Nr 10 (695—778) PAŹDZIERNIK 2006 Tom LI

POLIMERY

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII i PRZETWÓRSTWU POLIMERÓW

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Microcellular polymers and composites

Part I. TYPES OF FOAMING AGENTS AND TECHNOLOGIES OF MICROCELLULAR PROCESSING

Summary — In the review the principles of technology of microcellular polymers preparations were presented. The process consists of three steps: the bubbles nucleation, growth and stabilization. The examples physical foaming agents most often used such as carbon dioxide or nitrogen were given. Attention is paid to the fact that choice of foaming agent influences the structures of the foams obtained. An important group of chemical foaming agents, being organic or inorganic solid substances decomposing during the foaming process with carbon dioxide or nitrogen release, was also described. Three basic technologies used for microcellular materials preparation, *i.e.* MuCell (Fig. 1 and 2), Optifoam (Fig. 3) and ErgoCell (Fig. 4) were discussed in detail. The examples of applications of the materials prepared by the technologies mentioned above were given (Fig. 5—9).

Key words: microcellular polymers, microfoaming, physical foaming agents, chemical foaming agents.

POLIMERY I KOMPOZYTY MIKROPOROWATE. Cz. I. ŚRODKI SPIENIAJĄCE I TECHNOLOGIE MIKROPOROWACENIA

Streszczenie — W literaturowym przeglądzie omówiono podstawy technologii wytwarzania polimerów mikroporowatych. Proces ten składa się z trzech etapów polegających na zarodkowaniu powstawania pęcherzyków, ich wzrostu i stabilizacji. Podano przykłady najczęściej używanych fizycznych środków spieniających, takich jak ditlenek węgla i azot, zwracając uwagę na to, że wybór środka spieniającego ma wpływ na strukturę otrzymanych tworzyw mikroporowatych. Opisano także ważną grupę chemicznych środków spieniających, które są organicznymi lub nieorganicznymi substancjami stałymi rozkładającymi się podczas procesu mikroporowacenia z uwalnianiem ditlenku węgla i/lub azotu. Szczegółowo omówiono trzy podstawowe technologie stosowane do wytwarzania materiałów mikroporowatych, tj. MuCell (rys. 1 i 2), Optifoam (rys. 3) i ErgoCell (rys. 4). Przedstawiono przykłady użycia materiałów otrzymanych z zastosowaniem powyższych technologii (rys. 5—9).

Słowa kluczowe: polimery mikroporowate, mikroporowacenie, fizyczne środki spieniające, chemiczne środki spieniające.

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Microcellular polymers are closed cell plastic foams with a bubble densities in excess of 10^9 bubbles per cm^3 and cell diameters averaging 100 μm or less, typically between 5 to 50 μm in diameter, depending on the material and application. The idea to introduce very small bubbles in plastics by gas nucleation was originally advanced by professor Nam Suh at Massachusetts Institute of Technology. Introducing the idea to produce microcellular foams around 1980 as means to reduce the costs of many mass produced plastic items [1]. The rationale was that if bubbles smaller than the critical flaws that already exist in plastics could be introduced in sufficient numbers, then the material density could be reduced while maintaining the essential mechanical properties. The microscopic cell size and large number of cells in microcellular material can reduce material consumption as well as improve the thermodynamics, which results in quicker cycle times.

The fundamental principles of microcellular foam formation are bubble formation nucleation, bubble growth and bubble stability. The first step in foam producing is the formation of gas bubbles in a liquid system. If the bubbles are formed in an initially truly homogeneous liquid, the process is called 'self-nucleation'. If a second phase is initially present, especially if it is in the form of finely divided solids, the bubbles will usually form more easily at the liquid-solid interface: the bubbles are said to form by a 'nucleation processes'.

The classical work on bubble nucleation and growth, the pioneering modelling of the growth of a single gas bubble in a polymer matrix was carried out by Street et al. [2]. The latter authors introduced the concept of a finite influence volume around each bubble. They also considered the effects of heat, temperature, pressure, mass and mass transfer on bubble growth [3—17].

