

Current Trends in Nanocomposite Foams

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ABSTRACT: This article presents a brief but concise review of the current research efforts on polymeric nanocomposite foams production, characterization, and applications. Survey indicates that the emergence of nanocomposites has resulted in the development of a new group of materials regarded as nanocomposite foams. Nanocomposites result from the use of nano-sized (10^{-9} m) particles as fillers to modify and enhance the properties of polymers and other matrices. The combination of functional nanoparticles and foaming technologies such as supercritical fluid foaming, chemical foaming, syntactic foaming, aerogel foaming, phase inversion foaming etc. generate these new materials regarded as nanocomposite foams that have light weight, high specific strength, and multifunctional attributes. Enhanced thermo-mechanical properties of nanocomposite foams result from improved cell morphology that is mainly attributable to the role of nanoparticles as nucleation agents for bubble generation. High-specific mechanical properties and multifunctional characteristics of nanocomposite foams make them cost-effective and desirable in a multitude of application areas including structural, energy-dissipating/absorbing, acoustical insulation, flammability resistance, and others. Of particular importance in this study of nanocomposite foams is the flammability resistance effect of nanoparticles. The intumescent model (NIST, NMAB, and others) indicates that the flame barrier mechanism involves a high-performance carbonaceous-silicate char; this char build-up insulates the underlying material. Understanding this char build-up mechanism presents a challenge and area of

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research interest in the effort to develop new generation foams that are suitable in energy absorbing materials and structures.

KEY WORDS: Nanoparticles, Nanocomposites, Microspheres, Syntactic, Nanocomposite Foams, Nanocomposite-Syntactic Foams, Nanotubes, Nanofibers, Nanoclays, Nanoplatelets, Nucleation Agents, Morphology, Free Energy, Cone Calorimetry, Peak Heat Release Rate (PHRR), Smoke Density.

INTRODUCTION

Polymeric nanocomposite foams are currently subjects of attention in both the scientific and industrial communities. The combination of functional nanoparticles and foaming technology has a high potential to generate a new class of materials that are lightweight, high strength, and multifunctional. Small amounts of well-dispersed nanoparticles in polymer matrices serve as nucleation sites to facilitate the bubble nucleation process. Moreover, the nano-scaled particles are suitable for microscaled reinforcement, and can lead to the achievement of macroscopic mechanical enhancement [1]. Compared to conventional micro-sized nucleants, nanoparticles offer unique advantages for controlling both the foam structures and properties [2]. 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 these particles desirable as reinforcing elements for the cell walls.

NANOPARTICLES AND NANOCOMPOSITES

Table 1 indicates a healthy global trend in nanomaterials usage with a projected consumption volume of 10.3 million metric tons for 2010, and an annual average growth rate (AAGR) of about 2.7%. The 2010 projected nanomaterials market comprises of four major morphological types, nanoparticles (55%), thin films (25%), monolithics (17%), and composites (3%).

Table 1. Trends in global nanomaterials usage (Source: BCC, Inc.).

Year →	2004	2005	2010	AAGR (2005–2010)
Tons (metric)	8.7E + 06	9.0E + 06	10.3E + 06	2.7
\$ (Billions)	12.5	13.1	20.5	9.3

Business Communications Company Inc. (BCC) Report – RGB-334: 'Nanomaterials markets by type,' September 2005; AAGR = annual average growth rate.

There are three major types of nanoparticles, iso-dimensional nanoparticles, nanotubes and nanoplatelets based on the number of dimensions in the nanometer range (nanometer = 10^{-9} meter; average hair diameter = $70\ \mu\text{m}$). Figure 1 shows some of three types of nanoparticles. Iso-dimensional nanoparticles such as silica, aluminum oxide, carbon black, titanium dioxide, zinc oxide, silicon carbide, polyhedral oligomeric silsesquioxanes (POSS) have three dimensions in the nanometer range. Nanotubes (nanofibers or whiskers) such as carbon nanotubes (SWCNT, MWCNT), carbon nanofibers (NFs), boron nitride tubes, boron carbon nitride tubes, cellulose whiskers, gold, or silver nanotubes have at least two dimensions in the nanometer range, and form elongated structures (Table 2). Nanoplatelets such as layered silicates (nanoclays), layered graphite flakes and layered double hydroxides have only one dimension in the nanometer scale and are

