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Water expandable polystyrene (WEPS)
Part 1. Strategy and procedures

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Abstract

Conventional expandable polystyrene (PS) is prepared via the suspension polymerisation of styrene containing pentane isomers as a blowing agent. The polystyrene beads are expanded by heating above the glass transition temperature, T_g. During the expansion process, pentane, which contributes to the formation of ozone in the lower atmosphere, is released into the environment. The objective of this study was to replace pentane isomers with a harmless blowing agent, namely water.

The procedure adopted to use water as a blowing agent was as follows. Water was emulsified by means of a suitable emulsifier in a pre-polymerised styrene/polystyrene mixture possessing a high viscosity in order to fixate the emulsified water droplets. Subsequently, this inverse emulsion was suspended in water containing a suitable suspending agent and polymerisation was completed. This procedure resulted in spherical PS beads containing small water droplets which were capable of expanding the PS matrix upon heating above T_g. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Expandable polystyrene; Water; Blowing agent

1. Introduction

A number of processes have been developed to prepare polystyrene (PS) foams. The two most important processes are, respectively:

(a) extrusion for the production of foamed sheet or foamed board [1–3]; and
(b) the preparation of expandable beads [4].

In the former process, the blowing agent is mixed into the molten polymer in an extruder under pressure. The blowing agent vaporises as the pressure in the polymer melt decreases at the die-exit, causing the polymer to expand. The formed cellular structure is vitrified by cooling of the polymer melt.

Incorporation of the blowing agent in expandable PS beads can be achieved by the addition of the blowing agent during the suspension polymerisation process. In this process, the monomer is suspended as droplets in water, stabilised by a suspending agent and subsequently polymerised. The blowing agent (usually a mixture of pentane isomers) is introduced into the closed suspension reaction vessel during the final stage of polymerisation [5] at a temperature well above the glass transition temperature, T_g, of PS, resulting in dissolution of pentane in the PS beads. After cooling, the blowing agent is entrapped in the PS beads [6].

All organic blowing agents such as pentanes, industrially applied as physical blowing agents for the preparation of expandable polystyrene (EPS), have a major disadvantage in common; they are all harmful to the environment. Volatile organic hydrocarbons (VOCs) contribute to the generation of ozone in the lower atmosphere [7,8]. Extensive studies have shown that ozone is both a lung irritant and a phytotoxin; it is responsible for crop damage and is suspected of being a contributor to forest decline in Europe and the United States [8]. Besides, VOCs such as pentane are precursors for a multitude of other photochemical smog species that also have significant environmental consequences [8]. Moreover, carbon dioxide, which contributes to the greenhouse effect, is also formed during the photo-oxidation of pentane [8].

Since EPS is expanded on a small scale (delocalised) by a large variety of converters, advanced (and expensive) recovery systems are usually not feasible [9]. The world-wide annual production of EPS amounts approximately to 1.5

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Table 1
Formulation for suspension polymerisation DBPO, dibenzoylperoxide; TBPB, *tert*-butyl peroxybenzoate; AOT, sodium bis(2-ethylhexyl)sulfosuccinate; HEC, hydroxyethyl cellulose

Component	Content (g)
Styrene	$1000 - X$
DBPO	$0.004 \times (1000 - X)$
TBPB	$0.0015 \times (1000 - X)$
Surfactant (AOT)	$0.1 \times X$
Water (blowing agent)	X
Sodium chloride	$0.009 \times X$
Water (susp.)	3000
HEC	12

million tonnes which consequently leads to an annual release of 75 000 tons of organic volatiles (mainly pentane isomers) in the environment [10].

In this series of papers, a new process for the preparation of EPS using water as the blowing agent is described [11, 12], which besides being friendly to the environment also possesses the advantage of non-flammability. Moreover, water is in principle a very effective blowing agent as a consequence of its low molar mass (four times lower than pentane isomers). The basic concepts are explained in this paper.