Colton and Suh [18—21] developed a nucleation theory for microcellular thermoplastic foam. Three possible mechanisms of the nucleation of gas in polymeric systems are considered: homogeneous, heterogeneous and mixed mode nucleation.

Typically, microcellular plastics exhibit high Charpy impact strength [23—32], high toughness [33—35], high fatigue life [36—38], high thermal stability [39, 40], high light reflectability, low dielectric constant and low thermal conductivity [41]. These improvements are due to the presence of bubble cells which inhibit crack propagation by blunting the crack tip and increasing the amount of energy needed to propagate the crack.

Microcellular plastics have unique processing characteristics [42]. The processing temperature is substantially lower than in case of the conventional processes because the viscosity of plastics is substantially reduced due to the presence of gas between polymeric molecules. The total rate of a given extruder can be also greater because of the low viscosity. The cycle time of injection moulding machines is also reduced because the processing temperature is lower and the phase separation of gas from polymer instantaneously increases the rigidity of plastics. Furthermore, there is reduced shrinkage of the injection-moulded part because it is compensated by the internal expansion in the microcells, creating parts with minimal residual stress and warpage. Certain properties of microcellular plastics, such as modulus and strength, follow the rule of mixture, whereas such properties as toughness and coefficient of thermal expansion do not. When the cell size is smaller than a few microns, the toughness of certain microcellular plastics should be equal to or better than the plastic without the cells. Small cells also lower the thermal conductivity when they are smaller than a critical size.

FOAMING AGENT

Physical foaming agent

Physical foaming agents are the materials that liberate gases as a result of physical processes (evaporation, desorption) at elevated temperature or reduced pressure. They do not undergo chemical transformation themselves and they are volatile liquids or compressed gases that are injected into the plastic matrix, and change state during processing to form a cellular structure. Physical foaming agents that have been reported [43] to be used in microcellular processing include water, argon, nitrogen and carbon dioxide. Nitrogen and carbon dioxide are by far the most widely used and the easiest to use [44—51].

Carbon dioxide is the most versatile physical foaming agent as it can be readily made supercritical starting from either the liquid or the gas state. A different pumping system is required to use carbon dioxide in the liquid or the gas state.

Nitrogen is the least expensive physical foaming agent to use but it can only be economically used starting from the gas state. Unless required for food, medical, or other potentially regulated uses, microcellular foam process requires nitrogen or carbon dioxide of only industrial grade or better quality.

However, the choice of foaming agent affects the microcellular structure that is obtained. Therefore, the choice between nitrogen and carbon dioxide should be made depending on what microcellular structure is desired rather than on ease of use or foaming agent costs.

Chemical foaming agent

Chemical foaming agents (CFA) are substances which decompose at processing temperatures thus liberating gases like CO_2 and/or nitrogen. Solid organic and inorganic substances are used as chemical foaming agents. The solid residues react as nucleation centres. This leads to a finer cell structure and a better solubility of the gas in the polymer melt. There are several different types of chemical foaming agents, which differ mostly in the type of gas that is generated and the type of reaction that generates the gas. The reaction that produces the gas can either absorb energy (endothermic) or release energy (exothermic).

Requirements to an ideal chemical foaming agent [52] are:

— decomposition reaction has to be in a defined temperature range, according to used polymer,

— avoid very fast reaction (explosion) by decomposition of the CFA,

— prevention of a heat build-up or burning,

— easy mixing and uniform dispersion of the CFA in the polymer,

— high gas yield and feasibility of the CFA,

— CFA should not be corrosive for tools,

— no discoloration and plate out of the polymer.

