Society of Plastics Engineers

5th International Conference on Thermoplastic Foam

FOAMS 2006

September 13 - 14, 2006
Chicago, Illinois, USA

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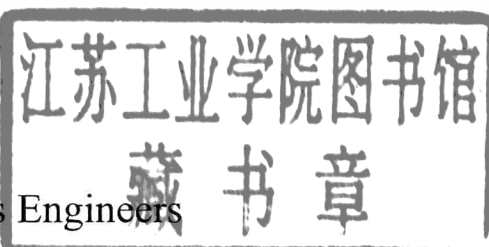# 5th International Conference on Thermoplastic Foam

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A PREDICTIVE METHOD FOR ESTIMATING THE MINIMUM DYNAMIC CRITICAL SYSTEM PRESSURE REQUIRED TO DISPERSE BLOWING AGENT IN POLYSTYRENE

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Abstract

A predictive method for estimating the minimum dynamic critical system pressure required to disperse the blowing agents in molten polystyrene has been introduced based on the relationship between dynamic and equilibrium solubility determined using the Theory of Corresponding States. This method can be used to estimate the minimum dynamic system pressure required to disperse new blowing agent systems as a function of temperature and blowing agent concentration in the foam extrusion line. A brief discussion on the effect of dynamic system pressure on the cellular structure, skin, quality, and the pressure drop calculations through the foam extrusion line will be given.

Introduction

The physical and environmental impact characteristics of potential blowing agents are very important in the selection of nontoxic, environmentally acceptable (VOC, ODP, GWP) alternative blowing agents that are sustainable and economically viable [1]. Selection of suitable blowing agents for each polymer is also important for producing dimensionally stable foams with desired cellular structures and physical properties required in various applications. Some of the desirable properties of suitable blowing agents are as follows:

A. High solubility of blowing agents at high processing temperatures and low solubility at the ambient temperature are desirable for improving processability due to lower system pressure, better blowing agent mixing, better cell size control, and also for improving physical properties because of less plasticization of cellular polymers at the ambient temperature.

B. The permeability of blowing agent or mixed blowing agents through the cellular polymers should be similar to or higher than that of air through the same cellular polymers. Nakamura [2] showed in his patent that in order to produce a dimensionally stable foam, the permeability of a mixed blowing agent system should be between 0.75 to 6 times that of air through the same styrenic polymers.

C. A suitable blowing agent or blowing agent mixture for the thermal insulation foam containing at least one insulating blowing agent should have low vapor thermal conductivity and low gas permeability to produce a thermal insulation foam with low long-term k-factor [3].

A successful selection of blowing agents depends on the solubility and permeability of blowing agents as described above and also on the ability to produce foams with desired cellular structures, cross-sectional size and shape, and properties required in end-use applications. Therefore, foam process and product developments often have been motivated by issues associated with the blowing agents. One example is the development of patented critical dynamic solubility concept at The Dow Chemical Company [4] and its application for the process control and process equipment design in producing low density extruded foam products with good quality. This development was motivated by the inability to predict the pressure drops through the process equipments using the equilibrium solubility data and the

computational fluid dynamics (CFD), resulting in significantly lower values than the experimental pressure drop values.

Experimental

Figure 1 shows the schematic diagram of experimental setup used for this investigation. The foam extrusion line consisted of a 1.25" extruder with mixing elements, temperature controlled jacketed quartz window, coolers, and a die. A manual valve was installed between the coolers and the die to control the pressure at the outlet of the quartz window. Temperature readings were also taken at the same area. The extruder was running at 13.6 lbs/hr set-point. At the time this work was done in the mid 1970's [5], Dow was interested in designing a new extrusion line for the super-critical blowing agent CO_2 in the pilot plant. CFC-12 was selected as a test blowing agent since it is a supercritical fluid at the foaming temperature as shown in Table 1.

