Optimization of Synthesis of Expandable Polystyrene by Multi-Stage Initiator Dosing

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Abstract

Suspension polymerization process is commonly used to produce expandable polystyrene. In the conventional method for producing this polymer, two different initiators are added to the process at two different temperature levels. In the industrial scale, this process is time consuming and difficult to control. A new method (Multi-Stage Initiator Dosing, MID) is proposed in which the initiator is dosed into the reactor. Laboratory and bench scale tests of this new method result in better control of the process, shorter reaction times and better quality of the product. Optimum temperature and dosing intervals are determined. The properties of the prepared samples by MID and conventional methods are compared with each other. According to the results, time process and consuming amount of initiator is reduced. Also, absorption of pentane was evaluated comparison to conventional methods. In fact, in this process the suspension control would be easier due to varying dose of initiator in several stages.

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1. Introduction

Suspension polymerization is an important heterogeneous polymerization technology used to produce specialty polymer granules. It is particularly suited to the production of polymer beads, typically in the range of 5-1000 μm [1]. Some of the main commercial resins produced by suspension polymerization processes are styrenic resins, such as general purpose polystyrene, expandable polystyrene (EPS), high-impact polystyrene (HIPS), poly (styrene-acrylonitrile) (SAN), poly (acrylonitile-butadiene-styrene) (ABS) and styrenic ion-exchange resins. These polymers are widely used in thermal insulation, packaging and architectural structures [2-4].

The process for production of expandable polystyrene by suspension polymerization of styrene with the addition of blowing agents (usually Pentane gas) is well known. This process results in the formation of polymer beads containing pentane as a blowing agent [5,6].

In the conventional industrial process EPS is produced using two different initiators, added at two different temperature levels, based on their half-life at the corresponding temperature. Benzoyl peroxide (BPO) is frequently used as the initiator of the first stage at a reaction temperature of between about 86°C and 92°C. Other initiators used include peroxy-2-ethylhexanoate, tert-butyl peroxy-2-ethylhexanoate, tert-amyl and 2, 5-dimethyl-2, 5-di (2 - ethylhexanoylperoxy) hexane [7]. Initiators such as tertbutyl benzoyl peroxide, tert-butyl phosphate (TBP) or dicumyl peroxide (DCP) are widely used for the high temperature second stage, which occurs between 115°C and 135°C. It should be noted, the second stage is usually a finishing step for minimizing the amount of residual monomer in the final EPS product [7].

In an industrial procedure both initiators are fed to the reactor from the very beginning. First stage polymerization lasts 4 h at a temperature of 90°C. Then, pentane is added to the system as a blowing agent and the temperature is increased to 130°C to initiate the second stage polymerization which lasts about 5 hours [8]. This process suffers from long process times and difficulties in the control of the polymerization process.

Precedence exists where initiator dosing has been successful in improving similar polymerization processes. For example, a process for the polymerization of styrene in the presence of brominated flame retardant is provided [9-12] during which the negative impact of the retardant agents on the molecular weight of polystyrene is corrected and a suitable molecular weight distribution is achieved [13-15]. Initiator dosing method is also successfully used in the production process of vinyl chloride copolymerization with vinyl acetate, ethylene, propylene, and styrene acrylonitrile [16-19]

In the present work, Multi-Stage Initiator Dosing (MID) is used in bench scale tests. The number of dosings and the dosing interval are optimized to achieve desirable number and weight average molecular weight, mechanical strength, residual monomer concentration and grain size distribution of the polymer product.

2. Materials and methods

2-1. Materials

Styrene (monomer-purity 99.7%), Pentane (blowing agent- pentane 99%) and deionized water (suspension media) were obtained from Tabriz Petrochemical Company. Reagent grade Calcium Phosphate (M_w=310.18 g/mol), Polyvinyl Alcohol (M_w=47000 and 98% hydrolyzed), Benzoyl Peroxide and tert-Butyl Benzoyl Peroxide were purchased from Merck.

