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Mathematical models and numerical simulations of a thermally expandable microballoon for plastic foaming

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HIGHLIGHTS

- A mathematical model of polymeric microballoon was developed to simulate the expansion behavior of a microballoon in air and in a polymer matrix.
- The viscoelastic properties of polymeric microballoon were taken into account in the model.
- The developed model showed quite good agreement with the observed thermal expansion behavior of a microballoon.

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ABSTRACT

Thermally expandable microcapsules, often called microspheres or microballoons, are utilized in compression, injection molding and extrusion processes to foam different types of polymers. Microballoons consist of a polymer shell and a liquid hydrocarbon core. Hydrocarbons are used as a physical blowing agent. In this study, a mathematical model was developed to describe the expansion behavior of a microballoon in air and in a polymer matrix. The model was used to determine the key factors in improving the expandability of the balloon at designated temperatures. The viscoelastic properties of the polymer shell, evaporation of hydrocarbons in the balloon and diffusion behavior of the blowing agent through the polymer shell were taken into account in the model. The results of the developed model showed quite good agreement with the experimentally observed thermal expansion behavior of a microballoon. A sensitivity analysis of the expansion behavior with respect to the properties of the microballoon was also conducted to devise an optimal design strategy for high-expansion microballoons.

1. Introduction

Recently, requirements for further reducing the weight of plastic parts, especially automotive parts for mileage improvement, have been established. Plastic parts other than those used in the automotive industry also require a reduction in weight without deteriorating their mechanical properties and appearance. Polymer foaming is one of the most promising techniques for realizing weight reduction. Polymer foaming methods can be roughly divided into two groups: chemical foaming and physical foaming. Chemical foaming uses chemicals that release gas, such as carbon dioxide (CO_2) and nitrogen (N_2), by thermal decomposition. The released gas dissolves into the polymer or directly leads to bubble expansion and the formation of a cellular structure. Physical foaming does not involve any chemical reaction. It simply uses butane, pentane, CO_2 or N_2 as a blowing agent.

Thermally expandable microballoons are used in physical foaming, in which polymeric capsules are used to foam polymers. A low-boiling-point hydrocarbon liquid, such as octane or pentane, is encapsulated by a polymeric shell. By mixing microballoons with a thermoplastic polymer and allowing them to thermally expand, the polymers can be foamed. When microballoons are heated, they expand to 50–100 times their initial volumes.

The polymeric microballoon was originally developed by Dow Chemical Co. (Morehouse and Tetreault, 1964) and has been advanced by others (Lundqvist, 1992; Yokomizo et al., 1997). Nowadays, microballoons are available in a variety of grades (Jonsson, 2006), and have been used in car parts (Mae, 2008a, 2008b), shoe sole production, vinyl plastisol formulations (Ahmad, 2001), as well as the rotational molding of linear low-density polyethylene and ethylene-vinyl acetate (Takacs et al., 2002; D'Agostino et al., 2003). Even though there a large number of patents and application reports have been issued, scientific papers, which discussed the synthesis and properties of the microballoon, have been still limited. In the early stage, the researches on

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polymeric microballoons were directed to the investigations of the effects of the existing microballoons on mechanical property of the foam (Lawrence et al., 2001; Mae, 2008a, 2008b; Gupta and Woldensenbet, 2004). Recently, some papers related to synthesis and expandability of the balloons (Kawaguchi and Oishi, 2004; Kawaguchi et al., 2005) developed a thermally expandable microballoon for foaming polypropylene (PP) that required high processing temperatures above 200 °C. This temperature range cannot be accommodated by conventional thermally expandable microcapsules. Jonsson et al. (2009, 2010) synthesized the microballoons and investigated the relation among their expandability, balloon size and the structure of crosslinker. Kawaguchi et al. (2010, 2011) consecutively investigated the expansion behavior of a conventional microballoon by visual inspection and developed a mathematical model for designing a new type of capsule. Their model consisted of Newtonian constitutive equation and equations for the diffusion and evaporation of the blowing agent. The model shows fairly good but not complete agreement with experimental data. In particular, the elastic behavior of the balloon could not be simulated by the researchers' model.

In this study, the microballoon model was re-designed by considering the viscoelastic behavior of the shell to improve the predictability of the microballoon's expansion behavior both in air (free expansion) and in a polymer matrix.

