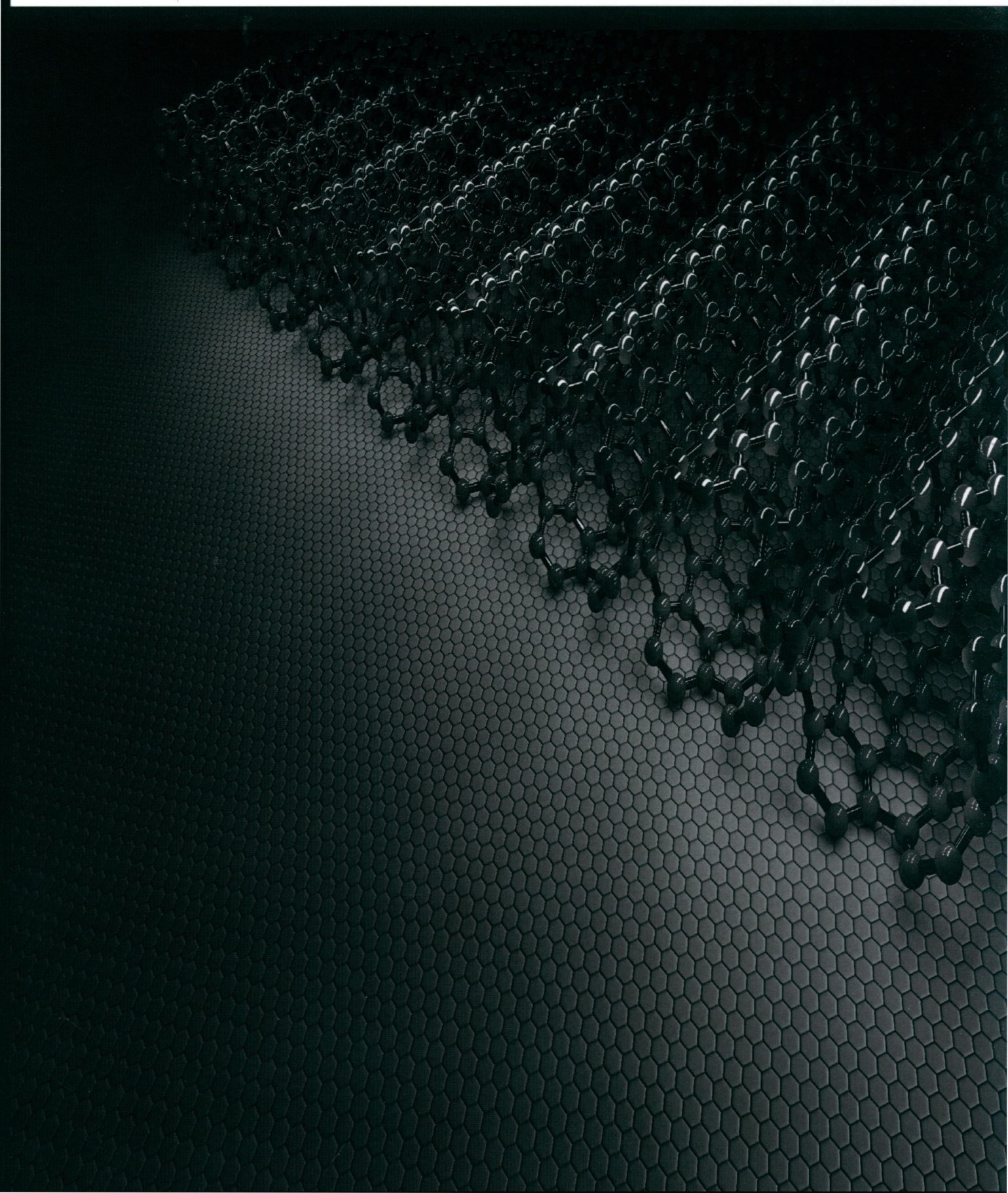
Surface Chemistry of Nanomaterials: Synthesis, Properties and Applications

Contributors: Deniz Rende, Linda S. Schadler, et al.



About the Book

Surface chemistry is the study of chemical reactions at surfaces and interfaces. Appreciating how molecules and atoms interact with surfaces and with each other while on surfaces is key to understanding desirable chemical reactions, such as in heterogeneous catalysis, and also those that are undesirable, such as in corrosion chemistry. Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future. Some nanomaterial's occur naturally, but of particular interest are engineered nanomaterial's (EN), which are designed for, and already being used in many commercial products and processes. Engineered nanomaterial's are resources designed at the molecular (nanometer) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts. The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviors. Nanomaterials are already in commercial use, with some having been available for several years or decades. Today nanophase engineering expands in a rapidly growing number of structural and functional materials, both inorganic and organic, allowing to manipulate mechanical, catalytic, electric, magnetic, optical and electronic functions. The production of nanophase or cluster-assembled materials is usually based upon the creation of separated small clusters which then are fused into a bulk-like material or on their embedding into compact liquid or solid matrix materials e.g. nanophase silicon, which differs from normal silicon in physical and electronic properties, could be applied to macroscopic semiconductor processes to create new devices. These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties.

