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Degradation Mechanism of Expanded Polystyrene (EPS) Foam in Lost Foam Casting, PIPS Approach for Synthesis and Novel Expansion Techniques for Cellular Foam

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Abstract

Lost Foam Casting (LFC) is a metal casting technology that facilitates fabrication of near-net shape metal castings using expanded polystyrene (EPS) foam patterns that are coated with refractory slurry and is effective for producing aluminum or iron castings of complicated geometry. However, the LFC process can produce considerable amount of scrap due to casting defects. Removing the EPS thermal decomposition products through the ceramic coating ahead of the advancing metal front during the liquid metal pour is a key factor in obtaining a defect free casting. Developing a fundamental understanding of foam degradation mechanism is essential in improving LFC process.

Modeling of the LFC process till date has completely neglected the effect of styrene on the overall thermal degradation of EPS foam. The dissolution effect of styrene is investigated by presenting the thermodynamic principles of polymer solution theory along with experiments to verify its impact on polystyrene degradation. By subjecting EPS Foam samples directly either to thermal radiation or to styrene vapor, it is demonstrated that styrene’s solubility of polystyrene significantly alters the degradation mechanism of EPS foam in LFC process and thus can control the metal fill process leading to reduction of defects in castings.
LFC process uses expanded polystyrene foam patterns in which isomers of pentane are used as blowing agents to achieve the expansion. In order to expand polystyrene, steam is used as a heat source and the expansion process takes place via conduction of heat from the surface of unexpanded polystyrene beads into the bulk. Pentane isomers are volatile organic compounds and greenhouse gases that are either liberated directly into the atmosphere or combusted using expensive setup. The environmental impact of the current process using pentane as an expansion agent has been considered and a new method for manufacturing of EPS foam has been developed with benign expansion agent. Laboratory experiments are demonstrated where PS pellets are successfully expanded into foam. Novel heating technology using microwave radiation is proposed and implemented in order to achieve efficient volumetric heating for the manufacturing of foam with target density.
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Chapter 1 Introduction

Polymeric foam is typically prepared from thermoplastic polymer with the introduction or generation of a gas within a polymer matrix. At present, the use of polymeric foam continues to grow at a rapid pace due to their desirable material properties such as light weight, excellent strength/weight ratio, superior thermal and acoustic insulation, and damping properties ideal for vibration isolation or shock absorption. Selections of polymers suitable for industrial foam applications depend on their chemical, mechanical and thermal properties, ease of manufacturability, and economic factors. A wide range of densities of polymeric foam are produced varying from 2 kg/m³ to 960 kg/m³. Open cell foams were the cell are connected by open channels, are generally flexible and widely used in cushioning and acoustic insulation. Closed cell foams with cells encased in thin permeable films of solid polymer, are generally rigid and used for packaging, and thermal insulation (Brody and Marsh, 1997). In addition to commercial applications, polymeric foams are also finding a niche in specialized technological applications like space research and electronics. Expanded polystyrene (EPS) foam was introduced in 1931 (Munters, 1935) and was extensively commercialized in the United States after World War II.

EPS has a higher flexural modulus at room temperature than other
thermoplastics (Wagner et. al., 2000). This is due to PS being an amorphous polymer which undergoes biaxial stretch induced hardening when foam cells are formed. Its higher rigidity along with its closed cellular structure leads to excellent thermal insulation and shock absorption properties ideal for use in packaging applications. The non-polar chemical nature of polystyrene and having a closed cellular structure in expanded form makes it hydrophobic and impermeable to water under ambient conditions. Thus it is effectively used in food packaging industry and for applications in floatation devices. EPS foam is also used in the casting industry for making patterns of complicated geometry in Lost Foam Casting (LFC).

LFC is a metal casting technology that facilitates fabrication of near-net shape parts by using expanded polystyrene (EPS) patterns coated with refractory slurry and packed in un-bonded sand that is subsequently compacted by mechanical vibration. LFC was developed from the principles of Investment Casting. Investment Casting is a process that has been practiced for thousands of years, with lost wax process being one of the oldest known metal forming techniques. Detailed explanation of the LFC process is presented in Chapter 2 as a background for the present study. LFC can be a cost effective process for producing aluminum or iron castings of complicated geometry. However, the LFC process can produce considerable amount of scrap due to casting defects. These casting defects
are attributed to the entrapment of the EPS degradation products inside the casting. Removing the EPS thermal decomposition products through the ceramic coating ahead of the advancing metal front during the liquid metal pour is a key factor in obtaining a defect free casting. Ceramic coatings absorb liquid fractions by wicking as they are formed. The liquid fractions degrade slowly into gaseous products and disperse into the sand. The coating also allows direct removal of the gaseous degradation products formed during the LFC process. (Cai et al., 2002) Developing a fundamental understanding of the foam degradation behavior is essential in improving the LFC process. An integrated approach for reducing defects in LFC thus involves:

1. Chemical modifications of expandable polystyrene to eliminate or minimize formation of defects and
2. Manufacturing process control and optimization of foam and coating physical properties

LFC process uses expanded polystyrene foam patterns in which isomers of pentane are used as blowing agents to achieve the expansion. In order to expand polystyrene, steam is used as a heat source and the expansion process takes place via conduction of heat from the surface of unexpanded polystyrene beads into the bulk. Pentane isomers are volatile organic compounds and greenhouse gases that are either liberated directly into the atmosphere or combusted using expensive setup (EPA report, 2005).
In both cases the plant producing EPS emits greenhouse gases into the lower stratosphere (Snijder, 2003).

The second Chapter of this dissertation provides background information necessary to all the subsequent chapters. In Chapter 2 the existing method for manufacturing EPS foam is reviewed and a recent attempt towards development of environmentally friendly foaming process is introduced. Chapter 2 also provides an introduction to the lost foam casting process and chemical degradation mechanism for polystyrene.

Modeling of the LFC process till date has completely neglected the effect of styrene on the overall thermal degradation of EPS foam. Chapter 3 discusses this dissolution effect by presenting the thermodynamic principles of polymer solution theory along with experiments to verify the impact of styrene on polystyrene degradation. It is demonstrated that styrene significantly alters the degradation mechanism of EPS in the LFC process and thus dictates the success of obtaining defect free casting.

Chapter 4 considers the environmental impact of the current process using pentane as an expansion agent and introduces a new method for manufacturing of EPS foam. Laboratory experiments are demonstrated where PS pellets are successfully expanded into foam. In this research an optimized new approach for manufacturing EPS foam is investigated where a benign and recyclable expansion agent is used to expand
polystyrene and novel heating technology is developed in order to achieve efficient volumetric heating for the expansion to take place during foam preparation. Chapter 4 investigates a novel method for foam production to achieve a cellular morphology and overall foam uniformity that may contribute to a better control over metal flow during LFC and thus reduce flow related casting defects.

REFERENCES


EPA (2005) “Maricopa County Environmental Services Department Title V Operating Permit Program Evaluation, Final Report”, 75 Hawthorne Street, San Francisco, CA

Chapter 2 Background of the Study
2.1 Current Method for Synthesis of EPS

Polystyrene can be foamed either by extrusion processes or by expansion from beads. Current study is focused on foam produced by the expansion technique.

2.1.1 Synthesis of expandable polystyrene beads

Expanded polystyrene (EPS) foam is manufactured from atactic polystyrene prepared via free radical polymerization in a standard suspension process. Spherical, expandable polystyrene beads are prepared from liquid styrene monomer suspended in an aqueous medium containing a suitable suspension stabilizer, an expansion agent, and a free-radical initiator. During the polymerization process a controlled hydrocarbon pressure is applied to incorporate approximately 7% by weight of the blowing agent in the beads. The most common expansion agents used are pentane isomers. A schematic of the EPS production process is presented in Fig.2.1. The specific applications of EPS foam are determined by the diameter of the expandable beads and the expansion agent. The manufactured grades and their specific applications are illustrated in Table 2.1. Scanning electron micrograph of a typical expandable polystyrene bead containing pentane as expansion agent is presented in Fig 2.2.
Table 2.1 Application for EPS foam depending on compact foam diameter [Lee, 2007]

<table>
<thead>
<tr>
<th>Bead diameter (μm)</th>
<th>Size classification</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>800-3000</td>
<td>Large</td>
<td>Insulation and building panels</td>
</tr>
<tr>
<td>500-1000</td>
<td>Medium</td>
<td>Molded items, e.g. Packaging material</td>
</tr>
<tr>
<td>200-800</td>
<td>Small</td>
<td>Thin walled containers e.g. coffee cups. Complicated foam geometry e.g. lost foam pattern</td>
</tr>
</tbody>
</table>

Figure 2.1 Schematic illustration of expandable polystyrene bead synthesis process [After Huntsman, 2001]
2.1.2 Pre-expansion of polystyrene beads

In the pre-expansion stage the expandable polystyrene beads are introduced into a vertical tank with an agitator having a controlled steam input. The pre-expansion stage is required to ensure a closed cell structure and to achieve the required uniform density at macro scale. Scanning electron micrograph of a typical expanded polystyrene bead is presented in Fig 2.3. The expandable bead has a glass transition temperature at approximately 85°C while the boiling point of pentane isomers is approximately 38°C. Being heated with steam at 100°C the internal vapor pressure in the beads increases. The vapor pressure of the blowing agent forces the PS matrix to expand as it reaches glass transition and a uniform
cellular structure with irregular polyhedral-shaped closed cells is formed [Benning, 1969]. The cell size can be regulated between 50\(\mu\text{m}\) and 750 \(\mu\text{m}\) by means of the expansion time and nucleating agents [Crevecoeur et al., 1998]. The target density is achieved by controlling the steam flow rate and the feed rate of the raw beads. The final density is also a function of the initial size of the beads and blowing agent content. Controlling the process time is an important factor since the beads might reach their minimum density limit and subsequently collapse due to pressure drop as the expansion agent diffuses out of the porous system (Fig 2.4). The expansion characteristics of PS, like foam stability and cell uniformity,
are also influenced by the rheological properties of the polymer matrix.

During the expansion process, expansion of a viscous medium takes place and a certain degree of melt strength or elasticity is required to prevent viscous flow failure of the cell walls [Benning, 1969]. The viscous flow properties of the polymer, as a function of temperature, are affected by its molecular weight and polydispersity. Stafford et al. [1998] investigated the effect of molecular weight, polydispersity and plasticizers on the microcellular structure of polystyrene. They concluded that molecular weight and polydispersity do not significantly affect the foaming process.
However, the presence of low molecular weight plasticizers was found to greatly influence the final structure of the foam. Viscous flow can be facilitated by the presence of plasticizers in the matrix [Blihi et al., 1994]. The viscous strength of the PS matrix during expansion can be enhanced by crosslinking or grafting of the PS chains [Benning, 1969] or by blending with PPE (poly 2, 6-dimethyl-1, 4-phenylene ether) [Crevecoeur et al., 1999]. Such blending also increases the glass transition by a few degrees and possibility of cell wall collapse can be reduced. The pre-expansion process is generally carried out in a continuous screw type pre expander machine. The pre-expanded beads exiting the pre-expander are usually fed to a fluidized bed drier where they are gently dried.

The pre-expanded beads leaving the fluidized bed drier is transferred to plastic mesh holding bins and allowed to reach steady state at ambient temperature. Depending upon the target density and thus bead size, this process can take four hours to three days. This stabilization stage is required for the elimination of excess water contained in and on the surface of the pre-puffed beads that is detrimental to the final molding process. For molding of high-density foams this stage also allows for the excess blowing agent to dissipate [Huntsman, 2001].

2.1.3 Molding of pre-expanded beads

Block molds are made from either steel or an aluminum alloy. The mold
walls are usually Teflon™-coated or stainless steel and have many small ports, nozzles or slits less than 1mm dimension for steam to enter and air to escape. Behind each wall a chamber is provided for vapor inlet and condensation water outlet.

Molding Cycle consists of

a. Filling Cycle - Filling the mold involves the closing of the mold and transport of the aged pre-puff beads into the cavity by controlled airflow.

b. Vacuum Cycle - A pressure drop inside the mold cavity is accomplished by a vacuum pump. This vacuum stage removes the air and water from the mold facilitating subsequent fusion.

c. Steaming Cycle - With the condensation outlets closed, the mold is subjected to steam until atmospheric pressure is reached. Steam pressure is then increased by sending the steam into the two side steam chambers with the outlet condensation valves open. The pre puffed beads reach glass transition and with no space for further expansion, fusion of bead walls occur.

d. Autoclave Cycle – During this stabilization period all condensation outlet valves are closed and the vapor pressure is maintained for 3 to 10 seconds.

e. Cooling Cycle – During this cycle, the condensation outlet valves are
Figure 2.5.a SEM image of a cut and fractured surface of rigid expanded polystyrene foam showing fusion of foam beads forming a mesh of dodecahedron structures. b. Image shows fused cell walls and detail of the inner closed cell structure.
opened, decreasing the pressure inside the mold. The valves are then
closed again and the vacuum is applied till mold pressure reaches
approximately 0.1bar. Any residual condensate remaining in the mold is
thus evacuated. The mold pressure is allowed to reach atmospheric
conditions, the mold is opened and rigid EPS foam (Fig 2.5) is ejected
using ejector pins.

