameter of 20 nm, the furthest location within observation is 20 nm below the polymer-air free surface. However, the most interested area is located near the substrate from the nanoparticle-reinforcing point of view. Therefore, gold particles with a larger size (up to
100 nm) are required to probe further into the film towards the substrate. One challenge is: once the particle size is increased, will gravitational force and hence the buoyancy of the particles play an important role? Also, will gold spheres be responsible for plasticizing the surface of PS films with an increased weight? All these issues need to be addressed in the future work.

Second, the nanoparticle embedding technique requires a top polymer-air free surface, which does not exist in real polymer nanocomposites. A polymer thin film sandwiched between to solid surface, instead, will be a more relevant configuration. However, the direct measurement of $T_g$ using the above-mentioned technique will not be practical in that case. Molecular dynamics simulation is thus required. Figure 7.2a shows the schematic $T_g$ profile of a polymer film between two solid surfaces. Assuming that the two solid substrates have identical physical and chemical proprieties, the $T_g$ profile will be symmetric. If the interactions between the polymer and the substrate are strong (such as PS and HOPG), the $T_g$ of films near the substrate will be higher than the bulk value, $T_g^b$ (the dash line). The length scale ($\lambda$) within which $T_g$ decreases to $T_g^b$ relies on the film thickness and the degree of polymer-substrate interactions. Either reducing the thickness (Fig. 7.2b) or increasing the interaction forces (Fig. 7.2c) will lead to a higher $T_g$ profile. If a model can be developed to predict this $T_g$ profile, the distance between two substrates required to obtain an overall $T_g$ enhancement can be theoretically determined (Fig. 7.2d). This can be further translated into the maximum distance between dispersed nanoparticles in the polymer domain, under which, an overall reinforcement can still be realized.
Figure 7.1: Screw elements: (a) kneading, (b) combing (c) conveying
Figure 7.2: Dash line: bulk polymer $T_g$, blue curve: $T_g$ profile within the film, $\lambda$: influencing length scale (a) schematic $T_g$ profile of a polymer film sandwiched between two solid surfaces with strong polymer-solid interactions (b) system with the same film thickness but stronger polymer-solid interactions than in case (a) (c) system with the same polymer-solid interactions but thinner film thickness than in case (a) (d) system in which $T_g$ at all locations are equal or higher than the bulk polymer $T_g$
APPENDIX A

CO₂ FOAMING BASED ON POLYSTYRENE/POLY(METHYL METHACRYLATE) BLEND AND NANOCLAY

A.1 Introduction

The use of polymer blends in the foam processing provides a high degree of freedom to manipulate the foaming processibility and foam properties. Through the adjustment of blend composition, the rheological properties [323-325], the absorption of the foaming agent [203, 326-329], the open/closed cell content [330, 331], and the mechanical strength [332-336] of foams can be manipulated. However, only limited researches have been focused on this area to date. For example, blends of low-density polyethylene (LDPE)/polystyrene (PS) were foamed with supercritical CO₂ (ScCO₂) by Lee et al. [337]. The effects of the CO₂ content and the die pressure were studied under one fixed blend composition. In Doroudiani et al.’s work, the foaming behavior of high-density polyethylene (HDPE)/isotactic PP (iPP) blends were studied [338]. Different blend compositions and foaming conditions were applied in his study. Suh et al. used
high impact polystyrene (HIPS), a blend of PS and rubber, to produce microcellular polymer foams [22]. Park has reported the microcellular structure of PE/iPP blend [338]. While the effects of blend composition and foaming conditions on the foam morphologies and properties have been discussed extensively, little has been done on the correlation between the phase morphology in the blend and the cell morphology in the foam.

A.2 Summary of experimental results

In our recent work, nanocomposite foams based on a PS/poly methyl methacrylate (PMMA) blend and nanoclay were synthesized. The experimental design focused attention on identifying the correlation between the blend morphology and the foam morphology. Here we only briefly summarize the experiment observation and one postulation based on it, more details can be found in the referenced paper [339]. It was found that the type of nanoclay and its location can both affect the ultimate foam morphologies.