The experimental critical dynamic pressure data were obtained by observing the appearance of blowing agent bubbles through the quartz window followed by blowholes in the foam and gassing at the die below the critical dynamic pressures and the disappearance of blowing agent bubbles followed by the absence of blowholes and gassing at the die above these critical dynamic system pressures. The latter critical dynamic system pressure was slightly higher than the former critical dynamic system pressure due to the difficulty of dissolving the foam particles inside the die area. However, when carrying out this experiment very carefully by slowly changing the line pressures and making sure that foam bubbles at the die area were all dissolved, the difference between these two pressures was small and within the experimental error (~5%). Most of the time, the pressure at which the blowing agent bubbles start to appear was taken to be the critical dynamic system pressure. Otherwise, the experiment was repeated after thorough line purge was completed. The observation through the quartz window was facilitated by the use of a cathetometer equipped with a microscope. High speed motion picture was also taken at the speed of 2300 frames per second. Tables 2 - 7 show the experimental data.

Results and Discussions

Figure 2 shows the experimental equilibrium and critical dynamic pressures for CFC-12 (or R-12) as a function of blowing agent concentration at 175 and 200 °C. The results show that the critical overpressure (P_{dyn} - P_{eq}) required to keep blowing agent in polystyrene solution increases rapidly as the blowing agent concentration or temperature increases as shown in Figure 3.

Since solubility and viscosity are related to the free volume, we have applied the Theory of Corresponding States advanced by Van der Waals in 1873 which states that all pure fluids manifest the same compressibility factors when measured at the same reduced conditions of pressure and temperature. According to this principle, the deviation of thermodynamic properties of different pure fluids would manifest the same departure from the properties of these substances in their ideal gaseous state when measured at the same reduced conditions of temperature and pressure.

Figure 4 shows the experimental solubility of CO_2 in molten polystyrene at high pressures by V.A. Khan and Esin Gulari at Wayne State University, and Figure 5 shows the minimum overpressure required to disperse CO_2 in polystyrene as a function of reduced temperature which was estimated by extrapolating Figure 3 and Table 1. Figure 6 shows the method of determining the minimum dynamic system pressure and the dynamic solubility of CO_2 at 130 °C using the Theory of Corresponding States. Figure 7 shows the minimum dynamic system pressure of CO_2 in polystyrene as a function of CO_2 concentration at three different temperatures, 130 °C, 150 °C, and 165 °C. This predictive method provided dynamic system pressures within the experimental error based on plant evaluations for various blowing agent mixtures. In these cases, it was assumed that the additive rule applies.

Figure 8 shows the minimum overpressure required to disperse R-12 and CO_2 vs. reduced temperature. It appears that there is a strong possibility to generalize the minimum or

critical dynamic overpressure required to disperse any blowing agent in a given polymer. Therefore, if the equilibrium solubility of a given blowing agent in polystyrene is available, the critical or minimum dynamic system pressure of this blowing agent in polystyrene can be estimated from Figure 8 in the supercritical temperature range (Tr > 1). If the equilibrium solubility is not available, then the Flory-Huggins equation can be used to calculate the equilibrium solubility as a first approximation which is adequate for most engineering purposes [6]:

$$\ln a = \ln v_o + v_p + x v_p^2 \qquad (1)$$

where $a = f / f^o = p / p^o$ and a = activity, f = fugacity, f^o = fugacity of pure blowing agent, p = vapor pressure above the polymer solution, p^o = vapor pressure of pure blowing agent, and v_o and v_p are volume fraction of blowing agent and polymer, respectively. x = Flory-Huggins interaction parameter, which can be expressed as:

$$x = 0.34 + V_o(d_o - d_p)^2 / RT \qquad (2)$$

where V_o is the molar volume of the blowing agent, and d_o and d_p are the solubility parameter of blowing agent and polymer, respectively.