The entire molding cycle generally lasts from 3 to 15 minutes, depending
on the product. The temperature of the block at the time of ejection is
approximately 90°C-95°C and the cells still contain a partial vacuum.
Fresh molded foam parts are usually allowed to stabilize for at least 24
hours in an atmosphere free of cold drafts to allow gradual cooling.
[Huntsman, 2001]

2.2 Expansion Agent

Hydrocarbons like pentane isomers or butane, classified under physical
expansion agents, are used for expansion of polystyrene beads. Criteria
for selection of a blowing agent are illustrated in Table 2.2. A major
disadvantage of pentane isomers is their high flammability and high
volatility. Pentane isomers are suspected to contribute to smog and to the
generation of stratospheric ozone. Within the next few years the polymer
industries will be forced by new regulations to drastically reduce the level
of volatile organic compound emission [Crevecoeur et al., Part 1, 1999].
Table 2.2 Considerations in selecting physical expansion agents

<table>
<thead>
<tr>
<th>Physical</th>
<th>Volatility, Boiling point, Latent heat, Thermal conduction, Critical Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>Henry Law constant, Reactivity, Stability, Solubility parameter</td>
</tr>
<tr>
<td>Transport</td>
<td>Diffusivity, Plasticization</td>
</tr>
<tr>
<td>Safety</td>
<td>Flammability, Toxicity</td>
</tr>
<tr>
<td>Regulatory</td>
<td>Ozone formation, Green house, Smog, Odor, FDA</td>
</tr>
<tr>
<td>Availability</td>
<td>Cost, Ease of handling, Storage</td>
</tr>
</tbody>
</table>

2.3 Water Expandable Polystyrene (WEPS)

Motivated by environmental concerns, Emile Snijders in her Doctoral dissertation titled “Water Expandable Polystyrene (WEPS) Computational and Experimental Analysis of Bubble Growth” [Snijders, 2003] presented detailed experimental and theoretical work on a novel expansion method for polystyrene using water as an expansion agent. The experimental study included synthesis of WEPS beads by a novel two-step process. Water is completely insoluble in styrene monomer. The first step in the process was [Crevecoeur et al., 1999] bulk polymerization where a physical surfactant was added to disperse water droplets in partially polymerized styrene thus yielding a stable emulsion. Partial polymerization was carried out to increase the viscosity of the liquid media sufficient enough to stabilize the emulsion. In the second step this emulsion was suspended in water in the presence of a suitable suspension stabilizer and standard suspension polymerization was carried out in order to obtain beads. The following are the problems reported in literature related to WEPS.
1. In commercial expandable polystyrene beads the expansion agent used is pentane isomers that form a single-phase solid solution with the polystyrene matrix. This is due to the high room temperature solubility in polystyrene. The expansion agent (Water) in WEPS is completely insoluble in styrene and polystyrene and thus has to be mechanically dispersed in the polymer matrix. This creates an inhomogeneous dispersion varying widely in phase size, concentration and distribution that finally result in large non-uniformity in cell structures of expanded beads.

2. The Glass transition temperature Tg for commercially available expandable PS beads is reduced from 100°C to approximately 70°C by the plasticizing effects of pentane. This enables the use of saturated steam at 100°C to be used as a source for heat in expansion and fusion process. For WEPS, the Tg of the bead is 100°C since water has no plasticizing effect on PS. Thus saturated steam was proposed to be replaced by either “hot air or superheated steam at temperatures substantially above 100°C” [Snijders, 2003] However, due to high diffusion coefficient of water through PS at elevated temperatures (above Tg) dry hot air lead to loss of blowing agent without foaming due to high diffusion rate at the high concentration gradient. Thus, superheated steam that is considerably more expensive to generate was considered the only option as a heat source. The problem identified with superheated steam was that of generating
sufficient pressure differential for expansion to take place. The expansion process, as applied for conventional EPS with saturated steam at atmospheric pressure as heating medium, cannot be applied for WEPS because identical pressures inside and outside the beads would exist in this case. “Moreover, since the Tg 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.” [Crevecoeur et al., 1999]

2.4 Lost Foam Casting (LFC)

Lost foam casting is a technology that facilitates fabrication of near-net shape parts by using expanded polystyrene (EPS) patterns coated with refractory slurry and packed in unbonded sand that is compacted by mechanical vibration (Fig. 2.6). EPS foam used in the LFC process is made from amorphous, linear polystyrene with a molecular weight ranging from 150,000 to 500,000. For a typical Aluminum casting, EPS foam has a density in the range of 0.020–0.030 g/cc and an average cell diameter ranges from 250 – 1500 μm depending on the product. If subjected to heat, EPS bead loses structural rigidity at about 120°C, becomes viscous at about 220°C, and almost fully volatilizes at about 430°C. The average heat of degradation of the EPS foam is ~190cal/g. The heat from the molten metal that is poured into the mold, acts as a source for chemical degradation of the polymeric foam and the metal eventually takes the
Figure 2.6 Schematic of basic foam degradation model in lost foam casting [Chen, 2005]

shape of the pattern. The objective for LFC is to shift value-added content of a final product from machining, finishing and assembly operations to the casting. Components with internal complexity and high machining parameters as well as assemblies with the potential for integration are ideal candidates for the LFC process. LFC also offers design engineers an opportunity to produce a detailed and refined design, as the foam patterns can be made in several parts and then glued together. By optimizing the LFC process machining and assembly costs can be reduced. Due to the use of loose sand in the LFC process, it is environmentally friendlier than conventional sand casting, which uses resin bonded sand that can have a negative impact on the environment. The LFC sand can thus be recycled. A comparative study in energy usage for both lost foam casting and
conventional green sand casting shows that LFC results in total energy savings of 27%, a productivity increase of 46% and cast metal saving by 7% [Campbell, 2000]. The benefits of the LFC process have led manufacturers such as General Motors, Mercury Marine, BMW and Kohler to embrace the process for casting their engine components. For instance, General Motors started to produce the 4.3L, V-6 diesel cylinder head using aluminum Lost Foam Casting at Massena, New York in 1981. According to Smith [Smith, 1996], General Motors had nine different products in Lost Foam production including aluminum cylinder head, aluminum cylinder block, aluminum driven sprocket supports for automatic transmission, iron crankshaft, iron differential case, and iron clutch housing for automatic transmission. Saturn Corp, a subsidiary company of General Motors, produced the engine blocks and heads at rates of up to 90 sets/hr. General Motors obtained success with its – the Vortec 4200 Inline 6 engine– by using LFC process.

A complex lost foam casting pattern is generally an assembly of smaller sections glued together and dipped into water-based refractory slurry and dried to provide a rigid coating. After drying operation, the coated foam pattern is placed in a steel casting chamber and packed with unbonded silica sand to fill all the pattern cavities. The sand is compacted by mechanical vibration to provide mechanical structure to the compacted mold. Molten metal is then poured down through the sprue. The foam
pattern degrades and permeates into the loose sand through the coating absorbing heat from the molten metal and eventually the target shape is obtained as metal replaces the expendable pattern. The final casting product is obtained by removing the sand and sand blasting off the refractory coating. The sequence of steps involved in the LFC process is illustrated in Fig. 2.7. During the LFC process the molten metal serves as a heat source and the foam pattern undergoes both physical and chemical changes, due to thermal degradation and oxidation. The foam pattern degrades into gas and liquid byproducts and vents into loose sand through the refractory coating after the molten metal is poured into mold. The metal filling rate is controlled by a dynamic balance between the rate of degradation of the foam pattern and rate of removal of the degradation products. The rate of degradation is controlled by parameters such as temperature, EPS composition, molecular weight, pattern density and extent of fusion between the foam cells. Rate of formation of degradation ultimately to the quality of the castings [Brown, 1992; Shivkumar, 1990]. The refractory coating controls the flow of the metal front by regulating flow of the polymer degradation products out of the mold and also provides structural rigidity to the mold so that it does not collapse under product is proportional to the molten metal temperature where as the rate of removal is determined mainly by the permeability and thermal diffusivity properties of the porous refractory coat and sand surrounding the coating. Also the initial foam morphology and subsequent local
Figure 2.7 Illustration showing different steps in LFC process
[Chen, 2005]
alterations in the foam pattern, induced by heating are deemed critical to the transport mechanism of the degradation products through the foam and the weight of packing sand. The optimized regulation of the degradation products out of the casting cavity has been reported as a major control process in order to minimize casting defects [Littleton et al., 1997; Liu et al., 1998].

Other factors such as the chemical nature of the foam material and density uniformity of the patterns also affect the quality of the castings. [Sonnenberg, 2003; Benson, et al. 2004]

2.5 Thermal Degradation of Polystyrene Foam

The thermal stability of commercial PS depends on various factors such as presence of excess initiator, additives, presence of number of weak bonds, method of synthesis, residual chemicals etc. EPS generally contains minute amount of residual initiators. Sometimes these initiators are deliberately added to enhance dissociation into free radicals when heat is applied. Usually these initiators are peroxides (Fig 2.8).

2.5.1 Components of degradation products

The thermal degradation of polystyrene is a radical chain process, which includes steps such as initiation, propagation, transfer and termination. Generally at temperatures below 300°C degradation is a decrease in the degree of polymerization. At temperatures greater than 300°C
intermolecular transfer results in a large drop in the molecular weight.

Further, degradation generates monomer, dimers, oligomers, and other low molecular weight fragments. The degradation process is controlled by several competing reactions. Kruz et al. reported a comprehensive model for the degradation mechanism [Kruz, 2002]. Thermal decomposition of polystyrene foam under controlled atmosphere and temperature conditions have been studied [Alajbeg, 1985] by collecting the volatiles and analyzing the components. The thermal degradation products of EPS have been analyzed under various conditions and a summary is presented in Table 2.3. In all these cases, styrene monomer is the major volatile product. The degradation products also contained oligomers of styrene such as dimer and trimer, toluene, benzene, ethyl benzene and methyl styrene. The organic products were very complex mixtures with several hundred components amounting from less than 0.01% to more than 50% of the mixture. This data on volatiles is useful in non-combusting situations like in LFC.
The products of EPS degradation, results are from Table 2.3 are summarized as follows:

- Most of the products are aromatic hydrocarbons. Predominant ones are styrene monomer and its homologues, styrene dimers and trimers.
- Styrene comprises approximately 52% of the collected products as a result of EPS depolymerization process.
- Many fused aromatic ring compounds such as indene, naphthalene, phenanthrene, and some with alkyl compounds are formed.
- In presence of air the oxidized decomposition products formed is

<table>
<thead>
<tr>
<th>Degradation Byproducts</th>
<th>EPS in N2 % At 950°C</th>
<th>EPS in Air % At 950°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>52.48</td>
<td>52.18</td>
</tr>
<tr>
<td>Toluene</td>
<td>12.05</td>
<td>12.34</td>
</tr>
<tr>
<td>Dimer</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Trimer</td>
<td>0.14</td>
<td>0.01</td>
</tr>
<tr>
<td>Bistyryl</td>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>5.99</td>
<td>4.75</td>
</tr>
<tr>
<td>Methyl styrene</td>
<td>4.32</td>
<td>3.94</td>
</tr>
<tr>
<td>Indene</td>
<td>0.84</td>
<td>1.18</td>
</tr>
<tr>
<td>Aromatic ketone1</td>
<td>0</td>
<td>0.02</td>
</tr>
<tr>
<td>Aromatic ketone2</td>
<td>0.002</td>
<td>0.03</td>
</tr>
<tr>
<td>C10H10</td>
<td>0.22</td>
<td>0.23</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1.2</td>
<td>2.28</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.37</td>
<td>2.05</td>
</tr>
<tr>
<td>Benzoyl peroxide</td>
<td>0.15</td>
<td>0</td>
</tr>
</tbody>
</table>
only about 2% of the total mixture. Oxygen reacts to give rise to phenols, alcohols, aldehydes, ketones and benzoic acid in appreciable amounts.

- It appears that degradation occurring does not get exposed to air since the oxidative degradation products are so low in concentration
- It is evident from the high percentages of styrene and toluene formed that depolymerization is predominant, and then dehydrogenation, followed by cyclization.

