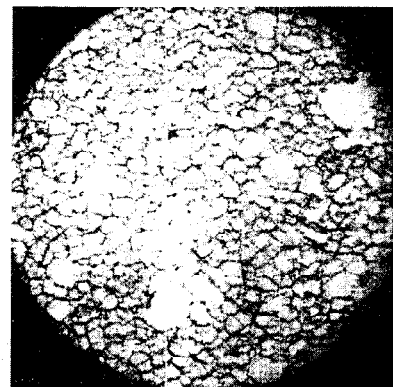


Full Paper: Heating of polystyrene beads containing pentane isomers as the blowing agent traditionally produces polystyrene foam. Undesirable emissions of the blowing agent and its high flammability are the complications of this process. A new process for the production of expandable polystyrene has been developed, using water as the blowing agent. Water is trapped inside the polystyrene matrix through the use of starch that is introduced as a separate phase during the suspension polymerization. The problems created by the incompatibility of starch with the organic phase can be partially overcome by "compatibilization" with maleic anhydride. The type of starch can influence the foam morphology of the pre-expanded beads, while the density is changed only in the range of the experimental error. The density of the pre-expanded beads is influenced by the blowing technique used (hot air or high frequency electric field). The use of these different blowing techniques does not influence significantly the foam morphology.



Typical pattern of the foam morphology of a sample with rice starch (average granule size 5 μm)

Expansion of polystyrene using water as the blowing agent

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Introduction

Expandable polystyrene (EPS) is an important industrial commodity with interesting properties that lead to a wide spectrum of applications, especially in the field of packaging and construction.

The standard procedure¹⁾ is based on the polymerization of styrene in suspension with the formation of polystyrene beads. Pentane, added during this polymerization process, is used as the blowing agent. Pre-expansion^{2,3)} of the beads before processing is realized by heating the pentane-containing polystyrene beads above their glass transition temperature.

Pentane is a volatile hydrocarbon and several reasons for its replacement by a less harmful solvent can be formulated.

The first argument is safety during manufacturing, processing, and transportation. Pentane is a highly flammable liquid with high explosion hazard. The second argument is the emission of this hydrocarbon during processing.

As a consequence it became evident to look for an alternative blowing process using a less problematic

blowing agent^{4–8)}. The already proposed alternatives, however, have some disadvantage: water is only a co-blowing agent⁶⁾ or contains emulsifiers^{7,8)} necessary to keep sufficient amount of water in the polystyrene matrix. In this article we present a new process for the preparation of EPS using water as the blowing agent without addition of any harmful chemical compound.

The solubility of water in polystyrene is very low. Consequently it is impossible to use the same procedure as the one used for pentane and water has to be introduced in a different way. Therefore a water soluble or swellable polymer will be dispersed in the polystyrene matrix. The natural polymer starch was chosen for this purpose.

The major sources of commercial starches are corn, wheat, potatoes, and rice. Starch is mainly composed of two polymers, *amylose*, a mixture of linear polysaccharides composed of D-glucose units linked by α -1–4 glycosidic linkages, and *amylopectin*, a mixture of branched polysaccharides of D-glucose units with α -1–4 glycosidic linkages in the linear region and α -1–6 glycosidic linkages at the branching points. The molecular weight of amylose is between one thousand and one million $\text{g} \cdot \text{mol}^{-1}$ and that of amylopectin can run into several millions $\text{g} \cdot \text{mol}^{-1}$, according to the botanical source of

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starch. Amylose is present in the granules of most starches in amounts of around 20–25 wt.-%. There are exceptions, such as the waxy varieties, which are composed entirely of amylopectin and also high amylose varieties which contain 50–80 wt.-% of amylose.

Starch, as natural polymer, is immiscible with most of synthetic polymers. This incompatibility can lead to agglomeration of the starch granules in a synthetic polymer matrix and to poor performance of these materials. Better properties can be obtained through the introduction of polar functional groups in the synthetic polymer chain. This will lead to a positive interaction between the two components⁹. A typical example is the blending of starch with a styrene-maleic anhydride copolymer (SMA). The anhydride groups of the copolymer can interact with the hydroxyl groups of starch and this will lead to a stabilization of the multi-domain morphology.