Surface Chemistry of Nanomaterials- Synthesis, Properties and Applications holds a special niche in describing the current state of the art in the fundamentals and applications of a variety of nanomaterials. This book enables the results of current research to reach those who wish to use this knowledge in an applied setting. The contributors cover the whole spectrum of nanomaterials, ranging from theory, synthesis, properties, characterization to application.

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ISBN 978-1-78802-162-3
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9 781788 021623

Rende,
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Published by Auris Reference Limited

www.aurisreference.com

United Kingdom

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ISBN: 978-1-78802-162-3

British Library Cataloguing in Publication Data
A CIP record for this book is available from the British Library

Printed in the United Kingdom

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Preface

Surface chemistry is the study of chemical reactions at surfaces and interfaces. Appreciating how molecules and atoms interact with surfaces and with each other while on surfaces is key to understanding desirable chemical reactions, such as in heterogeneous catalysis, and also those that are undesirable, such as in corrosion chemistry. Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future. Some nanomaterial's occur naturally, but of particular interest are engineered nanomaterial's (EN), which are designed for, and already being used in many commercial products and processes. Engineered nanomaterial's are resources designed at the molecular (nanometer) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts. The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviors. Nanomaterials are already in commercial use, with some having been available for several years or decades. Today nanophase engineering expands in a rapidly growing number of structural and functional materials, both inorganic and organic, allowing to manipulate mechanical, catalytic, electric, magnetic, optical and electronic functions. The production of nanophase or cluster-assembled materials is usually based upon the creation of separated small clusters which then are fused into a bulk-like material or on their embedding into compact liquid or solid matrix materials e.g. nanophase silicon, which differs from normal silicon in physical and electronic properties, could be applied to macroscopic semiconductor processes to create new devices. These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties.

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CONTROLLING FOAM MORPHOLOGY OF POLY (METHYL METHACRYLATE) VIA SURFACE CHEMISTRY AND CONCENTRATION OF SILICA NANOPARTICLES AND SUPERCRITICAL CARBON DIOXIDE PROCESS PARAMETERS

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ABSTRACT

Polymer nanocomposite foams have received considerable attention because of their potential use in advanced applications such as bone scaffolds, food packaging, and transportation materials due to their low density and enhanced mechanical, thermal, and electrical properties compared to traditional polymer foams. In this study, silica nanofillers were used as nucleating agents and supercritical carbon dioxide as the foaming agent. The use of nanofillers provides an interface upon which CO_2 nucleates and leads to remarkably low average cell sizes while improving cell density (number of cells per unit volume). In this study, the effect of concentration, the extent of surface modification of silica nanofillers with CO_2-philic chemical groups, and supercritical carbon dioxide process conditions on the foam morphology of poly(methyl methacrylate), PMMA, were systematically investigated to shed light on the relative importance of material and process parameters. The silica nanoparticles were chemically modified with tridecafluoro-1, 1,2,2-tetrahydrooctyl triethoxysilane leading to three different surface chemistries. The silica concentration was varied from 0.85 to 3.2% (by weight). The supercritical CO_2 foaming was performed at four different temperatures (40, 65, 75, and 85°C) and between 8.97 and 17.93 MPa. By altering the surface chemistry of the silica nanofiller and manipulating the process conditions, the average cell diameter was decreased from 9.62 ± 5.22 to 1.06 ± 0.32 μm, whereas, the cell density was increased from $7.5 \pm 0.5 \times 10^8$ to $4.8 \pm 0.3 \times 10^{11}$ cells/cm^3. Our findings indicate that surface modification of silica nanoparticles with CO_2-philic surfactants has the strongest effect on foam morphology.

INTRODUCTION

In nature, foams are found in the form of bone, natural sponge, coral, and natural cork. Inspired by these materials, processing of polymer foams has received considerable attention [1, 2]. Polymer nanocomposite foams are micro- and nanoporous materials that are used as thermal and sound barriers, shock absorbers, absorbents, cushions, and tissue engineering scaffolds [3, 4]. Recent advances in processing of polymer nanocomposite foams enabled new application areas in hydrogen storage [5], electromagnetic shielding [6], and sensing technology [7]. Various polymers are being used in foam applications such as polyurethane, polystyrene, polyethylene, polypropylene, poly(vinyl chloride), polycarbonate, and poly(methyl methacrylate) [8–14] as well as specialty polymers.