2.6 Use of brominated flame retardants [Sonnenberg, 2003]

Major product of thermal decomposition of EPS is styrene monomer, dimers, and various other fragments. The molecular weight reduction is exponential at the initial stage of the degradation by random chain scission and becomes linear after a threshold stage when unzipping occurs. Longer chain degradation products are liquid existing at temperatures above 145°C. The existence of thermal degradation products in the liquid state is considered a major cause for defects in LFC. One of the major quality problems in these castings is fold formation that occurs when pouring molten aluminum. A fold can occur when two metal fronts come together and do not completely wet one another. Brominated flame-retardants have been successfully used to eliminate fold formation in LFC. Brominated flame-retardants effectiveness depends on the quantity of the Bromine atoms they contain and also, very strongly, on the control
of the halogen release. Other considerations when choosing a flame retardant is cost and the effect of the flame retardant on physical properties, especially the solubility of the FR in the PS melts. The lower melting flame-retardants tend to be more soluble. Also they have positive effects on lowering the melt viscosity of fragments. But the soluble flame-retardants may cause blooming defect, i.e., migration onto the surface of molded parts. Solubility of the flame retardant can also interfere on heat resistance of the EPS. Bromine based flame-retardants (FR) act primarily by chemically interfering with the radical chain mechanism that occurs in the gas phase during combustion. The Br additive in the EPS releases free bromine radicals in the temperature range of about 650°C - 800°C In case of LFC Brominated flame retardants accelerate the kinetics of the reaction towards producing smaller chains by terminating free radicals through oxidation. The fragments of the degradation products are smaller and gaseous at LFC temperatures, hence passed easily through the refractory coating. Organic brominated additives were tried by trial and error method and evaluated. Tetrabromo cyclooctane (TBCO Fig.2.9) was found to produce fold free castings. This result was repeated in numerous pours at different times. Incorporation of organic brominated additives, into EPS beads was found effective in reducing folds, thereby eliminating a high number of defective parts. A new generation of EPS beads is tailored to serve the LFC market, a specialty market since it comprise only 0.4% of total EPS sales.
2.7 Role of refractory coating in LFC

Refractory coating applied on the foam pattern surface plays an important role in the success of LFC process. Defects that are commonly observed in the LFC process are strongly correlated to the coating properties. The coating requires appropriate mechanical properties in order to resist the stress from the un-bonded confining sand during metal fill as the polystyrene pattern degrades. The structural integrity and thermal stability of the coating provides resistance to compaction and thermal expansion forces during casting thus preventing coating fracture and metal infiltration into the surrounding sand [Goria et al., 1986]. The coating should, at the same time, have optimal permeability to allow transport of the degradation products of EPS through the coating into the sand and control the flow of molten metal by regulating the gas backpressure. Inadequate coating permeability has been reported to produce defects such as porosity, mis-fill, cold laps, and folds. Metal solidification before the complete expulsion of degraded materials through the coating causes porosity defects. A misrun is an incomplete fill...
of the cavity during pouring. Cold lap is a discontinuity on the casting surface that is a result of the metal being too cold to fuse at the confluence of two streams of metal fronts. High coating permeability, on the other hand leads to surface blisters and formation of a thin oxide layer beneath the cope surface of the casting. [Littleton et al., 1997]. High coating permeability may also cause turbulence in metal flow during pouring that subsequently shall increase the probability of folds formations. Folds are formed due to entrapment of degradation products between metal fronts and manifest as thin sheet-like discontinuities composed of carbon and aluminum and/or magnesium oxides [Bennett et al., 2000]. These flaws cause fatigue failure of the casting when subjected to cyclic thermal loading and/or mechanical stress.

The thermal diffusivity of the coating also determines the quality of the castings. Heat transfer between the molten metal and sand and thus solidification kinetics is guided by the coating thermal properties. Moreover, the specific heat of the coating also determines the heat content and its temperature and is extremely important in understanding degradation behavior and transport of liquid degradation products that wick into the coating during the LFC process. The insulating properties of coating also control the dendrite arm spacing and appropriate cooling rates need to be provided to obtain suitable strength and elongation properties. The mechanical properties, permeability and thermal
conductivity of coating are affected by the coating thickness, besides its chemical and physical properties. Increasing coating thickness will increase coating strength. At the same time, increasing coating thickness will decrease coating permeability while also increasing the overall thermal resistance of the coating [Tschopp et al., 2002]. The coating thickness can be optimized to obtain ideal permeability, wicking properties, and thermal diffusivity of the coating by controlling the coating viscosity and solids content [Tschopp, 2002].

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Chapter 3 Thermal degradation of EPS foam in LFC: Effect of Styrene
3.1 Introduction

Early modeling of the LFC process was done by Ohnaka [1993] and Sun et al. [1996] simulating the effect of backpressure in the Lost Foam Casting (LFC) process. Davami and Mirbagheri [2003] modified the advanced solution algorithm (ASOLA-VOF) technique and a finite difference code called FLOW3D developed by The Flow Science Institute [Nichols] offered a mold filling simulation (Fig.3.1). Wang et al. [1993] modified the existing computer program for simulation of a conventional sand casting to simulate the fluid flow and heat transfer during mold filling. Liu et al. [2002] developed a simple 1-D mathematical model predicting

![Figure 3.1 Flow-3D modeling for LFC showing advancing metal front through collapsing EPS foam](image)

Figure 3.1 Flow-3D modeling for LFC showing advancing metal front through collapsing EPS foam
metal front velocity and backpressure of decomposed gases for the LFC process. Recently Mirbagheri et al. [2006] proposed a model “capable of considering the effect of various parameters, such as burning foam rate, gas foam pressure, permeability and thickness of refractory coating and foam density”. To date, available modeling of the LFC process takes into account only heat transfer from the molten metal front and pressure from the gaseous degradation products front neglecting any heat transfer or dissolution effect from styrene. The simplifying assumptions associated with the current modeling of LFC are presented below:

1. Thermal conduction inside the foam is ignored, assuming it is negligible.
2. The foam is assumed to melt at a fixed temperature, instantly releasing all its latent heat similar to the behavior of a pure substance.
3. The complex physics at the metal foam interface, the formation of liquid and gaseous products and the escape of volatiles through the coating, foam and sand are all lumped into one single parameter—the overall metal/foam heat transfer coefficient.
4. The advancement of the metal front is controlled by velocity, which is derived from the rate of foam degradation. Foam degradation rate is a function of specific heat and overall metal/foam heat transfer coefficient.
The motivation behind the present study is to obtain better understanding of the foam degradation behavior in order to generate higher accuracy in modeling of the LFC process. The present study focuses on the effects of styrene vapors on the morphological alteration of the EPS. Experimental results are also presented describing the growth of temperature profile inside intact foam.

The LFC process is considered to occur within a confined space with permeable boundaries. During the process evolution of low molecular weight degradation products is experienced. The flow dynamics of polystyrene fractions and volatiles through the EPS patterns during mold filling is affected by the physical and chemical heterogeneity in the degrading pattern. The styrene vapors are absorbed by the EPS foam pattern leading to morphological changes and opening up of fast diffusion pathways [Benson et al., 2004]. Fig 3.2 shows a neutron radiographic image capturing generation and transmission of volatiles through these fast diffusion pathways instead of a uniform degradation front within the foam pattern. These paths lead to faster escape of volatiles from the mold space that in turn is expected to govern the metal flow through the pattern by altering the backpressure. As the styrene vapors are absorbed by EPS foam, the glass transition temperature decreases and deformation occurs at lower temperature. This is verified by differential scanning calorimeter (DSC) experiments with PS samples exposed to styrene vapors. Under
casting conditions depolymerization of the collapsed polymer foam results in formation of gaseous degradation products and significant amounts of a partially depolymerized viscous residue. [Alajbeg, 1985; Cai, 2002] The viscous residue consists of dimmer, trimer, tetramer and other oligomers (see Table 2.3). Styrene comprises approximately 52% of the degradation products as a result of PS depolymerization process. Many fused aromatic ring compounds such as indene, naphthalene, phenanthrene, and some with alkyl compounds are formed. In presence of air the oxidized decomposition products formed is only about 2% of the total mixture.
Oxygen entrapped inside the mold reacts with the polymer degradation products to give rise to phenols, alcohols, aldehydes, ketones and benzoic acid. Significant amount of partially depolymerized fragments may remain inside the cast even after the mold has been filled. The gaseous degradation products formed at the metal front at temperatures below 750ºC may consist primarily of monomer. At temperatures greater than 750ºC, the monomer molecules undergo additional fragmentation yielding lighter hydrocarbons [Mehta, 1994]. The degradation of polystyrene is known to be a multiple step process consisting of random chain scission with generation of oligomers and unzipping of polymer chain with generation of styrene monomer. The size of the oligomers and amount of styrene generated during thermal degradation of polystyrene depend on the temperature as well as the rate of temperature increase. At temperatures between 300ºC – 400ºC, polystyrene has been reported to yield approximately 45 wt% of styrene monomer [Cameron, 1967]. All published research report that a considerable fraction of styrene shall be generated during the LFC process. Styrene dissolves polystyrene and styrene-oligomers to form a viscous liquid. The complete expulsion of the liquid fractions from the mold cavity is determined by the molecular chain sizes in the viscous liquid and their chemical and physical interaction with the ceramic coating. For understanding the LFC process it is thus essential to take into account the dissolution effects of styrene vapor on the base EPS foam.
3.2 Theory

3.2.1 Comparison by the Hildebrand solubility parameter

The Hildebrand solubility parameter \( \delta \) [Hildebrand, 1916] is a numerical value that indicates the relative solvency behavior of a specific solvent at 25ºC. It is derived from the cohesive energy density of the solvent, which in turn is derived from the heat of vaporization.

Hildebrand proposed the square root of the cohesive energy density as a numerical value indicating the solvency behavior of a specific solvent.

\[
\delta = \sqrt{c} = \left[ \frac{\Delta H - RT}{V_m} \right]^{1/2}
\]  

(3.1)

where:

c=Cohesive energy density

\( \Delta H \)=Heat of vaporization

R=Ideal Gas constant

T=Temperature

\( V_m \)= Molar volume

The cohesive energy density of a liquid is a numerical value that indicates the energy of vaporization in calories per cubic centimeter, and is a direct reflection of the degree of van der Waals forces holding the molecules of the liquid together. For polymers the cohesive energy density as a function of temperature is not available since the polymer undergoes molecular degradation before it vaporizes at standard atmospheric
pressure. Thus the Hildebrand solubility parameters were determined by experiments. Hansen [1967] divided the total Hildebrand parameter value into three additive parts: a dispersion force component, hydrogen bonding component, and a polar component given by equation 3.2.

$$\delta t^2 = \delta d^2 + \delta p^2 + \delta h^2$$

(3.2)

where,

- $\delta t$: Total Hildebrand parameter
- $\delta d$: dispersion component
- $\delta p$: polar component
- $\delta h$: hydrogen bonding component

van der Waals forces result from the additive effects of the three types of components viz. dispersion forces, polar forces, and hydrogen bonding forces. Non-polar molecules, such as polystyrene, have strong intermolecular attractions although dipole moment is negligible. Random changes in electron cloud distribution cause mobile polar fluctuations along the molecular chain. Although no permanent polar configuration is formed, numerous temporary dipoles are created constantly, and disappear. In two interacting molecular chains, random polarities in each molecule tend to induce corresponding polarities in the other, causing the molecular polarities to fluctuate together. These induced attractions are called London dispersion forces, or induced dipole-induced dipole forces.
The degree of "polarity" that these temporary dipoles confer on a molecule is related to the chain length. A longer molecule, i.e. a molecule of higher molecular weight, shall have a greater number of temporary dipoles, and thus greater intermolecular attractions.

In polar molecules dipole-dipole forces, called Keesom interactions, are symmetrical attractions that depend on the same properties in each molecule. Because Keesom interactions are related to molecular arrangements, they are temperature dependent. Higher temperatures lead to increased molecular vibrations and thus a decrease in Keesom interactions. However, any molecule, even if non-polar, will be temporarily polarized in the vicinity of a polar molecule, and the induced and permanent dipoles will be mutually attracted. These dipole-induced dipole forces, called Debye interactions, are not as temperature dependant as Keesom interactions since the induced dipole is free to shift and rotate around non-polar molecules.

A particularly strong type of polar interaction occurs in case of hydrogen bonding. In such cases, the hydrogen's sole electron is drawn toward an electronegative atom like oxygen or a halogen, leaving the strongly charged hydrogen nucleus exposed. This exposed positive nucleus can exert a considerable attraction on electrons in other molecules, forming a protonic bridge that is substantially stronger than most other types of dipole interactions. Hydrogen bonding and Debye interactions in
Polystyrene are negligible, and is only existent due to impurities and presence of polar initiator molecules. The solubility parameter is a numerical value that indicates the relative solvency behavior of a specific solvent and is directly correlated to van der Wall’s interactions. [Jensen, 1984]

A 3-D graph can be plotted with the Hansen parameters forming the three coordinate axes. The Hildebrand parameter for each solvent can be plotted in this 3-D space by using the individual Hansen parameters as coordinates. For a polymer a sphere called solubility sphere can be geometrically constructed in this 3-D space. (Fig.3.3) The coordinates at the center of the solubility sphere are located by means of three component parameters (δd, δp, δh) of the polymer, and the radius of the sphere is indicated, called the interaction radius (R). A polymer has a high probability to be soluble in a solvent if the Hansen parameters for the solvent lie within the solubility sphere for the polymer. In order to determine this (without building a model) it must be calculated whether the distance of the solvent point from the center of the polymer solubility sphere (DS,P) is less than the interaction radius for the polymer. Values of R for different polymers have been experimentally determined by trial with many different solvents and reported in literature. Gharagheizi and Angaji [2006] used intrinsic viscosities of the polymer in different solvents and the molar volumes of the solvents to develop a correlation
Figure 3.3 Schematic illustrating the plotting of a solubility sphere in a 3-D Hansen plot. Ideal solvent coordinates lie on the sphere surface while bad and good solvent coordinates lie outside and inside the sphere respectively between Hansen parameters and the polymer interaction radius. The radius of interaction for PS is $R = 12.7 \text{ (MPa}^{1/2})$

$$D_{(S-P)} = \left[ 4(\delta_d S - \delta_d P)^2 + (\delta_p S - \delta_p P)^2 + (\delta_h S - \delta_h P)^2 \right]^{1/2}$$ (3.3)

where

$D_{S-P} =$ Distance between solvent and center of polymer solubility sphere

$\delta_{xS} =$ Hansen component parameter for solvent

$\delta_{xP} =$ Hansen component parameter for polymer If the distance $(D_{S-P})$

Table 3.1 tabulates the values of the Hansen solubility parameters for reagents under consideration. Comparing the calculated results in Table 3.2 it is evident that styrene is a stronger solvent for PS than either THF.
or Acetone. It should be noted that THF is a standard good solvent used for different chemical analysis technique for PS including gel permeation chromatography (GPC).