2-2. Equipment

The laboratory setup used in this work consisted of a 5 L stainless steel Buchi reactor equipped with baffles, thermostatically controlled hot oil jacket, with a three blade mixer. Dosing pump supplied the initiator to the reactor at the programmed time and dose. The reactor is equipped with a discharge valve at the bottom.

Varian 3800CP Gas Chromatographer was used to determine the percentage of pentane absorbed and the concentration of monomer remaining in the samples. Testing was conducted in accordance with ASTM 5135. Grain size analysis of the two products was carried out on the Retch AS-200 Grain Size Analyzer equipped with a series of sieves with the following meshes: 0.315, 0.5, 0.71, 1, 1.8 and 2.5. Typical samples are poured on the top sieve and after shaking the sieves the accumulated amount of grains on each sieve is collected and weighed. The mechanical strength of the prepared blocks, was tested using a Zwick Roll (model TI-FR010THA50) Germany according to ASTM 1621. The number and weight average molecular weights and polydispersity of the samples were measured by an Agilent 1100 gel permeation chromatography (GPC) system equipped with a refractive index detector. China Caution optical microscope Model NSZ-810 with a magnification of 150X was used to study cell structure.

2-3. Method of polymerization

The following methods were used:

Conventional method: 2400 g of water was charged into a 5-litre reactor, followed by 5.6 g (0.0181 mol) of tricalcium phosphate and 1600 g (15.385 mol) of styrene monomer. The reaction mixture was stirred at 360 rpm. When the reactor temperature reached to 40°C, 2.26 g (0.01164 mol) of tert-butyl benzoyl peroxide and 5.93 g (0.02448 mol) of benzoyl peroxide were added to the mixture. The temperature was further increased to 90°C at a rate of 0.83°C/min and kept at 90°C for 4 h.

During this "low temperature polymerization" stage, the size and growth of the particles were regularly checked because during this stage, the risk of agglomeration of polymer beads existed, which might result in formation of two-phase system or undesirable lumps. At the end of the 4 hperiod of the low temperature polymerization, 11.5 g (2.4468*10-4 mol) of polyvinyl alcohol (5wt%) followed by 128 g

(1.7741 mol) of pentane was added and the temperature was increased to 120°C at a rate of 0.5°C/min (7bar). It should be noted that the boiling point of the deionized Water in 7 bar pressure is equal to 164.97˚C. The reactor was kept at 120°C for 5 h and subsequently cooled to room temperature. It took about 1 hour for the temperature of the reactor to reach room temperature. Finally, the reactor was evacuated and polymer beads were filtered, washed with deionized water and dried.

Multi-Stage initiator dosing method: The equipment and materials were similar to those described for the conventional method. 2400 g of water, 5.6 g (0.0181 mol) of tricalcium phosphate, 11.5 g (2.4468*10-4 mol) of polyvinyl alcohol (5wt%) and 1491 g (14.3365 mol) of styrene monomer were charged into the reactor. The temperature was increased to 85°C at a rate of 1.083°C/min. Then the initiator solution (containing 4.448 g (0.01836 mol) benzoyl peroxide in 109 g (1.048 mol) styrene) was equally divided into 12 parts and charged at the specified dosing intervals and temperatures to the reactor (according to Table 1).

At the end of the so-called "low temperature polymerization stage", 128 g (1.7741 mol) of pentane and 2.26 g (0.01164 mol) of tert-butyl benzoyl peroxide as the initiator of the second stage were added. The reaction mixture was heated to 120ºC at a rate of 0.33°C/min, and polymerization was continued for 2.5 h (7 bar).