For the subcritical process temperature range where the phase separation can occur, a blowing agent having a high critical temperature (T_c), methyl chloride was selected as a test sample. Figure 9 shows the experimental equilibrium and dynamic system pressure as a function of blowing agent concentration at 175 °C and 200 °C at the quartz window area. Figure 10 can be extrapolated down to the glass transition temperature (or solidification temperature) of the blowing agent and polystyrene mixture. The results showed that the dynamic critical overpressure required to disperse a given blowing agent increases with increasing temperature and blowing agent.

Lastly, the effect of minimum dynamic critical system pressure on the cellular structure and skin quality is very similar to the pre-foaming condition which manifests itself as a fine smearing and streaking, and increased open cell content and blowholes, although the system pressure is greater than the equilibrium vapor pressure of the blowing agent and polystyrene mixture [7]. Another process problem encountered was the underestimation of calculated pressure drops through the process equipments by as much as 40 - 70% using a CFD (Computational Fluid Dynamics) and equilibrium solubility [8]. This may also apply to the computer simulation of the foaming process, nucleation, and other process simulations that include the solubility and viscosity of polymer and blowing agent mixtures.

Conclusion

A concept of critical dynamic system pressure has been introduced and the feasibility of predicting the minimum dynamic system pressure required to keep the blowing agent in solution has been demonstrated for any blowing agent in a given polymer. Secondly, the relationship between dynamic solubility and dynamic system pressure has been determined based on the Theory of Corresponding States. Further work is recommended.

Acknowledgments

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3. K.W. Suh, and G.W. Killingbeck, Canadian Patent 1,086,450, 1980 (To Dow); K.W. Suh, and G.W. Killingbeck, British Patent 1,537,421, 1978 (To Dow).

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Keywords

Equilibrium vapor pressure, minimum dynamic system pressure, dynamic critical overpressure, polystyrene foam.

Table 1. Reduced Temperatures, Tr (T/T_c)

$T(^oC)$	Methyl Chloride	CFC-12	CO_2
200	1.14	1.23	1.56
175	1.08	1.16	1.47
165	1.05	1.14	1.44
150	1.02	1.10	1.39
135	0.98	1.06	1.34
120	0.94	1.02	1.29
100	0.90	0.97	1.23
T_c	143	112	31

Table 2. Equilibrium and Dynamic Solubility of R-12

$T(^oC)$	Tr	R-12 pph	Equilibrium Press. MPa	Dynamic Press. MPa
175	1.16	4.1	1.45	1.90
		6.4	2.07	2.92
		10.8	3.07	4.83
		14.5	3.69	6.90
		18.5	4.17	8.41
200	1.23	3.0	1.45	2.59
		5.3	2.24	4.00
		11.7	3.86	7.07
		15.0	4.48	8.62
		18.5	4.93	10.00

Table 3. Minimum Overpressure Required to Disperse R-12 vs. Reduced Temperature

Tr	R-12 (pph)	ΔP_c (MPa)
1.16	1.0	0.1
	2.0	0.2
	4.0	0.5
	6.0	0.8
	8.0	1.2
	10.0	1.7
1.23	1.0	0.5
	2.0	0.9
	4.0	1.4
	6.0	1.9
	8.0	2.4
	10.0	2.9

Table 4. Solubility of CO_2 in Polystyrene (PS), V.A. Khan, "Solubility of Gases in Molten Polymers at High Pressures," Ph.D. Dissertation, Wayne State University, Detroit, MI, 1998.