2. Experimental

2.1. Materials

The styrene monomer was used without distillation from the inhibitor *tert*-butylcatechol (11–17 ppm), manufactured by Shell and supplied by B.P.M. Breda. The initiators, dibenzoylperoxide (active content, 75%; water, 25%) with a halflife ($t_{1/2}$) at 90°C of 75 min [13] and *tert*-butyl peroxybenzoate with $t_{1/2} = 70$ min at 120°C [13], were supplied by Akzo Nobel Chemicals.

The surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT) (98% purity) was supplied by Fluka and used as received. The suspension stabiliser hydroxyethyl cellulose was supplied by B.P.M.–Shell (Breda) and used as received.

2.2. Suspension polymerisation

Suspension polymerisations were performed according to the formulation presented in Table 1, where X represents the amount of dispersed water as a blowing agent. Samples with $X = 20$, 40, 60, 80 and 100 g, corresponding to 2, 4, 6, 8 and 10 wt.%, respectively, were synthesised.

After dissolution of the surfactant and initiator in styrene, the mixture was heated to 90°C and polymerised in the bulk for 100–120 min while stirring at 300 r.p.m. in a nitrogen atmosphere up to a conversion of approximately 50% (determined by solid content analysis). Subsequently, water containing 0.9 wt.% NaCl was emulsified by stirring at 800 r.p.m. for 5 min. Note that the emulsification of water can also be performed directly after the start of polymerisation if a high stirring rate is maintained throughout the complete prepolymerisation. The viscous reaction mixture was suspended in the suspension reaction vessel containing water and suspension stabiliser, and polymerisation was continued for 4 h at 90°C in a nitrogen atmosphere while stirring at 350 r.p.m. Subsequently, the temperature was raised to 125°C under a nitrogen pressure of 4 bar and the polymerisation was continued for another 3 h. Finally, the suspension was cooled to room temperature and the spherical beads were filtered and washed with water.

The suspension polymerisations were performed in a suspension reactor of 6.4 l. The ratio R of the reaction mixture/suspension medium was 1/3 (w/w).

2.3. Thermogravimetric analysis

In order to determine the water content of the water expandable polystyrene (WEPS) beads, the weight loss of a sieve fraction of 1.7–2.0 mm beads was measured using a Perkin–Elmer TGA7 under an air flow of 50 ml min^{-1}. The temperature program started at 30°C at a heating rate of 40 K min^{-1} to 120°C. After an isothermal period of 15 min at 120°C, the temperature was raised to 180°C at a heating rate of 40 K min^{-1} followed by another isothermal period of 15 min.

2.4. Gel permeation chromatography

Gel permeation chromatography (GPC) was used to determine the number average molar mass (M_n), the weight average molar mass (M_w), and the molar mass distribution (M_w/M_n) of the PS. The samples were measured on a Waters modular GPC system consisting of pump M510, injector WISP712, detector 440 (UV at 254 nm), detector 410 (refractometer) and two Shodex KF-80M linear columns (at 40°C). The eluent was THF (p.a., stabilised) injected at 1 ml min^{-1} with an injection volume of 100 ml and a sample concentration of 1 mg ml^{-1}. The columns were calibrated with Polymer Laboratories polystyrene standards in the range $M_w = 6.5 \times 10^6$ to 580 g mol^{-1}.

2.5. Scanning electron microscopy

Scanning electron microscopy (SEM) was performed on each WEPS sample. The morphology of both compact and expanded samples was investigated by SEM using a 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

The blowing agent (pentane isomers) of conventional EPS is incorporated in the PS beads during the suspension