3. Results and discussion
3-1. Determination of the optimal number of stages and the time interval between initiator dosing

In the conventional EPS production method, the typical monomer conversion in the first stage is about 50% [20-24]. A lower conversion results in a sticky paste and higher conversions result in low absorption of pentane in the following stage. Using the proposed initiator dosing procedure we were able to obtain 70% monomer conversion at the end of first phase [8]. The results of the initiator dosing experiments are summarized in Table 1. As can be seen in this table, in experiments 1 to 7, the percentage conversion of monomer at the end of the first phase was very high. The high conversion rate will result in lower absorption of the blowing agent, pentane (Note the results of test 7). In experiment 8 we tried changing the value of initiator, dosing intervals and reducing the time interval to 15 minutes, in order to achieve lower conversion in the first stage. Experiments 9 and 10 are conducted to ensure the reproducibility of the experiment 8. Experiments 11 to 15 use the same conditions as experiment 8, with the second stage carried out fully to the end. Experiments 12 to 15 have been carried out to check the repeatability of test 11. According to the results obtained, operational conditions of test 8 were considered as the optimal conditions in multiple stages dosing method.

Table 1
Measured and Calculated data of the experiments [25].

Experiment No.	Molar ratio of initiator consumed in dosing method to that of conventional method	Total time of the first stage of the polymerization (h)	Temperature for each of the 12 stages of initiator dosing (ºC)	Time interval between dosing	Measured monomer conversion at the end of the first stage	Total time of the second stage of the polymerization (h)	Measured monomer conversion at the end of the second stage	pentane Percent absorbed to polymer
1	1	4	85,89,94.5,99,104,109.5, 104,109.5 Other shots at 110	First 9 injections, every 15 minutes. The other shots every 30 minutes.	84.13	-	-	-
2	1	3.5	85,90,95,100,105, Other shots at 110	First 11 injections, every 15 minutes. The other shots every 30 minutes.	83.81	-	-	-
3	0.8	3.5	85,90,95,100,105, Other shots at 110	First 11 injections, every 15 minutes. The other shots every 30 minutes.	72.83	-	-	-
4	0.8	3	85, 98 Other shots at 110	Every 15 minutes	72.07	-	-	-
5	0.8	3.25	85, 95 Other shots at 110	First 3 injections, every 30 minutes. The other shots every 15 minutes.	72.85	-	-	-
6	0.8	3.25	85, 100 Other shots at 110	First 2 injections, every 30 minutes. The other shots every 15 minutes.	72.96	-	-	-
7	0.8	3.25	85, other shots at 110	First 2 injections, every 30 minutes. The other shots every 15 minutes.	73.59	2.5	99.77	4.2%
8	0.75	3	85, other shots at 110	Every 15 minutes	66.89	-	-	-
9 (Repeat 8)	0.75	3	85, other shots at 110	Every 15 minutes	67.15	-	-	-
10 (Repeat 8)	0.75	3	85, other shots at 110	Every 15 minutes	66.73	-	-	-
11	0.75	3	85, other shots at 110	Every 15 minutes	66.94	2.5	99.51	6.7%
12 (Repeat 11)	0.75	3	85, other shots at 110	Every 15 minutes	67.82	2.5	99.7	6.3%
13 (Repeat 11)	0.75	3	85, other shots at 110	Every 15 minutes	68.09	2.5	99.6	6.3%
14 (Repeat 11)	0.75	3	85, other shots at 110	Every 15 minutes	66.13	2.5	99.65	6.5%
15 (Repeat 11)	0.75	3	85, other shots at 110	Every 15 minutes	67.94	2.5	99.73	6.2%