When pentane as the blowing agent is replaced by water, incorporated in starch particles, an alternative pre-expansion technique has to be developed.

Experimental part

Materials

Styrene (99%) was donated by Shell Chemicals, maleic anhydride (99%), dibenzoyl peroxide (70%), and *tert*-butyl perbenzoate (98%) employed in the synthesis were obtained from Aldrich Chemical Co. and used as received.

Samples of starches were purchased by Cerestar R&D, company of Eridania Bèghin-Say. Starches were unmodified and used as purchased. Their basic characteristics are summarized in Tab. 1.

Suspension stabilizers hydroxyethyl cellulose and tricalcium diphosphate were provided by Bredase Polystyreen Maatschappij.

Tab. 1. Characteristics of the starches used in the formulations

Starch	Average granule size	Granule appearance	Amylose content
	μm		wt.-%
corn	15	angular	25
waxy corn	15	angular	0
high amylose corn	11	deformed, elongated	55 or 70 ^{b)}
wheat ^{a)}	6	small spherical and large lens-shaped	28
Rice	5	very angular	17
Potato	33	oval	22

^{a)} Starch wheat-B (bimodal granule size distribution, maxima in 5 μm and 30 μm).

^{b)} Two different varieties.

Pre-expansion in hot air

The pre-expansion is performed in a home-made device in which hot air is generated by an electrical heating-blowing system. The sample is introduced in the heated vessel for a well determined time and then quenched through the introduction of cold air, followed by elimination of the sample from the vessel.

Pre-expansion in high frequency electric field

The device consists of a electrical circuit, which transforms the conventional alternating voltage to a high frequency voltage of 3470 V and 38 MHz. The sample is placed on the lower horizontal electrode, exposed to the high frequency field for a well determined period of time and then quenched to room temperature.

Optical microscope

The foam morphology of the samples is examined by light microscopy using an Olympus BH-2 equipped with a CCD camera Photometrics CH-250. Computer images are evaluated using software V3.5 for Windows provided by Digital Optics, Ltd.

Experimental results and discussion

Preparation of water-blown expandable polystyrene (WEPS)

Basic principles

EPS is usually prepared in the form of beads via suspension polymerization. The blowing agent pentane is added during polymerization into the styrene/polystyrene mixture at a styrene conversion of about 70 wt.-%.

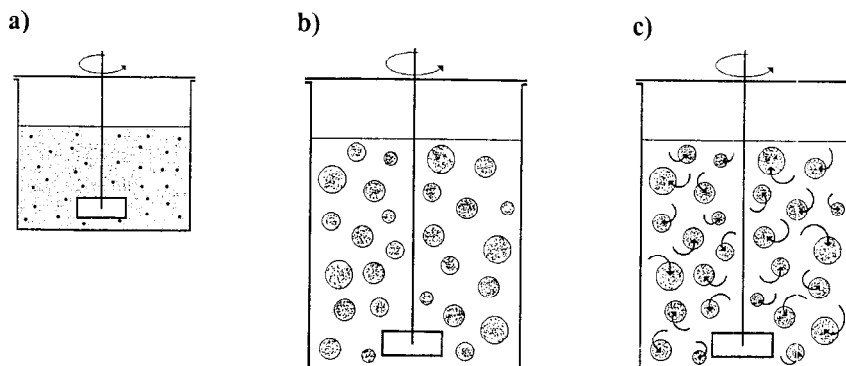
Water and polystyrene are nearly completely immiscible. Water has therefore to be introduced in a different way. This can be realized through the incorporation of a water swellable phase in the polystyrene matrix¹⁰. This phase should not be soluble in styrene or polystyrene and has to be introduced at the beginning or in the early stages of the polymerization. Starch has been chosen for this water swellable phase.

