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# Production of polystyrene-nanoclay nanocomposite foam and effect of nanoclay particles on foam cell size

P Saraeian, HR Tavakoli and A Ghassemi

## Abstract

This paper seeks to study the effect of nanoclay particles on polystyrene-nanoclay nanocomposite foam cells. In this study, first using a melt method, nanocomposites were injected into a mold in proportions of 4, 5 and 6% of nanoclay with a twin-screw extruder. To determine the distribution pattern of nanoclay particles in a polystyrene basis, X-ray diffraction and scanning electron microscope tests were conducted on the samples. To produce nanocomposite foam parts using mass foam process, first the samples were placed and maintained for 40 hours in a chamber pressurized to 60 bars. Removed and weighed, the samples were placed in a hot glycerin bath heated to 85, 95, 100 and 105°C. The foam samples were tested to measure the density and grain size using a scanning electron microscope. The results showed that proportions 4% and 5% of nanoclay caused an increase in density and a decrease in grain size. However, in the nanocomposite foam sample with a proportion of 6% nanoclay, there was a decrease in density and an increase in grain size due to accumulated nanoclay layers.

## Keywords

Nanocomposite foam, cell size, polystyrene-nanoclay

## Introduction

Plastics are materials that due to their unique properties have optimally replaced metals over the past decades. Among others, reference can be made to their light weight, low-cost of raw materials and easy formability. In recent years, too, to further reduce the weight, plastics have been replaced with their foams. However, in the process of foaming, plastics suffer from such problems as decreased strength and cell size control. Nowadays, using nanoparticles is a good way to overcome the above problems. Nanocomposite foam is applied to a class of foams where microcells are formed in the presence of reinforcing materials. For these foams, a neutral gas (i.e. nitrogen or carbon dioxide) or a chemical is used as a puffing agent.<sup>1</sup> Because of the limited cell size, the foams have better mechanical and physical properties, e.g. fatigue strength, impact strength, thermal properties and dielectric than non-foamed plastics. The advantage of microcellular nanocomposite foam over the current microcellular foams is the ease of control over the cell dimensions.<sup>2</sup> This is because the presence of nanoparticles slows down the growth of the cells; hence, the cell size is controlled with

less effort. Furthermore, addition of nanoparticles will not affect the physical properties; rather, it will enhance such properties as strength, processability and reduced flammability.<sup>3</sup> Polystyrene falls within the class of materials with a wide application in industry including insulation of buildings and roof blocks, food and beverage containers. Structurally, the material is amorphous softened at high temperatures. It is fully transparent, colorless and least resistant to sunlight.

## An overview of past works

The idea of formation of very tiny bubbles referred to as gas bubbling in plastics was introduced by Martini as a way to reduce the price of a large number of plastics.<sup>4</sup> Evidently, although this foam had a much higher strength than commonly used traditional foams, as

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the foam production method was not industrial in nature, it did not appeal to industries and was used on a laboratorial scale. Years later, microcellular with higher strength was first produced by extrusion. The method was not only economically and technologically justifiable but also appealed to academic circles.<sup>2</sup> Naturally, many a researcher sought to increase the strength of microcellular foam with partial success in this decade.<sup>5</sup> Nanoparticles have been used in different materials to reduce the cell size and increase the tensile strength.<sup>6</sup> Also, tests have been conducted on various nanoparticles including nanoclay particles, carbon nanotubes (CNTs), carbon nanofibers (CNFs) and metal nanoparticles which reportedly CNFs have produced the best results.<sup>7</sup> There are papers, too, on the production of polystyrene foam with nanoclay particles using in-situ polymerization and injection.<sup>8</sup> There are reports on using nanoparticles to use decomposable foams with delayed foam decomposition.<sup>9,10</sup> The aim of this study was to explore the possibility of producing nanocomposites foam using a mass method along with measuring the effect of the thermal parameter and proportion of nanoclay particles on the structure of the foam obtained. The difference between this and other past works lies in the method of producing nanocomposite and combination of nanoclay with polystyrene.