3-2. Comparison of polymerization time of two methods

In Fig. 1, the temperature profile of the system for the two methods of conventional and "MID" (with the optimal conditions of experiment 8 in Table 1) are drawn.
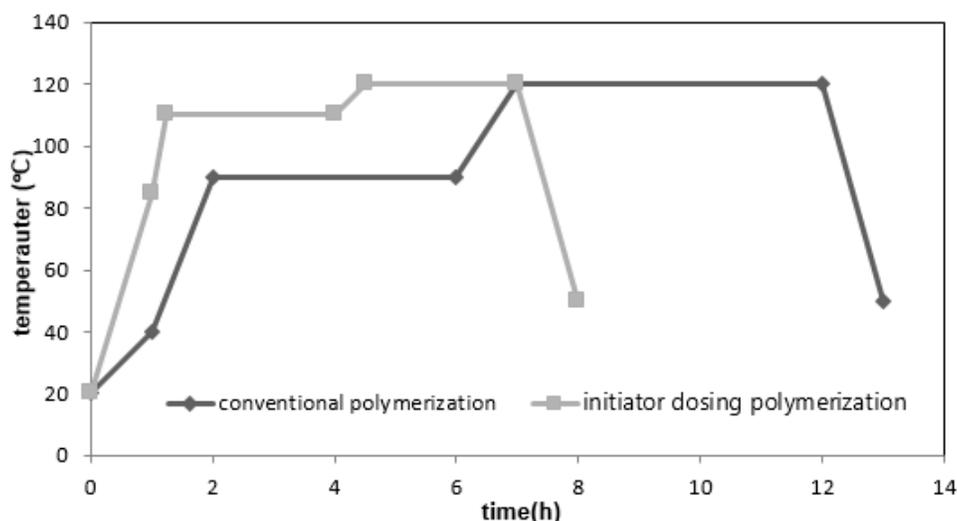
Figure 1. Temperature profile of the system for conventional and optimal dosing methods [25].

According to Fig. 1, the total time of the process in conventional and MID processes is 13 and 8 hours respectively. In other words, MID polymerization has led to 5 hours reduction in total time of the polymerization process. This reduction in time is due to the following reasons:

1) At the beginning of the MID process, there is no initiator in the reactor up to 85°C, thus the temperature can be increased very quickly. Therefore, the total time is reduced about 1 h.

2) First stage of the polymerization of the conventional method is done at 9°C and within 4 hours whereas this stage is done at 11°C in the MID process, requiring only 3 hours, which shortens the process by another 60 minutes.

3) At the beginning of the second stage of the conventional process, the temperature is increased from 85°C to 120°C which takes 1 hour. But in the MID process, temperature is increased from 110°C to 120°C requiring only half an hour.

4) The second stage of the conventional process continues for 5 h whereas in the MID process, this stage lasts only 2.5 h due to the higher amount of monomer conversion at the end of the first stage, resulting in 2.5 h of time saving.

On the whole, the MID process leads to 5 hours reduction in the total time of the polymerization process (about 40%) which is synonymous with increasing the production capacity of a manufacturing unit without any requirement to install new equipment [25].

3-3. A comparison of system consistency control type in two methods

In the conventional process for the production of expandable polystyrene, the most sensitive stage is the first polymerization stage. In this stage, phase separation threatens the process. First stage polymerization takes 4 h. Equilibrium exists between formation and deformation of polymer beads that overtime will shift towards higher diameter beads, which is

undesirable. Therefore, frequent sampling and control of these phenomena is needed. In the MID process, this problem does not occur, as the initiator is dosed into the system gradually and is not all present in the system at the outset of the process. Therefore, the polymerization rate is controlled and the risk of formation of gel or phase separation does not exist. Thus continual monitoring is no longer required, resulting in a simpler, more robust process.

3-4. Comparison of the amount of initiator utilized in the two methods

Consumption of the initiator in the MID process is 25% less than the common method. Reduction of the consumption of

benzoyl peroxide is significant, as it is an economic advantage and also results in a higher purity and a "greener" product