130 °C		150 °C		165 °C	
Press. (MPa)	Wt.%	Press. (MPa)	Wt.%	Press. (MPa)	Wt.%
17.36	12.26	19.29	11.70	18.33	10.65
15.62	11.40	17.24	10.97	16.25	10.18
13.93	10.54	15.31	10.20	14.05	9.01
12.12	9.77	13.27	9.36	12.19	8.31
10.64	8.77	11.55	8.45	10.47	7.49
9.22	8.08	9.96	7.69	8.39	6.48
7.48	6.95	8.04	6.58	6.80	5.43
6.01	5.73	6.45	5.62	4.70	3.64
4.14	4.21	4.46	3.88	2.63	2.02
2.32	2.39	2.50	2.17	1.18	0.82
1.03	1.04	1.16	0.91		
0.46	0.28				

Table 5. Minimum Overpressure Required to Disperse CO_2 in PS vs. Reduced Temperature

T(°C)	Tr	CO_2 pph	ΔP_c MPa	Equil. System Press. MPa	Critical Dynamic Press. MPa
130	1.33	2.0	1.80	2.00	3.80
		4.0	2.83	4.10	6.93
		6.0	3.55	6.20	9.75
		8.0	4.14	9.00	13.14
		10.0	4.56	12.60	17.16
150	1.39	2.0	2.37	2.30	4.67
		4.0	3.65	4.20	7.85
		6.0	4.50	7.30	11.80
		8.0	5.17	10.50	15.67
		10.0	5.74	14.80	20.54
165	1.44	2.0	2.83	2.70	5.53
		4.0	4.36	5.10	9.46
		6.0	5.32	7.90	13.22
		8.0	5.98	11.50	17.48
		10.0	6.62	16.30	22.92

Table 6. Equilibrium and Dynamic Solubility of Methyl Chloride

T(°C)	Tr	Methyl Chloride MPa	Equil. Press. MPa	Dynamic Press. MPa
175	1.08	8.30	2.55	3.10
		11.90	3.45	4.31
		12.50	3.72	4.83
200	1.14	8.30	3.24	3.79
		12.50	4.62	5.86
		16.50	6.00	6.90

Table 7. Minimum Overpressure Required to Disperse Methyl Chloride vs. Reduced Temperature

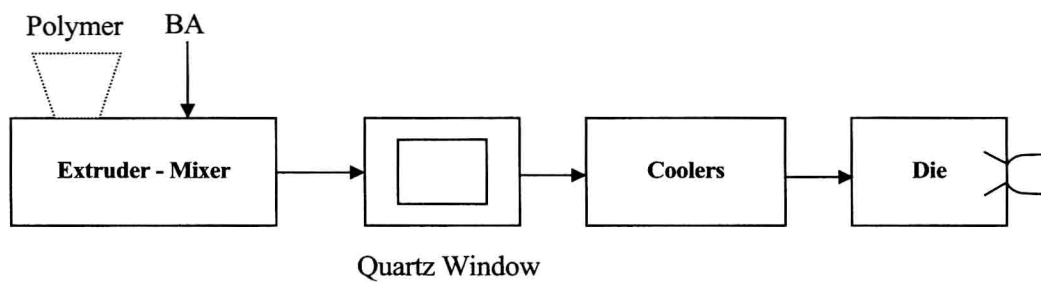| T(°C)	Tr	Methyl Chloride pph	ΔP_c MPa
150	1.02	2.0	0.14
		4.0	0.25
		6.0	0.38
		8.0	0.48
		10.0	0.61
175	1.08	2.0	0.17
		4.0	0.31
		6.0	0.48
		8.0	0.62
		10.0	0.79
200	1.14	2.0	0.21
		4.0	0.38
		6.0	0.59
		8.0	0.76
		10.0	0.97

