Society of Plastics Engineers
PLASTICS RESEARCH ONLINE

10.1002/spepro.000047

Using chemical blowing agents to make microcellular nanocomposites

Miguel Angel Rodriguez-Perez, Paz Garcia, Juan Arevalo, Cristina Saiz, Eusebio Solorzano, and Jose Antonio de Saja

A novel experimental setup for producing foams offers the advantages of simplicity and improved properties over conventional means of fabrication.

Microcellular plastics are foamed polymers that are characterized by cell sizes averaging 100μm or less, and typically between 5 and 50μm.[1] Some of these materials have been shown to have high impact strength, high toughness, high fatigue, and lower thermal conductivity than solid polymers, as well as better properties than conventional foams.[2] Due to their unique properties, it is possible to imagine a broad range of applications for these materials: for instance, pipes with high stiffness yet lower weight and cost, or lightweight automotive and aeronautical parts.

Over the last two decades, a substantial amount of research and development has been devoted to microcellular foams.[3–5] They are currently produced using a process based on dissolving a gas, typically CO_2, in a polymer matrix at high pressure. A thermodynamic instability (triggered by a rapid pressure drop or a temperature increase) is generated to nucleate the gas phase (i.e., to start the bubbles). The main limitation of microcellular foams is the stringent processing conditions required to produce them (e.g., very high pressures, extremely high pressure-drop rates, processing temperatures close to that of the glass transition, and the dual challenges of getting microcellular foams from semicrystalline polymers and of obtaining high density reductions (more foaming).[6,7] This limits the operating window for extrusion and the attainable size of foam products, and has considerably hampered the introduction of these materials onto the mass market.

We describe an alternative route, called improved compression molding,[8] for producing foams with cells in the micro range. Our method is based on three main concepts. First, we use chemical blowing agents to initiate the gas phase. Second, the foam is produced under pressure using a simple setup that is amenable to experiments. Third, we employ multifunctional nanoadditives. These additives have several advantages. They act as nucleating agents for the cells (i.e., more cells are created), which makes it possible both to reduce cell size—since for a given amount of gas the cells are smaller—and to narrow the distribution of the sizes, making the foam more homogeneous. The additives also act as nucleating agents for the polymer crystals by modifying the structure of the base polymer. Finally, the additives improve polymer rheology (melt strength) and thermal and mechanical properties, which in turn enhances the stability and physical qualities of the foam. The result is a material produced using a simple setup that has better cellular structure and properties than conventional foams.

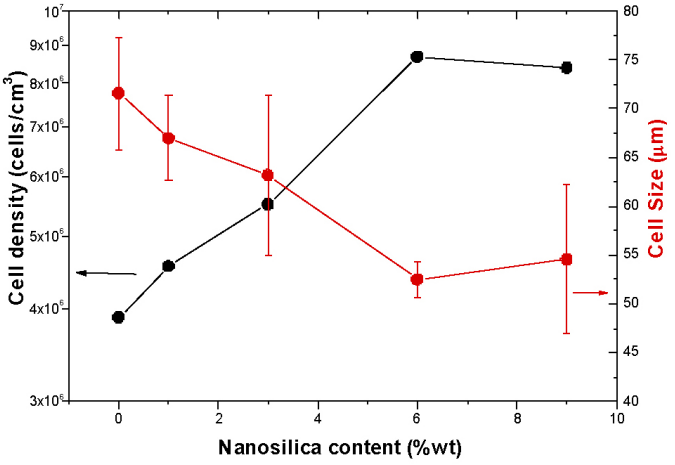

Figure 1. *Effect of nanosilica content on the cellular structure of the foam.*

To demonstrate our concepts, we chose a typical semicrystalline polymer—low-density polyethylene (Sabic LDPE 2404)— with nanosilica (Aerosil R-974 from Degussa) as an additive. The chemical blowing agent was a commercial grade of azodicarbonamide Uquifoam L (Uquinsa, Spain). A coupling agent (Fusabond MB-226DE from