The polymerization consists of different steps:

- Pre-polymerization of the styrene/starch mixture to a conversion of about 30% (Scheme 1, a) in order to increase the viscosity of the matrix so that agglomeration of the starch particles is limited as much as possible.
- Dispersion of the pre-polymerized styrene/starch mixture in water containing the appropriate suspension stabilizers (Scheme 1, b).
- Suspension polymerization to complete conversion. Water is directly absorbed into the starch inclusions (Scheme 1, c).

Scheme 1: Particular steps in the WEPS preparation: a) bulk pre-polymerization of the styrene/starch mixture, b) dispersion of the pre-polymerized mixture in water, c) adsorption of water into the starch inclusions in the polystyrene matrix during suspension polymerization.

● = starch, ⊙ = polystyrene, → = absorption of water into the starch inclusions



These different steps will be discussed in detail in the next paragraphs.

Pre-polymerization

tert-Butyl perbenzoate (0.025 wt.-% related to styrene) is dissolved in styrene (90 wt.-% of the total amount) and placed into a glass vessel with stirrer and thermocouple. Maleic anhydride is added if needed (0.5 wt.-% related to total amount of styrene). Starch (5 wt.-% related to the total amount of styrene) is dispersed in this solution. The reaction mixture is stirred at 120 °C under the nitrogen atmosphere until the desired conversion of styrene is reached. The prepolymerized mixture is then cooled to 60–70 °C and solution of initiators in styrene (10 wt.-% of the total amount) containing dibenzoyl peroxide (0.4 wt.-% related to the total amount of styrene) and *tert*-butyl perbenzoate (0.2 wt.-% related to the total amount of styrene) is added. The resulting mixture is homogenized and transferred into the suspension polymerization reactor.

Dispersion of the pre-polymerized mixture in water

The pre-polymerized mixture (100 cm³) is dispersed in water (500 cm³) containing hydroxyethyl cellulose (0.075 wt.-% related to water) and tricalcium diphosphate (0.43 wt.-% related to water) as the suspension stabilizers.

Suspension polymerization

Suspension polymerization is performed in a glass 1000 cm³ Büchi autoclave reactor with thermostatic system and data controlling device. The stirring rate is 400 rpm during all polymerization procedures and polymerization is performed under nitrogen atmosphere.

The temperature profile in suspension polymerization is as follows: 80 °C for 240 min, 90 °C for 60 min, and 120 °C for 120 min. Then the reaction mixture is cooled to room temperature and the product is recovered by filtration.

Pre-expansion of the polystyrene beads

The physical properties of water are very different from those of the hydrocarbons that are generally used in the traditional blowing procedures. The relatively high boiling point of water necessitates relatively high pre-expansion temperatures in order to generate sufficient vapour pressure inside the beads. The traditionally used heating devices (hot air or overheated steam) can be used for the pre-expansion of these beads. Several restrictions however have to be made.

These traditional heating media increase first the temperature of the polystyrene matrix, which has to transfer its energy to the blowing agent. This will take some time and during this period, water vapor will already diffuse through polystyrene, leading to a significant loss of water. When the maximum degree of pre-expansion is reached, a collapse of the foam can be observed because of relatively low cooling of the overheated matrix and simultaneous condensation of water inside the developed foam cells.

An alternative method has therefore been developed using electromagnetic energy -- a high frequency electric field -- as the heating source. Such a heating procedure will transfer the heat to the blowing agent, water. This heat will then be transferred to the polystyrene matrix that will reach temperatures above T_g . The boiling of water will result in an important volume increase of this phase and will lead to an expansion of the viscous matrix.