## Materials and equipment

Experimental tests at this stage fall into various categories: purchasing raw materials, producing nanocomposite granules, preparing nanocomposite samples, transmission electron microscopic (TEM) and X-ray diffraction (XRD) tests to ensure distribution of nanoclay particles in the nanocomposite basis, preparing nanocomposite foam, density measurement test and foam cell-size measurement, which will be discussed shortly. The materials needed for this study were polystyrene and nanoclay. The polystyrene was purchased from En-Chuan in Taiwan. The nanoclay needed for this study was obtained from Southern Clay in US on whose advice Cloisite 15A was selected for polystyrene.<sup>11</sup> Polystyrene contains non-polar molecules and can be said to be hydrophobic with no affinity to combine with hydrophilic materials. Moreover, nanoclay is a hydrophilic material; hence, it is very difficult for both materials to combine. A host of studies indicate that the polar interaction of polymer and clay surface plays a major role in the distribution and dispersion of nanoclay surfaces in the polymer basis. For most non-polar polymers, a polar compatibilizer such as maleic anhydride plays the major role in improving the polymer and clay compatibility. For this reason, as recommended by previous studies, a catalyst was used for this purpose.

Accordingly, polymethyl methacrylate (PMMA) was used for this purpose.<sup>12–15</sup>

## Experimentation

In this study, the stages of experimentation are drying nanoclay and polyamide granules in a vacuum oven heated to 80°C for 12 and 24 hours, respectively, mixing both materials in a twin-screw extruder, preparing nanocomposite granules, injecting nanocomposite, producing standard parts, XRD, SEM to learn about the nanocomposite morphology, density measurement test, preparing SEM images and measuring the cell size which will be addressed in detail in the ensuing sections.

### Production of nanocomposite granules

At this stage, polystyrene and nanoclay were dried by being placed and kept in an oven heated to 80°C for 24 and 12 hours respectively. A Brabender twin-screw extruder with a length-to-thickness ratio of 25 was used to mix nanoclay particles and polystyrene. To obtain nanocomposites with 4, 5 and 6% of nanoclay, first one kilogram of masterbatch with 10% nanoclay was prepared. To improve distribution of nanoclay PMMA was used as a compatibilizer. The proportions of polystyrene, nanoclay and PMMA within the nanocomposite were 900 grams polystyrene, 100 grams nanoclay and 100 grams PMMA, respectively. Then, to prepare nanocomposite, the samples with the above proportions were diluted with an adequate amount of polystyrene required. The temperature for the extruder was set at 180°C and the speed at 250 r/min.

### Preparation of nanocomposite sample using injection-molding machine

Nanocomposite granules produced to prepare parts for the production of mass foam, the granules should have been converted into standard parts. Hence, an injection mode was used to produce parts measuring  $3.4 \times 50 \times 10$  mm. The injection pressure within the injection equipment for production of samples was set at 30 bars and the temperature 220°C for nanocomposites with 4% and 5% nanoclay and the injection temperature was set at 230°C for the 6% nanocomposite sample.

### XRD test

To find out about the distribution of particles within the internal structure of nanocomposite, Phillips XRD equipment with a wavelength of 1.54 angstroms and a copper electrode capable of measuring the distribution

rate at angles 1–30 degrees with a speed of 0.04 degree per second was used. To ensure that the samples were good enough at the first stage, scanning was performed at low to 30 degree-angles and then repeated at zero to 5-degree angles. The results are shown in Figure 1.