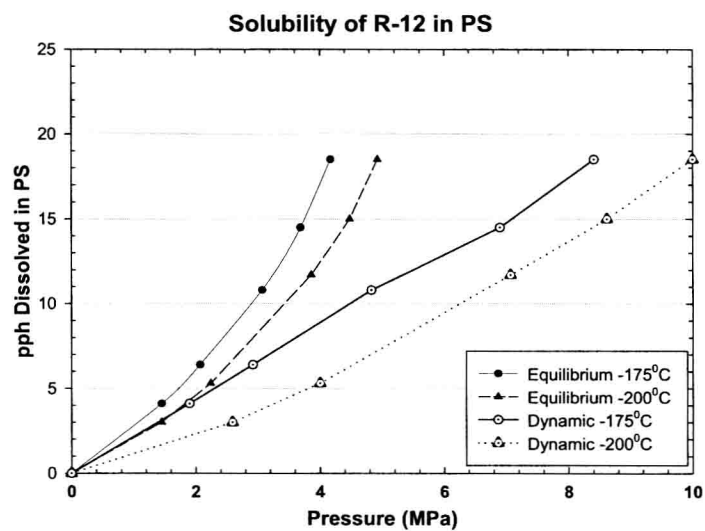Figure 1: Schematic Diagram of Experimental Setup

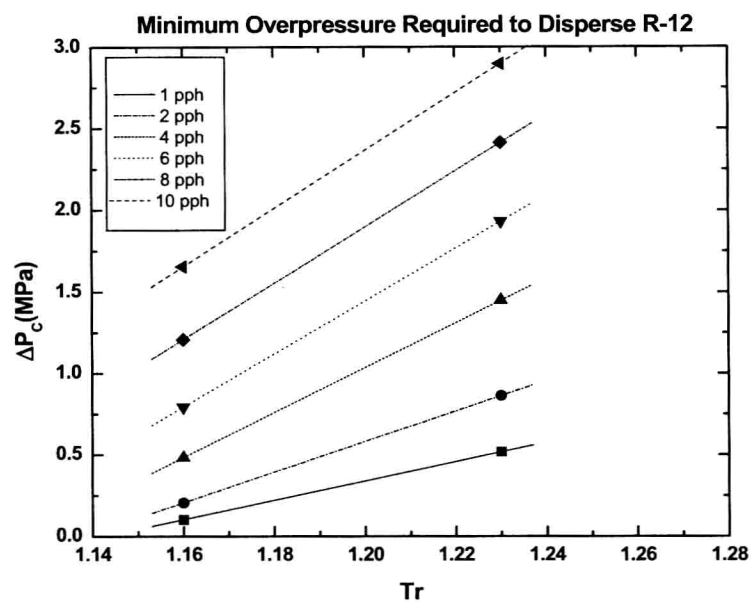Figure 2: Equilibrium and Dynamic Solubility of R-12 at 175 °C and 200 °C

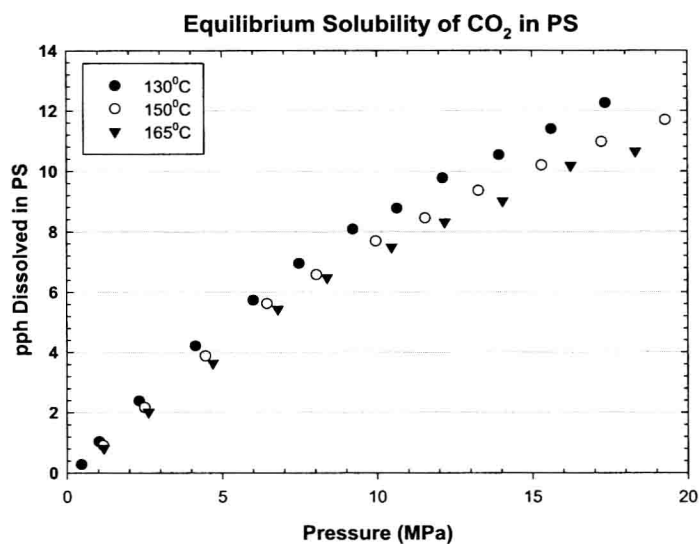Figure 3: Minimum Overpressure Required to Disperse R-12 vs. Reduced Temperature

