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Water expandable polystyrene (WEPS)
Part 3. Expansion behaviour

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Abstract

In Part 1 (Polymer 1999;40:3685) of this series, the concept for the preparation of expandable polystyrene (PS) applying water as a blowing agent was presented. This paper focuses on the expansion characteristics of water expandable polystyrene (WEPS) beads. The influence of temperature, amount of blowing agent, molar mass of the PS matrix and slight crosslinking of the matrix were investigated in view of the expansion performance in hot air. A maximum volume expansion by a factor of 25 was achieved for WEPS in hot air (135°C) as the heating medium. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Expandable polystyrene; Water; Blowing agent

1. Introduction

In our previous studies, we introduced the concept for the preparation of water expandable polystyrene (WEPS) [1] via the partial polymerisation of the continuous phase of an inverse emulsion (water-in-styrene) followed by a suspension polymerisation, up to complete conversion, of the prepolymerised mixture. Moreover, a novel route for the in-situ preparation of (block)copolymer surfactants possessing an enhanced compatibility with the matrix, compared with the tested, commercially available surfactants, was introduced in order to improve the stability of the inverse emulsion during polymerisation [2]. This paper focuses on the expansion characteristics of EPS beads containing water as a blowing agent.

Conventional EPS typically contains 7–8 wt.% of pentane isomers (mainly *n*-pentane and iso-pentane) as the physical blowing agent [3]. This blowing agent is capable of expanding the compact PS beads upon heating the material above its glass transition temperature (T_g). The vapour pressure of the blowing agent forces the softened PS matrix to expand and a homogeneous cellular structure with irregular polyhedral-shaped closed cells is formed [4]. The cell size can be regulated between 50 and 750 μm by means of the expansion time and nucleating agents.

Some essential differences in expansion behaviour can be expected for WEPS with respect to conventional EPS. Due to the incompatibility of water and PS, the blowing agent of WEPS is located in discrete pools, entrapped by the PS matrix. The size distribution and number of these pools can be assumed to determine the dimensions of the final foam cells. The use of a nucleating agent is redundant for WEPS since the droplets themselves initiate cell growth. Another distinction of water as a blowing agent, is its low molar mass with respect to pentane, 18 versus 72 g mol^{-1}. This results in a theoretical maximum expansion which is four times higher compared with EPS expanded by pentane with the same amount of blowing agent at the same temperature. These differences can be considered advantageous. However, water also possesses some intrinsic disadvantages as a blowing agent for PS. The expansion process, as applied for conventional EPS with saturated steam as heating medium, cannot be applied for WEPS because identical pressures inside and outside the beads would exist in this case. Furthermore, due to the very quick diffusion of water through PS [5], a substantial fraction of the blowing agent will permeate out of the beads during the period of expansion. Finally, the relatively high boiling point of water requires a relatively high expansion temperature in order to generate sufficient vapour pressure inside the beads. Moreover, since the T_g of PS is equal to the condensation temperature of water at atmospheric pressure, an increased risk of foam collapse can be expected during cooling of the foam. It is anticipated that these disadvantages are (partly)

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Table 1
Compositions of grade A DBPO dibenzoylperoxide; TBPB, *tert*-butylperoxybenzoate; AOT, sodium bis(2-ethylhexyl)sulfosuccinate

Sample grade number	DBPO (wt.% S)	TBPB (wt.% S)	AOT (wt.%)	Emulsified water (wt.%)	Incorporated water (wt.%)	$M_{w,PS}$ (kg mol^{-1})
A-1	0.4	0.15	0.2	2.0	3.2	183
A-2	0.4	0.15	0.4	4.0	7.1	180
A-3	0.4	0.15	0.5	5.0	7.9	179
A-4	0.4	0.15	0.6	6.0	8.6	174
A-5	0.4	0.15	0.8	8.0	9.3	174
A-6	0.4	0.15	1.0	10.0	11.3	186

compensated by the high theoretical maximum expansion of WEPS (as a result of the low molar mass of water).

The expansion behaviour of WEPS samples containing different contents of blowing agent is evaluated at different temperatures and exposure times in this paper.

2. Experimental

2.1. Materials

The WEPS grades that were applied for expansion experiments are listed in Tables 1 and 2 together with the most important characteristics (incorporated water content, molar mass and additives). These grades are prepared according to the procedures described in Part 1 [1] (grade A) and Part 2 [2] (grade B) of this series. $M_{w,PS}$ represents the weight average molar mass of the PS fraction soluble in tetrahydrofuran.