3-5. Comparison of molecular characteristics of the samples

In order to compare the molecular characteristics of the samples, number and average molecular weight and polydispersity of the sample obtained from dosing method with the optimal conditions (experiment 8 in Table 1) and the sample obtained from the conventional method are measured by GPC. The elugram of the samples are shown in Fig. 2 and the average molecular weights are brought in Table 2 [25].
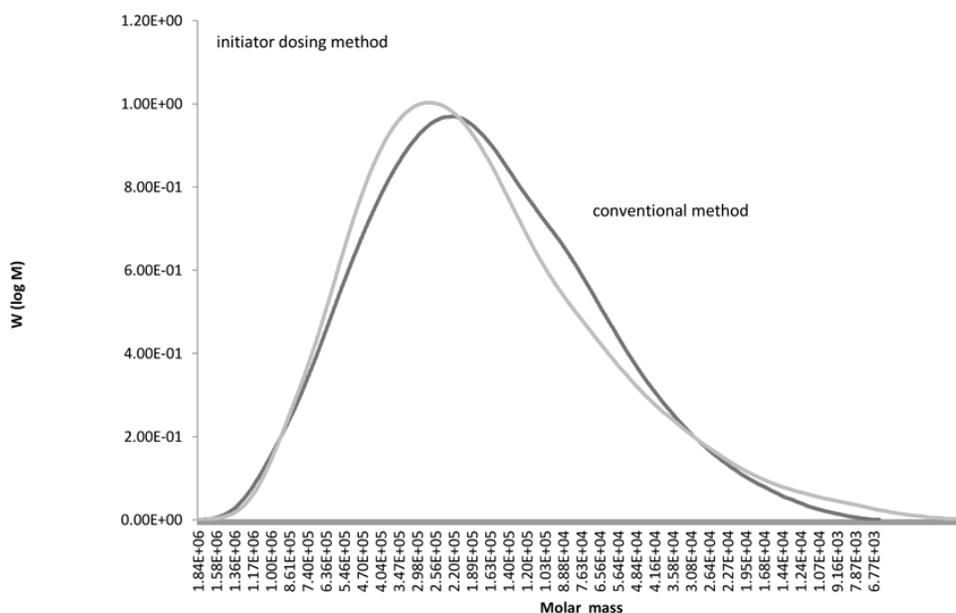
Figure 2. Elugram of the samples obtained from the conventional and dosing methods [25].

Table 2

Comparison of the molecular characteristics of the samples.

Polymerization method	M_w (g/mol)	M_n (g/mol)	PDI
Conventional	2.5282×10^5	1.0559×10^5	2.4
Dosing method	2.9591×10^5	1.0526×10^5	2.8

According to the obtained results, the molecular characteristics of the samples of two methods are nearly the same.

3-6. Comparison of the residual monomer in samples resulting from the two methods

It may be expected that shorter polymerization time should result in an increase in the residual monomer concentration and the resulting health and environmental concerns. GC analysis was carried out on typical samples from both processes to compare the amount of residual monomer. The results reflected in Table 3 show that the concentration of residual monomer remains constant (within the experimental error) between the two processes. This is, at least partially, due to the fact that in the initiator dosing method, first stage polymerization is carried out at higher temperatures, resulting in higher polymerization rates.

Table 3
Comparison of residual monomer percentage in samples resulting from both methods [25].

Polymerization method	residual monomer %
Conventional	0.360 ± 0.037
MID	0.362 ± 0.039

3-7. Comparison of pentane absorbed in samples resulting from both methods

Average and standard deviation of pentane concentration from 5 different batch products using GC analysis is reflected in Table 4. The initiator dosing method results in higher pentane concentration. A higher pentane concentration is considered an advantage if it produces a foam with regular cell structure and uniform cell size distribution. Thus microscopic analysis of the cell structure is required.

Table 4
Comparison of the percentage of pentane absorbed in samples resulting from the two methods.

Polymerization method	Pentane Concentration (wt%)
Conventional	5.3 ± 0.08
MID	6.4 ± 0.09