Figure 4: Solubility of CO_2 in Molten Polystyrene at High Pressure, V.A. Khan, "Solubility of Gases in Molten Polymers at High Pressures," Ph.D. Dissertation, Wayne State University, Detroit, MI, 1998.
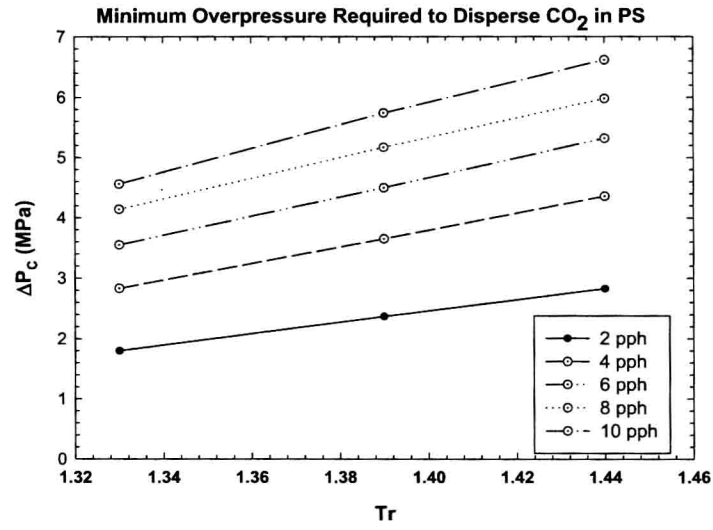
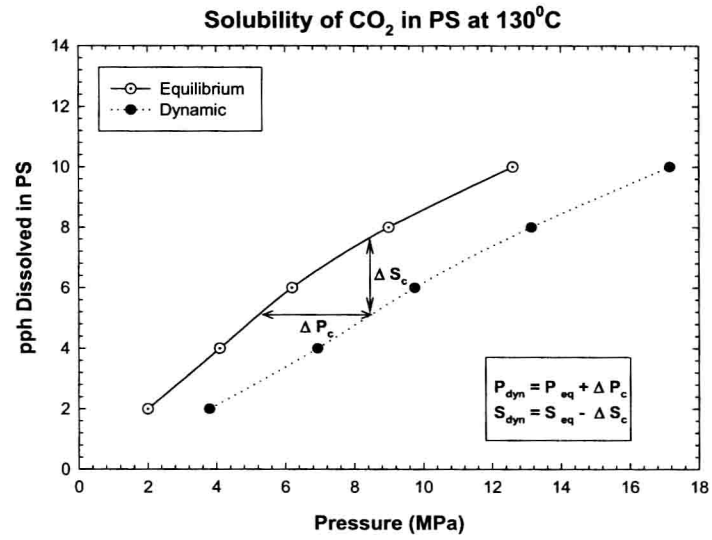Figure 5: Minimum Overpressure Required to Disperse CO_2 in PS vs. Reduced Temperature

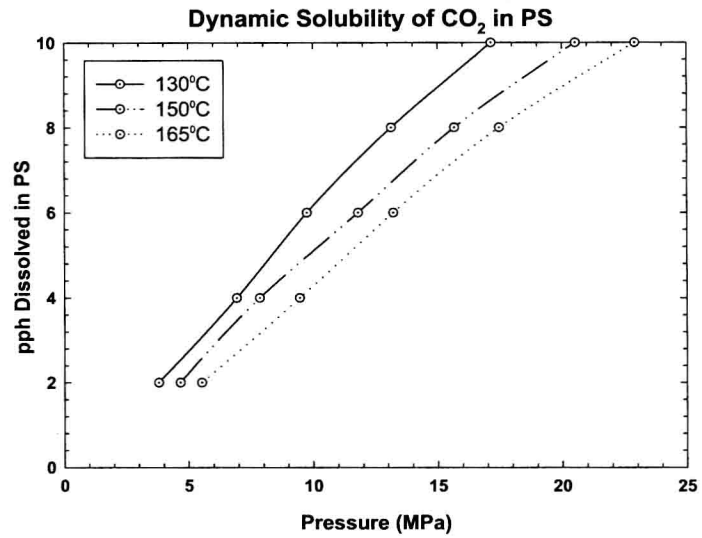Figure 6: Equilibrium and Dynamic Solubility of CO_2 in Polystyrene at 130 °C