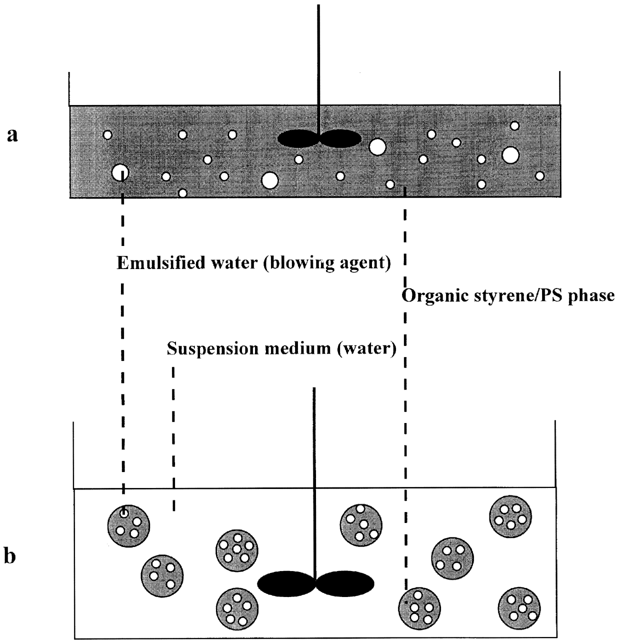

Fig. 1. Schematic representation of the preparation process of WEPS: (a) emulsification of water (blowing agent) in a styrene/PS mixture, and (b) suspension polymerisation of styrene/PS droplets containing emulsified water.

polymerisation process. After polymerisation, the pentane isomers are automatically incorporated in the PS matrix. This straightforward procedure for the incorporation of the blowing agent is possible due to the partial miscibility of PS and pentane.

In order to incorporate water as a blowing agent, the described procedure (via dissolution) cannot be applied due to the nearly complete immiscibility of water and styrene/PS. However, water can be incorporated into a solid PS matrix as small dispersed droplets via the continuous phase polymerisation of a water-in-styrene emulsion [14–26]. This can be accomplished by emulsifying water in styrene or in a partly converted styrene/PS mixture using appropriate surfactants to obtain a so-called inverse emulsion (see Fig. 1(a)). After a polymerisation step in the bulk up to a styrene conversion between 20 and 60% (prepolymerisation), which is necessary to fixate the water droplets in the viscous continuous phase, the reaction mixture is suspended in water containing a suitable suspending agent (see Fig. 1(b)). The bead polymerisation is continued in the thus obtained water-in-oil-in-water (w/o/w) system to complete conversion. This procedure leads to spherical compact PS beads containing small water droplets which are capable of expanding the beads upon heating the material above the glass transition temperature of PS.

For the preparation of foam with good thermal and mechanical properties, it is of essential importance to create small and monodisperse foam cells [27,28]. This implies the preparation of compact (before expansion) WEPS beads containing small water droplets with a narrow size distribution. Therefore, the establishment of a suitable morphology is of crucial importance.

In order to achieve this, several water-in-oil (w/o) emulsifiers (surfactants that preferably form inverse emulsions due to their hydrophile–lipophile balance (HLB) [29,30] value and molecular geometry [31,32]) were tested with respect to their emulsion stabilities and the obtained morphologies after polymerisation.

The influence of the presence of a salt in the aqueous phase, which can strongly affect the stability and droplet size of inverse emulsions [33–35], was investigated. For anionic surfactants, a decreased repulsion between the ionic head groups in the interior of the water droplets is realised by an enhanced exchange of counter ions in the presence of an electrolyte. This decrease in repulsion permits the ionic head groups to approach each other more closely, leading to an increase in emulsion stability.

Morphologies were evaluated on samples which were, after prepolymerisation, further polymerised in test tubes. Emulsion stabilities were investigated by the rate of separation in bulk phases of the emulsion. From this study, it appeared that AOT was the most effective of the tested surfactants in establishing stable water-in-styrene emulsions. Moreover, a low concentration of NaCl (0.9 wt.% based on emulsified water) proved to improve the morphology of the precursor material. Therefore, AOT combined with NaCl was used as emulsifying system for the preparation of WEPS beads.