2. Mathematical models of microballoon

2.1. Assumption for model development

A mathematical model was developed to describe the expansion behavior of a microballoon both in air and in a polymer matrix. It was considered that the expansion behavior comprises three basic phenomena: (1) deformation (expansion) of the polymeric shell, (2) evaporation of the liquid hydrocarbon blowing agent and establishment of a vapor pressure in the microballoon and (3) diffusion of the hydrocarbon blowing agent from the inside to the outside of the balloon.

Microscopy images of a microballoon before and after expansion are illustrated in Fig. 1. From these images, a simple microballoon structure was constructed to have three major components: (1) a polymeric shell (outer layer), (2) a hydrocarbon liquid layer (middle layer) and (3) a hydrocarbon gas phase (inner layer), as illustrated in Fig. 2.

To develop a microballoon model, the following assumptions were made for the abovementioned microballoon structure:

(a) The balloon expands uniformly along the radial direction. In other words, the radius of the balloon changes while maintaining the balloon's spherical shape.

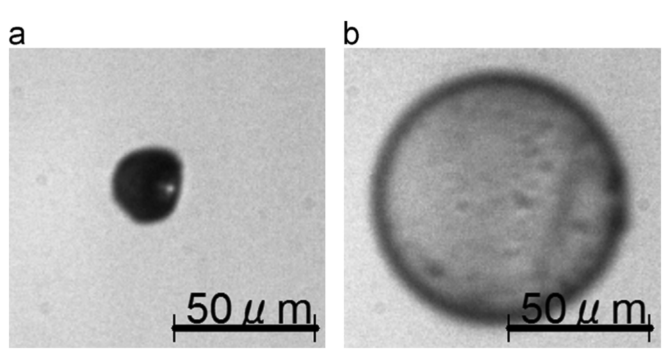

Fig. 1. Microscopic images of microballoon (a) before expansion and (b) after foaming.

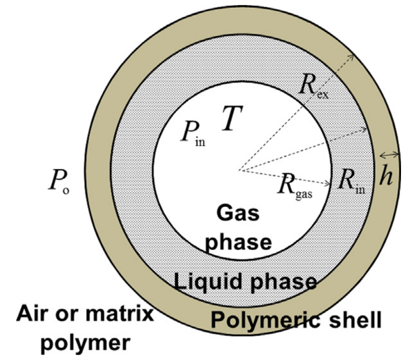

Fig. 2. Schematic structure of microballoon.

(b) The polymeric shell is deformed uniformly along the radial direction only without any degradation (reactions) or breakup. The polymer properties are not altered by expansion.
(c) The change in the density of the polymer shell with temperature is negligible.
(d) The heat transfer in the balloon is so fast that the temperature of the balloon can be considered to be uniform and equal to the temperature of the surrounding media.
(e) The effect of inertia on the deformation and fluidization of the polymeric shell is negligible because of the low Reynolds number: because the radius of the balloon is several micrometers and the viscosity of polymer is high, the Reynolds number could be considered to be low.
(f) There is no stress distribution in the polymer shell. The stress in the shell is uniform.
(g) The shell polymer and the matrix polymer are viscoelastic and incompressible.
(h) The blowing agents satisfy the ideal gas law.
(i) The permeability of the liquid in the shell polymer is negligible compared with that of the gas. Only the permeability of the gaseous blowing agent in the shell polymer is considered.
(j) The driving force of the permeability of the gas in the polymeric shell is governed by the difference in the partial pressures of the blowing agent inside and outside of the balloon.

With these assumptions, three basic equations, i.e., an equation of continuity, a momentum balance equation and the material balance equation of the blowing agent, were developed using a constitutive viscoelastic equation and the ideal gas law.

2.2. Model equations of free expansion in air

In the developmental stage of a microballoon, the expandability of the microballoon is experimentally tested in free-expansion mode: a specified number of microballoons are placed in a temperature-controlled transparent vessel, the vessel is heated to expand the balloons at a given temperature under atmospheric pressure and the volumetric change before and after expansion is measured. Therefore, we first developed a model of an isolated microballoon suspended in air to describe the expansion behavior during the course of heating.

2.2.1. Equation of continuity

With the assumption of the incompressibility of the shell polymer (g), the equation of continuity of the polymer is given by

$$\nabla \cdot \mathbf{v} = 0 \tag{1}$$