It has been proven [52] that chemical foaming agents will reduce the melt viscosity significantly. After the decomposition of the chemical foaming agent, the generated gas is dissolved in the polymer melt. At the high pressures in the extruder or injection moulding machine, the gas will stay in the polymer melt until the pressure drops at the die, therefore the chemical foaming agent acts as processing aid during the processing of plastic composites. After the profile exits the die the dissolved gas is decompressed and starts forming the cells. This leads to a weight reduction and improved workability of the profile. The chemical foaming agents influence the viscoelastic properties of the matrix and the cell morphology of foamed plastics in different manners, because of the differences in their thermal decomposition behaviors.

Generally chemical foaming agents are divided by their enthalpy of reaction into two groups that means exothermic and endothermic foaming agent. Nowadays, a combination of exothermic and endothermic chemical foaming agents is also used for the foaming. Mostly used exothermic chemical foaming agent is azodicarbonamide. Substances like sodium bicarbonate, citric acid and its salts are used as endothermic chemical foaming agents.

New findings have shown that azodicarbonamide decomposes into semicarbazide and it has weak carcinogenic activity in laboratory animals and weak genotoxicity. Due to these reasons, European Commission ruled the suspension of the use of azodicarbonamide as blowing agent to materials and articles intended to come into contact with foodstuffs [53] after August, 2005.

Endo/exothermic chemical foaming agent is a combination of endothermic and exothermic foaming agents. This newer development in the masterbatches, the advantages of the two groups are connected to improve further the foaming of the thermoplastics.

The foaming process is affected by some parameters such as polymer, processing temperature and application. There is no universal foaming agent for all applications. A certain polymer processing temperature needs a special decomposition temperature of the foaming agent. The different produced gases of the foaming agent must agree with the ideal of foamed polymer.

The form of a chemical foaming agent, which can be handled most simply, is the masterbatch (granules). These granules, which contain up to 70 % of foaming agent and a carrier polymer, show different advantages:

— increase in dispersion of the foaming agent,

— by a good compatibility of the carrier polymer, the distribution of CFA is improved.

The carrier system, which consists mainly of different polymers, provides optimal distribution of gas for a CFA. The softening point of these polymers, usually 80 to 100 ^{o}C, is thereby under the decomposition temperature of the chemical foaming agent. Further components of the carrier can be talcum powder, silicates and other inert solids, which act as nucleation agents and improve the fine cell distribution during process.

MICROCELLULAR PROCESSING

There are generally following technologies to produce microcellular foams with use of physical foaming agents [43]:

— MuCell by Trexel Inc. (USA),

— Optifoam by Sulzer Chemtech AG (Switzerland),

— ErgoCell by Demag (Germany).

The first method at all to produce microfoamed parts *via* microcellular injection molding technique was MuCell technology, developed in the early 1990s at Massachusetts Institute of Technology [1]. It consists of: creation of a single-phase solution, homogenous nucleation, cell growth and part formation [54]. As a processing technique and trade mark MuCell was marketed by Trexel Inc. (Woburn, MA, USA), and it is still worldwide the leading microfoaming technology.

An injection molding unit according to MuCell technology is shown in Figure 1. At the start of plasticising, the injector 1 opens and will continue to dose the supercritical fluid (SCF) for the length of the wiping section. Injector 1 is closed when the wiping section reaches the injector position. At this point the second injector is aligned with the start of the wiping section and is allowed to open. Injector 2 can dose SCF until the end of the wiping section reaches its position. This is the maximum screw position permitted for SCF dosing. The two phase solution of molten plastic and SCF will move into the mixing section of the screw where it is continuously divided and recombined by the dynamic mixing action of this section, until the SCF completely diffuses into the melt creating a single phase solution. The single phase solution preparation is the first of four main steps in the production of a microcellular injection molded foam structure. The other 3 steps, cell nucleation, cell growth and shaping take place during injection as the mold cavity is filled.