According to Flory, for a polymer-solvent system to be miscible throughout the entire compositional range, the polymer-solvent interaction parameter ($\chi$) must be less than 0.522. The polymer-solvent interaction parameter can be written as: [Mark, 1996].

$$\chi = 0.34 + \frac{V_i}{RT} (\delta_i - \delta_j)^2$$

(3.4)

Where the enthalpic contribution $\chi_H$ is given by
\[ \chi_H = \frac{V_i}{RT} (\delta_i - \delta_j)^2 \]  

(3.5)

Where \( V_i \) is the molar volume of the solvent \( i \)

\( R \) is the Ideal gas constant

\( T \) is the absolute temperature

\( \delta_i \) is the total Hildebrand solubility parameter for the solvent \( i \) and

\( \delta_j \) is the total Hildebrand solubility parameter for the polymer \( j \)

Using equation 3.5, the interaction parameter \( \chi \) was calculated at various temperatures and tabulated in Table 3.3. All values of interaction parameter \( \chi \) for the PS-styrene system within the calculated temperature range are lower than the critical value of 0.5. This indicates that styrene is a good solvent for polystyrene over the entire temperature range of 298K to 473K. Also it is important to note that \( \chi \) decreases with increasing temperature. At higher temperatures, interaction parameter decreases favoring conditions for dissolution.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( \chi_H )</th>
<th>( \chi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.133</td>
<td>0.473</td>
</tr>
<tr>
<td>373</td>
<td>0.106</td>
<td>0.446</td>
</tr>
<tr>
<td>473</td>
<td>0.084</td>
<td>0.432</td>
</tr>
</tbody>
</table>
3.2.2 Behavior of polymer chains in solvents [Rubinstein and Colby, 2003].

“Linear polymer melts and concentrated solutions have practically ideal chain conformation because the interactions between monomers are almost completely screened by surrounding chains”. Considering ideal chain behavior in a polymer melt, the mean end-to-end chain distance ($\langle R_m \rangle$) for a polymer molecule will be given by

$$\langle R_m^2 \rangle \approx C_\infty n l^2$$

Where $C_\infty$ is Flory’s characteristic ratio, $n$ is the number of main chain bonds and $l$ is the bond length.

In a Polystyrene melt with molecular weight of $M_w=200,000$, $n \approx 2,000$, $C_\infty = 9.5$ and $l=1.54 \AA$ the mean end-to-end distance for a chain is estimated to be

$$R_m = 212.3 \AA$$

A good solvent for a polymer is defined as one in which a polymer chain coil swells in order to maximize the number of polymer-fluid contacts. A polymer chain coils in good solvent has larger size while in a thermodynamically bad solvent they behave like solid spheres. Flory's Theta solvent marks the boundary between the good and bad solvents.
Considering acetone as a Theta solvent for PS at room temperature and a semidilute solution the mean end to end chain distance ($R_o$) is given by

$$R_o = b n^{1/2}$$

where $b$ is the Kuhn length for monomer styrene.

For PS with $n = 2,000$ and considering $b = 18 \, \text{Å}$ we get

$$R_o = 805 \, \text{Å}$$

When a polymer repeat unit is chemically identical with the solvent, there are practically no energetic interactions between the solvent and a solute and the solution behaves as an athermal solution where the excluded volume ($v$) of the polymer becomes independent of temperature. PS in styrene monomer forms an athermal solution where the mean end-to-end chain distance is given by

$$R_a \approx b n^{0.588}$$

For PS considering $b = 18 \, \text{Å}$ and $n = 2,000$ we get

$$R_a \approx 1571.4 \, \text{Å} = 0.16 \, \text{μm}$$

Thus the estimated swelling ratio for a polystyrene chain dissolved in styrene is given by
\[ \frac{R_a}{R_m} \approx 7.4 \]

Polymer chains begins to overlap when their volume fraction \( \phi \) exceeds the volume fraction of repeat units inside each isolated coil, called the overlap concentration \( \phi^* \).

\[ \phi^* = \frac{nb^3}{R_a^3} \]  

(3.9)

For PS under consideration \( \phi^* = 0.003 \) or 0.3%

Mehta and Shivkumar had indicated the possibility of achieving maximum of 80% styrene under the lost foam casting conditions. [Mehta, 1994]. Considering a minimum of 0.3% of polystyrene in solution with styrene, it is evident that in case of LFC the semi-dilute regime with chain overlap shall be experienced. The analysis of polymer chain swelling is critical in understanding the expulsion mechanism of viscous liquid residue through the LFC ceramic coating and thus can provide valuable information for modeling the LFC process.

3.3 Experimental

Materials

The EPS foam patterns were obtained from a supplier in the shape of plates of dimension 80x60x8 mm. Sections of these plates were used to investigate the effects of styrene and infrared radiation on the morphology. Styrene monomer of high purity (\( \geq 99\% \)) was purchased
Sections of foam were also used to obtain temperature profiles inside foam when subjected to heating by infrared radiation. EPS foam pattern was coated with ceramic coating to obtain a lost foam mold for partially filled casting experiment.

### 3.3.1 Exposure to Infrared Radiation

Sections of EPS foam samples were exposed to radiation from molten aluminum (Al 356 alloy) maintained at 750°C in a cylindrical furnace (Fig. 3.4). The heat source was positioned vertically at a distance of approximately 10” below the horizontally positioned EPS foam plate. The

---

**Fig. 3.4 Experimental setup for exposure of EPS to thermal radiation**
3.3.2 Exposure to Styrene Vapor

radiation source was circular in geometry with a diameter of 2”. Time of exposure was varied manually by using a stopwatch. A glass cylinder of dimensions 8” x 3” as shown in Fig.3.4 was used to obtain a separation distance of 10” between the radiation source and EPS foam samples.

Sections of EPS samples were exposed to styrene vapor emanating from boiling styrene at 145oC. A volume of 10ml of styrene monomer was taken in a 4” diameter glass Petri dish. A glass cylinder (See Fig. 3.5) of dimensions 8” x 3” was used to provide a separated volume to generate saturated styrene vapors. The cylinder was covered with a metal plate which was manually replaced quickly by sample EPS plates, on
observation of simultaneous signs of boiling and condensation of styrene vapors inside the glass cylinder, indicating saturation by vapors. Exposure time was varied manually using a stopwatch. DSC experiments were carried out with samples collected from exposed EPS foam to check for alterations in glass transition temperature due to plasticization effect of styrene of PS. A Mettler DSC 821 was used. The heating rate was 10°C/min and for each sample two heating runs from 30°C to 120°C were recorded with 100 ml/min N₂ as the purge gas. An isotherm at 30°C was run for 15 minutes to obtain thermal equilibrium within the sample. Indium was used for temperature and heat of fusion calibration.

The morphological changes related to exposure to styrene vapor were documented using scanning electron microscope. A Leo Scanning Electron Microscope 1525 was used to study the morphological changes of the EPS foams exposed to radiant heat and styrene vapor. All micrographs were obtained using voltage of 20.K volts.

3.3.3 Partially Filled EPS Foam Pattern

The samples were generated by partially filling the lost foam molds during the lost foam casting process. After cooling the remaining EPS foam patterns were removed and subjected to Gel Permeation Chromatography (GPC) analysis to obtain for changes in the molecular characteristics such number average molecular weight, weight average molecular weight and molecular weight distribution. GPC analysis was
performed on sections removed from the partially degraded pattern (Fig. 3.6, Fig. 3.7). The samples were measured using a Waters modular GPC. Temperature of column and detector were kept at 40°C. Solvent was THF at 1ml/minute with an injection volume of 50ml and a sample concentration of 2 mg/ml. The columns were calibrated with Toyo Soda polystyrene standards.

3.3.4 Measurement of Temperature Distribution inside Intact Foam

An experimental setup, consisting of a radiant heat source, thermocouples and a data acquisition device was used to obtain one dimensional temperature profile inside square section foam samples. Foam samples of different steam time were first characterized for morphological variations using SEM imaging. Foam samples were cut out from patterns of different steam time with a surgical blade, dimensions of samples being 3.81 cm x 1.27 cm x 1.27 cm. One of the square surfaces was kept as original pattern surface and marked as Top Surface. The other surfaces were then wrapped with insulating tapes to approach a one-dimensional heat flow model. Six graduations were marked on the insulation surface at separations of 0.3175 cm starting from the Top Surface. A center-line was drawn and 0.625 cm deep holes were drilled into the sample with 8mm drill bit. Six thermocouples (30 gauge) were inserted into the holes while one was placed on the Top Surface with the welded junction inserted into the foam. The Thermocouples were marked and fed into a
Figure 3.6 a. partially filled EPS foam pattern; b. close-up view of the degrading front

Figure 3.7 Position of the samples selected for used GPC studies
The Temperature measurement system consists of a Terminal Block (SCXI-1303) with Thermistor Cold Junction Compensation, a Signal Conditioning Module (SCXI-1202), a DAQ board (PCI6035E) and Data Logger Software. The radiant heat source was a stainless steel cylinder with a 500W heating element connected to a temperature control system. The sample was mounted on a cylindrical base using double-sided tape. The heat source was secured above the sample with a separation distance of 1” (See Figure 3.8). The distance between the heat source and foam surface was kept constant and temperature of the heat source was steadily increased from 150°C to the temperature when first sights of bead deformation were seen at the foam Top Surface. The foam was then allowed to cool by cooling the heat source and allowing the foam to reach a steady state (see Fig. 3.9).

The temperature at which the first signs of bead collapse occurred (critical surface temperature, Tsc) was noted and temperature distribution in the foam corresponding to that particular surface temperature was plotted.

3.4 Results and discussion

3.4.1 Morphological Changes

Recent investigations from our laboratory clearly provide support for difference in morphological changes in EPS foam patterns subjected to
Figure 3.8 Schematic of experimental setup for measuring temperature distribution inside intact foam (Benson et al., 2004)

Figure 3.9 Thermocouple readings to obtain temperature profile at critical surface temperature (Tsc)
radiant heat and styrene vapors. The morphological changes from exposure to thermal radiation and styrene vapors are presented in Fig. 3.10. The EPS foam samples exposed to infrared radiation at 750°C exhibits morphological changes that include reduction in bead size and separation at the junction between fused beads. The morphological changes generated by thermal radiation were observed approximately 2 seconds after initial exposure to the source. Expanded bead structure collapse has been reported to be noticeable above 140 - 150°C. The average bead size for a polymer with density of 0.021 g/cc decreases from 1.4 mm at 140°C to 0.5 mm at 200°C. The average beads return to their unexpanded size at approximately 250°C. At 260°C the beads melt to produce a viscous residue [Mehta, 1994].

The morphological alterations observed in EPS foams exposed to thermal radiation and styrene vapor are markedly different. The irradiated foam shows a pattern with distinct contraction of the beads. The morphology of the EPS foams exposed to styrene vapor exhibit highly distorted beads attached through a fibril-like structure. Morphological changes induced by exposure to styrene vapor occur over a similar period of time although the temperature of the styrene source was only at 145°C compared to the molten metal source at 750°C. This is expected since styrene is a solvent for polystyrene and its absorption should lead to loss of EPS structural integrity.
Figure 3.10 SEM micrograph showing morphological changes in of EPS foam exposed to: (a) infrared radiation from a 2” diameter cylindrical source of Aluminum at 750°C for 2 sec. (b) same thermal conditions for 4 sec. (c) for 8 sec. (d) Styrene vapor for 2 sec. (e) Styrene vapor for 4 sec. (f) Styrene vapor for 8 sec.
3.4.2 Changes in glass transition

Solvents can drastically reduce the glass transition of a polymer [Mark, 1996]. The absorption of styrene by the EPS foam lowers the glass transition temperature (Tg) of polystyrene through a plasticizing effect. The decrease in the Tg should support structural collapse of foam during the LFC. The DSC result shown in Fig.3.11 clearly depicts absence of Tg step near 100°C in the foam samples exposed to styrene vapor for 4 sec and 8 sec. Evidence from neutron radiography images obtained during real time pouring of metal studies and image analysis results indicate the presence of a gap between the position of the foam and metal front. (Fig 3.2) In the case of partial filling a similar gap between the fronts of the solidified metal and PS pattern was observed (Fig 3.6). This gap can only be justified if the rigid foam pattern never comes in direct contact with the molten metal.