Foams are divided into various categories depending on their pore morphology (open versus closed) or density (low versus high). Open cell morphology consists of pores (bubbles) that are connected to each other, making the material softer and more absorbent. In the closed cell morphology, the pores are isolated from each other, which makes the foam more rigid. In addition to these categories, polymer foams can also be characterized according to their density, cell size, cell density, and wall thickness, all of which influence the properties of the foam. In general, polymer foams have low thermal conductivity, poor mechanical properties, and poor surface quality due to the underlying porous structure. However, their low density, low thermal conductivity, and sound barrier properties make them highly attractive for a variety of applications. For example, low density foams are primarily used in packaging and insulation applications, and high density foams are used in structural applications [3, 15] as thermal or sound barriers. Polymer foams can also be categorized by their flexibility: flexible, semiflexible, and rigid. Flexible and semiflexible polymer foams are used to produce cushions, textiles, toy parts, and sporting goods. On the other hand, rigid polymer foams have applications in insulation, construction, durable goods, and infrastructure.

In general, the foam morphology is formed via the use of foaming agents, which undergo phase transition either due to physical or chemical changes creating a gas phase that expands forming gas bubbles inside the polymer matrix. The nucleation of the bubbles occurs via two different classical mechanisms: homogeneous or heterogeneous nucleation. In the homogeneous nucleation case, concurrent initiation and growth of bubbles are observed leading to a wide cell size distribution in the final foam structure. The heterogeneous nucleation, however, requires the existence of a secondary material that promotes simultaneous growth of bubbles inside the polymer matrix, resulting in a narrow cell size distribution. The addition of inorganic nanoparticles, which act as nucleating agents, induces heterogeneous nucleation and provides a large number of nucleation sites. Furthermore, the presence of micro- or nanosized fillers dramatically decreases the energy barrier for cell nucleation compared to that required for homogeneous nucleation [9, 13, 16, 17]. Existing models based on classical nucleation theories sometimes fail to explain the nucleation satisfactorily. Other models, for example, consider microvoids as nucleation sites. Microvoids lead to stress induced bubble formation, and the population of sufficiently large viable microvoids that overcomes surface and elastic forces can then be related to the cell density [18–20].

The synthesis of nanofillers is of recent interest because they provide a high density of nucleation sites at low concentrations. The highest nucleation efficiency is achieved when nucleation on the filler surface is energetically favorable and the filler is uniformly distributed and dispersed within the polymer matrix. Therefore, heterogeneous nucleation conditions could be controlled to some extent via filler type, geometry (size, aspect ratio, etc.), and surface chemistry [1, 21, 22]. Selection of the filler type is an important step to achieve the final desired properties. For instance, carbon based nanofillers (carbon nanotubes and graphene) enhance the strength and conductivity [8, 23]. The flat surfaces of clays offer an excellent surface for nucleation; however only when dispersion is controlled, uniform cell size and remarkable mechanical properties are achieved [24–29]. Spherical nanofillers are another class of fillers that are being used to create polymeric foams [21, 30], polymer blends [31], and copolymers [32]. Among spherical nanoparticles, silica nanoparticles have been widely used as bare or after surface modification with vinyl or fluorinated silane coupling agents to foam polymers. Studies using bare silica nanoparticles showed a reduction in the average cell size with increasing concentration [33]. The surface modification of silica nanoparticles was reported to lead to enhanced interaction between the foaming agent and the nanofiller, thereby reducing the average cell size further [34]. For example, Goren et al. reported an 8-fold decrease in average cell size after modifying silica nanoparticles with fluorinated silane coupling agents [21]. However, spherical nanoparticles do not improve properties as much as nanosized rods or sheets.