2.2. Expansion in hot air

Expansion of WEPS beads was performed with hot air as the heating medium. Laboratory-scale equipment was constructed from a 500 ml three-necked flask and a hot air gun (BOSCH PHG 630-2 LCE). Hot air was introduced from the hot air gun in the flask through a silicone tube. A magnetic stirrer was attached to the tube in order to induce rotation of the tube, resulting in a homogeneous temperature profile in the flask. The temperature inside the flask was measured by a thermocouple. The inlet was connected to a pressurised air tap, which enabled quenching of the WEPS beads and simultaneous removal through the outlet. This resulted in an apparatus possessing the characteristics of good heat exchange, small temperature deviations, good control of exposure time and the possibility of quenching.

After equilibrating at the desired temperature for 30 min, expansion measurements could be executed. A sieve fraction of 1.70–2.00 mm beads was used. The initial diameter of an individual bead (d_0) was measured with an accuracy of ± 0.01 mm and the bead was introduced into the flask through the inlet. After the desired exposure time to the hot air, which was measured with a stopwatch, the flask was flushed with a cold air flow and the bead was transported out of it and quenched at the same time. Finally, the diameter of the expanded bead (d_e) was measured (accuracy, ± 0.05 mm) and the expansion ratio (ϵ) was calculated by:

$$\epsilon = V_e/V_0 = (d_e/d_0)^3$$

The average expansion ratio was determined from five measurements at each exposure time.

2.3. Characterisation by scanning electron microscopy

The morphology of both compact and expanded samples was investigated by scanning electron microscopy (SEM). Micrographs were made of fractured or cut surfaces, with a

Table 2
Composition of grade B SSS, sodium styrene sulphonate; PTC, phase transfer catalyst; TOMAC, trioctylmethylammonium chloride

Sample grade number	SSS (wt.%)	PTC type	PTC (mol% SSS)	Emulsified water (wt.%)	Incorporated water (wt.%)	$M_{w,PS}$ (kg mol^{-1})
B-1	1.0	TOMAC	10	10.0	13.6	189

Cambridge Stereoscan 200 microscope operating at 20 kV. Compact samples were fractured at liquid nitrogen temperature and the expanded samples were cut with a razor blade. Subsequently, the samples were coated with a gold layer.

3. Results and discussion

3.1. Expansion characteristics of WEPS

WEPS samples containing different contents of blowing agent and possessing comparable droplet sizes were expanded in hot air. The weight average molar mass of the different samples was approximately 180 kg mol^{-1} (see Table 1). In Fig. 1, the expansion ratio of samples A-1 and A-5 containing, respectively, 3.2 and 9.3 wt.% of blowing agent is shown versus the exposure time in hot air of 130°C.

Both samples show a different expansion behaviour to conventional EPS with pentane as the blowing agent. During the expansion process of WEPS, three different stages can be distinguished: a period of induction, expansion up to maximum expansion, and collapse. During the induction period, the material is heated, but the temperature is too low to build up sufficient vapour pressure and to soften the PS matrix enough for expansion. However, the content of blowing agent is reduced during this induction period due to the high diffusion rate of water through PS [5]. This was observed by thermogravimetric analysis measurements which show that a complete depletion of blowing agent can take place within a few minutes (depending on the temperature and content of blowing agent).

Subsequent to the induction period, fast expansion takes place as soon as the water vapour pressure exceeds the retractive forces of the softened PS matrix. A quite simultaneous initiation of cell growth throughout the complete bead seems to take place after the induction period, as can be observed from SEM micrographs at different stages during the expansion process (see Fig. 2). In Fig. 2(a), the morphology of a bead during the period of expansion up to maximum expansion is depicted, showing a fairly homogeneous distribution of partly expanded foam cells. Fig. 2(b) shows the foam morphology at maximum expansion (expansion ratio ≈ 14). In contrast to conventional EPS, the maximum expansion does not approach its theoretical value, but is immediately followed by collapse of the bead, starting from the edge where the blowing agent escapes (Fig. 2(c)).

The dependence of the maximum expansion of WEPS on the content of blowing agent is depicted in Fig. 3 (grade A samples expanded at 130°C). An increase in maximum expansion ratio is observed with an increasing content of blowing agent, although not to the extent theoretically expected, which can be attributed to the excessive premature escape of blowing agent (via both diffusion and cell-wall damage). This phenomenon becomes more pronounced with an increasing content of blowing agent. SEM micrographs of foam morphologies reveal an increase in fraction of large cells with an increasing blowing agent content. This is probably due to the enhanced susceptibility to coalescence of foam cells during the expansion process as a result of the larger number of water domains.

