Nucleation Effects of Nanoparticles on Microcellular Polystyrene Foams

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Introduction
Microcellular foams with cell sizes less than 10 µm and cell densities larger than $10^9$ cells/cm$^3$ [1] are gaining commercial importance as lightweight structural materials. The idea of introducing small bubbles in solid polymers was first proposed by Num P. Suh [2] in 1890s and the rationale was that if the bubbles are even smaller than the critical flaws in the polymer matrix and can be introduced in a sufficient number, the material density could be reduced while maintaining the essential mechanical properties. However, in order to drive the nucleation of a myriad of microcells, a high thermal insatiability is required, which in turn requires the stringent operation conditions such as high pressure, high pressure drop rate, and low foaming temperature [3, 4]. In this context, nucleating agents (nucleants) such as talc [5-6] are used to reduce the nucleation energy and produce microcellular foams under relative milder conditions. More recently, nanoparticles such as nanoclay have been studied as foaming nucleants as well. Compared to micro-sized nucleants, nanoparticles offer unique properties such as a high aspect ratio and large surface area, which are valuable for controlling both the foam structures and foam properties [7-15]. In this study, we explored the use of carbon nanofibers (CNFs) as the nucleants to produce polystyrene (PS) microcellular foams. Supercritical CO$_2$ was chosen as the blowing agent because it is low cost, non-toxic, non-flammable and environmentally benign. Considering different particle dispersion, surface curvature and surface energy, the nucleation efficiency of CNF was compared to that of nanoclay, which has been studied in our previous work.

In order to maximize the number of nucleating sites and minimize the occurrence of skewed cell morphologies, a uniform spatial distribution of nucleants is required. In this work, both high-shear mixing and ultrasonication were used to facilitate the dispersion of CNFs. PS nanocomposites were first prepared by means of in-situ polymerization. The resultant composites were foamed via the batch foaming process.

Experimental
CNFs (PR-24-PS) were supplied by Applied Science Inc. The average diameter of CNF is 100 nm. The original fiber length ranges from 30 to 100 µm. Styrene and 2,2'-azobis(isobutyronitrile) (AIBN) were purchased from Aldrich and used as received. PS (CX5197) was from AtoFina Petrochemicals.

Different amounts of CNFs were added to the styrene monomer, with AIBN as the initiator. The mixture was then shear-mixed for 3 minutes and sonicated for 30 minutes. Polymerization was carried out isothermally at 60°C for 20 hours and the composites were post-cured at 105°C for 2 hours.

PS/CNFs nanocomposites were foamed with supercritical CO$_2$ as the blowing agent via a batch foaming process. Samples were placed in a stainless steel vessel and CO$_2$ was delivered via a syringe pump. The system was allowed to equilibrate at 13.8 MPa and 120°C
for 24 hours. The pressure was rapidly released and the foam cells were fixed by cooling with a mixture of ice and water right after depressurization.

Particle dispersion in the polymer matrix was characterized by TEM. Images were obtained from a Phillips CM12 apparatus using an accelerating voltage of 80 kV. Samples were micromilled at room temperature with a diamond knife and mounted on a 200-mesh copper grid. The foam morphologies were characterized by 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 cell density.

**Results and Discussions**

A series of PS/CNF nanocomposites with CNF contents of 0.3, 1.0, and 1.5wt% were synthesized. These nanocomposites were subsequently foamed at 120°C and a CO₂ pressure of 13.8 MPa. The cell morphologies are depicted in Figures 1a-1c. Pure PS foam [7] (Figure 1e) synthesized at the same foaming conditions is shown for comparison. In the presence of only 0.3wt% CNFs, the cell density increased from $8.23 \times 10^7$ cells/cm$^3$ (pure PS foam) to $1.07 \times 10^9$ 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%, cell density increased to $2.61 \times 10^9$ cells/cm$^3$ and the cell size decreased to 6.2 µm. Further increasing the CNF content to 1.5 wt% yielded foams with the cell density of $4.59 \times 10^9$ cells/cm$^3$ and the cell size of 4.82 µm. All PS/CNF foams exhibit uniform cell size distribution. These results clearly indicate that CNFs serve well as heterogeneous nucleation agents during the foaming process. Moreover, the monotonic increase of cell density with increasing fiber content indicates that bubble nucleation is dominated by the heterogeneous mechanism with the addition of CNFs. 