Thus the morphological changes in the PS foam pattern are due to contact with volatile degradation products. Current studies in modeling of LFC process also support this justification. [Liu, 2002; Cai, 2002; Mirbagheri, 2006]

3.4.3 Molecular Weight Analysis by Gel Permeation Chromatography

The concentration of styrene monomer for foams samples obtained from the partially filled patterns exhibits position dependence.
Figure 3.11 Sample DSC results showing (a) Tg at 101°C for intact foam and (b) broadening of Tg for Foam exposed to styrene vapors for 4 sec (c) for 8 sec
The higher concentration of styrene is obtained from position closest to the metal front. Decrease in styrene concentration is obtained for samples taken middle and back position. Comparison of the molecular weights of samples taken from the same three positions presented in Table 3.4 clearly indicates that samples closest to metal front undergo reduction in the molecular weigh and broadening of the molecular weight distribution. The molecular weights of samples taken from position (middle and back) further away from the metal front remained unchanged (Table 3.4). The molecular weight and styrene concentration of the unmodified polystyrene foam remains constant (Table 3.5). These results indicate the presence of a styrene concentration gradient within the foam during lost foam casting. This observation is expected since the LFC process is performed in confined space and polystyrene is known to yield at least 40% styrene monomer upon thermal degradation [Grassie, 1956]

3.4.4 Temperature Distribution inside intact foam

Foams of three different steam times were used in this experiment. The morphological variations in the cellular structure in these foams are evident from SEM imaging (Fig. 3.12). The temperature distribution within the foams prepared at steam times of 11, 17, and 20 seconds is summarized in Table 3.6. The temperatures provided in the Table 3.6 represent the actual reading of the thermocouples at the initiation of bead collapse (Tsc) at surface. The temperature distribution clearly exhibits a
Table 3.4 Comparison of molecular weight distribution and styrene presence at various positions within a polystyrene foam pattern

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Description</th>
<th>Mw</th>
<th>Mn</th>
<th>Mw/Mn</th>
<th>Styrene (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA51751</td>
<td>Front edge</td>
<td>138,000</td>
<td>39,000</td>
<td>3.55</td>
<td>5360</td>
</tr>
<tr>
<td>AA51752</td>
<td>Middle</td>
<td>242,000</td>
<td>96,000</td>
<td>2.53</td>
<td>104</td>
</tr>
<tr>
<td>AA51753</td>
<td>Back</td>
<td>249,000</td>
<td>98,000</td>
<td>2.55</td>
<td>79</td>
</tr>
</tbody>
</table>

Table 3.5 Coolecular weight distribution and styrene presence at various positions within the unmodified polystyrene foam pattern

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Mw</th>
<th>Mn</th>
<th>Mw/Mn</th>
<th>Styrene (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA52130</td>
<td>Front</td>
<td>245,000</td>
<td>100,000</td>
<td>2.45</td>
<td>6</td>
</tr>
<tr>
<td>AA52131</td>
<td>Middle</td>
<td>246,000</td>
<td>96,000</td>
<td>2.56</td>
<td>7</td>
</tr>
<tr>
<td>AA52132</td>
<td>Back</td>
<td>249,000</td>
<td>97,000</td>
<td>2.51</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3.6 Temperature distribution in foams as function of steam time

<table>
<thead>
<tr>
<th>Foam Type</th>
<th>Normal Steam Time (17 sec.)</th>
<th>Low Steam Time (11 sec.)</th>
<th>High Steam Time (20 sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bead Collapse Temp. (Tsc)</td>
<td>92.78</td>
<td>92.53</td>
<td>90.24</td>
</tr>
<tr>
<td>T1</td>
<td>63.89</td>
<td>70.53</td>
<td>60.35</td>
</tr>
<tr>
<td>T2</td>
<td>45.75</td>
<td>48.99</td>
<td>41.9</td>
</tr>
<tr>
<td>T3</td>
<td>38.02</td>
<td>40.28</td>
<td>35.8</td>
</tr>
<tr>
<td>T4</td>
<td>35.42</td>
<td>37.34</td>
<td>33.5</td>
</tr>
<tr>
<td>T5</td>
<td>32.04</td>
<td>33.5</td>
<td>30.5</td>
</tr>
<tr>
<td>T6</td>
<td>28.9</td>
<td>32.3</td>
<td>27.8</td>
</tr>
</tbody>
</table>
Figure 3.12 SEM images of EPS cellular structure as a function of steam time. (a) Low steam time (underexpanded, 11 sec). (b) Normal steam time (Optimum expansion, 17 sec). (c) High steam time (Partial collapse after maximum expansion, 20 sec) [Benson, et al. 2004]
Table 3.7 Characteristic thermal properties of foam using the proposed model

<table>
<thead>
<tr>
<th>Foam Type</th>
<th>Low Steam Time Foam (11 seconds)</th>
<th>Normal Steam Time Foam (17 seconds)</th>
<th>High Steam Time Foam (20 seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Collapse Temp. (Tsc)</td>
<td>92.53</td>
<td>92.78</td>
<td>90.24</td>
</tr>
<tr>
<td>A</td>
<td>-31.87</td>
<td>-32.482</td>
<td>-32.79</td>
</tr>
<tr>
<td>B</td>
<td>84.541</td>
<td>90.34</td>
<td>88.053</td>
</tr>
<tr>
<td>Correlation Coefficient</td>
<td>0.9491</td>
<td>0.9679</td>
<td>0.9637</td>
</tr>
</tbody>
</table>

dependence on the steam time. The temperature distribution data that was experimentally obtained was modeled using simple mathematical expression to characterize the foams. The mathematical expression was chosen to represent the foam property using two parameters (A and B) and Tsc. The result of the mathematical analysis is presented graphically in Figure 3.13 and the corresponding parameters are tabulated in Table 3.7. The parameters A and B are envisaged as having the potential use in the future characterization of foams.

3.5 Conclusions and future recommendations

Theory and experimental results from morphological study, GPC and DSC prove that styrene is an athermal/good solvent for polystyrene and its effect is significant in the degradation mechanism of the foam pattern and thus casting quality in LFC. The effect of styrene has to be accounted for in developing a comprehensive model for the LFC process.
Morphological and thermal characterization of intact foam clearly shows the variation of temperature profiles within intact foam as a function of steam time. Experimental parameters were developed for characterizing EPS foam for different steam times.

Future recommendation includes research and development of constitutive models accounting for styrene dissolution effects in LFC process at various temperatures. Contributions in the field of modeling the LFC process would be to generate an overall heat transfer coefficient as a modeling parameter that takes into account the dissolution effect of styrene. The thermal conductivity and diffusivity of the intact foam as

**Figure 3.13 Temperature distribution within intact foam as a function of processing conditions**
well as that of the “kinetic zone” can be experimentally determined and can be included as modeling parameters. A transient plane source technique (Eg. Hot disk, http://www.hotdisk.se/) is recommended for measurement of thermal properties for different zones of the degrading foam. The radiation effects from the degrading front should be considered instead of the radiation from the molten metal front in order to determine the velocity of the receding rigid foam front.

REFERENCES


Flory, P.J., (1953) “Principles Of Polymer Chemistry”, Cornell University Press (pg. 596)


Chapter 4 Novel expansion process for polystyrene
4.1 Introduction

4.1.1 Motivation and Objectives

Generally spherical, expandable polystyrene beads are prepared from liquid monomer suspended in an aqueous medium, containing an expansion agent. The most common expansion agents used are pentane isomers which are liberated into the atmosphere. These blowing agents are classified as greenhouse gases [Greenhouse Gas Technology Center Southern Research Institute, 2002] and volatile organic compounds (VOC) that contribute to smog. VOC also contribute to the generation of lower stratospheric ozone [Snijders, 2003]. Pentane emissions from EPS producing plants are generally uncontrolled. As an example the following text is quoted from a recent report from Environmental Protection Agency (EPA) while reviewing the compliance of two expanded polystyrene (EPS) producing plants. “Two of these plants gave fairly extensive information and, of these, one reported an overall uncontrolled VOC emission rate of 9.8 g/kg of product. For the other, an overall uncontrolled VOC emission rate of 7.7 g/kg is indicated.” [EPA, 1983 a, b] A major disadvantage of pentane isomers is their low flash point and high evaporation rate (see Table 4.2). Pentane isomers are five carbon saturated hydrocarbons and are excellent fuels with heat of combustion of 48.8 kJ/gm for n-pentane. (In comparison, octane, an eight carbon saturated hydrocarbon and a standard automobile fuel has heat of combustion value of 47.9 KJ/gm) [CRC Handbook, 2006-07]. Since pentane forms explosive mixtures with
air, precautions must be taken whenever it is used. “For example, after storage containers are opened, a time lag of 10 minutes is suggested to allow fumes or pentane vapors to dissipate out of the containers. Care must be taken to prevent static electricity and sparks from igniting the blowing agent vapors” [Benning, 1969]. Three general classes of pentane emissions from EPS foam production are as follows:

“manufacturing emissions; prompt foam cell losses, which are losses that typically occur during storage and shipping; and banked emissions, which are losses that occur through slow diffusion of blowing agents out of the foam over the life of the product” [EPA, 1990]. In coming years the polymer industry will be forced by new regulations to drastically reduce the level of VOC emission [Snijders, 2003].

The current production process of foam uses steam as the energy source for expansion of solid polystyrene beads. The machinery associated with steam generation and transmission takes up a substantial floor space as well as ceiling space in ducting. It is a common industrial practice to reduce components in the process chain through industrial engineering design since lesser components decrease maintenance cost, probability of process shut down due to component failure and probability of product rejection due to defect (See Fig 4.1). A list of gaseous emissions originating in the existing process of manufacturing of EPS foam is presented in Table 4.1 [Boustead, 1999]. Protection of industry human
Figure 4.1 Schematic showing current process of steam generation and transmission as a multi step process.
resource and reduction of flammable emissions require expensive plant
ventilation and gas collection systems. An appropriate approach for
reducing the health hazards associated with production of EPS foam is to
replace currently used expansion agents. A chemical reagent that is
benign, recyclable and susceptible to selective heating by appropriate
electromagnetic (EM) radiation has been identified and its
infusion/dispersion during polymerization of styrene to PS with target
molecular weight and distribution has been developed in this study.
Heating by EM radiation would lead to a fast (induction) volumetric
heating in comparison with the slower diffusion heating (conduction) that
takes place from the surface of the polymer beads to the core, in the
current industrial process of polystyrene bead expansion. An identical
principle is applicable during the molding process where microwave
radiation may be used to expand the pre-expanded beads further, until
fusion of beads occurs, to produce rigid foam. Development of a novel
production process that would eliminate the intermediate pre-expansion
step and carry out the entire expansion and fusion process inside the mold
is recommended in section 4.6 of this chapter. This new process is
expected to lead to an environmentally friendly, economic and efficient
production process, reducing raw material cost, cost of maintaining
stringent safety standards and reducing shop floor space.

Snijders, [2003] in her doctoral thesis presented experimental and
theoretical work on a novel expansion method for polystyrene using water as an expansion agent. The problems associated with this method have been described earlier in Chapter 2. Meyer and Kinslow [1991] developed the foaming of polystyrene using supercritical CO₂. “Supercritical CO₂ is a non-toxic, environmentally benign solvent with a unique ability to diffuse rapidly through small voids because of its high diffusivity and negligible surface tension” [Abbett et al, 2003]. Expansion using supercritical CO₂ is mainly based on extrusion principles and is ideal for making foam of simple geometry like boards and pellets [Meyer and Kinslow, 1991]. Recently, a microwave foaming process has been described for making molded starch foams from extruded pellets [Zhou, 2004]. The study presented in this dissertation is another PS foaming technological development for making rigid EPS foam of complex geometry, with an alternative approach that addresses environmental issues of greenhouse emission and provides a mechanism to overcome problems faced when water was used as an expansion agent.

From the perspective of LFC, it has been reported that the morphology of the cellular foam and variations in local density drastically affects foam degradation and thus the quality of the casting [Benson, 2004]. For example “patterns having a low degree of fusion degraded with an average recession velocity of 2.8 cm/s, about 25% faster than the normally fusion patterns” [Sun, 2005]. A novel method for foam production is hereby
Table 4.1 Gross gaseous emissions arising from the production of 1 kg of EPS. [Boustead, 1999]

<table>
<thead>
<tr>
<th>Emission</th>
<th>Total in gm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dust</td>
<td>1.8</td>
</tr>
<tr>
<td>CO</td>
<td>1.6</td>
</tr>
<tr>
<td>CO₂</td>
<td>2,500</td>
</tr>
<tr>
<td>SOₓ</td>
<td>9.7</td>
</tr>
<tr>
<td>NOₓ</td>
<td>12</td>
</tr>
<tr>
<td>*Hydrocarbons</td>
<td>4.5</td>
</tr>
<tr>
<td>*Methane</td>
<td>9.5</td>
</tr>
</tbody>
</table>

* Byproducts from commercial expansion agents.

investigated to achieve a cellular morphology and overall foam uniformity that may contribute to a better control over metal flow during LFC and thus reduce flow related casting defects.