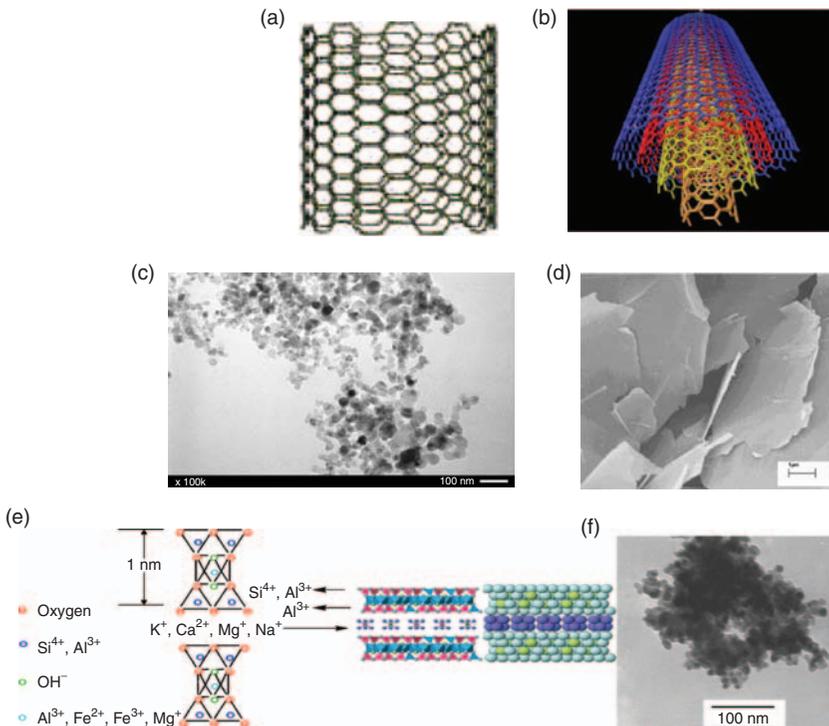


Figure 1. (a) SWCNT; (b) MWCNT; (c) Silica nanoparticles; (d) Graphite flakes; (e) Nanoplatelet - Layered Silicate Montmorillonite (MMT) Clay (stacks of plate-like structures, or platelets); (f) In-lab (aerogel process) AP- SrTiO₃ Nanoparticles.

Table 2. Nanoparticles manufacturers and costs.

Nanoparticle-type	Manufacturer(s)	Typical costs (\$/Lb)
Nanoclay	<ul style="list-style-type: none"> • Nanocor Inc. • Southern Clay 	2–5
Carbon black	<ul style="list-style-type: none"> • Degussa • Cabot 	0.40–0.80
Titanium dioxide (TiO ₂)	<ul style="list-style-type: none"> • Degussa • Huntsman • Millennium Chem. • Others 	≈10
Metals, Oxides, Nitrides, Carbides	<ul style="list-style-type: none"> • Nanopowder Enterprise 	N/A
Zinc oxide	<ul style="list-style-type: none"> • Rheox • Inframat Advanced Materials 	40–600
POSS	<ul style="list-style-type: none"> • Hybrid Plastics 	10–50
Carbon nanotubes (CNT)	<ul style="list-style-type: none"> • Hyperion Catalysis • Nanolab • SES Research (Fullerenes) • Materials & Electrochemical Research (+Fullerenes) • Carbon Nanotechnologies (SWCNT) • Deal (MWCNT) • Others 	Up to 2500–4500

Sources: www.nanovip.com
www.cheaptubes.com
<http://statusreports.atp.nist.gov/reports/98-01-0059.htm>
<http://nanomaterialstore.com/inc/sdetail/589>
<http://www.advancedmaterials.us/30N-0801.htm>

characterized by sheet-like forms of one to several nanometers thickness and lengths of hundreds to thousand nanometers (Figure 1(e)).

The infusion of nanoparticles into polymeric and other matrices results in nanocomposites; materials with enhanced multifunctional characteristics. Nanocomposites are fundamentally new materials or hybrids in which at least one of the components has dimension(s) in the nanometer scale. The presence of nanoscale components gives nanocomposites intrinsically new properties and characteristics that are not present in conventional composites or the pure components. The structure-property relationship of nanocomposites is very much influenced by surface area/volume ratio of the nano-inclusions. The change in particle diameter, layer thickness, or fibrous material diameter from micrometer to nanometer, changes the surface area/volume ratio by three orders in magnitude. At this scale, there is often distinct size dependence of the material properties. With the increase in interfacial area, the properties of the composite become

Table 3. Textural properties of mixed metal oxide nanoparticles.

SrTiO ₃ sample	Crystallite size (nm)	Surface area (m ² /g)	Total pore volume (cc/g)	Avg pore size d (Å)
CM-SrTiO ₃ S	145	1.0	0.003	93
NCM-SrTiO ₃	25	17	0.12	290
SrTiO ₃ (methanol)	25	82	0.58	280
SrTiO ₃ (ethanol)	8	159	0.62	150
AP-SrTiO ₃ (isopropanol)	20	121	0.59	190

CM – commercial; NCM – commercial nanosized, AP – aerogel process samples.

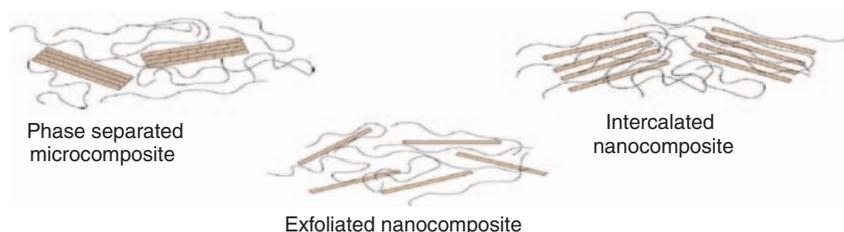


Figure 2. Dispersion of nanoparticles in polymer matrix.

dominated by the properties of the interface or interphase. CNCMM's Nanoparticles Synthesis Program focuses on the synthesis and characterization of high surface area mixed metal oxide nanoparticles (Table 3) via the aerogel process (AP or modified sol gel method). Also of importance in nanocomposites design, formulation, and production is the dispersion, intercalation (partial dispersion), and exfoliation (almost complete dispersion) (Figure 2) of nanoparticles in the matrix.