The influence of the temperature on the expansion characteristics of WEPS is illustrated in Fig. 4. WEPS containing 9.3 wt.% of blowing agent (sample A-5) was expanded at 120°C, 130°C and 150°C. With increasing temperature, the respective expansion stages become shorter, the required expansion time is substantially decreased and the expansion window becomes narrower. The deformation of the polymer matrix evolves faster and the foam stability deteriorates as a result of the reduction in melt viscosity with increasing temperature.

An optimum expansion temperature of approximately 130°C exists as a consequence of two opposing effects. At relatively low temperatures, the vapour pressure is insufficient to accomplish an accurate expansion of the viscous

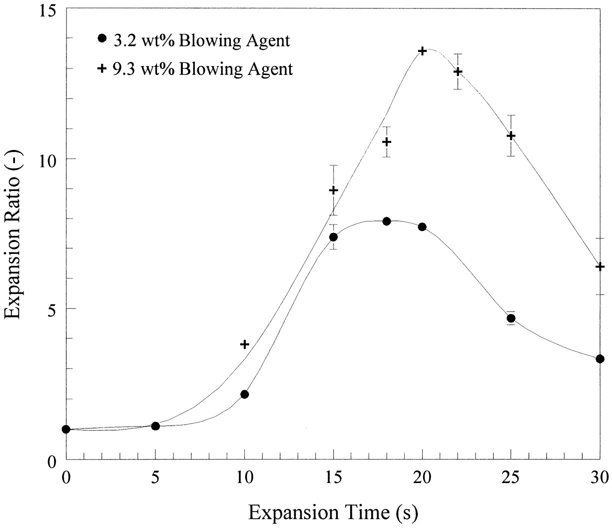

Fig. 1. Expansion ratio versus exposure time for WEPS samples A-1 and A-5, containing 3.2 and 9.3 wt.% water as the blowing agent, respectively, at 130°C.

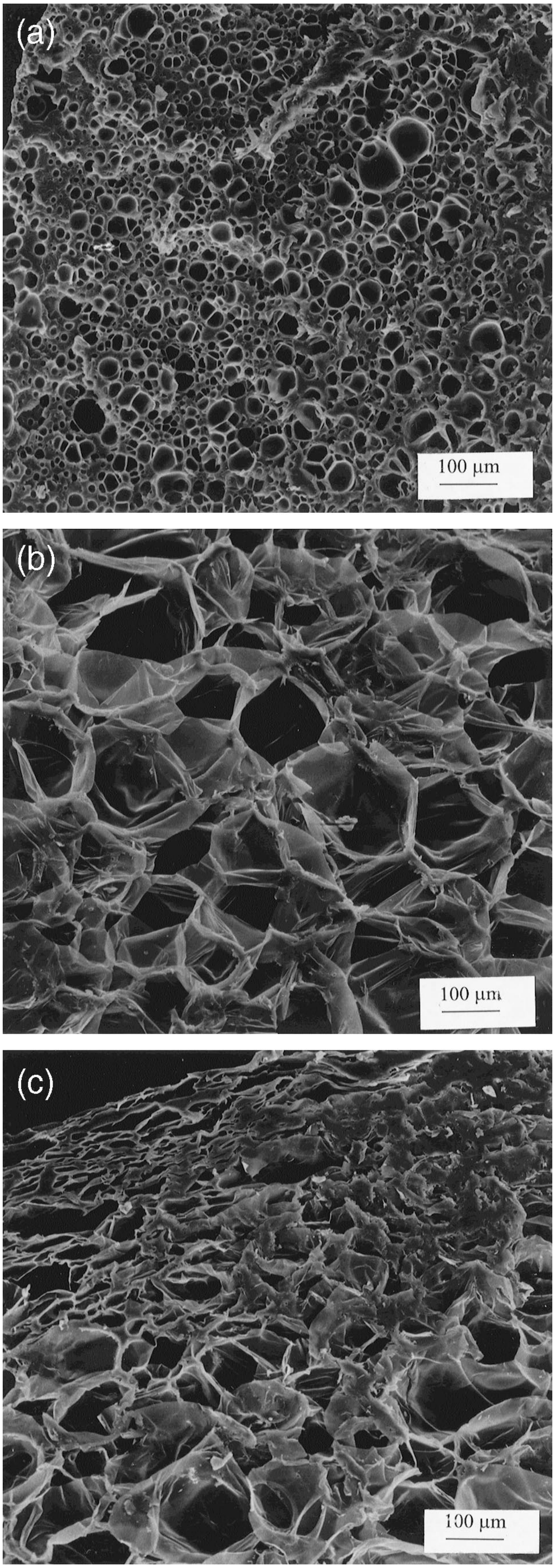

Fig. 2. SEM micrographs of foam morphology during the expansion process: (a) before maximum expansion, (b) at maximum expansion and (c) after maximum expansion.