### Preparation of nanocomposite foam

To prepare nanocomposite foam, the mass method was used. For this purpose, a chamber was used to store the samples at high pressure. The pressure within the carbon dioxide chamber was 60 bars and the following formula was used to compute the storage duration:<sup>16,17</sup>

$$t \approx \frac{h^2}{D}$$

where,  $h$  is the penetration depth (half the thickness of the part) in cm and  $D$  penetration coefficient in cc/s. Thus,  $t$  is obtained in seconds. Given the fact that the value of  $D$  for polystyrene and carbon dioxide is approximately 0.08 at a pressure of 50 megapascal and a thickness of 3.2 mm of the part, duration of 40 hours is obtained for the penetration of the gas into the sample. To determine the quantity of the gas absorbed by the samples before and after they were removed from the chamber, a precision scale made by Adam Equipment with an accuracy of 0.0001 gram was used to weigh the samples. Then, the samples were stored in a glycerin bath with a capacity of 1000 cc heated to temperatures 85, 95, 100 and 105°C for 60 seconds.

### Measuring the density of foam samples

Measuring the density of a part is illustrated by the following example. Assume that a vessel containing water with a density of  $\rho_w$  is placed on a precision scale. If an object with a mass of  $M_b$  and volume of  $V_b$  is submerged in the water in such a way that the entire surface of the object is covered by water, the scale will indicate the change in the mass  $\Delta M$ , which when the object is submerged equals the mass of the equal

volume of water of the object submerged. The density is calculated from the following formula by reading the change in the mass from the scale when the object has been submerged, the density of water determined and the mass of the samples calculated before submergence:

$$\rho_b = \frac{M_b}{V_b} = \frac{M_b}{\Delta M} \times \rho_w$$

### Measuring the cell size

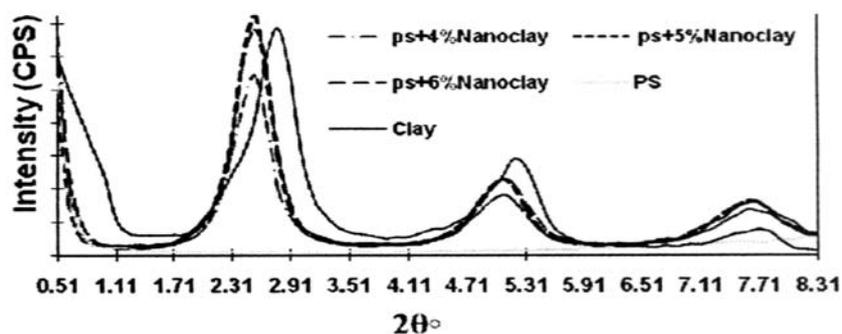
As the aim of this work was to measure the effect of the proportion of nanoclay particles on the cell size in nanocomposite foams, an SEM type XL30 made by Phillips in the Netherlands, was used to measure the mean cell size and some software was used to determine the number of cells per unit of volume. The cell size was determined by dividing each image into four zones and using some software, the size of each cell was measured in two directions of the largest and smallest diameter. The mean of the two measurements was taken as the average cell size. Finally, too, the mean cell size was determined for the zone and then the mean cell size was determined for the four zones. The findings are presented under the 'Findings'. It should be noted that for some images, particular images were measured to enhance the accuracy and assurance.

## Findings

The findings from the experiments conducted are presented in the following sections: the results of XRD, images studied by SEM and TEM, the quantity of gas absorbed by nanocomposite samples, density measurement and cell size measurement in nanocomposite foam presented with the test results subsequently.

### XRD findings

Prepared in various proportions of nanoclay, nanocomposite was subjected to XRD test; Figure 1



**Figure 1.** Results of X-ray diffraction (XRD) in samples of pure nanocomposite and pure polystyrene.

**Table 1.** Values of angles and interlaminar distances for various nanocomposites

Material description	Angle of first peak (in degrees)	Interlaminar distance (in angstroms)	Morphology
Nanoclay (Closite 15 A)	2.75	30	Blank
Nanocomposite with 4% weight of nanoclay	2.5	35	Interlaminar
Nanocomposite with 5% weight of nanoclay	2.55	34	Interlaminar
Nanocomposite with 6% weight of nanoclay	2.6	33	Interlaminar