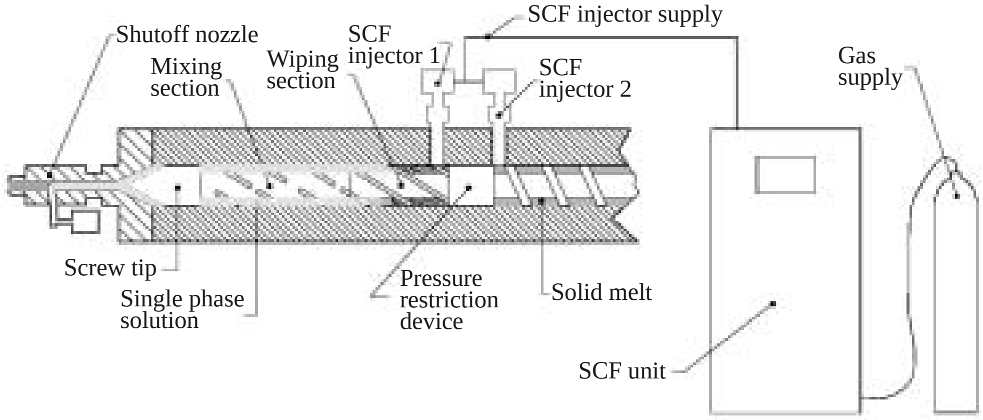

Fig. 1. MuCell injection molding system (according to [54], changed)

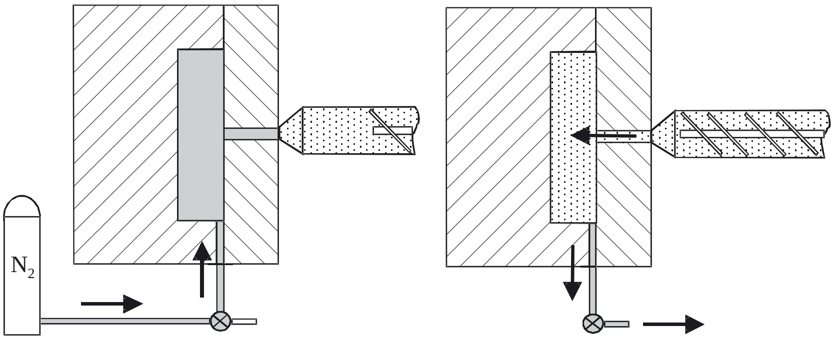

Fig. 2. Gas counter pressure process (GCP) (according to [55], changed)

Microfoaming can also have some disadvantages. The surface of resultant components is very often of inferior quality. Because of drifting of the fluid flowing out at the glaze front the polymer bubbles were destroyed by shear at the surface of the mold. However, the surface quality can be significantly improved by the gas counter pressure (GCP) process, presented in Figure 2 [32].

MuCell with gas counter pressure process (MuCell/GCP) developed by Institut für Werkstofftechnik, Universität Kassel in Germany gives visual differences in the surface quality: very smooth and glossy. An example can be the surface of polycarbonate samples produced by MuCell technology. The surface roughness (R_z) decreased from 23 µm to 0.85 µm by using of gas counter pressure process. Generally by GCP in the early injection phase some precise gas pressure — mostly N_2, is provided directly in a tool. This gas pressure prevented bubbles development at the surface during the injection. Microfoams produced by GCP technology exhibit the better mechanical properties like elongation at break in comparison with the conventional injection molding [55]. It is well known that microfoaming can significantly reduce the production cost. An economical analysis of the manufacture cost and amortization time for the MuCell technology has been presented [56, 57]. It has been proven that, dependent on clamping force and process parameters the amortization time and the investment themselves would be returned after about 2 years. To achieve a higher (more than 15 %) weight reduction of the parts, it is possible to combine the MuCell process with new technology so-called "precision opening". During this process the cavity of the mold is volumetrically filled and directly after injection enlarged to the desired part thickness [56].