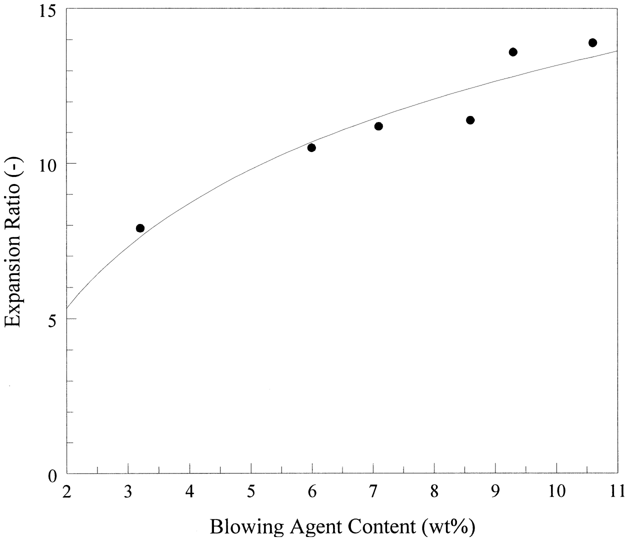

Fig. 3. Maximum expansion ratio versus blowing agent content for grade A samples expanded at 130°C.

polymer matrix, while a substantial amount of blowing agent is lost by diffusion out of the bead, e.g. WEPS appears to be unexpandable below 115°C. On the other hand, cell-wall rupture leading to premature escape of the blowing agent is promoted at temperatures higher than the optimum temperature, as a result of the decreased melt strength. This is demonstrated by the presence of voids at the outer surface of expanded beads, which increase in number with increasing expansion temperature, as observed by SEM.

From the discussed observation, it can be concluded that for the expansion of WEPS, relatively high temperatures (approximately 130°C versus 100°C for conventional EPS) are required in order to establish sufficient vapour pressure of the blowing agent. However, at such a temperature, failure of the matrix can cause the formation of voids by which the blowing agent can easily escape without contributing to expansion. This suggests that an improvement of the melt strength of the polymer matrix can contribute to an enhancement of the maximum expandability of WEPS.

The expansion characteristics of WEPS as described in this paper were obtained from investigations performed on samples prepared with the commercial surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT) (see Part 1 of this series [1]). However, WEPS beads containing amphiphilic copolymers of styrene and sodium styrene sulphonate, which were prepared in-situ during the polymerisation [2], were also tested with respect to their expansion behaviour. The maximum expansion ratio of sample B-1 in hot air (see Table 2) was 25 (corresponding with a density of approximately 40 kg m^{-3}) at a temperature of 135°C. This value is substantially higher than the maximum expandabilities

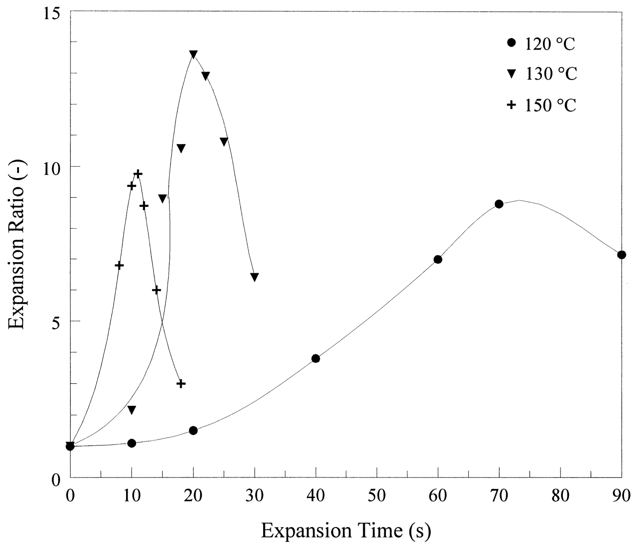

Fig. 4. Expansion ratio versus expansion time for sample A-5 (9.3 wt.% of blowing agent) at different temperatures.

obtained with samples prepared with AOT as surfactant. This is possibly caused by the better compatibility of the in-situ formed copolymers with respect to AOT, resulting in a more homogeneously distributed interfacial tension. This might reduce the probability of cell rupture and consequently improve foam stability [6]. However, since the trends (as a function of content of blowing agent, expansion time, matrix properties, etc.) appeared to be similar to those of samples prepared with AOT as surfactant, this paper focuses on the expansion characteristics of samples prepared with AOT.