Foam characteristics

Cell diameter

The average cell diameter of the pre-expanded foam is measured in the following way. Six beads are taken from the population of beads pre-expanded in one experiment. From each bead the microtome cut is made and the dia-

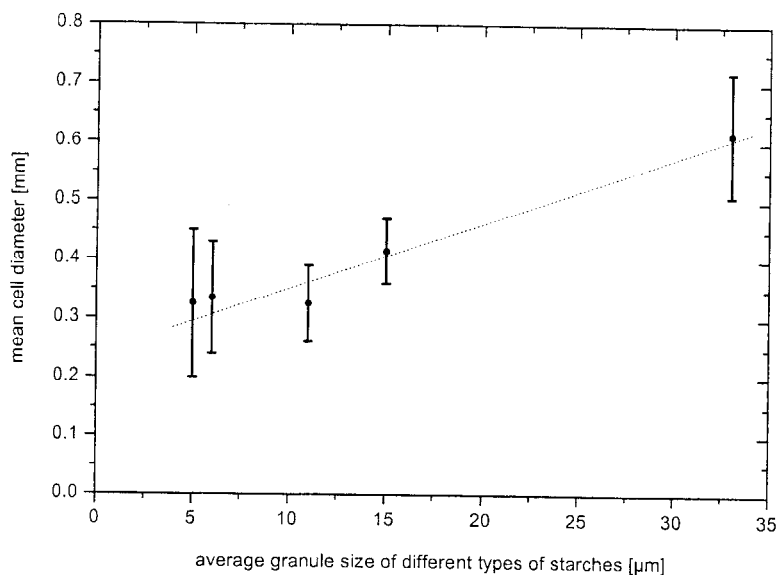


Fig. 1. Dependence of the mean cell diameter of the foam on the average granule size of different types of starches

meters of ten cells are recorded. Such observations are made with an optical microscope. To select the ten cells, a straight line is passed through the middle of the microtome cut. The diameters of ten consecutive cells on this line are recorded. The cell diameters are calculated according to the Eq. (1):

$$d = d_s/0.785 \quad (1)$$

where d is the cell diameter and d_s is the diameter of the circular segment in the cut¹¹⁾.

The factor 0.785 takes into account that the cut does not always pass through the center of a cell.

The set of the cell diameters is evaluated by means of descriptive statistics and basic parameters (mean, standard deviation, standard error, 95% confidence interval, etc.) are calculated. This procedure provides a suitable number of data for a valid statistical evaluation even for irregular foams in which the variation of the cell size is extreme.

Bulk density

The density of the pre-expanded beads is estimated in the following way. The vessel of fixed volume is filled with the pre-expanded beads and the weight is measured. This procedure is repeated at least six times and the basic parameters are again calculated by means of descriptive statistics.

Experimental factors affecting the process

Concentration and type of starch

WEPS was prepared making use of various types of starch (corn, wheat, potato, and rice) at concentrations

ranging from 1 to 40 wt.-%. The beads were hard and possessed good expandability up to a starch content of 15 wt.-%. At starch contents of 15 wt.-% and higher beads appear brittle or powdery and are difficult to expand. The best results were obtained at a starch content of 5 wt.-%. At this concentration the amount of absorbed water was about 8–10 wt.-%, which seems to be the optimal amount.

The foam morphology and the bulk density were evaluated after pre-expansion of the WEPS beads. The pre-expansion was performed using two different techniques: heating in hot air or in high frequency electric field.

The results presented here were obtained under these experimental conditions.

It is known that according to the botanical source of starch the size and shape of the starch granules vary significantly (see Tab. 1). A series of experiments was performed using the starch from the following sources: rice, wheat, corn, high amylose corn, and potato. They possess different granule size and size distribution. The dependence of the mean cell size of the pre-expanded foam on the granule size of starch is shown in Fig. 1. From these experiments it is clear that the size of the cells does not only depend on the formulation and pre-expansion technique, but also on the amount of the water inclusions present in the polystyrene matrix. The different foam morphologies are illustrated in Fig. 2.

This observation supports the idea that the foam morphology is improved when starch with smaller granule size is used. A larger number of smaller water containing inclusions is introduced in the polystyrene matrix for the same overall starch content.