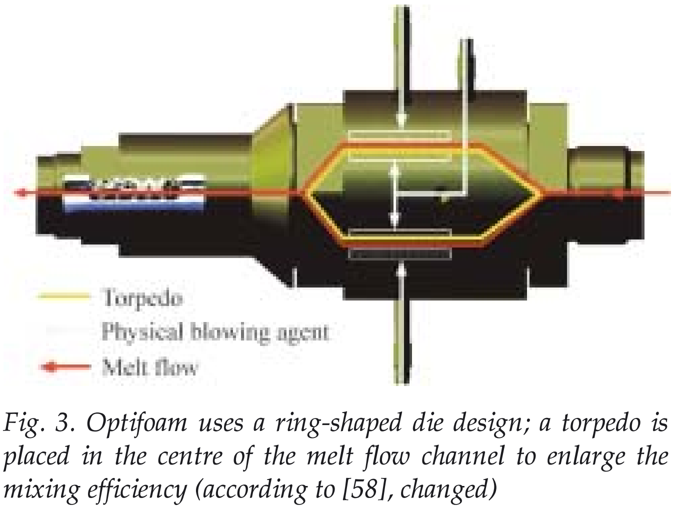

Fig. 3. Optifoam uses a ring-shaped die design; a torpedo is placed in the centre of the melt flow channel to enlarge the mixing efficiency (according to [58], changed)

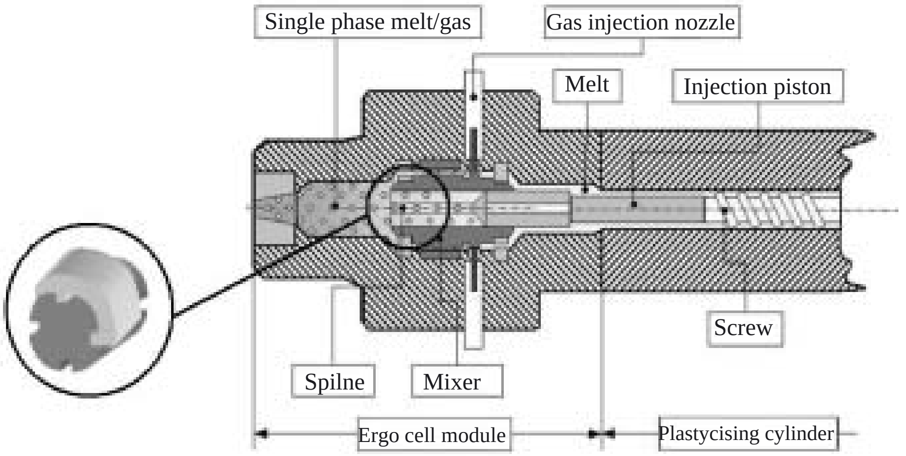

Fig. 4. ErgoCell — mixing and metering module (source: Demag Plastic Group Handout, changed)

The Sulzer Optifoam system, *i.e.* gas injection into the melt is much different in comparison with MuCell technology. The system mainly consists of a special nozzle, which is mounted between the plasticizing unit and the shut-off nozzle of a conventional injection molding machine, illustrated in Figure 3 [58—60]. In the Optifoam process the polymer is prepared in the plasticising unit in the same way as in a conventional compact molding. During the injection phase the melt fed through an additional annular flow channel manufactured from sintered steel. Through this special module the gas is introduced (usually CO_2) under pressure. The channel is narrow, just a couple of millimetres, and providing the gas with a very large surface area and short, diffusion length.

Demag Ergotech (Schwaig, Germany) has been pursuing in-house developments in the field of direct gas injection in 2001. The outcome has been a stand-alone solution that has been patented to Demag Ergotech and is being marketed under the name of ErgoCell. Analogical to Optifoam technology, the heart of the ErgoCell is an external module for gas metering and mixing to be installed upstream of a standard plasticising unit. This module enables homogenizing of the melt/gas mixture to be effected independent on plasticising. Apart from this module, the ErgoCell package comprises a hydraulic shut-off nozzle, full integration of its manipulation into the machine controller, and the gas station. A source of gas (*e.g.* carbon dioxide) is required in addition to the machine itself and can be provided *via e.g.* a bank of gas cylinders or a central supply system. An injection accumulator for dynamic and fast injection is recommended as additional equipment to realise the full efficiency of the process. As shown in Figure 4, the ErgoCell module consists of the following key components [61—63]:

— injection plunger (placed direct at screw),

— mixer (extern joined to the plunger, intern is built-in the casting of the module),

— gas nozzle.