In addition to filler characteristics, foaming conditions also influence the final foam structure. Conventional foamed products can be produced either by chemical or physical blowing agents. Chemical blowing agents are mixed into polymer matrix and decompose when heated up yielding a gas release. This process requires an additional step to eliminate the residual chemical blowing agent [35]. Due to the challenges in the removal of side products, physical foaming is often preferred over chemical foaming. Physical foaming involves the saturation of the polymer

matrix with a gas at high pressure followed by a rapid decrease in pressure. This rapid decrease in pressure leads to the expansion of the gas and, therefore, results in the formation of bubbles within the polymer matrix. The lack of hazardous chemical solvent use during physical foaming makes this technique the preferred method in the production of polymeric foams. Supercritical fluids have also become an attractive option for the production of polymer foams. Due to stable, nontoxic, inflammable, low cost and its easily attainable critical conditions, supercritical carbon dioxide has been widely used to create polymer foams [14, 21–23, 29]. Supercritical CO_2 exhibits relatively high solubility in polymers, acts as a plasticizer by lowering the glass transition temperature, easily diffuses into the polymer, reduces the viscosity and surface tension of the polymer melt, and assists in polymer processing. Foaming with supercritical CO_2 can be performed either as a batch process, where the samples are kept in a pressure chamber and saturated with supercritical carbon dioxide [14, 21, 36], or as a continuous process such as the inside of an extruder [37–39]. After the polymer is saturated with supercritical CO_2, the rapid decrease in pressure generates a thermodynamic instability, which leads to phase transition from supercritical to gaseous state and causes the nucleation of gas bubbles. Saturation (CO_2 soaking) pressure, temperature, time, and depressurization rate are critical parameters in determining the final morphology of the polymer foam [40]. At high pressures, more carbon dioxide is absorbed into the polymer, leading to an increase in cell density [41]. In addition, high pressure enhances the driving force for cell growth.

Many researchers investigated the silica/PMMA nanocomposite systems foamed with supercritical CO_2 and a review article by Chen and coworkers [42] discusses many of the recent developments. Siripurapu et al. [33] studied the effect of concentration of untreated (bare) silica nanoparticles at 1, 5, and 8% silica concentrations. The foamed material was produced with CO_2 at 40°C and 6.83 MPa. An increase in nanosilica concentration led to reduced average cell diameter and increased cell density under isothermal and isobaric conditions. Yeh et al. [34] highlighted the importance of surface modification of silica nanoparticles, which might influence the interaction of filler with CO_2. For example, at various concentrations untreated and vinyl-modified silica nanoparticles containing PMMA composites were foamed at 150°C and 13.8 MPa. The cell sizes achieved in this process ranged from 10 to 23 μm. The surface modification of silica nanoparticles was also performed with fluorinated silane coupling agents by our group [21], in which the silica nanoparticle sizes ranged from 60 to 150 nm. PMMA nanocomposites having 1% silica with 66, 80, 149, and 157 nm silica nanoparticles were foamed under supercritical CO_2 at 40°C and 17.93 MPa. In this study, the particle size was shown to have an important contribution to cell density and fluorination of the silica nanoparticles was shown to facilitate the dispersion of the silica nanoparticles inside the PMMA matrix.

Although nanofiller concentration and surface chemistry are known to have strong influence on the final cell size and cell density [14, 21, 43, 44], the extent of surface coverage (tethering density) of the functional groups on the foam morphology is yet to be reported in a systematic manner. In the current study, we aim to investigate the effect of tethering density of fluoroalkanes on the foam morphology of silica/PMMA nanocomposites. Fluorinated surface modifiers were chosen because they were shown to exhibit CO_2-philic behavior [21]. The effects of silica concentration, foaming temperature, and saturation pressure on the final foam morphology were also investigated.

EXPERIMENTAL

Materials

To synthesize silica nanoparticles, tetraethyl orthosilicate (TEOS, 98% reagent grade, Sigma, 131903) and ammonia solution (NH_3, 28%, Sigma, 338818) were used as received. Tetrahydrofuran (THF, Fisher Scientific, T397-1) was used to purify the silica nanoparticles. The surface modification of the silica nanoparticles was performed with silane coupling agent tridecafluoro-1,1,2,2-tetrahydrooctyl triethoxysilane (F-TEOS, Gelest, SIT8175). Poly(methyl methacrylate), PMMA, was chosen as the matrix polymer because of its outstanding chemicophysical properties [45] and relatively high affinity for CO_2. Commercial grade PMMA (Plexiglas V920-100) was donated by Altuglas International.

Preparation of Silica Nanoparticles

The method used in the synthesis of silica nanoparticles is an adaptation of the Stöber's procedure [46]. To prepare 100 nm bare silica nanoparticles, 87.5 g ethanol, 4.37 g distilled water, and 4.12 g ammonia solution was mixed with 8.62 g of TEOS. The reaction mixture was stirred overnight at room temperature and unreacted solvents were removed by rotary evaporator at 60°C and 90 rpm for 2 hours. The sample was then kept in vacuum dryer overnight at 60°C. In order to remove any organic and inorganic impurities and unused reactants, the dried sample was first washed with THF and vacuum-filtered through 0.45 μm hydrophobic filtering paper, then washed with distilled water, and vacuum-filtered through 0.45 μm hydrophilic filtering paper. Finally, the sample was dried again in vacuum oven

overnight at 60°C. This procedure approximately yields 1.5 g of bare silica nanoparticles with an average size of ~100 nm.