In summary, the objectives of the developed technology are to:

1. Identify a benign expansion agent that can be heated by microwave radiation
2. Maximize recovery and recycling of a novel expansion agent
3. Maximize efficiency with microwave radiation as volumetric heating source
4. Minimize workshop space with microwave expansion
5. Minimize maintenance cost by single component design
6. Eliminate cost of expensive tooling and stainless steel molds by using economic radiation transparent thermoset polymer or glass molds
4.1.2 Selection of the expansion agent

Many different organic solvents were considered as potential expansion agents. Non-polar molecules such as aromatic hydrocarbons (e.g. Benzene, Toluene, Diethyl Ether) were excluded due to their toxicity and incompatibility with microwave heating. Organic solvents like aldehydes, ketones and halogenated hydrocarbons (e.g. Methyl Ethyl Ketone, Methylene Chloride and Chloroform) were rejected due to their toxicity, volatility and/or high flammability. Alcohols were selected for the study based on their volatility, flammability, boiling point, toxicity and commercial availability. 2-butanol, 2-propanol and ethanol were identified as the most appropriate expansion agents. Experiments were conducted using 2-butanol as a model expansion agent. The criteria for selection of 2-butanol as an expansion agent is mentioned below:

**Pure** 2-butanol boils at 99°C, which is close to the glass transition temperature of polystyrene, which is approximately 100°C. This temperature correlation is used as a fundamental principle to obtain expansion using selective heating by electromagnetic radiation. The 2-butanol phases volumetrically absorb EM radiation and heat the polymer matrix through conduction. As the liquid 2-butanol changes phase to gas above its boiling point, the polymer matrix simultaneously reaches the glass transition and becomes rubbery, allowing the gaseous phase to expand the matrix under a pressure differential.
2-butanol is an alcohol with a dipole moment of 1.8 Debye (water 1.8546 Debye) [CRC Handbook, 2006-07] and is thus susceptible to microwave heating. Alcohols have a very distinct infrared absorption band for wave numbers in the range of 3200 cm\(^{-1}\) and 3600 cm\(^{-1}\). Thus selective heating by IR sources in addition to microwave is also a possibility. It should be noted that the heating mechanism using IR radiation is by selective absorption of energy, which is fundamentally different from heating mechanism in case of microwave radiation. Microwave heating uses the principles of ionic conduction and molecular interaction through dipole rotation. Fundamental aspect of microwave heating is explained in section 4.2.2. 2-butanol was found to be completely soluble in the styrene monomer and it has been shown in this study that 2-butanol is soluble in polystyrene of a target molecular weight, below a critical saturation concentration. This principle was used to achieve polymerization induced phase separation (PIPS). The phase separation is expected to produce morphology with an even distribution of the spherical alcohol phase (droplets) within the polymer matrix. Chan and Rey [1996] described the process of condensation polymerization of a tri-functional monomer in presence of an inert and low molar mass solvent. Their model proposed spherical phase separated morphologies distributed in a polymer matrix.

Unlike pentane isomers (current expansion agent), 2-butanol is a nonvolatile, low flammable and nontoxic organic alcohol (Table 4.2) In
addition 2-butanol can be easily recovered and recycled by using a room temperature trap, due to its high boiling point and low volatility. In addition economic benefits could be achieved due to relaxation of the rigorous flammable safety standards, currently practiced in the EPS foam industry. The molar mass of 2-butanol (74.12gm/mol) is very close to the molar mass of pentane (72.15gm/mol). The higher boiling point and lower volatility of 2-butanol is due to the hydrogen bonding present as a result of the hydroxyl group. The high molar mass accounts for slower expulsion of 2-butanol from PS matrix as compared to water in WEPS. High rate of water escape through PS at elevated temperatures (above Tg) leads to loss of blowing agent without foaming.

4.2 Background theory:

4.2.1 Polymerization Induced Phase Separation (PIPS)

When a polymerization reaction is carried out from a monomer, in the presence of a miscible oligomer, a soluble polymer or a small molecule like a solvent, a phase separation process usually occurs as the polymerization proceeds. This leads to phase separated morphologies and distribution of the separated phases depending strongly on the initial composition, reaction kinetics and thermodynamics (Fig.4.2).

PIPS can occur via two different modes, namely Spinodal Decomposition (SD) and Nucleation and Growth (NG). NG process can be subdivided
Table 4.2 Relevant physical properties of 2-butanol compared to n-pentane [CRC Handbook; SIRI MSDS]

<table>
<thead>
<tr>
<th>Name</th>
<th>2-butanol</th>
<th>n-pentane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Formula</td>
<td>C₄H₁₀O</td>
<td>C₅H₈</td>
</tr>
<tr>
<td>Molecular weight gm/mol</td>
<td>74.12</td>
<td>72.15</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>99°C</td>
<td>36°C</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.808</td>
<td>0.626</td>
</tr>
<tr>
<td>Flash point</td>
<td>26°C</td>
<td>-49°C</td>
</tr>
<tr>
<td>Explosion limits</td>
<td>1.7% - 9.8%</td>
<td>1.4% - 8.3%</td>
</tr>
<tr>
<td>Auto ignition temperature</td>
<td>405°C</td>
<td>260°C</td>
</tr>
<tr>
<td>Evaporation rate</td>
<td>0.67</td>
<td>28.6</td>
</tr>
<tr>
<td>Butyl acetate = 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor pressure at 99°C in mm Hg</td>
<td>797</td>
<td>882</td>
</tr>
<tr>
<td>Loss Tangent at 2.45 GHz</td>
<td>0.447</td>
<td>0</td>
</tr>
<tr>
<td>General Toxicology</td>
<td>Irritant by inhalation, ingestion or through skin absorption.</td>
<td>Harmful by inhalation, ingestion or skin absorption. Irritant. Narcotic in high concentration.</td>
</tr>
<tr>
<td>Risk Phrases</td>
<td>Flammable</td>
<td>Extremely flammable</td>
</tr>
<tr>
<td></td>
<td>Irritating to eyes, skin and respiratory system</td>
<td>Harmful by inhalation, to skin, if swallowed</td>
</tr>
<tr>
<td>Toxicity</td>
<td>Oral- rat- concentration 50 percent kill</td>
<td>Inhalation-rat-lethal concentration 50 percent kill 364 gm/m³/4hr</td>
</tr>
<tr>
<td></td>
<td>2193 mg kg⁻¹</td>
<td></td>
</tr>
</tbody>
</table>
into homogeneous and heterogeneous nucleation and growth. PIPS by SD mechanism takes place by a continuous and spontaneous process and the developed morphologies generally display a co-continuous connected structure. NG mechanism on the other hand is a slower random process that takes place at the metastable region of a phase diagram of the binary mixture, and is characterized by non connected separated phases [Rubinstein, 2003]. NG rate has a high dependence on the interfacial tension between the polymer and the separating phase. It has been reported in case of rubber modified epoxy, that for an interfacial tension value of $\gamma_{12} = 0.4$ mN/m practically no phase separation occurs by the nucleation-growth mechanism, and demixing proceeds by spinodal decomposition.” [Verchere et. al., 1991].

Polymerization-induced phase separation is used in practice to synthesize
useful materials such as high-impact polystyrene (HIPS), rubber-modified thermosets, thermoplastic-thermoset blends, polymer-dispersed liquid crystals, thermally reversible light scattering films and nanostructured thermosets. The morphology and dynamics of polymerization-induced phase separation in the initially homogeneous solution of a non-reactive component in reactive monomers have been investigated by Luo (2006). In PIPS, instability of the system has been reported to be driven by the progressive increase of the average molecular weight of the polymerizing species [Verchere et. al., 1991]. After initiation of polymerization, the non-equilibrium phase separated structure will manifest depending on the competition between phase separation dynamics and polymerization reaction kinetics [Luo, 2006]. Rey and co-workers used numerical analysis of PIPS based on an idealized assumption of reaction-driven phase separation using time-dependent Cahn–Hillard (CH) equation.

The CH equation for the rate of change of polymer volume fraction $\varphi_1$ is given by

$$\frac{\partial \varphi_1}{\partial t} = \nabla \cdot \nabla \Lambda_{12} \frac{\delta F}{\delta \varphi_1}$$

(4.1)

where $F$ is the Flory-Huggins free energy of mixing, $\Lambda_{12}$ is the mutual diffusion coefficient that can be expressed in terms of the self diffusion coefficients of the individual polymer and solvent. They showed that both the spatial distribution and morphology in PIPS are sensitive to the magnitudes of the diffusion coefficient and reaction rate constant. [Oh
and Rey, 2000]. Kyu and Lee reported time-resolved light scattering results for the case of PIPS of methylene dianiline in carboxyl terminated polybutadiene acrylonitrile. They observed reduction of the initial length scale at the early period of the reaction. By incorporating the polymerization kinetics into the Cahn–Hilliard equation, they analyzed the dynamics of phase separation and attributed the phenomena of reduction of the initial phase separated length scale to nucleation initiated spinodal decomposition (NISD). In their later experiments, the reduction of initial length scale was considered as criterion whether the phase separation goes through the nucleation growth (NG) mechanism or not [Kyu and Lee, 1996]. However, Luo reported that NISD was not the unique mechanism for the reduction in initial length scale of separated phase and the evidence for NG mechanism cannot be directly concluded by observation of reduction of initial length scale. [Luo, 2006].

Flory-Huggins theory predicts an equilibrium phase diagram for a particular polymer and solvent system. In our case the solvent is also the expansion agent. The thermodynamic phase diagram of polymer solution exhibiting a critical solution temperature can be established from equation 4.2, the Flory-Huggins free energy of mixing: [Strobl, 1997].

\[
\Delta F = kT \left[ \frac{\varphi_1}{n} \ln \varphi_1 + \varphi_2 \ln \varphi_2 + \chi_{12} \varphi_1 \varphi_2 \right]
\] (4.2)

where, \( n \) is the statistical polymer segment length, \( \varphi_1 \) and \( \varphi_2 \) are the
volume fractions of polymer and the solvent (expansion agent in this study) respectively and $\chi_{12}$ is the Flory-Huggins (FH) interaction parameter between the polymer and the solvent. In general the equilibrium state of the mixture depends on the sign of the free energy of mixing $\Delta F$ at a particular composition of interest. A negative value of the free energy favors a homogenous mixed system.

The first term in the equation $\frac{\varphi_1 \ln \varphi_1 + \varphi_2 \ln \varphi_2}{n}$ is the total mean field entropic contribution while the second term ($\chi_{12} \varphi_1 \varphi_2$) is the residual free energy of mixing, representing the effect of local interactions and motion of the monomers. Typically in polymer solutions the value of $n$ is large and $\varphi_1 << \varphi_2$. However in this study the situation is reversed where the value of $\varphi_2$ is in the range of 0.07 to 0.08 i.e. $\varphi_2 << \varphi_1$. The first (entropic) term of the FH equation is negative and always favors mixing. In case of styrene-2-butanol system this term is non trivial since $n=1$.

The mean field entropic (first) term in equation 4.2 is calculated based on the assumption that the conformational entropy of a polymer is identical both in the mixed and pure states. Another important assumption is that there is no volume change during mixing. These are good assumptions in this study since the solvent phase has very low volume fraction.

The second term in the FH equation involves the FH interaction parameter $\chi_{12}$, which has an energetic origin and can have positive (opposing
mixing), zero (ideal mixtures) or negative (promoting mixing) values. “If there is a net attraction between species (i.e. they like each other better than they like themselves), \( \chi_{12} < 0 \) and a single phase mixture is favorable for all compositions. More often there is a net repulsion between the species (they like themselves more than each other) and the Flory interaction parameter is positive” [Rubinstein, 2003] The later is the case for PIPS and the equilibrium state of the mixture does not depend any more on the sign of the free energy of mixing \( \Delta F \) at a particular composition of interest, but on the functional dependence of this free energy on the composition \( \varphi \).

Differentiating FH equation for ideal polymer solution (only entropic contribution) we get

\[
\frac{\partial \Delta F}{\partial \varphi_i} = kT \left[ \frac{\ln \varphi_i}{n} + \frac{1}{n} \ln(1 - \varphi_i) - 1 \right]
\]

(4.3)

It is evident from equation 4.3 that purely entropic contribution diverges at both extremes of composition (i.e. as \( \varphi_1 \to 0 \), \( \frac{\partial \Delta F}{\partial \varphi_1} \to -\infty \) and as \( \varphi_1 \to 1 \), \( \frac{\partial \Delta F}{\partial \varphi_1} \to \infty \)). This indicates “a small amount of either species will always dissolve even when there are strong unfavorable energetic interactions [Rubinstein, 2003].
The FH interaction parameter is given by

\[ \chi_{12} = A + (\chi_c - A)T_c / T \]  \hspace{1cm} (4.4)

Or in terms of Hildebrand solubility parameters [Mark, 1996]

\[ \chi_{12} = 0.34 + \frac{V_i}{RT}(\delta_p - \delta_s)^2 \]  \hspace{1cm} (4.5)

\( A \) is the entropy correction factor, \( T \) the absolute temperature, \( T_c \) is the critical temperature, \( V_i \) is the volume for the polymer chain segment, \( \delta_p \) and \( \delta_s \) are the total Hildebrand solubility parameters for the polymer and the solvent respectively and \( \chi_c \) is the critical interaction parameter given by

\[ \chi_c = 0.5(1 + \frac{1}{\sqrt{n}})^2 \]  \hspace{1cm} (4.6)

It should be noted that equation 4.5 does not work in mixtures with strong polar or hydrogen bond interactions. [Rubinstein, 2003] This equation cannot be applied to PS-2-butanol or styrene/2-butanol systems where hydrogen bonding and polar interactions are strong [Krevelen, 2003].