3-8. Comparison of cell structure of beads resulted from the two methods

The cell structure of both products was studied under a light microscope at 150 times magnification. Figures 3 and 4 are typical snapshots of the two products. The cell structure is largely the same, and uniform in both samples. The average cell size is larger in the product of MID process, due to higher absorption of pentane. These conclusions are also supported by the results of mechanical property analysis.
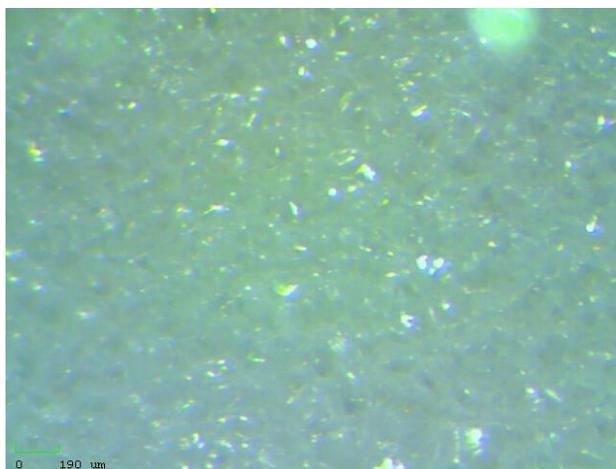
Figure 3. Microscopic image of EPS produced using the conventional method (150X magnification).
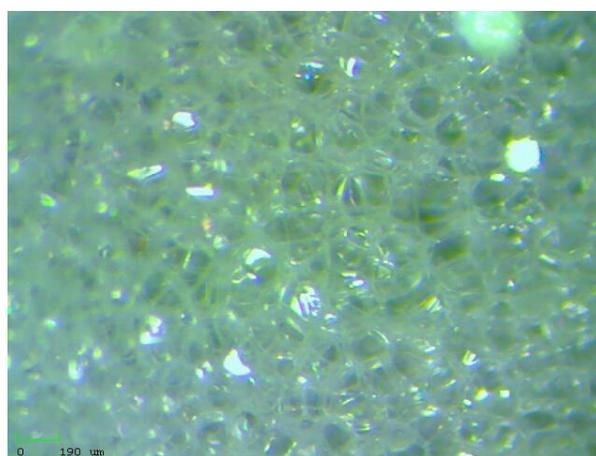
Figure 4. Microscopic image of EPS produced using MID (150X magnification).

3-9. Comparison of the distribution of sizes of beads resulted from the two methods

Figure 5 summarizes the results for both products (conventional and MID) from 5 different batches. MID results in a narrower distribution of grain sizes and larger population in the desirable range of 0.7 to 1 millimeter.
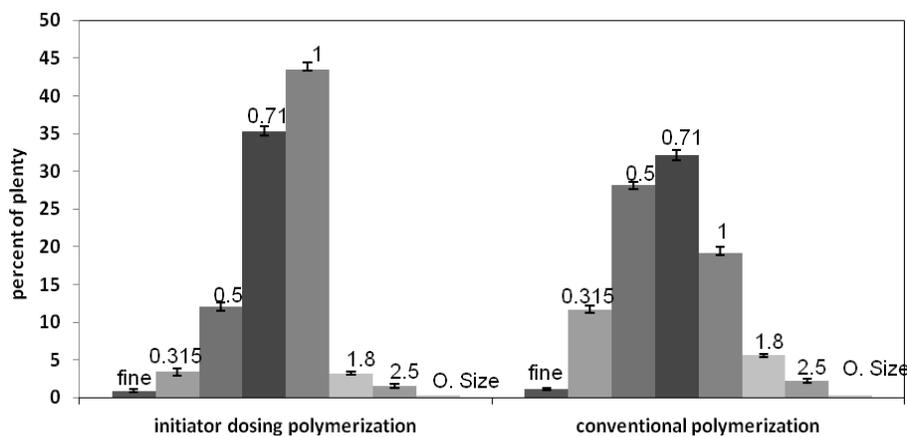
Figure 5. Comparison of EPS grain size distribution from both methods.