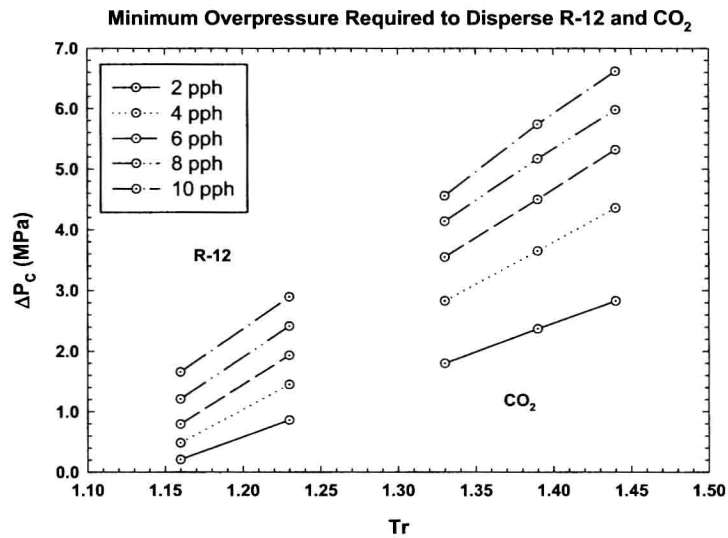Figure 7: Critical Dynamic Pressure Required to Disperse CO_2 in Polystyrene

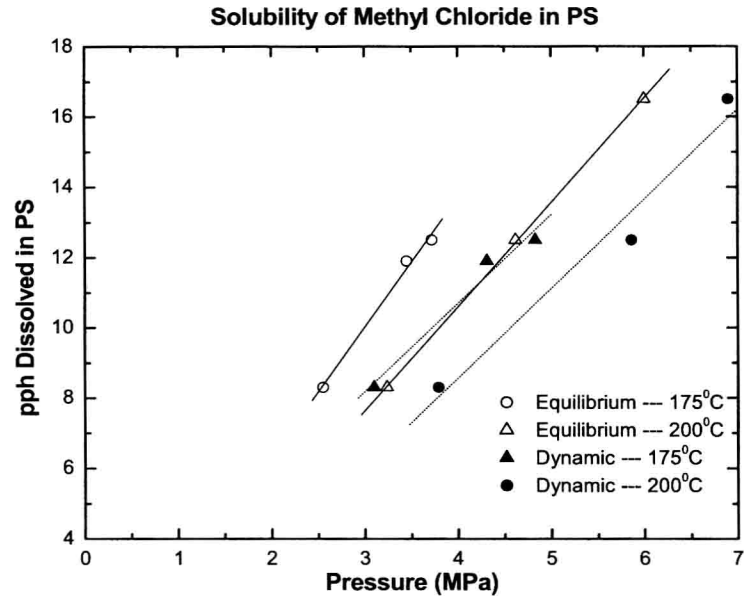Figure 8: Minimum Overpressure Required to Disperse Blowing Agents vs. Reduced Temperature