3.2. Influence of matrix properties

The expansion characteristics of PS are, besides the nature of the physical blowing agent and the expansion conditions (temperature, pressure and heating medium), influenced by the properties of the polymer matrix. The visco-elastic behaviour of the matrix during the expansion process influences the foam stability and the expandability. On the one hand, expansion of a viscous medium has to take place and, on the other hand, a certain degree of melt strength or elasticity is required to prevent viscous flow failure of the cell walls [7]. In the latter case, the polymer is pulled apart by the pressure of the expanding gas and the foam collapses.

The viscous flow properties of the polymer are, at a certain temperature, mainly determined by the molar mass and the molar mass distribution of the polymer. Besides, viscous flow can be facilitated by the presence of plasticisers in the matrix [8]. The melt strength of the matrix during expansion can be enhanced by crosslinking or grafting of the PS chains [7] or by blending the PS with poly(2,6-dimethyl-1,4-phenylene ether) (PPE). The presence of PPE effectuates an increase in melt viscosity which also affects the expansion characteristics. Moreover, the risk of foam collapse is reduced for this blend as a result of the enhanced T_g.

All the mentioned approaches to improve the rheological behaviour of the matrix during expansion were evaluated. A substantial increase in foam stability could be obtained by slight crosslinking of the PS matrix, and an enhancement of the foam structure (smaller cells) was realised by the addition of 1 wt.% of plasticiser or by blending with 5 wt.% of PPE. However, the maximum expandability (read minimum foam density) remained far below the theoretically expected value for WEPS. This is obviously the result of premature escape of blowing agent during the expansion process, which can occur both by diffusion of water through the PS cell walls and by rupture of the cell walls resulting in interconnection of cells and ‘channel formation’. However, extensive attempts to reduce the premature escape of blowing agent via cell-wall rupture by improving the melt strength of the polymer matrix during expansion did not result in significant improvements of the expandability of WEPS. It is therefore believed that the most important part of premature escape occurs via diffusion of water through PS. This is also confirmed by the important contribution of steam to the expansion process of conventional EPS. In this process, the steam is capable of diffusing during the period of expansion in the PS beads [9]. Accordingly, water can diffuse out of WEPS beads quickly when hot air is used as the heating medium. It can be expected that much higher expansion ratios (lower densities) can be achieved if superheated steam is used as heating medium instead of hot air. However, these technological details are beyond the scope of the present paper.

4. Conclusions

Hot air appeared to be useful as a heating medium for the expansion of water expandable polystyrene (WEPS) beads at laboratory scale, because of the relatively good control of temperature. However, due to the high diffusion rate of water through PS, the expandability was much lower than theoretically expected. Even the maximum expandability of samples prepared via the ‘in-situ surfactant’ approach, which showed a significantly higher expandability than ‘AOT samples’ (max. expansion ratio of 24 versus 15), remained far below the theoretical value.

Expansion can be enhanced by reducing the relative degree of diffusion out of the beads in the hot air flow by an increase in blowing agent content. An optimum expansion temperature exists for all WEPS samples, which originates from two opposing effects. At low temperatures, the water vapour pressure is not sufficient to expand the highly viscous PS matrix and a considerable amount of blowing agent is lost by ‘drying’. On the other hand, the decreased viscosity enhances viscous flow, resulting in more pronounced cell-wall failure and increased escape of blowing agent at high temperatures.

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References

[1] Crevecoeur JJ, Nelissen L, Lemstra PJ. Polymer 1999;40:3685.
[2] Crevecoeur JJ, Nelissen L, Lemstra PJ. Polymer 1999;40:3691.
[3] Ingram AR, Fogel J. In: Frisch KC, Saunders JH, Editors. Plastic foams, Part 2. New York: Dekker, 1973:525.
[4] Benning CJ. Plastic foams: the physics and chemistry of product performance and process technology, vol. 1. New York: Wiley-Interscience, 1969.
[5] Pogany GA. Polymer 1976;17:690.
[6] Klempner D, Frisch KC. Handbook of polymeric foams and foam technology. Munich: Hanser Publishers, 1991.
[7] Benning CJ. Plastic foams: the physics and chemistry of product performance and process technology, vol. 2. New York: Wiley-Interscience, 1969.
[8] Blihi S, Brons HMJ, Cureton RW, Schaerlaken A, Vliers DP. Eur Pat EP63444 A2, 1995.
[9] Hinselmann K, Stockburger D. Kunstoffe 1971;61:152.