NANOCOMPOSITE FOAMS

Recently researchers have been investigating polymeric nanocomposites (PNCs) containing nanoparticles to improve their physical, mechanical, and chemical properties [3]. Polymeric matrices infused with nanoparticles have attracted increasing interest because of the unique properties displayed by nanoparticles. Nanoparticle-polymer nanocomposites synergistically combine the properties of both the host polymer matrix and the infused nanoparticles. Such nanocomposite materials are expected to have novel electrical, flammability resistance and mechanical properties. The presence of nanoparticles such as nanoclay may enhance cell nucleation, provide foam reinforcement,

lower gas escape rate, and result in char formation when foam is exposed to fire. This makes polymer-clay nanocomposite foam an excellent choice for applications requiring high strength, lightweight, and enhanced flammability resistance [4,5]. Conventionally, foams are characterized and classified as per three main parameters [6], across-cell nominal diameter or cell size, BET (Brunnauer-Emmett-Teller) surface area (m^2/g) and cell density (number of cells per unit volume (cells/cm^3)). Microcellular foams (cell size less than $10\ \mu\text{m}$, surface area between 10 and 20 (m^2/g) and cell density between 10^7 and $10^9\ \text{cells}/\text{cm}^3$) and ultracellular foams (cell size less than $0.1\ \mu\text{m}$, surface area between 100–400 (m^2/g) and cell density between 10^9 – $10^{12}\ \text{cells}/\text{cm}^3$) have shown many promising properties compared to conventional foams. Conventional foams typically have cell size of about $100\ \mu\text{m}$ and cell density less than $10^6\ \text{cells}/\text{cm}^3$. Ultracellular foams require very stringent conditions such as extremely high pressure and high pressure drop rate to produce though. This greatly limits the processing window and the attainable size of the foam products. The use of nanoparticles should help to overcome this bottleneck.

NANOCOMPOSITE FOAMS SYNTHESIS AND PROCESSING TECHNIQUES

Limited work has been done regarding the study of foaming of polymer/nanoparticle (e.g., layered silicate) nanocomposites. Here, polymer foam is defined as a two phase material in which air bubbles are entrapped in a continuous macromolecular phase [7]. Nanocomposite foams can be obtained by several methods, mainly depending on the type of polymer matrix and foaming agent used. Polyolefin (PO) matrix-based foams are very popular as polyolefins account for more than 40% of the polymer market. PO matrix-based foams are commercially produced by three different methods, depending on the production process and final shape of the product:

1. extruded polyolefin foams, where a foam is directly obtained at the exit of an extrusion die,
2. crosslinked polyolefin foams, in which a partially crosslinked PO matrix stretches during foaming, minimizing gas escape, and
3. molded PO foams, where previously extruded PO materials (with all the foaming additives, mainly crosslinking and foaming agents), are foamed in a machine that allows careful regulation of temperature and pressure (hot-plate press, modified oven, thermoforming, etc.) in order to gradually crosslink and foam the material.

In addition to utilizing a blowing agent, porous polymeric and other materials can also be prepared by other methods such as aerogel, phase inversion, leaching, syntactic, supercritical fluids (SCF), etc.

Nanocomposite foams may show improved cell morphology, with smaller and more isotropic cells, resulting in enhanced thermo-mechanical properties with respect to the neat polymer foams [5,7]. Particularly, clay nanoparticles may act as nucleation agents for bubble generation in foams using CO₂ as a physical foaming agent, via batch process or by direct extrusion. In both cases it has been shown that small amounts of clay nanoparticles greatly reduce the cell size of the foams and increase the cell density. Microcellular and ultracellular foams (showing pores with <10 μm in size) can be produced by adjusting the interaction between the polymers, the clay surface and CO₂, as well as the foaming conditions, leading to cost savings and better processing control. Cell nucleation, in which it is known that the size, shape, and distribution of the particles affect the efficiency of the nucleation process, could be improved considerably if an exfoliated-type of structure is achieved for the clay particles, with finer particles reducing the nucleation energy for the growth of the gaseous phase. This affects cell growth and results in more isometric and smaller cell sized foams. Also clay nanoparticles act as a reinforcing agent; this could expand the range of properties of this type of materials and create mechanically improved foams for structural applications.

There are far fewer studies on thermoset nanocomposite foams than their thermoplastic counterparts. Most thermoset nanocomposite foam systems are polyurethane based; this is understandable as polyurethanes are the most used thermosetting plastics with an annual consumption volume of about 6.0 billion pounds. More than 50% of this are used in- flexible foams. Polyisocyanurate and phenolic nanocomposite foams are also popular. Several patents on polyurethane nanocomposite foams claim significant property improvement, such as improved compressive strength, thermal insulation, and flammability resistance. To prepare thermoset nanocomposite foams, nanoparticles are first dispersed uniformly in one or more monomers. The mixture is then foamed by adding other monomers. Foaming agents could be either physical or chemical blowing agents. Similar to the synthesis of thermoplastic nanocomposites, the surface modification of nanoparticles is essential for nanoparticle dispersion. In most studies, the layered silicates were modified with functional surface modifiers that can react with one of the reactants to form an intermediate leading to a uniform nanoparticle distribution in the polymer matrix during foaming.

NANOCOMPOSITE FOAMS MORPHOLOGY AND CHARACTERISTICS

To obtain foam cells with a controlled structure and uniform distribution [1], a common practice is to add particles, nanoparticles that serve as nucleation agents to reduce the nucleation free energy. It is generally known that the size, shape, and distribution of the particles, as well as the surface treatment, can affect the nucleation efficiency [8–11]. In a recent study, Zeng et al. determined that nanoclay serves as an efficient nucleation agent in thermoplastic nanocomposites, and that foam nucleation efficiency increases with enhanced nanoclay dispersion [11]. Enhanced nucleation efficiency is attributable to the accumulation of gas on the polymer-particle interface and creation of nucleation sites. Foams with finer fillers show a higher cell density at a high saturation pressure; nanoparticles exhibit higher catalytic activity and selectivity due to enhanced surface properties than their bulk counterparts [12–14]. The amount and distribution of the nucleation agents are also important factors in determining foam quality. The extremely small dimensions and large surface area of nanoparticles provide much more intimate contact between the particles, polymer matrix, and gas.