The cycle sequences in the ErgoCell process basically correspond to the sequences in the standard injection molding process. The decisive difference is in the gas delivery which takes place simultaneously with plasticising. As the screw draws in, melts and delivers material into the space ahead of the screw and, in the process, is being pushed back against the back pressure, gas is fed into the melt from a gas metering station. In other words, the screw moves back at a speed that is a function of the plasticising capacity of the screw. Simultaneously, an amount of gas as preset by the operator is delivered into the melt. Demag has an arrangement with Trexel for ErgoCell users to pay a reduced license fee to Trexel [43].

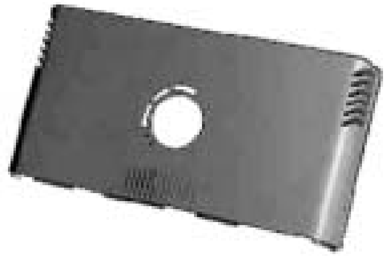

Fig. 5. LCD projector cover (source: MuCell Process News, 12, March 2005, changed)

Fig. 6. Microcellular PP (120 cm × 100 cm) transport palette (source: MuCell Process News, 12, March 2005, changed)

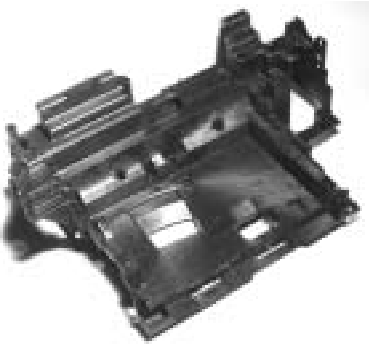

Fig. 7. Microcellular PC 20 % GF printer chassis produced using MuCell technology (source: [48], changed)

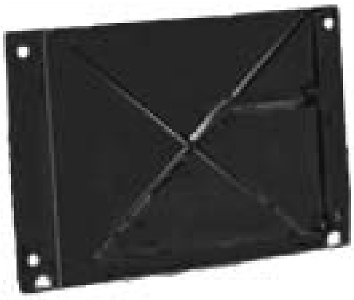

Fig. 8. Example of ABS battery tray (truck) produced using ErgoCell technology (source: Demag Plastic Group Handout, changed)

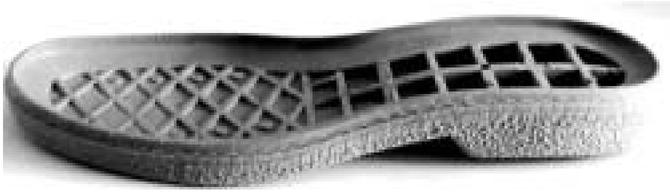

Fig. 9. TPU shoe soles injected by Optifoam system (source: Sulzer Technical Review 2/2004, changed)

Fig. 10. Example of microcellular PP panel, produced by MuCell precision opening (according to [56], changed)

Using the basic principles for microcellular processing developed at the Massachusetts Institute of Technology, chemical foaming agents and their concentrates have been modified to make thermoplastic microcellular molded parts. The chemical foaming agents manufacturers have started producing the chemical foaming agents and their concentrates in uniform fine particle sizes for better dispersion and more homogeneous decomposition of the chemical foaming agent itself. Additionally, the chemical foaming agents and their concentrates have been formulated to decompose into carbon dioxide or nitrogen at lower temperatures to generate a molten polymer/foaming agent single-phase solution prior to injection into a mold, much like the MuCell process.

Microcellular processing of thermoplastic materials found rapidly industry acceptance and it is now used to make the products for automotive, electronic and other demanding end-use applications. Some examples of applications of microcellular injection molded parts are shown in Figure 5—10.

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Received 8 III 2006.