Four blends were prepared in this study: blend 1: PS/9wt%PMMA-LMA (low molecular weight); blend 2: PS/9wt%PMMA-HMA (high molecular weight); blend 3: PS/PS/(9wt%PMMA/1%MHABS) (MHABS, organoclay covalently bonded with PMMA [46]); and blend 4: PS/1wt%20A/9wt%PMMA-LMW (20A, organoclay). For each composition, blends with different morphologies were obtained from different locations along the extruder. These blends were further batch foamed using CO₂ as the foaming agent. In each case, the foaming conditions (120°C, 13.8 MPa) were identical.
Samples were soaked in CO$_2$ for 24 hours. Based on our former experiment of the solubility measurement using a volumetric method, this time period is far beyond enough to saturate similar-sized batch foaming samples at the same saturation conditions [340]. Subsequently, the pressure was quickly released (1~2 seconds) to initiate the bubble nucleation. The final foam morphologies were fixed by cooling the foam using a mixture and ice and water. We seek to correlate the cell morphology (cell size and cell density) with the blend morphology (dispersed domain size).

A similar trend was found for the first three blends: the larger the domain size in blends, the smaller the cell size in foams. The phase morphologies and the corresponding foam morphologies of blends taken from two locations along the extruder, L/D of 14 and 36, were selected for illustration. Figure A.1 shows the blend morphology. The white dispersed phase is PMMA and the dark continuous phase is PS. Those dark particles in Figures A.1c and e are nanoclay (MHABS). Figure A.2 shows the corresponding foam morphology. Comparing Figure A.1 to A.2, it is clear that for blends with smaller PMMA domain size and larger domain density, the foam cell size is larger and the cell density is lower.

In Figure A.3, the foam morphology (cell size, cell density) versus the dispersed domain size is plotted for all four blends. Within the investigated range, an increase of the domain size leads to a decrease in the cell size and an increase in the cell density. Further, the data for the first three blends tend to merge into two uniform curves, shown as the dash lines in Figure A.3. In addition to characterizing the effect of domain size, our results suggest that the location of nanoclay also plays an important role in determining the ultimate foam morphology. When nanoclay remained in the dispersed phase (in
A.3 Discussion

Foaming based on polymer blend nanocomposites is a very complex process. Our results revealed an interesting correlation between the blend morphology and the foam morphology. However, the intrinsic physics behind these observations remains veiled. In this complicated foaming system, four processes are coupled with each other: homogeneous nucleation and bubble growth in PS, homogeneous nucleation and bubble growth in PMMA, heterogeneous nucleation at the PS/PMMA interface, and the interfacial CO$_2$ transfer between the two polymer phases. The final morphology of PS/PMMA blends is thus determined by the competition of the time scales for these processes. To make the situation more complicated, the direction of the interfacial CO$_2$ transfer depends on the consumption rate of CO$_2$ and therefore the dynamic CO$_2$ change in each phase. It is well know that due to the affinity of the carbonyl group in PMMA to
CO₂, the equilibrium concentration of CO₂ in PMMA is higher than that in PS. If the consumption of CO₂ in the PMMA phase is slower than that in the PS phase (as shown in Figure A.5a), the CO₂ concentration in PMMA will be higher within the entire time frame for foaming. Thus, a CO₂ outflow from the PMMA phase to the PS phase is expected. In this case, PMMA may serve as the gas reservoir and the foaming within the PMMA phase will be reduced or even suppressed. On the other hand, if the consumption of CO₂ in the PMMA phase is faster than that in the PS phase (as shown in Figure A.5b), there will exist a point (t'), after which the CO₂ concentration in PMMA is lower than that in PS. The direction of the CO₂ transfer will thus change at this point. Further, whether the supplement of CO₂ from one phase to the other enhances the nucleation or bubble growth highly depends on the mass transfer rate. As a result, the domain size in a blend will also affect the final foam morphology. The smaller the domain size, the larger the interfacial area, and ultimately the faster the interfacial mass transfer.

Unfortunately, with limited experimental results and the lack of theoretical supports, we cannot provide a clear explanation of the observed correlation between the domain size and the foam morphology. A hypothesis was proposed to rationalize the experimental results and will be introduced later. In that hypothesis, it is assumed that the PMMA phase serves as the gas reservoir and mainly enhance the bubble nucleation near the PS/PMMA interface. In order to verify this hypothesis, continuing efforts should be addressed on both experimental work and theoretical studies. First, it is highly desirable to theoretically estimate the change of CO₂ chemical potential in both phases after the pressure release. With this information, the existence of the interfacial gas diffusion and its direction during this transient stage can be confirmed. Secondly, it is suggested to
conduct a series of experiments using a triple-layer polymer configuration, PS/PMMA/PS. PMMA layer of varying thickness ranging from a few tens to several hundreds of microns, can be sandwiched between thick (millimeter-scaled) PS layers. This layered geometry offers a simplified but relevant resemble to the extruded PS/PMMA blends. Similar to manipulating the dispersed PMMA size in blends, the thickness of the middle PMMA layer can be controlled. Based on our current work, it is expected to observe a thickness (PMMA)-dependence of the foam morphology. Finally, in order to achieve a better understanding of this complicated process, a conceptual model is required. Classical models for bubble nucleation and growth can still be applied within each polymer phase or at the PS/PMMA interface. However, it is desirable to integrate the process of the interfacial mass transfer into these models. The relative rate of the interfacial mass transfer to that of the CO\(_2\) consumption for foaming will jointly determine the final foam morphology. The validity of the model can be evaluated using the experimental results of both extruded blend foams and layered blend foams.