**Table 2.** Proportion of gas absorbed by samples

Samples	Proportion of gas absorbed
Pure polystyrene	9.654
Polystyrene + 4% nanoclay	8.251
Polystyrene + 5% nanoclay	8.301
Polystyrene + 6% nanoclay	7.652

indicates the findings of XRD for polystyrene nanocomposite with improved proportions of clay as well as pure polystyrene and pure nanoclay (Closite 15 A). The peaks in the graph indicate the presence of nanoclay and the locus of the peaks indicates the distance between nanoclay surfaces. The rate of XRD distribution will not provide precise data on the sample behavior for it heavily depends on the quantity of the test sample. As seen in the figure, the clay has three distinct peaks. The first of the above three peaks for the approximate angle of  $2\theta = 2.75$  indicated the interlaminar distance of 30 angstroms. The second peak placed like a comb beside the first peak is at an interlaminar distance of  $2\theta = 5.2$  of 16 angstroms. This peak pertains to a group of montmorillonite silicate layers with imperfect corrective operations for the correction time has a great influence on the interlaminar distance. The third peak at an angle of  $2\theta = 7.7$  is at an interlaminar distance of 11.5 angstroms which pertains to the uncorrected clay layers. Hence, insertion of the string of polymer into the interlaminar distance was more difficult with less frequent separation. In Table 1, the interlaminar distance values pertaining to nanocomposites are presented. As can be seen, the greatest interlaminar distance occurs in nanocomposites of 4% nanoclay. The XRD results indicate increased interlaminar distance and development of an interlaminar structure. With a 5% increase in clay, a decrease in interlaminar distance occurs

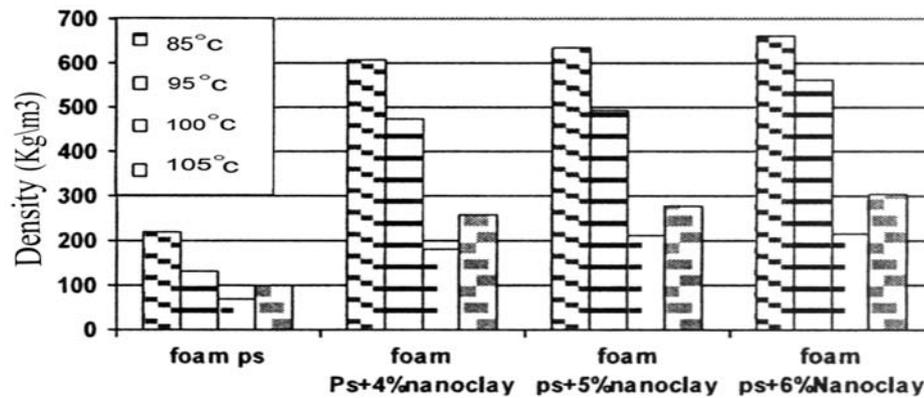
probably due to a decrease in polymer string inserted into the interlaminar distance. In nanocomposites with 6% clay, the interlaminar distance decreases.

### Findings on the quantity of gas absorbed by samples

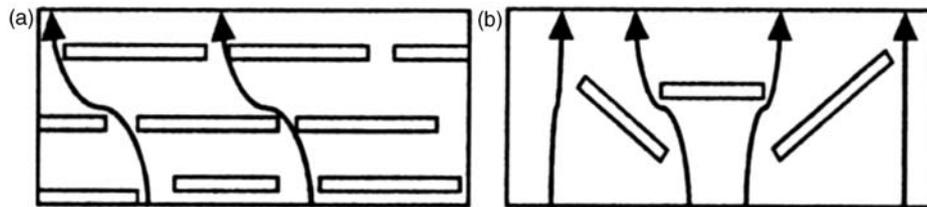
The quantity of gas absorbed by the samples while still in containers has a major influence on the volumetric expansion ratio of the foam. Also, nanoclay particles exert a major influence on the penetration factor. Hence, this section is devoted to the quantity of gas absorbed. As can be seen in Table 2, the largest quantity of gas absorbed is linked to pure polystyrene. With an increase in nanoclay, the quantity of gas absorbed in a given length of time and at a constant gas pressure is decreased and that the greatest decrease occurred in the sample with the largest proportion of nanoclay (6%). The reason for decreased gas absorption in nanocomposite samples can be traced to the nanoclay layers as a gas proof layer between strings that are shown in Figure 3. This property is evidently used as an advantage for production of nanocomposites to prevent against incoming and outgoing gases for certain packages such as those beverage bottles, packages for bread, food and dairy products. However, here it is used as an agent preventing gas penetration and foaming of samples. Evidently, viewed from another perspective, the phenomenon can be seen as an advantage in foam production for after the samples are removed from the containers and before they are placed in the hot oil bath, it seems that pure polystyrene lose their gas faster than nanoclay samples. If the rate of the gas escaping the samples is plotted against time, pure polystyrene loses gas at a faster rate and at a slower rate when nanoclay is increased.