Continued on next page

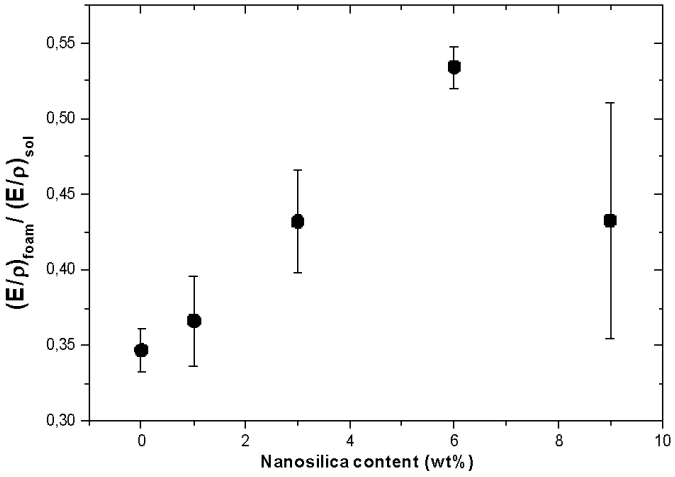

Figure 2. *Ratio between the relative Young's modulus of the foam and that of the continuous solid.*

Dupont) was also used in the formulations to promote adhesion between the polymer and the nanoparticles. The improved compression molding route described above was used to generate the foams, enabling cell sizes below 100μm and excellent control of density. In fact, density and cell size can be controlled independently.[8]

Figure 1 shows cell density and cell size as a function of the nanosilica content. A significant reduction of cell size was observed (about 26% for 6wt% of nanoparticles). Moreover, cell size dispersion (error bars in the figure) was narrower for this concentration of nanosilica. We concluded that this additive acts to reduce cell size during foaming, possibly due to a nucleating effect of the nanoparticles or to improvement in the polymer rheology. Figure 2 shows the ratio between relative Young's modulus (a measure of stiffness) of foams and solids versus nanosilica content. It is clear that the ratio increases with the concentration of nanoparticles up to 6%. We assume that there are two contributions to the result: first, the reinforcement offered by the nanoparticles, also observed in the solid, and second, modification of the cellular structure (see Figure 1), which affects the mechanical behavior of the material.

In summary, we have produced novel nanocomposite foams by combining functional nanoparticles and a controlled and homogeneous cellular structure using a simple setup conducive to experimentation. We have also shown the multifunctional role of nanoparticles in fabricating materials with improved properties compared with conventional foams and more easily than is typical for cell sizes in the micro range. As next steps, we intend to test our foaming method with other combinations of polymers and nanoparticles to more fully understand its potential.

Author Information

Miguel Angel Rodriguez-Perez, Paz Garcia, Juan Arevalo, Cristina Saiz, Eusebio Solorzano, and Jose Antonio de Saja
University of Valladolid
Valladolid, Spain

Miguel Angel Rodriguez Perez is an associate professor and the technical director of the Cellular Materials Group (CELLMAT) at the University of Valladolid. In the last 10 years, he has participated in 30 research projects in the field of foams and has published more than 70 scientific papers on the subject.

References

1. K. T. Okamoto, **Microcellular Processing**, Hanser Publishers, Munich, 2004.
2. C. B. Park, **Foam Extrusion: Principles and Practice**, ch. 11, Technology Publishing Company, 2000.
3. J. Colton and N. P. Suh, *Nucleation of microcellular thermoplastic foam with additives. Part I. Theoretical considerations*, **Polym. Eng. Sci. 27**, p. 485, 1987.
4. R. E. Murray, J. E. Weller, and V. Kumar, *Solid-state microcellular acrylonitrile-butadyne-styrene foams*, **Cell. Polym. 19**, pp. 413–426, 2000.
5. V. Kumar and J. E. Weller, *A process to produce microcellular PVC*, **Int'l. Polym. Proc. 8**, pp. 73–80, 1993.
6. C. P. Park, C. B. Baldwin, and N. P. Suh, *Effect of the pressure drop rate on cell nucleation in continuous processing of microcellular polymers*, **Polym. Eng. Sci. 35**, pp. 432–440, 1995.
7. X. Han, K. W. Koelling, D. L. Tomasko, and L. J. Lee, *Continuous microcellular polystyrene foam extrusion with supercritical CO_2*, **Polym. Eng. Sci. 42**, pp. 2094–2106, 2002.
8. M. A. Rodriguez-Perez, J. Lobos, C. A. Perez-Muñoz, J. A. de Saja, L. Gonzalez, and B. M. A. Del Carpio, *Mechanical behaviour at low strains of LDPE foams with cell sizes in the microcellular range: advantages of using these materials in structural elements*, **Cell. Polym. 27**, pp. 347–362, 2008.