**A.4 Proposed hypothesis**

Here, a simplified explanation of the observed experimental results is proposed based on the heterogeneous nucleation at the PS/PMMA interface and the dynamic diffusion of CO\(_2\) across the PS/PMMA interface. Due to the affinity of the carbonyl group in PMMA to CO\(_2\), PMMA can absorb more CO\(_2\) under the same saturation temperature and pressure compared to PS. Once the pressure is released, the system shifts away from the equilibrium state and the CO\(_2\) concentration gradient across the
PS/PMMA interface would cause the CO\textsubscript{2} diffusion between the PMMA domain and the PS domain depending on the CO\textsubscript{2} concentration and the solubility in each phase. One possible diffusion pattern is shown in Figure A.6. If the CO\textsubscript{2} saturation concentrations in both PMMA and PS phases are $S^{\text{PMMA}}(t)$ and $S^{\text{PS}}(t)$ at the time of pressure release, the CO\textsubscript{2} concentration in PMMA would be then less than $S^{\text{PMMA}}(t)$, while that in PS is higher than $S^{\text{PS}}(t)$ due to the CO\textsubscript{2} diffusion from PMMA to PS. Thus, the cell nucleation in the PMMA phase is hindered by the reduction of the super-saturation level. On the other hand, the extra CO\textsubscript{2} in the PS phase may increase or prolong the super-saturation stage, leading to an enhanced cell formation. In short, the PMMA domains may work as a CO\textsubscript{2} reservoir to support the interfacial nucleation in the PS phase.

The dependence of foam morphology on the blend size is further explained using the concept of interfacial volume. As shown in Figure A.6, an interfacial volume is defined as the area around a PMMA domain, within which the CO\textsubscript{2} concentration decreases from a high value in the PMMA phase to a low value in the PS phase. This is analogous to the boundary layers for a typical mass transfer process. At the initial stage, the system is at equilibrium and the CO\textsubscript{2} concentration profile is described as curve a. Once the pressure is released, CO\textsubscript{2} begins to diffuse from the PMMA domain to the PS domain, following two possible curves b and c. If the PMMA domain is large (case b), a sharp gradient of the CO\textsubscript{2} concentration exists within the interfacial region, thus the supersaturation of CO\textsubscript{2} remains high near the PMMA/PS interface, resulting in more cells. In a like analysis, a smaller PMMA domain size corresponds to a larger interfacial area, leading to a faster CO\textsubscript{2} diffusion. In this case, the CO\textsubscript{2} concentration within the interfacial region may drop more quickly (curve c). Consequently, the CO\textsubscript{2} concentration
near the interface, the most likely nucleation region, will be less. In summary, it is postulated that the dispersed domain size affects the nucleation by changing the CO$_2$ concentration profile in the interfacial volume.

### A.5 Dynamic observations of the foaming process

All our previous work was focused on the final foam morphology rather than the dynamic foaming process. The lack of this information greatly impedes the understanding of the complex foaming process. The visualization of the foaming process has been reported for both foam injection molding and batch foaming process. Using a rectangular mold cavity with glass windows on both sides, the dynamic behavior of the bubble growth was recorded [341]. The evolution of the bubble radius and the bubble growth rate were quantified. The batch foaming process of PP-clay nanocomposites was observed in-situ using a high-pressure autoclave equipped with two sapphire windows [223, 224]. Upon the pressure release, the foaming process was captured with by high-speed camera recording at a 0.02-minute interval. With the aid of image processing technique, the impact of the nanoclay on both bubble nucleation and growth was revealed.

In our recent work, the dynamic observation of the batch faming processes was established. As illustrated in Figure A.7, a high-pressure autoclave equipped with two sapphire windows on both sidewalls (Figure A.7) was used as the visible foaming chamber. Samples were saturated under a CO$_2$ pressure of 6.9 MPa and a temperature of 800ºC. After equilibrium, the pressure was released (6~7 seconds) and the dynamic
expansion process was recorded. Although the current set-up cannot be used to directly observe the bubble nucleation, the difference in the expansion behaviors can be quantitatively detected. We tested the feasibility of this new apparatus using two sets of samples: (1) PS and PS nanocomposites (PS-nanoclay and PS-carbon nanofibers) and (2) PS, PMMA and PS/50wt%PMMA bilayers (thickness ratio 1:1).