The effect of nanoparticles on cell size is a subject of current studies; in the presence of nanoparticles, cell size is reduced. As more bubbles start to nucleate concurrently, there is a less amount of gas available for bubble growth, leading to a reduction of cell size. Moreover, presence of nanoparticles can significantly increase melt viscosity. The surface chemistry of clay nanoparticles not only affects the particle dispersion but also has a tremendous effect on the nucleation efficiency in a polymer-clay-foaming agent system. The high aspect ratio and large surface area of nanoparticles offer the potential for high reinforcing efficiency, good barrier properties, and improved dimensional and thermal stability. The nanometer dimension is especially beneficial for reinforcing foam materials, considering the thickness of cell walls is in the micron and submicron regime. It is, therefore, ideal to use nanoparticles to reinforce microstructures in order to achieve macro-scale property improvement of the final products.

It has been found that the surfactant, introduced onto the clay surface to achieve good compatibility between the inorganic clay and the organic polymer or monomer for good clay exfoliation, is a fire hazard material. Natural clay without surface modification, however, can only disperse well in water-soluble polymers. Using water as a nanoclay carrier may achieve surfactant-free nanocomposites with good clay dispersion in hydrophobic polymers.

Nanoparticles may behave as stress concentrators in foam matrices [15,16], and can serve as prospective media for generating open cell foams under external fields such as ultrasonic fields. Open cell polymer foams are one of the most commonly used scaffolds for tissue engineering [17]. This may lead to a new mass production technology for tissue engineering scaffolds. The high surface area and rich surface chemistry make nanoparticles potentially useful as carriers for desired biofunctionalities (e.g., adhesion sites and signaling molecules).

NUCLEATION AGENTS

Foam cell density is determined by the concentration of the foaming agent. A nonuniform distribution of the nucleation agent results in a foam that has more cells in the agent rich area and less cells in agent deficient areas, leading to a non-uniform cell size distribution in the foam product. Because the number and size of the bubbles are determined by the concentration of the foaming agent, the uniformity of the cell structure and the cell density are limited by the method used to mix the foaming agents and the polymer. In fact, it is difficult to obtain a uniform cell structure with a high cell density in the conventional foaming process [1,18–21]. Compared to conventional micron-sized filler particles used in the foaming processes, nanoparticles offer unique advantages for enhanced nucleation. The effect of particle concentration on the foam nucleation has been investigated, and the cell density was found to increase linearly with clay concentration at low clay concentration, and starts to level off as clay concentration increases to 10% in some cases, while in other cases, an abrupt increase of cell density was observed as the clay concentration is increased.

The incorporation of nano-sized clay induces heterogeneous nucleation because of a lower activation energy barrier compared with homogeneous nucleation. However, the competition between homogeneous and heterogeneous nucleation is no longer discernible [22].

The classical nucleation theory is the approach currently used to describe bubble nucleation in polymeric foams, although its prediction of the nucleation rate can easily be off by several orders of magnitude. Within the polymer foaming community, the discrepancy between the classical theory and experiments is sometimes attributed to the intervening heterogeneous nucleation or has led to modifications of the classical theory by incorporating certain aspects specific to the polymer foaming process. The essential content of the classical theory

as per the discussions of Lee and others [1,23–25] is as follows. The steady state nucleation rate, N_0 , is given by:

$$N_0 = C_0 f_0 \exp\left(-\frac{\Delta G_{\text{crit}}}{k_B T}\right) \quad (2)$$

where ΔG_{crit} , k_B , and T are the free energy of critical nucleus formation, the Boltzmann constant, and the absolute temperature, respectively. C_0 is the number of gas molecules dissolved per unit volume of the primary phase, and f_0 is a kinetic pre-exponential factor that is believed to be weakly dependent upon temperature. The presence of ΔG_{crit} in the exponent implies that it has a strong impact on foam quality. ΔG_{crit} is described as per Equation (3).

$$\Delta G_{\text{crit}} = \frac{16\pi\sigma^3}{3\Delta P^2} \quad (3)$$

ΔP is the difference between the pressure of the nucleating phase if it existed in bulk at the same temperature and chemical potential as the metastable phase, and the pressure of the metastable phase (created by imposing a thermodynamic instability on a stable polymer/gas solution). If the polymer is fully saturated with CO_2 and the partial molar volume of CO_2 in the polymer is zero, ΔP can be taken as the difference between pressures inside and outside the nucleating bubble or as the pressure drop required to induce nucleation ($P_{\text{initial}} - P_{\text{final}}$).