3-10. Comparison of mechanical characteristics

To study the mechanical characteristics of produced EPS using the two methods, the blocks supplied were compared with pressure test of ASTM 1621 standard. The results are reflected in Fig. 6.
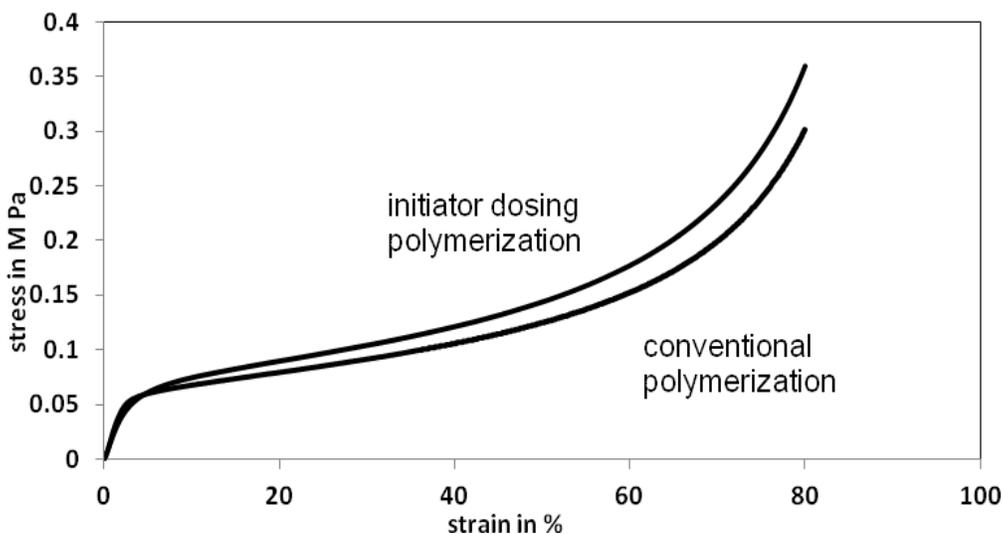
Figure 6. Pressure test results obtained by both methods for blocks made from EPS.

Values obtained for Young's modulus, compressive strength and minimum compressive resistance are compared in Table 5. The Young's modulus shows a slight decrease, perhaps as a result of higher pentane content in the product from the MID process. Both compressive strength and minimum compressive resistance show significant increases, which are desirable in most applications where EPS is used.

Table 5

Young's modulus, compressive strength and minimum compressive resistance.

Polymerization method	Young 's modulus MPa	Compressive strength (at 10% strain) MPa	Minimum compressive resistance MPa
Conventional	2.3	0.30	0.041
MID	2.1	0.35	0.047
change%	-8.7%	+16.6%	+14.63

Overall, it can be concluded that MID can produce a comparable product to the conventional method through a significantly easier and more robust process with considerably reduced batch time. More efficient use of the initiators in the MID process results in less residual material in the

final product, making it healthier and more environmentally friendly.

4. Conclusions

1. It is shown that by using an initiator dosing method significant savings in polymerization times can be achieved while keeping the quality of the product largely unchanged and without major changes to the equipment

2. Initiator dosing results in better control of the polymerization process and better control of the rate of polymerization, resulting in lower occurrences of in this conditions.

3. Under optimum initiator dosing method conditions, 25% less initiator is consumed.

4. Tests show that absorbed pentane will increase, resulting in higher expansion ratio.

5. Residual monomer remained constant between the two methods.

6. Polymer blocks made from both methods exhibit similar mechanical properties.

7. Regarding the results of the molecular characteristics analysis and pentane absorption measurement, it was found that the initiator dosing method had no significant effect on the average molecular weights of the sample but increased the pentane absorption in the product

Acknowledgement

References

[1] Dowding, P. and Vincent, B., "Suspension polymerization to form polymer beads", *Colloid Surface A.,* **161** (7), 259 (2000).

[2] Lenzi, M. Silva, F. and Lima E *et al*., "Semi-batch styrene suspension polymerization processes", *J. Appl. Polym. Sci.,* **89** (17), 3021 (2003).

[3] Yuan, H. Kalfas, G. and Ray, W., "Suspension polymerization", *J. Macromol. Sci-rev.,* **2** (84), 215 (1999).