The first set of experiments is designed to reveal the effect of nanoparticles on the dynamic foaming process of PS. Earlier studies indicated that the addition of nanoparticles led to a reduced cell size and an increased cell density in foams. However, most of these conclusions were made based on the final foam morphology, which cannot exclude the impact from the possible cell coalescence. The present dynamic expansion experiment provides support for the existence of the nucleation effect of nanoparticles. Upon the pressure release, it was observed that the PS nanocomposites expanded much faster than the neat PS. Since the addition of nanoparticles generally increases the extensional viscosity of polymer melts and hinders the bubble growth [220], it is reasonable to infer that the observed faster expansion is more likely due to a faster nucleation rather than a faster bubble growth. In addition, PS-CNFs showed a dramatic acceleration in expansion compared to that of PS-clay at the same particle loading. This observation agrees with our earlier analysis that CNF possesses superior nucleation efficiency on the PS-CO$_2$ foaming than nanoclay (Chapter 3).

The second set of experiments is designed to reveal the interactions between PS and PMMA during the foaming process. Our earlier study shows that when a poorly mixed PS/PMMA blend was foamed, a bimodal cell distribution was obtained, as illustrated in Figure A.8a. Energy Dispersive Spectrum (EDS) analysis further indicated
that the regions with larger cells were foamed PMMA phase. However, when PS and PMMA are foamed separately under the same foaming conditions, PS exhibited larger cell sizes (Fig. A.8b) and a lower cell density compared to PMMA (Fig. A.8c).

Using this visualized foaming apparatus, the dynamic expansion of a PS/PMMA rectangular bi-layer was observed. PS/50wt%PMMA bi-layer with a thickness of 0.5mm for each side was prepared using a compression molding process. The foaming conditions were the same as described earlier (CO₂, 6.9 MPa, 800°C). Before the CO₂ saturation, the bi-layer sample stood vertically, with the left side of PMMA and the right side of PS (Fig. A.9a). After reaching an equilibrium state, the bi-layer bent towards the PMMA side (Fig A.9b) due to the CO₂ sorption in both phases. Interestingly, after the pressure was released, the bi-layer sample changed back to the vertical state during the expansion and eventually, bent towards the opposite side (PS side, Figs. A.9c-d). Due to the limitations of the current sample design and imaging accuracy, we cannot conclude which side of this bi-layer expanded faster or where the expansion started first (near the interface or in the bulk region). However, the above observation clearly indicated that in this bi-layer blend, the PMMA phase expanded largely compared to the PS phase. This dynamic observation is in consistent with our findings from the bi-model cell distribution in the extruded PS/PMMA blends (Fig. A 8a).

We are currently designing a layered blend based on PS and PMMA which can be more relevant to the well-mixed extruded blends. A triple-layer blend (PS/PMMA/PS) with the PMMA phase of a micro-scaled thickness will be a better choice. The dynamic expansion of these blends will be examined in future study. We seek to obtain more
information and confirm our hypothesis on the interplay between the mass transfer and the foaming process in polymer blends (session A.5).
Figure A.1: Blend morphologies from TEM at L/D=14: (a) PS/9%PMMA-LMW; (b) PS/9%PMMA HMW; (c) PS/(9%PMMA/1%MHABS); and at L/D=36: (d) PS/9%PMMA-LMW; (e) PS/9%PMMA-HMW; (f) PS/(9%PMMA/1%MHABS)
Figure A.2: Foam morphologies with a foaming temperature of 120°C and a saturation pressure of 13.7MPa at L/D=14: (a) PS/9%PMMA-LMW; (b) PS/9%PMMA-HMW; (c) PS/(9%PMMA/1%MHALS); and at L/D=36: (d) PS/9%PMMA-LMW; (e) PS/9%PMMA-HMW; (f) PS/(9%PMMA/1%MHALS)
Figure A.3: Cell size (solid symbols) and cell density (open symbols) of polymer blend nanocomposite foams as a function of volume average domain size of the dispersed phase: triangles are PS/9%PMMA-LMW; diamonds are PS/9%PMMA-HMW; and squares are PS/(9%PMMA/1%MHABS) (the lines are only to guide eyes). PS/1wt%20A/9wt%PMMA-LMW is shown in circle symbol, here clay is at the interface of PS/PMMA
Figure A.4: TEM micrograph of blend 4 (PS/1wt%20A/9wt%PMMA-LMW), dark lines are nanoclay at the PS/PMMA interface
Figure A.5: Schematic CO$_2$ concentration change during foaming, green arrow: the direction of CO$_2$ transfer between two phases
Figure A.6: Interfacial volume of PMMA dispersed domains in blends of PS for foam cell nucleation in which curve a shows the initial equilibrium state, and curves b and c represent transient CO$_2$ concentration after the pressure release with a slow and a fast CO$_2$ diffusion. $S^{PMMA}(t)$ and $S^{PS}(t)$ are the saturation concentrations at the time $t$ when nucleation starts.
Figure A.7: Apparatus for the visualization of a batch foaming process
Figure A.8: Foam structures at a foaming temperature of 120°C and a saturation pressure of 13.7 MPa: (a) PS/9%PMMA (LMW) (b) neat PS, cell size: 30.9 µm, cell density: $2.8 \times 10^7$ cells/cc (c) neat PMMA (LWM), cell size: 17.2 µm, cell density: $1.71 \times 10^8$ cells/cc
Figure A.9: Dynamic expansion of PMMA(left)/PS(right) bi-layer, thickness 0.5mm/0.5mm (a) before saturation (a) equilibrium with CO$_2$ (6.9 MPa, 100°C) and before the pressure release (c) 60 seconds after the pressure release (d) 90 seconds after the pressure release (e) 120 seconds after the pressure release
APPENDIX B