Six samples containing different contents of blowing agent were prepared according to the formulation as described in Section 2. A typical bead size distribution that is obtained after the suspension polymerisation of samples 1–6 is presented in Fig. 2. This figure demonstrates that it is feasible to synthesise WEPS beads with a fairly narrow bead size distribution, despite the high viscosity after the pre-polymerisation step. This is, for potential

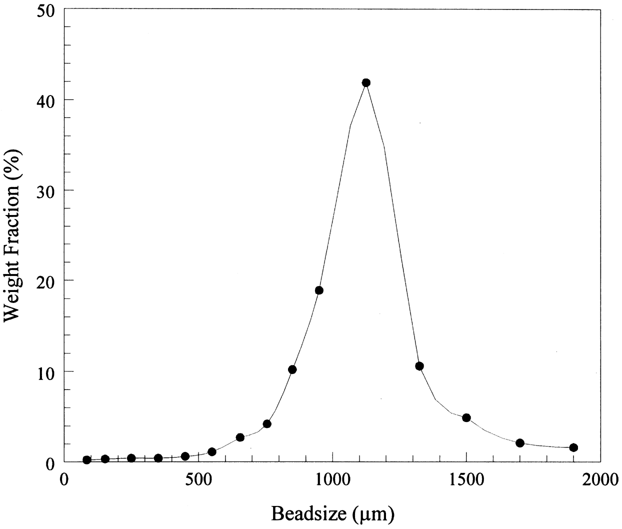

Fig. 2. Typical bead size distribution of WEPS samples.

Table 2
Specifications of synthesised samples AOT, sodium bis(2-ethylhexyl)sulfosuccinate

Sample number	AOT (wt.%)	Emulsified water (wt.%)	Incorporated water (wt.%)	M_w (kg mol^{-1})
1	0.2	2.0	3.2	183
2	0.4	4.0	7.1	180
3	0.5	5.0	7.9	179
4	0.6	6.0	8.6	174
5	0.8	8.0	9.3	174
6	1.0	10.0	11.3	186

industrial applications, a factor of essential importance, since only beads within a limited size range can be applied for expansion.

The amount of blowing agent that is incorporated as tiny droplets in these beads was evaluated with thermogravimetric analysis (TGA). In Table 2, it is demonstrated that the amount of blowing agent in the final product is a few wt.% higher than initially emulsified. This excess of blowing agent is obviously the result of incorporation of suspension medium in the beads. This is also visible on the SEM micrographs presented in Fig. 3, which reveal the presence of an increased number of droplets that are also larger in size, near the edge of the bead. This effect is caused by the diffusion of suspension water to the emulsified droplets present at the edge of the beads, causing these droplets to grow. Because the beads contain ionic groups, a driving force for diffusion of water into the beads exists (osmosis). The emulsified droplets of blowing agent swell (observed by the increased size) as a result of this. The degree of diffusion can be reduced by lowering the permeability of the styrene/PS barrier (higher conversion after prepolymerisation) or by diminishing the driving force (decrease the concentration of ionic groups in the beads).