The botanical source of starch or its genetic modification also determines the content of amylose and this will

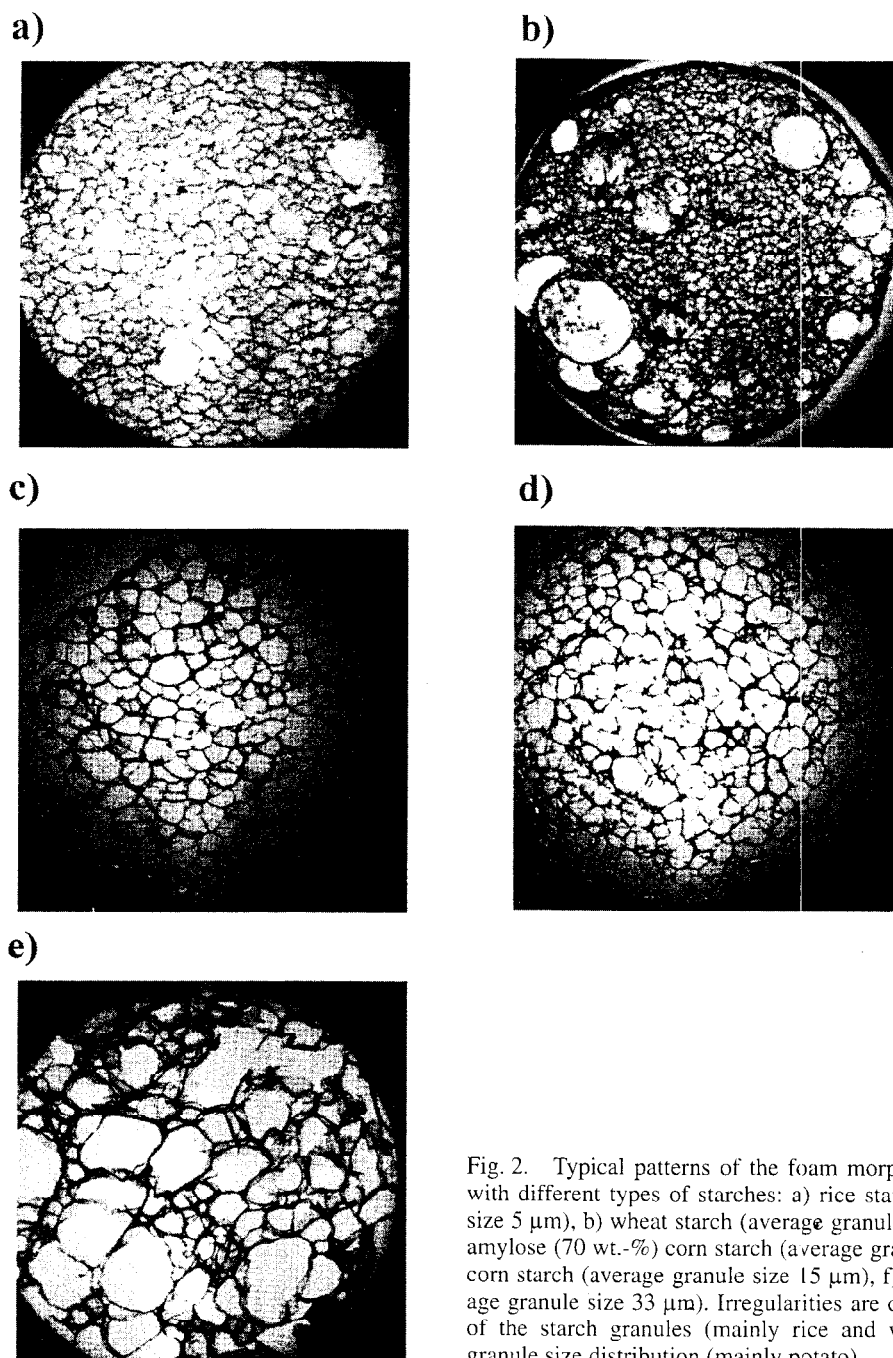


Fig. 2. Typical patterns of the foam morphologies of samples with different types of starches: a) rice starch (average granule size $5\ \mu\text{m}$), b) wheat starch (average granule size $6\ \mu\text{m}$), c) high amylose (70 wt.-%) corn starch (average granule size $11\ \mu\text{m}$), d) corn starch (average granule size $15\ \mu\text{m}$), e) potato starch (average granule size $33\ \mu\text{m}$). Irregularities are due to agglomeration of the starch granules (mainly rice and wheat) and/or broad granule size distribution (mainly potato)