### Findings for the density of nanocomposite foam samples

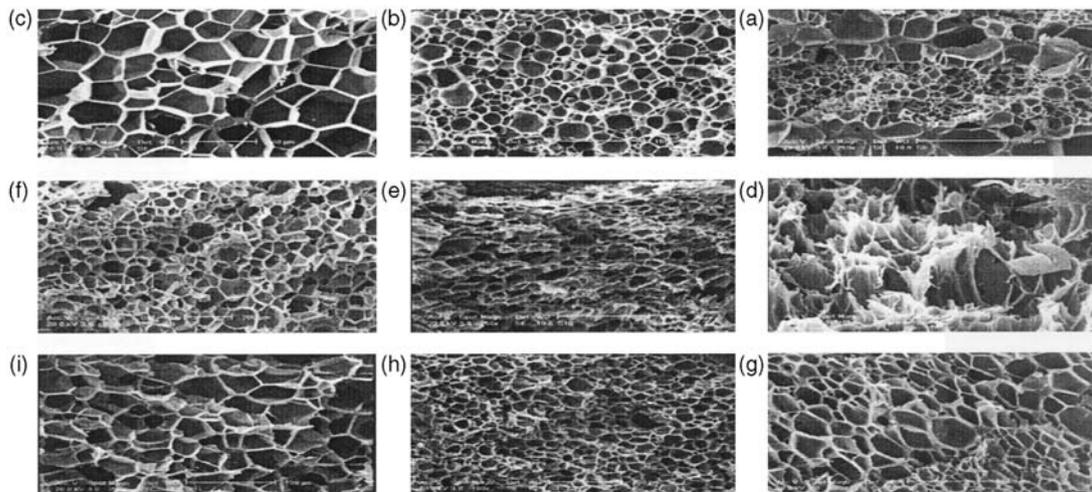
The findings from the measurement and comparison of the density of foamed nanocomposites with pure polystyrene foam are shown in Figure 2. As can be seen in the graph, the density observed at 100°C is minimal. The density of foam samples at 85°C is maximal, decreased with an increase in temperature such that it reaches minimum at 100°C. Then, at the higher temperature of 105°C, the density increases. It can also be seen that the density of nanocomposite samples compared to pure polystyrene foam is much higher even though for nanoclay samples with an increase in nanoclay weight the density increases and that samples with 4% nanoclay have a minimal density. As seen in the succeeding section, the size and density of cells vary widely. In nanocomposite samples, density increases due to decreased cell size.