[4] Kajimura, M. and Kaisha, S., US Pat. 4303757, (1981).

[5] Nikfarjam, N. Qazvini, N. T. and Deng, Y., "Cross-linked starch nanoparticles stabilized Pickering emulsion polymerization of styrene in w/o/w system", *Colloid. Polym. Sci.,* **292** (13), 599 (2013).

[6] Pascal, N. and Jacques, C. US Pat. 012798, (2011).

[7] Shaghaghi, S. and Mahdavian, A. R., "The Effect of Sodium Dodecyl Benzene Sulfonate on Particle Size in Suspension Polymerization of Styrene", *Polym-Plast. Technol.,* **45** (16), 109 (2006).

[8] Herman, H. A. Enschede, O. and Bart, F. et al, US Pat. 069983, (2011).

[9] Scheirs, J. and Priddy, D. Modern Styrenic Polymers. Wiley Series in polymer science, England (2003).

[10] Boevenbrink, H. G. and Hoogesteger, F. J. US Pat. 0111529 A1, (2006).

[11] Meulenbrugge, L. and Vanduffel, K. A. K. and Westmijze, H., US Pat. 0122330 A1, (2006).

[12] Swieten, A. P. V. and Westmijze, H. and Schut, J., US Pat. 6639037 B2, (2003).

[13] Rene, G. and Jacobus, S. and Willibrordus, O. J. *et al*, US Pat. 000916 A1, (2012).

[14] Meulenbrugge, L. and Swieten, A. P. V. and Vanduffel, K. A. K. *et al*, US Pat. 7173095 B2, (2007).

[15] Westmijze, H. and Swieten, A. P. V. and Meulenbrugge, L. *et al*, US Pat. 0046328 A1, (2011).

[16] Speikamp, H. and Kiihnle, A. and Bretschneider, J., US Pat. 5189069, (1990).

[17] Zhang, L. and Shi, T. and Wu, S. *et al.*, "Sulfonated graphene oxide: the new and effective material for synthesis of polystyrene-based nanocomposites", *Colloid. Polym. Sci*., **291** (7), 2061 (2013).

[18] Parsa, M. A. andGhiass, M. and Moghbeli, M. R., "Mathematical Modelling and Phase Separation Kinetics of Polystyrene/Polyvinylmethylether Blend", *Iran. Polym*., **20** (9), 689 (2011).

[19] Li, H. Wu, S. and Wu, J. *et al*., "A facile approach to the fabrication of graphene-based nanocomposites by latex mixing

and in situ reduction", *Colloid. Polym. Sci.,* **291** (8), 2279 (2013).

[20] Wang, S. Chen, H. and Liu, N., "Ignition of expandable polystyrene foam by a hot particle: An experimental and numerical study", *J. Hazard. Mater.,* **283** (8), 536 (2015).

[21] Chen, W. Hao, H. and Hughes, D. *et al*., "Static and dynamic mechanical properties of expanded polystyrene", *Mater. Design*., **69** (10), 170 (2015).

[22] Ferrándiz-Mas, V. and García-Alcocel, E., "Durability of expanded polystyrene mortars", *Constr. Build. Mater.,* **46** (7), 175 (2013).

[23] Vaitkus, S. Granev, V. Gnip, I. *et al*., "Stress Relaxation in Expanded Polystyrene (EPS) Under Uniaxial Loading Conditions", *Proc, Eng.,* **57** (9), 1213 (2013).

[24] Su, J. J. Yang, G. and Zhou, T. N. *et al*., "Enhanced crystallization behaviors of poly(ethylene terephthalate) via adding expanded graphite and poly(ethylene glycol)", *Colloid. Polym. Sci.,* **291** (6), 911 (2012).

[25] Derakhshanfard, F. Fazeli, N. Vaziri, A. and Heydarinasab, A., "Kinetic study of the synthesis of expandable polystyrene via "multi-stage initiator dosing" method", *J. Polym. Res.,* **22** (6) (2015).