influence to some extent the properties of starch. Therefore, WEPS was prepared using corn starches with different content of amylose: 0, 25, 55, and 70 wt.-%, respectively. The influence of the amylose content on the mean cell size of the pre-expanded foam was examined. The results are reported in Fig. 3. A slightly lower cell size is obtained with corn starch containing 70 wt.-% of amylose. The reason for this could be a slightly lower granule size and the higher thermal stability of high amylose corn starch. This starch (70 wt.-% of amylose) is far more resistant to swelling and its crystalline structure is more

resistant to destruction in hot water than that of ordinary native starches. Heating up to 140°C or higher is necessary to destroy completely the organization.

This difference in thermal stability is important as during the suspension polymerization process the temperature goes up to 120°C in the presence of water. This results in complete swelling, gelatinization and disintegration of the granules. Swelling of starch with an amylose content of 70 wt.-% will be very limited and the granules will maintain an observable degree of crystalline order. This was observed by optical microscopy.

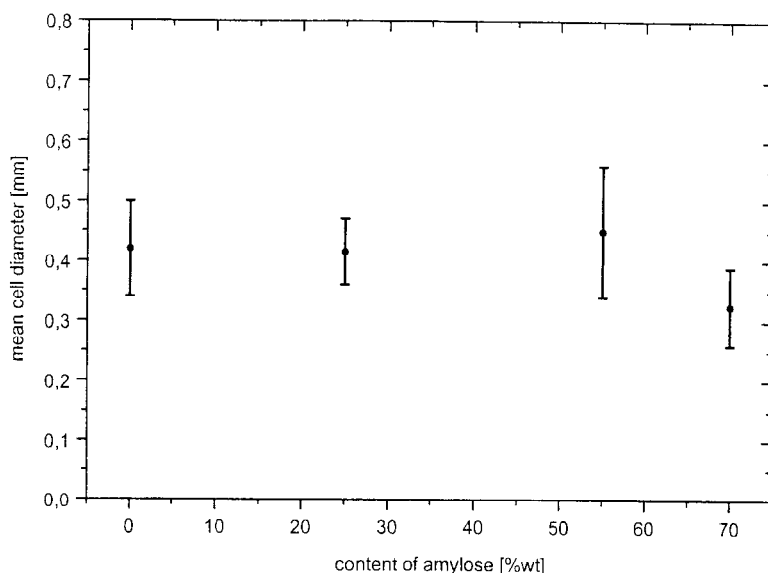


Fig. 3. Dependence of the mean cell diameter of the foam on the amylose content of corn starches