$T_g$ PROFILE OF A POLYSTYRENE FILM 
SUPPORTED ON AN OXIDIZED SILICON WAFER

The focus of Chapter 5 is PS-CBN nanocomposites and thus most effort was addressed on the thin film $T_g$ of a PS film supported on HOPG. However, nanoclay-reinforced polymer composites represent another large group of materials for strength-demanding applications. Since the main component of natural clay is silicon-oxygen [1, 51-53], it is reasonable to use oxidized silicon wafer ($SiO_x/Si$) to mimic the nanoclay surface. Recently, we carried out similar experiments to study the $T_g$ profile of a PS film supported on bard $SiO_x/Si$ surface. On-going research will be focused on the $T_g$ profile investigation of PS films covered on the surfactant treated $SiO_x/Si$.

While the interactions between PS and carbon surface are confirmed to be strong, previous studies indicated weak interactions between PS and silica (SiO$_2$) [241]. Bulk $T_g$ of PS-SiO$_2$ nanocomposites showed a negative dependence on the SiO$_2$ content. A filler loading of 40wt% led to an approximately 11°C depression in $T_g$. Correspondingly, a non-wetting interface between PS and SiO$_2$ was observed. In our previous work, a similar
reduction in $T_g$ with respect to the particle content was observed in the PS-clay nanocomposites. As shown in Figure B.1, PS containing 20wt% nanoclay possesses a $T_g$ 20°C lower than the bulk value [342]. Investigation on the integrated $T_g$s of PS thin films supported on the $SiO_x/Si$ substrate revealed the same phenomenon. As presented earlier, as the film thickness decreased, the thin film $T_g$ reduced to a level sufficiently below the bulk $T_g$, signifying the lack of favorable polymer-substrate interactions [237].

Using the nanoparticle embedding technique, the $T_g$ profiles of PS films coated on the $SiO_x/Si$ substrate were measured. Results are summarized in Figure B.2. Films with two thicknesses were prepared: 2 µm and 92 nm. All $T_g$s within investigation are lower compared to the bulk $T_g$ (dash line). In addition, as the film thickness decreases, the $T_g$ profile is further suppressed. These observations agree well with earlier statement that in PS-$SiO_x$ systems, the interactions between the polymer and particles are weak. Thus, in a supported polymer thin film configuration, the free surface-induced $T_g$ reduction dominates.

From the reinforcing point of view, it is desirable to achieve strong interactions at the particle-polymer interfaces. Therefore, surface modification of nanoclay is generally required in the synthesis of polymer nanocomposites. In order to provide a more relevant thin film configuration to these polymer-treated nanoclay composites, a polymer film coated on a surfactant-treated silicon substrate will be used in later study. Self-assembly monolayer (SAM) technique has been widely used to treat the solid surface and, in particular, to graft polymers on solids. For this particular study, assemblers possessing reactive sites to the styrene monomer are favorable choices. We expect the $T_g$ profile of a
PS film grafted on the Silicon wafer to show a similar trend as those observed in the PS/HOPG systems. On-going research is been carried out in this area.
Figure B.1: Bulk $T_g$ of PS-nanoclay nanocomposites
Figure B.2 $T_g$ profiles of PS films supported on $SiO_x/Si$.
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