Nanoparticles serve as heterogeneous nucleation agents and their effect on cell density has been qualitatively described by the classical nucleation theory. For heterogeneous nucleation, the nucleation rate is expressed as:

$$N_1 = C_1 f_1 \exp\left(-\frac{\Delta G_{\text{crit}}^{\text{het}}}{k_B T}\right) \quad (4)$$

where f_1 is the frequency factor of gas molecules joining the nucleus and C_1 is the concentration of heterogeneous nucleation sites. The work of forming a critical nucleus in a heterogeneous system, $\Delta G_{\text{crit}}^{\text{het}}$, is considered proportional to the work in a homogeneous system (Equation 3) by a factor dependent on the contact angle θ between the gas and polymer and particle surface:

$$\Delta G_{\text{crit}}^{\text{het}} = \frac{16\pi\sigma^3}{3(PG - PL)^2} S(\theta) \quad (5)$$

$$S(\theta) = \left(\frac{1}{4}\right)(2 + \cos\theta)(1 - \cos\theta)^2 \quad (6)$$

In addition to the contact angle, the surface curvature of particles also plays an important role in the critical nucleation energy. The dependency of $\Delta G_{\text{crit}}^{\text{het}}$ on both the surface curvature and the contact angle can be described by Equation (7).

$$\Delta G_{\text{crit}}^{\text{het}} = \frac{16\pi\sigma^3}{3(P_G - P_L)^2} \frac{f(m,w)}{2} \quad (7)$$

The energy reduction factor, $f(m,w)$ is a function of θ and the relative curvature (w) of the nucleant surface (radius R) to the critical radius (r_{crit}) of the nucleated phase:

$$f(m,w) = 1 + \left(\frac{1-mw}{g}\right)^3 + w^3 \left[2 - 3\left(\frac{w-m}{g}\right) + \left(\frac{w-m}{g}\right)^3 \right] + 3mw^2 \left(\frac{w-m}{g} - 1\right) \quad (8)$$

$$m = \cos\theta, \quad w = \frac{R}{c_{\text{crit}}}, \quad r_{\text{crit}} = \frac{2\sigma}{P_G - P_L}, \quad g = (1 + w^2 - 2mw)^{1/2}$$

In heterogeneous nucleation, the highest nucleation efficiency is achieved when the nucleation on the nucleant surface is energetically favored (relative to its homogeneous counterpart) and the nucleant is 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. The potential nucleant density in a heterogeneous nucleation system can be estimated via Equation (9).

$$\frac{\text{nucleants}}{\text{cm}^3} = \frac{w}{\rho_P} \frac{\rho_{\text{blend}}}{V_P} \quad (9)$$

Here, w is the weight fraction of the particle in the composite, ρ_P is the density of the particle, ρ_{blend} is the density of the polymer blend, and V_P is the volume of the individual particle.

Non-uniform distribution of temperature, gas pressure, and gas concentration in polymer system, as well as a secondary nucleation process, can result in a broad cell size distribution because the cells do not generate simultaneously [21]. Therefore, shortening of the nucleation time interval is a main means to obtain narrow cell distribution in microcellular foams. An increase in cell nucleation rate obviously

decreases the time interval for nucleation process, and is expected to narrow the cell size distribution of the final foam. On the other hand, the heterogeneous nucleation induced by the nucleating agents, especially nano-scaled nucleating agents, decreases dramatically the energy-barrier for cell nucleation, increases the cell nucleation rate, and is expected to narrow the cell size distribution as well.

The application of SCF to the preparation of composites is through one of two approaches: *in-situ* polymerization of the dispersed phase in a SCF-swollen polymer matrix, or dispersive mixing of the nanoscale phase into the polymer matrix using the SCF to reduce the matrix viscosity and/or nucleate nanoscale bubbles in the material [26]. While the basic feasibility of the *in-situ* processes was demonstrated in the mid-1990s, recent work has concentrated on reducing the dispersed phase domain size and isolating the nanoscale features in the composite materials. In many of the applications discussed above the supercritical fluid acts primarily as a diluent/swelling agent for the polymer phase, solvent for monomers or reactants, and a blowing agent to produce foams. During the dispersion of nanoparticles in a polymer matrix, or during the formation of nanofoam bubbles, the viscosity of the polymer/gas system plays a pivotal role. As a result, increased attention has been given to understanding the rheological properties of polymer/gas melt or solution systems. In general, viscosity is observed to decrease as CO₂ is dissolved into various polymers. Once the nanometer-sized fillers are dispersed in the polymer matrix, the rheological behavior becomes more complex due to synergetic effect of nanofillers and CO₂. Another fundamental area relevant for nanocomposite research is the behavior of CO₂ confined in nanoscale systems. Recent results show that SCF (CO₂ in particular) exhibit unique behavior in nanoscale systems including pores and films. This behavior most often manifests itself near the critical point of CO₂ where the isothermal compressibility is at its highest.

SCF have received a great deal of attention and are currently being used as environmentally friendly solvents for a range of materials synthesis and process applications including polymerization, polymer purification and fractionation, coating applications, and powder formation. In general, SCFs offer mass transfer advantages over conventional organic solvents because of their 'gas-like' diffusivity, liquid-like density, low viscosity, and surface tension. In particular, supercritical carbon dioxide (scCO₂) has emerged as an important SCF due to its many desirable attributes such as low cost, abundance, low toxicity, and readily accessible supercritical conditions. One research effort [18] exploits the physicochemical properties of supercritical carbon

dioxide (scCO_2) to disperse and/or coat nanoclays for use in polymeric nanocomposites. Specifically, the ability of scCO_2 processing to delaminate CO_2 -philic nanoclays in their dry state is demonstrated and it is shown that the type of surface modification impacts the CO_2 -philicity of the nanoclay and hence the extent of delamination.