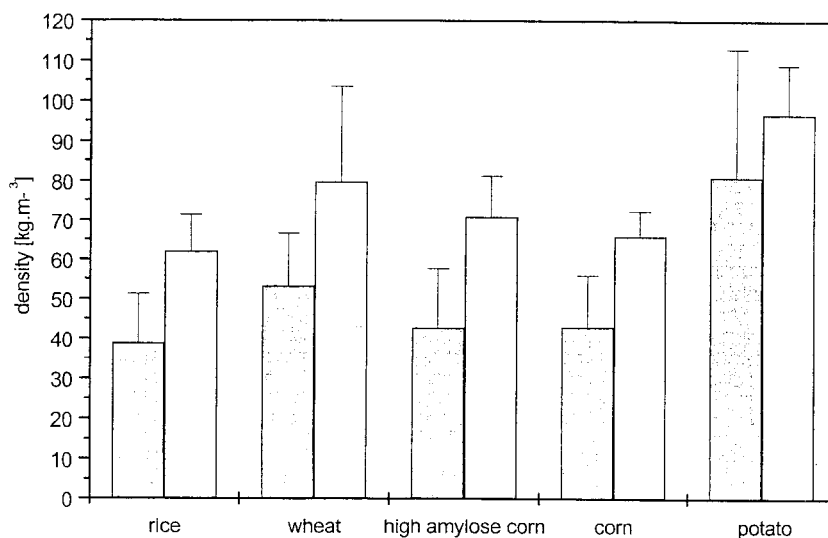


Fig. 4. Influence of the pre-expansion technique and the type of starch on the bulk density of the pre-expanded beads. ■ = pre-expansion in high frequency electric field, □ = pre-expansion in hot air

We suggest that during the pre-expansion process the granules of high amylose starch can act as heterogeneous nucleating agent and improve the formation of the final foam.

We can therefore conclude that the type of starch has a not negligible influence on the foam morphology (Fig. 1–3). However, the only significant parameter seems to be the granule size of starch.

No real influence is observed on the density of the pre-expanded beads. Small differences can only result from differences in the bead size distribution and the slightly different amount of water present in these beads.

The only significant factor is the pre-expansion technique (Fig. 4). As one can see, blowing in a high frequency electric field results in a lower density of the pre-

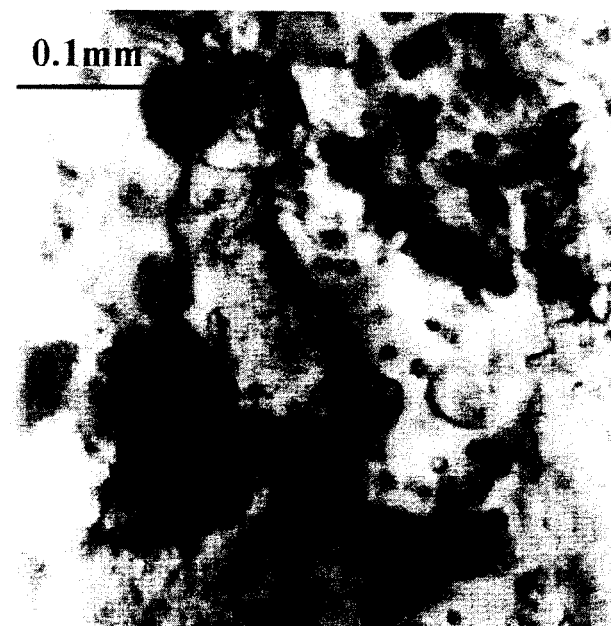
expanded beads. Though the density is influenced significantly, the foam morphology of the pre-expanded beads is not; however, the mean cell diameter is slightly higher in the range of the experimental error.

The poor data obtained with the potato starch containing sample is due to the large granule size and distribution.

Effect of compatibilization

The use of starch with a very small granule size improves the foam morphology. But these granules, once swollen with water, tend to agglomerate despite the prepolymerization step. They also were partially washed-out from the polymerizing system. This leads to an irregular foam morphology. In order to cope with this problem, maleic

a)



b)