Figure 1f shows a PS nanocomposite foam with 5wt% MHABS, a surface modified nanoclay leading to an exfoliated clay distribution (Figure 2a) prepared at the same foaming conditions [21]. Even with an exfoliated structure and a higher particle content, the cell density ($4.02 \times 10^8$ cells/cm$^3$) was still lower and the cell size (10.8 µm) higher than any of the PS/CNF foams attained in this study.
To minimize cell interactions and cell coalescences, a sparse and stable nucleant distribution is preferred. However, we noticed that in the early stage of polymerization, the system viscosity is not high enough to fix the fibers in separate locations. Thus, the CNFs are still inclined to attract each other, causing a reduced distance between individual fibers. Therefore, in Sample d, we added 10 wt% PS into the mixture of styrene/CNFs to achieve a higher initial viscosity. We also increased the initiator concentration from 0.5 to 0.75wt% to achieve a higher rate of viscosity increase. These two changes resulted in a sparser and more stable fiber suspension. Figure 2b is the transmission electron microscopy (TEM) image of the final nanocomposite (Sample d), which shows a complete dispersion of CNFs (the dark lines) in the PS matrix. The corresponding foam morphology is shown in Figure 1d. Compared to foam Sample b (Figure 1b), the cell density was increased from $2.61 \times 10^9$ to $2.78 \times 10^{10}$ cells/cm$^3$, while the cell size decreased from 6.2 to 2.64 µm. Considering the same nominal fiber content in these two samples, this dramatic change of the cell morphology may result from the improved fiber dispersion.

In heterogeneous nucleation, the highest nucleation efficiency can only be realized when the nucleation on the nucleant surface is energetically favored (relative to its homogeneous counterpart) and the nucleants are dispersible 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 a poor dispersion. Here we compare the nucleation efficiencies of CNF and exfoliated nanoclay from a simple analysis.

In the case of PS/CNF foam, the potential nucleant density with a complete fiber dispersion as shown in Figure 2b can be estimated by Equation 1:

$$\frac{\text{Nucleants}}{\text{cm}^3} = \frac{w \rho_{\text{blend}}}{\rho_{\text{CNF}} V_{\text{CNF}}}$$

where $w$ is the weight fraction of CNFs in the composite, $\rho_{\text{CNF}}$ is the density of CNF, $\rho_{\text{blend}}$ is the density of the PS/CNF blend and $V_{\text{CNF}}$ is the volume of the individual CNF. The potential nucleant density of PS composite containing 1wt% CNFs is $1.41 \times 10^{12}$/cm$^3$ according to equation (1). Experimentally, the cell density of the foam with the same fiber content is $2.78 \times 10^{10}$ cells/cm$^3$ (shown in Figure 1d). Similar calculations were conducted for PS/MHABS and the results are listed in Table 1. Comparing these two systems, the PS/CNFs system provides better nucleation efficiency. The proximity of the potential nucleant density and the final cell density indicates that most of the fibers effectively served as nucleants and there was no severe cell collapse. On the other hand, in the PS/clay system, there is a huge difference (five orders of magnitude) between these two numbers, implying that clay has lower nucleation efficiency compared to CNFs.
The reduction of nucleation energy on the particle surfaces was estimated using the classical heterogeneous nucleation theory. It shows that on the CNF surface, the energy is reduced by 99.7%, while on the clay (MHABS) surface it is only 30%. Furthermore, in a PS/clay system, although exfoliated, stacks of multiple clay layers are still observable. The effective number of nucleants is thus substantially lower than the calculated value. Consequently, for nanoclay, the combination of a higher energy barrier and a lower nucleant density results in a lower nucleation rate and ultimately a lower cell density.

Conclusions

We have demonstrated the use of CNFs as a highly efficient nucleating agent to form PS microcellular foams. A complete dispersion of CNFs in the PS matrix can be achieved by high-shear mixing and ultrasonication. The presence of a small amount CNFs significantly increases the cell density and reduces the cell size. For PS foams, such small cell sizes have not been reported before in either batch or continuous foaming process.

Reference


<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>wt%</th>
<th>Dispersion</th>
<th>Potential Nucleant density $^{[b]}$ ($#/cm^3$)</th>
<th>Measured cell density $^{[b]}$ ($#/cm^3$)</th>
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<tbody>
<tr>
<td>CNF</td>
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<td>Complete</td>
<td>1.41x10$^{12}$</td>
<td>2.78x10$^{10}$</td>
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<tr>
<td>Nanoclay</td>
<td>5</td>
<td>Exfoliated</td>
<td>5.45x10$^{13}$</td>
<td>4.02x10$^{8}$</td>
</tr>
</tbody>
</table>

$^{[a]}$ actual particle dispersion observed by TEM images  
$^{[b]}$ calculated (Eqn. 1) with the assumptions of complete particle dispersion and no cell bread-up or coalescence