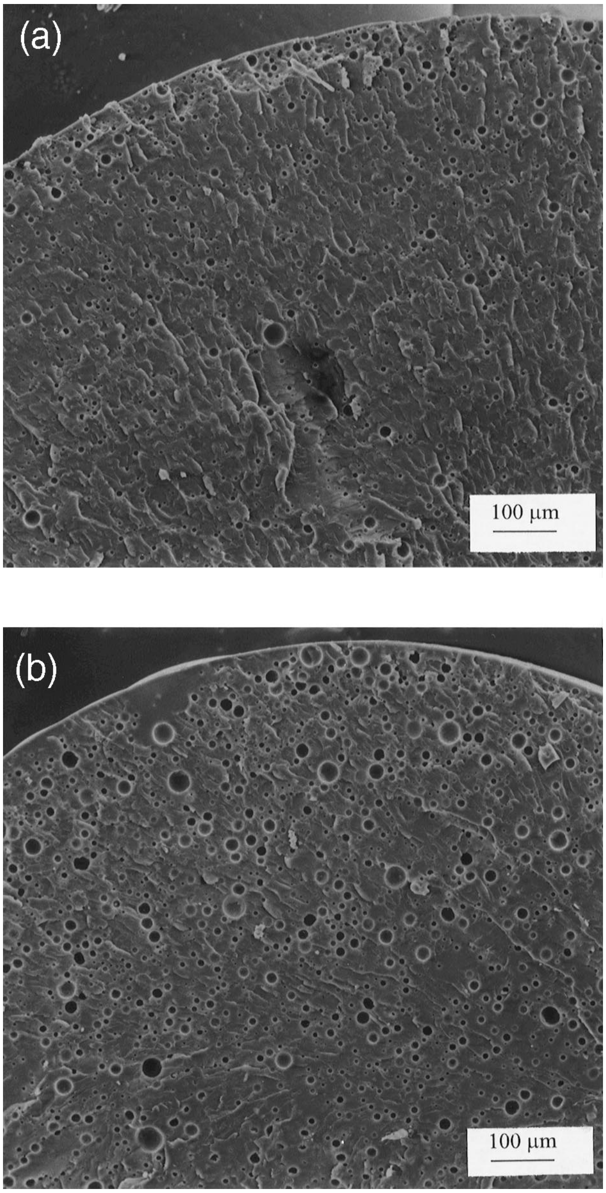

Fig. 3. SEM micrographs of samples (a) 1 and (b) 5, prepared via suspension polymerisation.

All samples were prepared with a constant AOT/emulsified water ratio of 0.1 (w/w), in order to prepare products possessing comparable water domain sizes. In Fig. 3, the SEM micrographs of fractured beads of samples 1 and 5 are presented. Both samples, in which, respectively, 2 and 8 wt.% of water was emulsified, indeed show a very similar water droplet size distribution as a result of the normalisation of the AOT concentration to the water content.

WEPS beads could be expanded by exposing them to hot air (optimum temperature was 130°C) followed by quenching with cold air. A typical foam structure of expanded WEPS samples is depicted in Fig. 4. A reasonable regular and fine foam structure can be observed in this micrograph. The structure of the foam is important with respect to the mechanical and thermal properties of the final material. Part 3 of this series [36] gives a more detailed picture of the expansion behaviour of WEPS in hot air. Especially, the influence of matrix properties (crosslinking, molar mass, etc.) on the expansion potency and the foam structure are investigated.

4. Conclusions

It has been demonstrated that expandable polystyrene (EPS) beads, containing water as a blowing agent can be

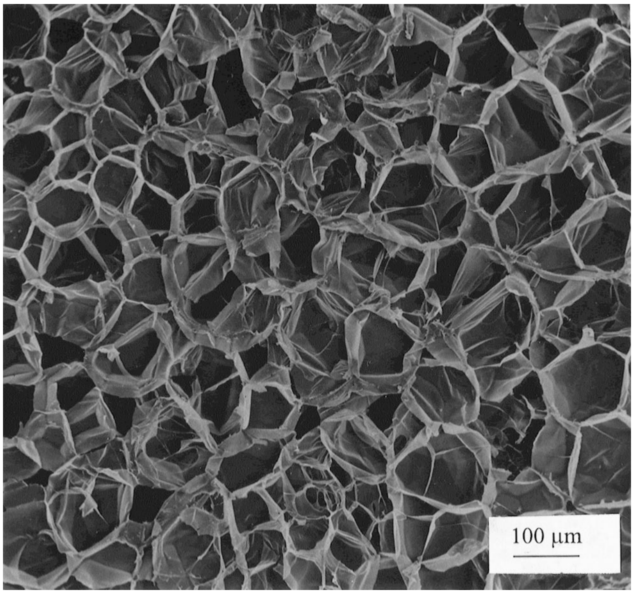

Fig. 4. SEM micrograph of a typical foam morphology of an expanded WEPS sample.

synthesised via a conventional suspension polymerisation process. The blowing agent was dispersed as tiny droplets in a partly polymerised styrene/PS mixture by emulsifying it with a suitable surfactant (AOT). This viscous mixture was subsequently suspended in water and polymerised up to complete conversion. The water expandable polystyrene (WEPS) beads prepared in this manner could be expanded in hot air, resulting in foamed particles possessing a fine and homogeneous cell structure.

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