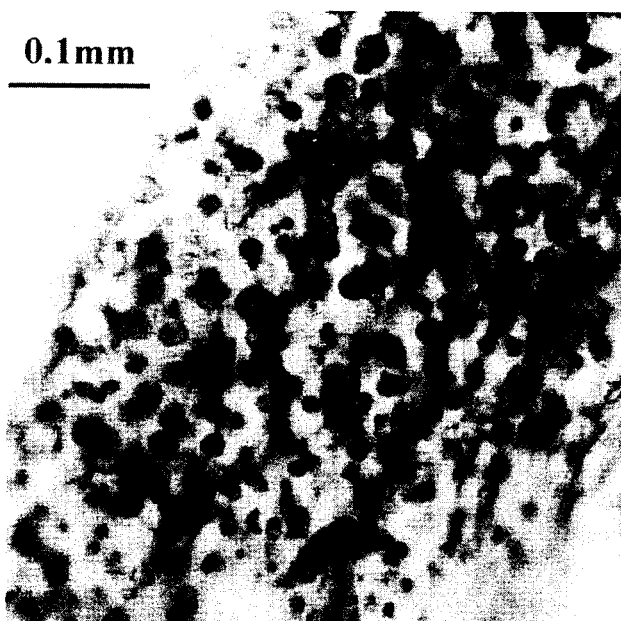
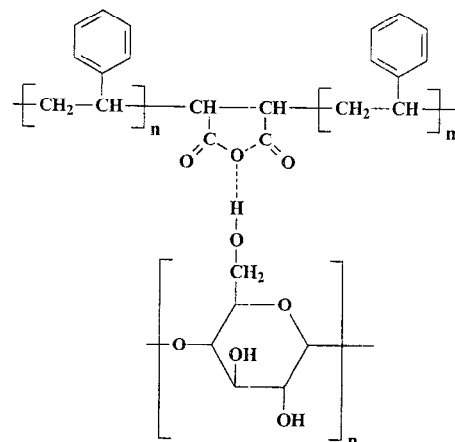


Fig. 5. Patterns of the starch dispersion in the not pre-expanded beads (black regions are swollen starch inclusion). a) starch not compatibilized with the polystyrene matrix, b) starch compatibilized with the polystyrene matrix using 0.5 wt.-% of maleic anhydride

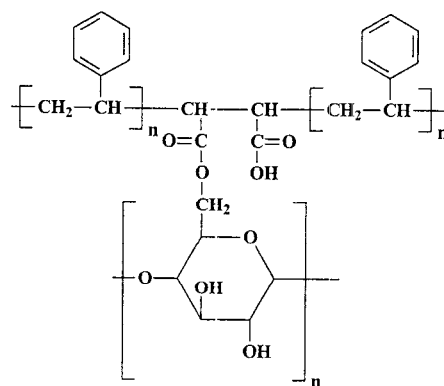
anhydride was used as compatibilizer. Maleic anhydride in concentration 0.5 wt.-% related to styrene was added directly to the prepolymerization mixture and copolymerized with styrene. The "compatibilizing" effect can be ascribed to reaction (ester) or interaction (H bond) of the

Scheme 2: Structure of possible products formed as the result of compatibilization. a) interaction of starch and styrene-maleic anhydride copolymer via H bond, b) starch grafted with styrene-maleic anhydride copolymer via esterification reaction

a)



b)



cyclic anhydride groups in the copolymer with hydroxyl groups of the starch macromolecule (Scheme 2). The significant compatibilizing effect and sufficient stabilization of the fine dispersion of the starch granules can be clearly seen in the microtome cuts of the not pre-expanded beads prepared without and with maleic anhydride (Fig. 5).

However, the results of the foam mean cell size do not correlate with the positive effect of compatibilization on the regularity of the starch dispersion in the matrix, though the regularity of the foam is improved. The improved regularity of the foam supports the idea that a fine and regular distribution of the starch granules determines the regular distribution of the cells, but the role of maleic anhydride in the foam formation process is still uncertain. We suggest that this contradiction is the result of different water desorption properties of starches caused by reaction/interaction of the starch granules with the matrix. A systematic investigation of the water desorption properties of starch made compatible with polystyrene is currently in progress.

Conclusion

EPS using water as the blowing agent was successfully prepared by suspension polymerization of the prepolymerized mixture of starch and styrene. It was shown that the fine dispersion of starch granules within the polystyrene matrix could be improved by compatibilization with maleic anhydride. The mean cell size of the foam of pre-expanded WEPS beads depends on the type of starch used in the formulation, mainly on its granule size distribution. The improvement of the pre-expanded foam density can be obtained using the alternative pre-expansion technique.

The possible improvement of both the foam morphology and the density is investigated to make the WEPS suitable for a whole range of EPS applications.

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