SELECTED RESEARCH ON NANOCOMPOSITE FOAMS

Crosslinked LDPE/hectorite nanocomposite closed-cell foams were prepared by a two-step compression-molding process and studied, focusing on their foaming behavior, and characterized in terms of final foam densities and expansion behavior, cell structure and crystalline characteristics [7]. Higher hectorite loadings resulted in more isometric foams in terms of the cell aspect ratio. The foamed nanocomposites underwent faster collapsing when compared to the pre-foamed, hectorite-free polyethylene foams, related to a lower crosslinking degree of the polymer matrix in the nanocomposites. The foaming process affects the delamination of the hectorite particles, helping to create a nanocomposite type of structure, but also exfoliation changes the morphology of the foams (cell size, distribution and shape), as well as their foaming behavior.

The use of CNFs as nucleating agents to produce polystyrene nanocomposite foams was demonstrated [2,3]. With the addition of CNFs, microcellular foams with uniform cell size distributions were obtained. Compared to nanoclay and single-walled carbon nanotubes (SWCNTs), CNFs exhibit substantially higher nucleation efficiency in the foaming process. The homogeneous fiber distribution and favorable surface and geometrical characteristics of CNFs make them ideal nucleating agents. The presence of a small amount of CNFs can significantly increase the cell densities and reduce the cell sizes. This may be due to its good dispersion in the polymer matrix, as well as the favorable wettability and surface curvature in this foaming process. It was found that, with a complete dispersion and favorable particle size and surface properties, an energy reduction of 99.7% 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 strong interactions between the clay surfaces and the polymer matrix lead to a deteriorated nucleation efficiency.

The typical process used to synthesize water expandable polystyrene was modified and applied to prepare water expandable polystyrene-clay nanocomposite [3]. The natural clay can be uniformly dispersed in water due to its hydrophilicity. The presence of water cavities significantly enlarges the cell size and leads to a foam product with ultra-low density (~ 0.03 g/cc) and low thermal conductivity. The addition of nanoclay can trap more water in the beads during synthesis and reduce the water loss during storage.

Polyurethane (PU)/montmorillonite (MMT) nanocomposites were synthesized with organically modified layered silicates (organoclays) by *in situ* polymerization and foams were prepared by a batch process [19]. The morphology and properties of PU nanocomposites and foams greatly depend on the functional groups of the organic modifiers, synthesis procedure, and molecular weight of polyols because of the chemical reactions and physical interactions involved. Silicate layers of organoclay can be exfoliated in the PU matrix by adding hydroxyl and organotin functional groups on the clay surface. The presence of clay results in an increase in cell density and a reduction of cell size compared to pure PU foam. Good dispersion of clays in the PU matrix has been achieved through the modification of MMT with active surfactants containing more than two hydroxyl groups. The presence of hydroxyl groups enhanced intra-gallery polymerization, which in turn led to better clay dispersion. Several advantages can be expected in using a PU nanocomposite as the matrix of PU foams. The presence of nanoparticles may improve the mechanical strength of the PU matrix and in turn the strength of the PU foam. Nanoscale-dispersed clay may act as nucleation agents during the foaming process to produce finer cell structure and higher cell density. With the inclusion of 5% functional organoclays, nanocomposite foams show a higher cell density with a smaller cell size. Depending on the chemical structure of polyurethane, as high as 650% increase in reduced compressive strength were observed in PU nanocomposite foam with relative low crosslinking density and urethane content but opposite effect was observed in PU nanocomposite foams with highly crosslinked structure and high urethane content.

Agglomerated nanoparticles act as defects and can have detrimental effect on polymer performances. The improved properties mainly depend on the fine dispersion of nanoparticles inside the matrix. The effects of different process parameters of sonication technique for the doping of CNFs into rigid polyurethane foam have been investigated [1]. Sonication time varies inversely with the power amplitude of the sonicator. Higher sonication time is required for higher weight percentage of nanoparticles with the total amount of material fixed.

Polymethylene polyphenylisocyanate (Part A) was mixed with nanoparticles such as SiC and TiO₂, and irradiated with a high power ultrasound liquid processor [4]. In the next step, the modified foams containing nanoparticles are mixed with Part B (containing polyol resin systems, surfactant, and an amine catalyst) through a high-speed mechanical stirrer. The foam cells are well ordered and uniform in size and shape. The TGA analyses indicate that the modified foams are thermally more stable than the parallel neat system. Quasi-static flexure tests under three-point bend configuration show a significant increase (approximately in the range of 50–70%) in the flexural strength and stiffness of the nanophased foams over the neat system. Gain in strength is attributed to the delay in the formation of initial cracks during loading. It is believed that nanoparticles embedded in the cell walls and edges and the associated interfaces surrounding the nanoparticles resist crack formation/coalescence at the earlier stage of the loading. Accordingly this allows higher sustainability of load.

Neat polycarbonate (PC) foam showed a quite broad distribution of cell sizes. Under the same foaming conditions, the addition of nano-silica resulted in PCSN foams having uniform cell size distribution, reduced cell size of 0.3–0.5 μm and increased cell density of 10¹¹–10¹³ cells/cm³. The heterogeneous nucleation of nano-silica aggregates dramatically increased the nucleation rate, decreased the nucleation time interval, and hence facilitated the almost instantaneous growth of cell size. Combined with the well-dispersed nucleation sites, resulted from the uniform dispersion of nano-silica aggregates, the narrow-distributed cell size was obtained in PCSN foams [21]. With cell size smaller than 10 μm, microcellular foams can reduce significantly the amount of plastics used while improve some mechanical properties, and may offer special properties which are not possessed by the conventional foams and the nonfoamed polymers. To obtain polymeric microcellular foam with desirable cell size, the process typically requires higher nucleation rates and higher inert gas concentrations than the conventional processes.