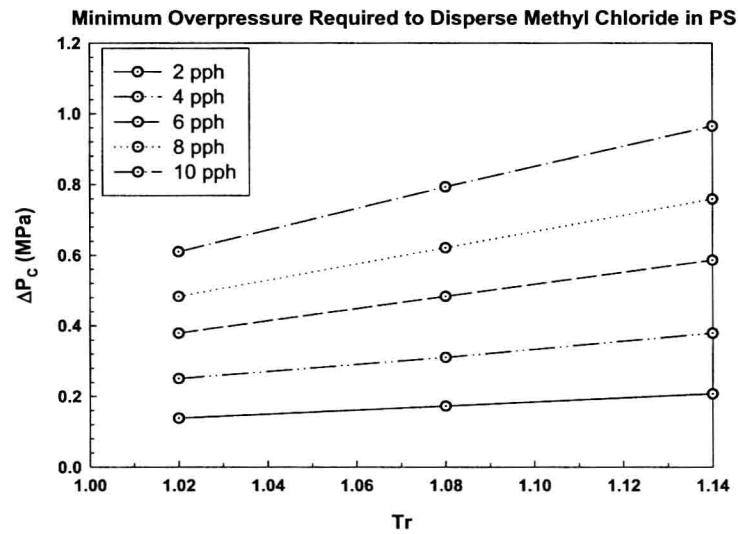Figure 9: Equilibrium and Dynamic Solubility of Methyl Chloride at 175^0C and 200^0C

Figure 10: Minimum Overpressure Required to Disperse Methyl Chloride
in Polystyrene vs. Reduced Temperature

NUCLEATION PROCESSES IN THE PRODUCTION
OF WATER BLOWN EXPANDED POLYSTYRENE.

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Abstract

The expansion of polystyrene using water as the blowing agent has been investigated. Water is ad- or absorbed by a hydrophilic additive that is introduced in styrene before the polymerization. The different additives used in this work are ordinary corn starch and high amylose starch, zeolite A and Y, and SiO_2. The influence of additive and water content, of the type of additive, and the polymerization conditions on the density and the morphology of the expanded product were investigated. The characteristics of the foam depend on the expansion procedure. The density obtained with high frequency electric field heating is lower that what can be realized with hot air.

Introduction

A standard procedure for the production of expanded polystyrene (EPS) is based on the suspension polymerization of styrene (ST) with the formation of polystyrene (PS) beads. Pentane, added during this polymerization process, is used as the blowing agent. The expansion results from the boiling of the homogeneous solution of pentane in PS. Nucleation additives like polyethylene waxes are added in order to promote this boiling process.

In recent years however, several methods have been proposed to replace this organic blowing agent by water, an environmental more friendly and a more save blowing agent. Procedures using water in combination with organic volatile substances [1-6] or water in an inversed emulsion process [7-11] have been presented. The use of carbon black, graphite or other inorganic substances has also been proposed[12].

Our attention has been focused on the introduction of pure water, using a water absorbing polymer as a separate phase[13-16]. This procedure has to be followed as the solubility of water in PS is very low. A typical example is starch, used as a pure material or grafted onto PS [14]. This polymer is suspended in styrene that is subjected to a radical suspension polymerization. Preliminary data have revealed the importance of parameters like the concentration and type of starch and the expansion technique. Both hot air and high frequency electric field heating have been used. In this contribution the use of different nucleation agents for the production of water blown expanded polystyrene (WEPS) will be discussed in detail.

Experimental

Experimental details about the materials and the polymerization procedure can be found in previous papers [13-16]. Only the most important aspects are reported here.

The polymerization consists of three steps:

i. pre-polymerization of the styrene/additive mixture to a conversion of about 30% in order to increase the viscosity of the matrix so that agglomeration of the additive and washing out of these particles is limited as much as possible;

ii. dispersion of the pre-polymerized mixture in water containing the appropriate suspension stabilizers;

iii. suspension polymerization to complete conversion.

Additives used in this work are ordinary corn starch (OCS), high amylose corn starch (HACS), two types of zeolites and SiO_2. Properties of these additives will be discussed in the text.

Experimental results

Starch as nucleation agent: characteristics

Types of starches.

A large variety of starches are commercially available. Two typical examples, namely ordinary corn starch (OCS) and high amylose corn starch (HACS), will be used. The difference between the two starches lies in the different content of amylose. Some physical characteristics are reported in table 1.

Thermal transitions in OCS:

i. Dynamic measurements

The transitions in starch can be detected by DSC and optical microscopy. When a suspension of starch granules