**Figure 2.** Findings on the density of nanocomposite foam samples compared to pure polystyrene.



**Figure 3.** Effect of arrangement of nanoclay particles on the gas escaping the matrix.

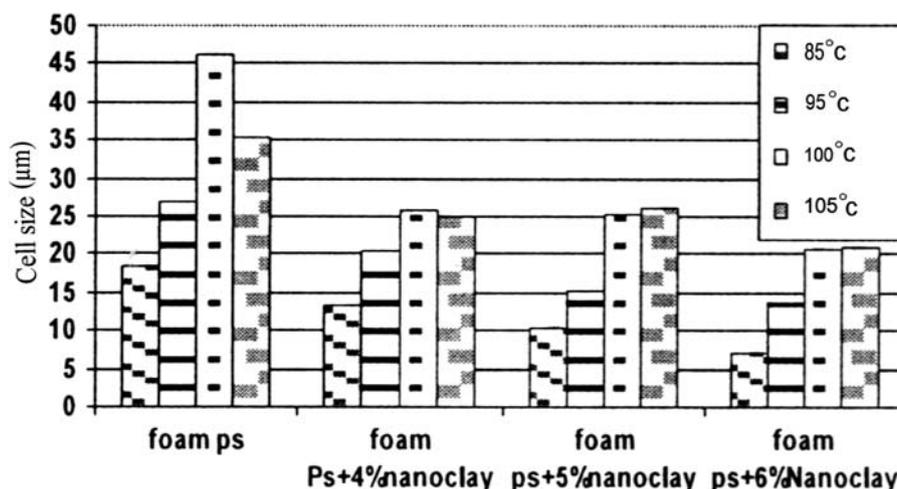


**Figure 4.** Scanning electron microscopy (SEM) images of nanocomposite foam samples (a, b, c, e, h, i = 100 X), (f = 200 X), (d = 20 X), (g = 50 X), (a, d and g, t = 95°C), (b, e and h, t = 100°C), (c, f, i, t = 105°C), (a, b, c = pure polystyrene foam), (d, e, f = 4% nanocomposite foam), (g, h, i = 5% nanocomposite foam).

### Findings of nanocomposite foam cell size

The findings from measurement of cell size and density are shown in Figure 4. Evidently as it was not possible to show the entire SEM images of nanocomposite foam and of pure polystyrene, in Figure 5, the cell sizes of samples are shown in microns at different temperatures.

As seen from the graph, the cell size decreases by adding in nanoclay. The decrease is due to the presence of nano surfaces and prevented penetration and development of cells. Evidently, the presence of nanoclay particles affects the thermal properties too, making changes to the softening temperature and consequently proportions of 5 and 6%.



**Figure 5.** Findings on the cell size of nanocomposite foam samples compared to pure polystyrene.

Obviously as seen from some figures, cell distribution is influenced by distribution of nanoclay particles and where nanoclay particles are not properly distributed, the cell size is affected. The presence of nanoclay particles in certain cases causes non-uniform distribution of the cells in samples such that in certain samples the cell size is much smaller than elsewhere. However, all the samples thus obtained are within the bounds of micro-foam cells. Evidently, in samples with 6% nanoclay, the particle size decreases further, but it is impossible to ensure their complete distribution. To ensure XRD test findings, TEM images were produced.

As seen in Figure 3, with an increase in temperature, the cell size increases due to softened matrix. Obviously this holds true up to a temperature of 100°C and at higher temperatures, as seen, the cell size decreases due to over-softening of the basis and the rapid gas escape from within the basis. Hence, at 105°C, the cell size begins to decrease.

## Discussion and conclusion

From the findings of this study, reference can be made to the influence of nanoclay particles on decreased cell size. Nanoclay particles also prevent entry and escape of gas and the duration for storage in the gas chamber for saturation must be altered. Further, the time for the gas to escape from nanocomposite samples is increased. Among other findings of this study, reference can be made to the influence of temperature on the cell size. Accordingly, as temperature increases, the number of cells emerged increases. Obviously, should the temperature exceed a given limit, as a consequence of the softening of matrix, the gas contained in the matrix escapes and the cell size decreases. Another finding is the way nanoclay particles are mixed with polystyrene matrix. As discussed earlier above, this material is

hydrophobic and reportedly difficult to mix. This problem can be overcome by re-mixing. Evidently, by allowing polystyrene to re-cross the extruder, the probability for failure of polymer string increases, damaging both the mechanical and thermal properties.

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## Conflict of interest

None declared.

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