The foam processing of neat polylactide (PLA) and two different types of PLA-based nanocomposites has been conducted using supercritical carbon dioxide (CO₂) as a foaming agent [22]. The incorporation with nanoclay induced heterogeneous nucleation because of a lower activation energy barrier compared with homogeneous nucleation as revealed by the characterization of the interfacial tension between bubble and matrix. The grown cells having diameter of ~200 nm were localized along the dispersed nanoclay particles in the cell wall. The dispersed nanoclay particles acted as nucleating sites for cell formation and the cell growth occurs on the surfaces of the clays.

In vitro hydrolytic degradation behavior was examined for nanofibrous (NF) poly(L-lactic acid) (PLLA) foams prepared by phase separation. NF foams were incubated in phosphate-buffered saline at 37°C for 15 months. Upon removal, changes in mass, molar mass, morphology, BET specific surface area, mechanical properties, and thermal properties were compared with those of similarly incubated solid-walled (SW) PLLA foams. Initial surface area in NF foams was over 80 times higher than in SW foams [27]. These results suggest that the high surface area in NF foams accelerated the rate of hydrolytic degradation.

Synthetic biodegradable polymer matrix composites incorporating bioactive ceramic phases are being increasingly considered for use as tissue engineering scaffolds due to their improved physical, biological, and mechanical properties, as well as having the capacity for tailoring their structure and degradation rate to the specific need at the implant site. In general, scaffolds should have appropriate mechanical properties such as elastic constants, with values in a similar range to those of the tissues at the site of implantation. Much research is focused on the development of such porous bioactive and biodegradable composite scaffolds for the repair and regeneration of bone tissue. Among this group of materials, porous degradable polyglycolide, polylactide, or their co-polymers, are especially relevant for bone tissue engineering, with additions of inorganic particles or fibers, such as bioactive glass and hydroxyapatite to impart bioactivity and improve mechanical properties. TiO₂ nanoparticles have been recently proposed as attractive filler materials for biodegradable polymer matrices since they enhance cell attachment and proliferation on the composite surfaces. Poly(lactide-co-glycolide) (PLGA) foams and PLGA/titanium dioxide (TiO₂) nanoparticle-filled composite foams (porosity >90%) were produced by thermally induced solid-liquid phase separation and subsequent solvent sublimation. The scaffolds exhibit bimodal and anisotropic pore structures, with tubular macropores (~100 μm in diameter) interconnected by a network of micropores. A study of the collapse mechanism [28] of the foams porous structure revealed that when compressed in the main pore direction, the scaffolds failure mechanism involves an initial 'accommodation' of large regions of the porous structure, followed by the collapse of individual pores in different modes. An increase in storage modulus was observed with addition of 20 wt% TiO₂, with regard to the unfilled PLGA.

A novel biocomposite of nano-apatite (NA)/polyamide₆ (PA₆) was prepared with a co-solution method [29]. Molecular interaction and

chemical bonding existed between NA and PA₆, which greatly improved the mechanical properties and integrity of the composite. It was found that the composite with a high NA content (around 65%) has good homogeneity and mechanical strength, which are close to the natural bone.

The fabrication of gold/carbon nanocomposite foam by laser ablation of an organometallic gold salt was reported [30]. The produced material consists of gold nanoparticles diluted within nanostructured carbonaceous matrices, comprising both disordered carbon and graphitic structures. A new family of metal/carbon nanocomposite foam materials can be envisioned by employing the simple, versatile laser ablation technique described in this work.

Mesocellular carbon foams and ordered mesoporous carbon materials were synthesized from the direct carbonization of as-synthesized silica/triblock copolymer nanocomposites [31].

A nanostructured silver (Ag) catalyzed nickel foam cathode for an aluminum–hydrogen peroxide fuel cell was prepared using an electro-deposition technique [32]. The nanostructured silver catalyzed Ni foam cathode showed high catalytic activity and gave stable electrode performance. The electrode provides a high surface area in the catalyst layer and offers lower mass transport resistance, which is suitable for the application of Al–H₂O₂ fuel cell.

SCF have been used to synthesize and foam a variety of polymer nanocomposite materials [33]. *In situ* processes for producing nanocomposites apply a two-step procedure. Initially, the polymer substrates are infused with the precursor reactants dissolved in the SCF and then a reaction is induced (typically thermally) to generate a new dispersed phase. The SCF functions as a swelling agent for the polymer to enhance diffusion, a solvent for the precursor reactants and byproducts, and nonsolvent for the reaction products. The resulting nanoparticle or nanophase products are restrained from agglomerating by the polymeric continuous phase.

Nanoclay hybrid syntactic foams are developed for applications requiring high energy absorption and damage tolerance [34]. Four types of hollow glass particles with different densities and two volume fractions of nanoclay particles (2 and 5%, respectively) are used for fabrication. Results indicate that tensile strength increased upon the addition of nanoclay particles. Modulus decreased, which indicates a large increase in fracture strain and toughness of syntactic foams due to the presence of nanoclay particles. Presence of nanoclay particles plays a significant role in delaying crack initiation and growth, resulting in enhanced tensile strength and toughness.