Considering 8% by volume of 2-butanol the free energy for styrene-2-butanol system can be written as

\[ \Delta F = kT[-0.254 + 0.065x \chi_{12}] \]  \hspace{1cm} (4.7)
Thus the critical value for $\chi_{12}$ exceeding which phase separation shall occur can be estimated by setting $\Delta F = 0$

Or $\chi_{12} \approx 4$

This value is substantially larger than expected $\chi_{12}$ values ($\chi_{12} = 0.713$ estimated using equation 4.5) and it was clearly observed during experiments that styrene and 2-butanol form a homogeneous mixture at room temperature.

Chan and coworkers showed that a major contribution for phase separation is due to the change in the Flory-Huggins interaction parameter $\chi_{12}$ resulting from associated changes in the chemical structure produced by polymerization [Chan, 1996]. Bernardo [2007] experimentally determined the interaction parameter ($\chi_{12}$) for a series of alcohols and polystyrene (Mw = 230,000) system (Table 4.3). The values of the interaction parameter ($\chi_{12}$) for 2-butanol-PS system at different temperatures were estimated to be approximately equal to that of 1-butanol due to lack of data in literature. The difference in literature values of interaction parameter between 1-propanol and 2-propanol served as measure for estimation. It has been experimentally shown in this study that phase separation at room temperature do not occur until a critical concentration of approximately 8% by volume of 2-butanol is reached. Below this critical composition PS-2-butanol system (Mw=200K) exists in a
Table 4.3 Interaction parameter ($\chi_{12}$) for alcohols in PS at different temperature [Bernardo, 2007]

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>$\chi_{12}$ at 65°C</th>
<th>$\chi_{12}$ at 75°C</th>
<th>$\chi_{12}$ at 95°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-propanol</td>
<td>1.6502</td>
<td>1.5408</td>
<td>1.3066</td>
</tr>
<tr>
<td>2-propanol</td>
<td>1.7470</td>
<td>1.5958</td>
<td></td>
</tr>
<tr>
<td>1-butanol</td>
<td>1.5356</td>
<td>1.4449</td>
<td>1.2039</td>
</tr>
<tr>
<td>2-butanol (estimated)</td>
<td>1.6</td>
<td>1.49</td>
<td>1.2039</td>
</tr>
</tbody>
</table>

homogeneous single-phase mixture. Verchere and co workers [1991] analyzed PIPS in rubber modified epoxies. They reported that the change in mean field entropy, due to growth of polymeric chains is more significant in their case of PIPS than changes in the value of $\chi_{12}$. The occurrence of uniform spherical phase separated structures in a continuous polymer matrix has encouraged many authors to describe the PIPS process using NG mechanism. However, Verchere and co workers concluded that inspection of SEM images to determine the mode of PIPS to be either NISD or NG may be grossly misleading.

They recommended a detailed analysis of thermodynamics and kinetic process during polymerization in order to conclude the mechanism leading to formation of separated phases in PIPS.

In this study, PIPS technique has been used in order to achieve a uniform distribution of separated phases of 2-butanol in polystyrene matrix instead of mechanical dispersion as in WEPS. In case of WEPS, water is
completely insoluble in styrene monomer. The first step in the WEPS process was bulk polymerization where a surfactant was added to disperse water droplets in partially polymerized styrene thus yielding a stable emulsion [Crevecoeur, 1999]. Partial polymerization was carried out to increase the viscosity of the liquid media sufficient enough to stabilize the emulsion. In the second step this emulsion was suspended in water in the presence of a suitable suspension stabilizer and standard suspension polymerization was carried out in order to obtain beads. The detailed thermodynamic and kinetic modeling of PIPS in PS-2-butanol system is outside the scope of this dissertation. Thus a simpler comparative treatment using room temperature solubility parameters is used to support the already discussed process of phase separation in PS-2-butanol system. Later in this chapter thermodynamics of phase separation has been analyzed by comparison of theory with experimental results.

Solubility and thus phase separation can be expressed in terms of the Hildebrand parameter denoted by $\delta t$ [Hildebrand, 1916]. Practically it is possible to use this parameter without a thorough understanding of the molecular dynamics (MD) on which it is based. Hansen [1967] divided the total Hildebrand parameter value into three additive parts: a dispersion force component, hydrogen bonding component, and a polar component given by equation 4.8.

$$\delta t^2 = \delta d^2 + \delta p^2 + \delta h^2$$ (4.8)
where

\[ \delta_t = \text{Total Hildebrand parameter} \]
\[ \delta_d = \text{dispersion component} \]
\[ \delta_p = \text{polar component} \]
\[ \delta_h = \text{hydrogen bonding component} \]

The Hildebrand parameter for each solvent at 25°C can be plotted in a 3-D space by using the individual Hansen parameters as coordinates. For a polymer, a solubility sphere can be geometrically constructed in this 3-D space (Fig. 4.3).

The coordinates at the center of the solubility sphere are designated by means of three component parameters (\( \delta_d, \delta_p, \delta_h \)) of the polymer, and radius of the sphere, called the interaction radius (R). A polymer has a high probability to be soluble in a solvent at 25°C, if the Hansen parameters for the solvent lie within the solubility sphere for the polymer.

In order to determine this (without rigorous MD simulations) the distance of the solvent point from the center of the polymer solubility sphere (DS-P) needs to be evaluated and should be less than the interaction radius for the polymer. Values of R for different polymers have been experimentally determined by trial with many different solvents and reported in literature. Gharagheizi et al. [2006] used intrinsic viscosities of the polymer in different solvents and the molar volumes of the solvents to
Figure 4.3 Schematic illustrating the plotting of a solubility sphere in a 3-D Hansen plot.

develop a correlation between Hansen parameters and the polymer interaction radius. The radius of interaction for PS is reported to be $R = 12.7 \text{ MPa}^{1/2}$ [Krevelen, 2003]

Ideal solvent coordinates lie on the sphere surface while bad and good solvent coordinates lie outside and inside the sphere respectively.

$$D_{(S-P)} = [4(\delta_{dS} - \delta_{dP})^2 + (\delta_{pS} - \delta_{pP})^2 + (\delta_{hS} - \delta_{hP})^2]^{1/2}$$ (4.9)

Where $D_{(S-P)} = \text{Distance between solvent and center of polymer solubility sphere}$

$\delta_{xs} = \text{Hansen component parameter for solvent}$

$\delta_{xp} = \text{Hansen component parameter for polymer}$
Table 4.4 Hansen parameters of monomer, polymer and expansion agents at 25°C [Krevelen, 2003]

<table>
<thead>
<tr>
<th>Species</th>
<th>$\delta_t$ (MPa$^{1/2}$)</th>
<th>$\delta_d$ (MPa$^{1/2}$)</th>
<th>$\delta_p$ (MPa$^{1/2}$)</th>
<th>$\delta_h$ (MPa$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentane</td>
<td>14.5</td>
<td>14.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2-butanol</td>
<td>22.2</td>
<td>15.8</td>
<td>5.7</td>
<td>14.5</td>
</tr>
<tr>
<td>Styrene</td>
<td>19</td>
<td>18.6</td>
<td>1</td>
<td>4.1</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>18.6</td>
<td>21.3</td>
<td>5.8</td>
<td>4.3</td>
</tr>
</tbody>
</table>

See Table 4.4. Equation 4.9 was used to calculate the distance between 2-butanol and polystyrene. Based on the value of $D_{(2\text{-butanol-PS})} = 17.96$ which is greater than $R=12.70$, PS is expected to be completely insoluble in 2-butanol and a complete phase separation of expansion agent in polystyrene matrix is expected at 25°C for all compositions. It should be noted that in the commercial process n-pentane as an expansion agent dissolves inside polystyrene beads by the process of diffusion while 2-butanol is thermodynamically dispersed in the laboratory experiment as separated phases by PIPS technique.

4.2.2 Theory of heating by Microwave radiation

Microwaves are electromagnetic waves that typically have a frequency range from 0.3 GHz (there is no actual specified lower frequency limit) to 300 GHz with corresponding wavelengths of 1 m to 1 mm. Microwaves travel at the velocity of light and are comprised of oscillating electric and magnetic fields. Microwaves are coherent and polarized in contrast to visible electromagnetic waves (apart from lasers). They obey the laws of optics and can be transmitted, absorbed or reflected depending on the type
of material. [Kappe and Stadler, 2005] The microwave heating process is fundamentally different from the heating process used in conventional ovens. With microwaves, heat is generated internally within the material as opposed to originating from external heating sources. The energy injected in the material is transferred through the material surface electromagnetically, and does not flow as heat flux, as in conventional heating. The heating rate is not a function of the thermal diffusivity of the material and surface temperature. As a result, the thermal gradients and flow of heat is the reverse of those in materials heated by conventional means. Thus, it is possible by using microwave to heat both large and small complex shapes very rapidly and uniformly. As per Meridith [1998], “Heating times can often be reduced to less than 1% of that required using conventional techniques, with effective energy variation within the workload of less than 10%”. As the absorption of microwave energy varies with composition and chemical structure it is also possible to have selective heating. All domestic microwave ovens and commercially available microwave sources for chemical synthesis operate at 2.45 GHz corresponding to a wavelength of 12.25cm in order to avoid interference with cellular phones and telecommunication frequencies. Energy of a microwave photon at a frequency of 2.45 GHz is 1.6 x10^-3 electron volts, which is much lower than covalent bond energies or even hydrogen bond (0.04eV to 0.44eV). Thus, microwaves cannot induce chemical reactions by direct absorption of electromagnetic energy. [Leadbeater, 2006]
Microwave dielectric heating is dependant on the ability of a material to absorb mainly the electric component of microwave energy and generate heat. The heating is caused by two main mechanisms that are dipole polarization and ionic conduction. In a polar molecule a partial negative and partial positive charge is developed due to deformation of the electronic cloud during bond formation. The permanent electric dipole moment \( \mu \) in such a molecule is defined as the moment due to the force from the centre of partial negative charge \((-\delta_q)\) to the centre of partial positive charge \((+\delta_q)\) distance \(r\) away. The units are usually given in Debye.

\[
\mu = \delta_q r
\]

In presence of an oscillating electric field, the dipoles attempt to continuously reorient in the direction of the electric field vector. (Fig 4.4) Depending on the frequency of the field, the dipole may move synchronously in time to the field, lag behind it or remain unaffected. When the dipole vector lags behind the field vector, interactions between the dipole and the field vectors lead to an energy loss by heating, the extent of which is dependent on the phase difference between these vectors. Heating effects reaches a maximum value twice during each cycle [English and MacElroy, 2003]. “Debye (1929) when investigating dielectric relaxation obtained the relation between relaxation time \(\tau_D\), now known as Debye relaxation time, and the coefficient \(\varsigma\) of molecular
Figure 0.4 Dipole polarization effect on water molecule. a. Water dipole moment is aligned to the field; b. Dipole moment rotates in order to follow the field; c. Dipole moment rotates in opposite direction trying to align with the field.

friction.” “The Debye theory of relaxation is based on the consideration of rotational Brownian motion of polar molecules.” The Debye relaxation time is expressed as [Gaiduk, 1999]

\[
\tau_D = \frac{\zeta}{2k_B T}.
\]  

(4.11)

where \( k_B \) is Boltzmann constant and \( T \) is the absolute temperature of the media. The ease of relaxation depends on the viscosity of the liquid subjected to the field and the mobility of the electron clouds in its molecules. In molecules like alcohols these, in turn, depend on the strength and density of the hydrogen bonded network. In free liquid water this movement occurs at GHz frequencies (microwaves) and in ice at kHz frequencies (long radiowaves). The re-orientation process may be modeled.
using a 'wait-and-switch' process where the water molecule has to wait for
a period of time until favorable orientation of neighboring molecules
occurs and then the hydrogen bonds switch to the new molecule [Kaatze,
2002]. Since the frequency of typical microwave is 2.45 GHz, the time
period of microwave radiation is in order of nanoseconds \(10^{-9}\) sec). The
molecular relaxation rate in liquid state during cooling by conduction is
in the order of microseconds \(10^{-6}\) sec) [Leadbeater, 2006]. In a microwave
coupled thermodynamic control volume of a liquid, where energy input is
by the mode of microwave radiation and energy output is by mode of
molecular vibrations (Conduction) and mass transport (Natural
convection), the accumulation of energy is extremely fast. Thus in a
coupled system, an almost constant energy accumulation is achieved at a
rate far greater than the rate at which energy can be dissipated by
conventional modes of cooling. As a result an absorbing liquid medium
can have almost instantaneous local superheating and temperatures can
reach much higher above its boiling point. It should be noted that gas
molecules cannot be heated by microwave radiation since distance
between rotating dipoles are too high to create molecular friction.