Surface Modification of Silica Nanoparticles

In order to increase the interaction of silica and CO_2, silica nanoparticles were modified by tethering fluoroalkane chains (F-TEOS) onto their surfaces. To prepare the surface modified nanoparticles, silica nanoparticles were synthesized as described before and each batch was divided into multiple parts; one was left as is (bare silica) and the other parts were modified with F-TEOS. This ensured that the starting silica nanoparticles on average had the same size. Two different amounts (0.1 and 0.7 g) of F-TEOS were added to two different silica batches to create two different surface tethering densities. The surface modification reaction took 24 hr at room temperature. Unreacted solvent was removed by rotary evaporator at 60°C and 90 rpm for 2 hours, and the samples were dried in a vacuum oven overnight at 60°C. To remove any residual solvent and impurities, each sample was subsequently washed with THF and water, filtered, and dried in vacuum oven overnight at 60°C.

Structural Analysis of Silica Nanoparticles

The size of the bare and surface modified nanoparticles was characterized by field emission scanning electron microscopy (SEM), transmission electron microscopy (TEM), and image processing. After the synthesis, the bare and surface modified silica nanoparticles were dried and the nanoparticles were first subjected to gold sputtering to form a 10–15 nm layer of gold on the sample surface. SEM images were obtained with a JEOL JSM-6332 using an accelerating voltage of 10 kV. TEM images were collected with a Philips CM12 with an accelerating voltage of 120 kV. Subsequently, both SEM and TEM images were analyzed with ImageJ [47] and diameter measurements of at least 100 nanoparticles were recorded in order to have statistically significant results.

The extent of the surface modification was determined by thermogravimetric analysis (TGA). Each silica nanoparticle sample was analyzed by TA Instruments TGA Q50 by heating up to 900°C at a rate of 20°C/min. The resulting percent weight changes between 200 and 800°C were used to calculate the percent coverage of the silica surface. Both bare and surface fluorinated samples were tested for at least three times.

The surface area of the silica nanoparticles was measured with Quantachrome BET Surface Analyzer Autosorb. Before BET analysis, the samples were degassed at 150°C under nitrogen atmosphere for 24 hrs.

Preparation of Polymer Nanocomposites

The polymer nanocomposite samples were prepared by melt mixing with a benchtop twin-screw extruder (Haake MiniLab). The extruder was equilibrated for 2 hrs at 220°C before each use. The rotation speed of the screws was set to 60 rpm. Before each operation, 5 g of neat PMMA was passed through the system to clean the screws. The samples with different concentrations of bare and surface modified silica nanoparticles were mixed with PMMA and each sample was cycled within the extruder for 4 min and flushed in 3 min. These parameters were chosen because they were previously shown to disperse and distribute silica nanoparticles effectively [21]. Neat PMMA samples were also processed in the same way as silica containing PMMA as control samples.

Although silica was added to PMMA in premeasured amounts, due to the chaotic nature of the twin-screw extruder used, silica concentration in silica/PMMA composites was subsequently measured again by thermogravimetric analysis (TA Instruments). For statistical accuracy, three different samples, each being approximately 40 mg, were analyzed with a TA Instruments TGA Q50 by heating to 900°C at a rate of 20°C/min. The silica concentration was determined from the remaining weight at 800°C, after which the weight remains constant. The melt mixing process led to several composite samples each having slightly different amount of bare or surface modified silica nanoparticles. In order to establish statistical significance, these samples were separated into two groups of "low" and "high" silica concentrations. The low silica concentration group contained 0.85–1.38% silica and the high concentration group contained 2.5–3.2% silica. All silica concentrations are reported as weight percentages. Another 2.9% silica/PMMA nanocomposite sample was prepared with highly surface modified silica nanoparticles. This sample was used specifically to investigate the effect of supercritical CO_2process parameters on foam morphology while eliminating sample variations and effect of surface modification. The nanocomposite samples were labeled according to their silica surface tethering density (B: bare; F: fluorinated with low tethering density; and FF: fluorinated with high tethering density) and silica concentration (low or high). For instance, B-Low indicates a nanocomposite sample containing bare silica nanoparticles at low concentration (0.85%). The neat PMMA control sample was labeled as "PMMA." This labeling convention was necessitated by the fact that during sample preparation neither the surface tethering density nor the silica concentration could be controlled accurately.