The Center for Nanocomposites and Multifunctional Materials (CNCMM) is currently involved in the development of nanocomposite/syntactic foams for blast mitigation applications. CNCMM's blast mitigation systems are designed for structural integrity, toughness, ballistic penetration resistance, and flammability resistance. The nanocomposite foams [16] of this particular study are produced by casting, compression molding and vacuum infusion techniques. Materials used include marine laminating epoxy and vinyl ester resins, nanoclay and silicon carbide nanoparticles, and microspheres. System is cured at room temperature for 24 h, and post-cured at 100°C for 3 h. The nanocomposite matrices are prepared by dispersing the nanoparticles in the epoxy and vinyl ester resins via sonication at 35–65°C for 10–30 min. Experimental data indicate that higher density microspheres produce higher density foams, and higher density foams exhibit synergies in mechanical properties. Addition of silicon carbide nanoparticles also results in density increase. The 2% silicon carbide-S60HS microsphere-epoxy nanocomposite foams exhibit increases in impact strength over that of neat epoxy. These nanocomposite foams also show increases in stiffness and dimensional stability properties.

Figures 3, 4, and others (not shown) show the cone calorimetric flammability resistance properties of these nanocomposite foams. The epoxy nanocomposite foams exhibit much lower heat release rate (HRR) than neat epoxy; the S60HS syntactic foam shows a peak heat release

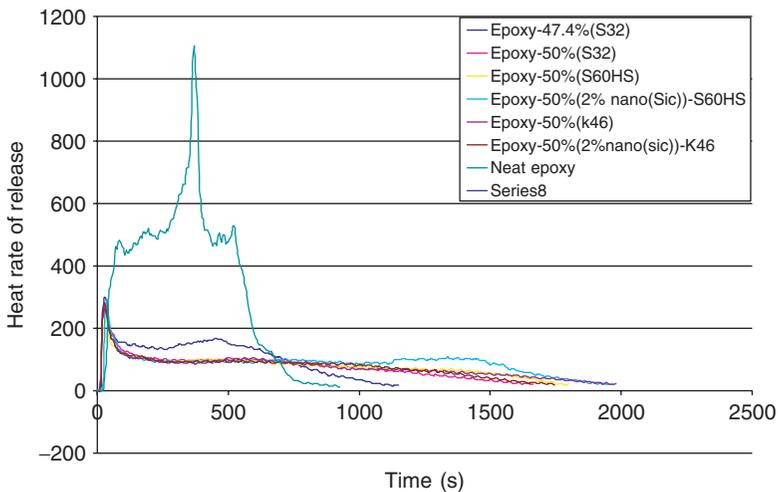


Figure 3. Cone calorimetry heat release rate data for epoxy-silicon carbide nanocomposite foams.

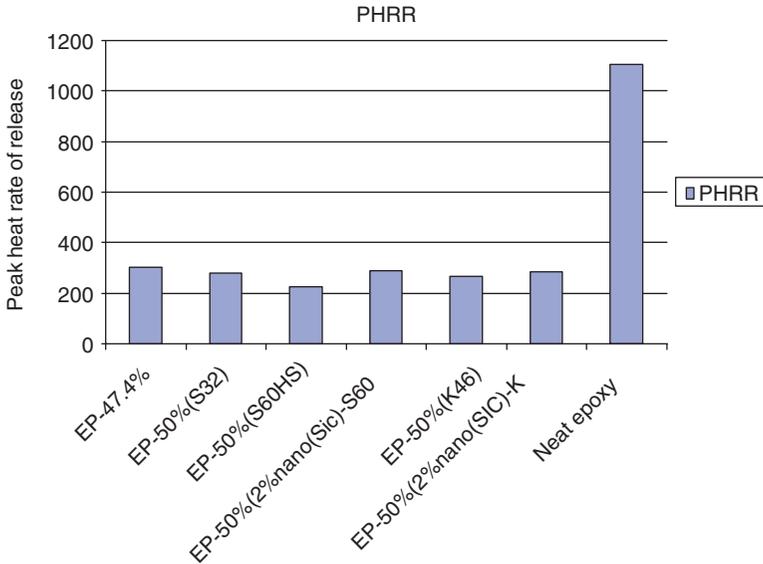


Figure 4. Peak heat release rate (Kw/m^2) of nanocomposite foams (as per Figure 3).

rate (PHRR) of 200 Kw/m^2 compared to 1100 Kw/m^2 for the neat epoxy. These and other cone calorimetric data such as mass loss rate (MLR), ignition time, effective heat of combustion (EHC) indicate enhanced flammability resistance properties for epoxy-silicon carbide nanocomposite foams.

CONCLUSIONS

Nanoparticles show great potential as reinforcement in nanocomposite foams for property enhancement. Enhanced thermo-mechanical properties of nanocomposite foams result from improved cell morphology that is mainly attributable to the role of nanoparticles as nucleation agents for bubble generation.

High-specific mechanical properties and multifunctional characteristics of nanocomposite foams make them cost-effective and desirable in a multitude of application areas including structural, energy-dissipating/absorbing, acoustical insulation, flammability resistance, and others.

The need for mass production of nanocomposite foams present challenges with regards to cost-effective processing techniques. Techniques for preparing exfoliated nanocomposite foams with required

cell morphologies, structural, flammability, and other properties must be developed, through the successful control of nucleation and growth of bubbles. Factors that affect the mechanical properties are sonication time, sonication power amplitude, amount of nanoparticles, foaming temperature etc.; these have to be controlled to attain optimum mechanical properties.

Of particular importance in this study of nanocomposite foams is the flammability resistance effect of nanoparticles in nanocomposite foams. The intumescent model (NIST, NMAB, and others) indicates that the flame barrier mechanism involves a high-performance carbonaceous-silicate char; this char build-up insulates the underlying material. Understanding this char build-up mechanism presents a challenge and area of research interest in the effort to develop new generation foams that are suitable in energy absorbing materials and structures.

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