Ionic conduction (Fig 4.5) on the other hand involves oscillation of
dissolved charged particles in a liquid and creates heating effect due to
molecular collision. The ionic conductivity effect has a much stronger
heating effect than the dipole rotation mechanism. The heating
Figure 0.5 Ionic conduction effects on Chlorine ion. a. Negatively charged Chlorine ion is attracted to the positive portion of microwave; b. is repelled by the negative section of microwave; c. causing oscillation of the ion through the liquid media

characteristic of a material is dependant on its dielectric properties expressed by its loss tangent (tanδ) [Meridith, 1998]. An introductory mathematical treatment of dielectric heating effect in liquid with hydrogen bonding is presented as follows. [Smyth, 1995; Metaxas & Meredith, 1983; Chaplin, 2007]

If two charges $q_1$ and $q_2$ are separated by distance $r$, the potential energy $V$ (joule) in vacuum is expressed as

$$V = \frac{q_1 q_2}{4 \pi \varepsilon_0 r}$$  \hspace{1cm} (4.12)

where $\varepsilon_0$ is the ability of a vacuum to store electrostatic energy, called the
permittivity in vacuum (= 8.854 x 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1} )

The potential energy due to charges separated in a material medium with medium permittivity $\varepsilon$ is expressed as

$$V = \frac{q_1 q_2}{4\pi \varepsilon r}$$

(4.13)

The relative permittivity ($\varepsilon_r$) of a material medium is expressed as

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$

(4.14)

In the case of dilute gases the relative permittivity approaches unity. In hydrogen bonded molecules like liquid water and alcohols the dielectric constant is high and there is a linear correlation between the dielectric constant and the density of hydrogen bonds [Yoshii, 2001].

The polarization ($P$, coulombs) of a material is its electric dipole moment density.

$$P = (\varepsilon_r - 1)\varepsilon_0 E$$

(4.15)

Where $E$ is the applied field potential ($E$, volts) of electromagnetic radiation and is expressed as

$$E = E_{\text{max}} \cdot \cos(\omega t)$$

(4.16)
where $E_{\text{max}}$ is the amplitude of the potential, $\omega$ is the angular frequency in radians/second and $t$ is the time (seconds).

The relative permittivity ($\varepsilon_r$) is related to the molar polarization of the medium ($P_m$) using the Debye equation

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{\rho P_m}{M}$$

(4.17)

where $\rho$ is the mass density ($\text{kg} \, \text{m}^{-3}$), $M$ is the molar mass ($\text{kg}$). The molar polarization of the medium ($P_m$) is defined as

$$P_m = \frac{N_A}{3\varepsilon_0} \left( p + \frac{\mu^2}{3kT} \right)$$

(4.18)

where $p$ is the polarizability of the molecules, which is the proportionality constant between the induced dipole moment $\mu^*$ and the field strength $E$ ($\mu^* = pE$), $N_A$ is the Avogadro number, $k$ is the Boltzmann constant ($=R/N_A$) and $T$ is the absolute temperature. The second term in equation (4.18) is due to the contribution from the permanent dipole moment and is negligible when the medium is non-polar or when the frequency of the applied field is sufficiently high that the molecules do not have time to change orientation.

If the polarization lags behind the field vector by the phase ($\delta$, radians) then the polarization ($P$, coulombs) can be expressed as
\[ P = P_{\text{max}} \cos(\omega t - \delta) \]  
\hspace{1cm} (4.19)

where \( P_{\text{max}} \) is the maximum value of the polarization

The power (\( P^* \), watts) lost as heat by the dielectric material media is expressed as

\[ P^* = 0.5 P_{\text{max}} E_{\text{max}} \omega \sin(\delta) \]  
\hspace{1cm} (4.20)

Power lost as heat is zero if there is no lag (that is, if \( \delta = 0 \))

The relative permittivity can be expressed in terms of complex dielectric permittivity (\( \varepsilon_r^* \)) given by

\[ \varepsilon_r^* = \varepsilon_r' - i \varepsilon_r'' \]  
\hspace{1cm} (4.21)

where \( \varepsilon_r'' \) is the dielectric loss factor indicating the efficiency with which electromagnetic radiation is converted into heat and \( \varepsilon_r' \) is the dielectric constant indicating the polarizability of the molecules in the electric field.

Also \( \tan(\delta) = \varepsilon_r''/\varepsilon_r' \)  
\hspace{1cm} (4.22)

The terms \( \varepsilon_r^* \), \( \varepsilon_r'' \) and \( \varepsilon_r' \) are all functions of the frequency of the electromagnetic radiation. The dielectric constant as a function of the wavelength, is expressed as
where $\varepsilon_s$ is the dielectric constant at low frequencies (static region), $\varepsilon_\infty$ is the dielectric constant at high frequencies (optical region) and $\lambda_S$ is the critical wavelength for maximum dielectric loss. The dielectric constant can also be expressed in terms of the dipole relaxation and is given by

$$
\varepsilon_r' = \frac{\varepsilon_r - \varepsilon_\infty}{1 + (\lambda_s / \lambda)^2} + \varepsilon_\infty
$$

where $\tau$ is the dipole relaxation time expressed as

$$
\tau = \frac{4\pi r^3}{kT}
$$

where $r$ is the molecular radius, $k$ is the Boltzman constant and $\eta$ is the viscosity of the liquid.

As the temperature increases, both the strength and density of the hydrogen bond network decrease. This effects dielectric heating by

(a) lowering the static dielectric constant $\varepsilon_s$,

(b) lessening the difficulty for the movement of dipole and thereby allowing the liquid molecule to oscillate at higher frequencies, and

(c) reducing the drag to the rotation of the water molecules, thereby
reducing the molecular friction coefficient and hence the dielectric loss.

Most of the dielectric loss is within the microwave range of electromagnetic radiation (~0.3 to ~300 GHz, with wavenumber 0.033 cm\(^{-1}\) to 10 cm\(^{-1}\), and wavelength 0.3 m to 1.0 mm respectively). The frequency for maximum dielectric loss lies higher than the 2.45 GHz (wavenumber 0.0817 cm\(^{-1}\), wavelength 12.24 cm) produced by most microwave oven [Chaplin, 2007].

The electromagnetic penetration is infinite in a perfectly transparent substance and zero in reflective material (for example, metals). The attenuation (\(\alpha\)) is given by:

\[
\alpha = \frac{2\pi}{\lambda} \sqrt{\frac{\varepsilon_r \, \{\sqrt{(1 + \tan^2 \delta)} - 1\}}{2}}
\]

(4.26)

Considering plane waves, the penetration distance \(D_p\) for incident microwave radiation intensity to decrease to 1/e (63% absorbed) in a given media is expressed as

\[
D_p = \frac{1}{2\alpha} = \frac{\lambda}{2\pi \tan \delta \sqrt{\varepsilon_r}}
\]

(4.27)

At 2.45 GHz:
\[ D_p = 1.947 \frac{\sqrt{\varepsilon'_r}}{\varepsilon''_r} \text{ cm} \]  

(4.28)

From the equations 4.26 and equation 4.20 it is clear that a reaction medium with a high tanδ is required for efficient absorption and rapid heating. At 2.45GHz, 2-butanol has a tanδ = 0.447 and heats more rapidly than water with a tanδ of 0.123. Also at 2.45GHz the loss tangent (tanδ) for polystyrene is 0.0003 and attenuation (α) is ≈ 0 (from equation 4.26). Thus a negligible microwave heating effect of polystyrene matrix is expected from microwave radiation. Table 4.5 lists loss tangent values for various alcohols and water. [Kappe and Stadler, 2005]

The main advantage of using microwave as a heating source for expansion of PS using alcohols as expansion agents lies in the high coupling efficiency that can be achieved when heating alcohols doped with ionic salts [Metaxas & Meredith, 1983]. Dissolved salt depresses the dielectric

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility Parameter</th>
<th>Boiling Point °C</th>
<th>Vapor pressure at 100°C in mm of Hg</th>
<th>Microwave Coupling (tanδ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>26.2</td>
<td>78.4</td>
<td>1683</td>
<td>0.941</td>
</tr>
<tr>
<td>2-propanol</td>
<td>23.5</td>
<td>82</td>
<td>1500</td>
<td>0.799</td>
</tr>
<tr>
<td>2-butanol</td>
<td>22.2</td>
<td>99</td>
<td>806</td>
<td>0.447</td>
</tr>
<tr>
<td>Water</td>
<td>48.0</td>
<td>100</td>
<td>764</td>
<td>0.123</td>
</tr>
<tr>
<td>PS</td>
<td>18.6</td>
<td>N/A</td>
<td>N/A</td>
<td>0.0003</td>
</tr>
</tbody>
</table>
constant dependent on its concentration \((C)\) and the average hydration number of the individual ions \((H_N)\). This is expressed as

\[
\varepsilon'_\infty = \varepsilon_\infty - \frac{2H_N C - \varepsilon_\infty}{1 + \omega^2 \tau^2} + \varepsilon_\infty
\]  

(4.29)

By salt addition the dielectric loss factor is increased by a factor that depends on the ionic conductivity \((\Lambda, \text{ S cm}^2 \text{ mol}^{-1}; \text{ S (Siemens)} \text{ } \Lambda (\text{mho}))\), concentration and frequency. It increases with rise in temperature and decreasing frequency.

\[
\varepsilon'' = \frac{(\varepsilon_\infty - 2H_N C - \varepsilon_\infty)(\omega \tau)}{1 + \omega^2 \tau^2} + \frac{\Lambda C}{1000 \omega \varepsilon_0}
\]  

(4.30)

Thus with addition of very small amounts of salt, increase in dielectric loss factor and decrease in dielectric constant causes a major increase in the value of the loss tangent and in turn an increasing in dielectric heating efficiency. Zhou and Song [2005] used Calcium Chloride (CaCl2) and Sodium Chloride (NaCl) to improve microwave coupling in their experiment to expand starch pellets into foam. It was observed that it took approximately 30 sec for the pellets with the salts to foam compared with 45–60 sec for those without the salt additives. Another advantage is the high microwave frequency that leads to fast superheating of coupled liquid much above its boiling point [Leadbeater, 2006]. This is especially effective in the case of PS-alcohol system where initially the alcohol phases are encapsulated within the polymer matrix and thus can be
superheated without an immediate phase change. The polymer matrix is expected to act like an impermeable high-pressure vessel that confines the alcohol phases until heat transfer from the superheated alcohol raises the matrix temperature above glass transition. The heat transfer by conduction within a polymer of low thermal diffusivity, as well as mass transport through a glassy polymer below Tg, is a much slower process than superheating small volume fluid phases (in the order of micro liters) by microwave coupling.

It should also be noted that the concentration of 2-butanol in the PS matrix and uniformity of dispersion shall determine the overall heating efficiency and thus optimization of 2-butanol distribution is critical in achieving maximum process efficiency. The selection of 2-butanol as a model expansion agent was based on its boiling point of 99°C, which is within glass transition range (98°C ~105°C) of the PS matrix. The intent was to achieve selective microwave superheating of the 2-butanol phase above its boiling point and heating of the PS matrix to its glass transition temperature indirectly by the mode of conduction from the 2-butanol phase. Although 2-butanol has been used as a model expansion agent, an alcohol like ethanol can be used as an expansion agent, exploiting its high loss tangent (microwave coupling) even though its boiling point (78.2°C) is lower than the glass transition of PS. This is due to the fact that ethanol temperatures much higher than Tg of PS can be achieved by fast superheating.
A third advantage of using microwave is the complete transparency of PS matrix towards microwaves compared to the high coupling of the expansion agent. Penetration depth for microwave at 2.45GHz in PS is calculated from equation 4.28 as \( D_p = 103.64 \text{m} \) (considering dielectric constant = 2.55 [CRC Handbook, 2006]). This facilitates microwave heating of large volumes of PS with a small volume fraction of 2-butanol. When the temperature of the PS matrix is below \( T_g \), the matrix acts like an impermeable vessel containing phases of 2-butanol. Once the matrix temperature exceeds \( T_g \), the PS matrix expands since the vapor pressure of the superheated 2-butanol exceeds the viscoelastic stresses offered by the rubbery polymer. Expanded cells with permeable cell walls are formed due to biaxial stretching of the viscoelastic polymer and expansion agent 2-butanol escapes from the polymer matrix through the permeable cellular structure. Since microwave heating is directly related to the mass of 2-butanol in the PS matrix, the heat input to the system, should decrease at the same rate as the 2-butanol escape rate and become negligible as this mass approaches zero. Fast cooling of the expanded polymer surfaces below glass transition temperature is essential to prevent collapse of the newly formed cell walls [Benning, 1969]. It is important to note that for thermal insulators like PS, cooling occurs by the heat transfer mode of radiation and convection both of which are strong functions of surface area. Thus convection and radiation cooling of the PS matrix is facilitated near the end of the microwave heating process especially with the
formation of large new polymer cellular surface area due to foaming. This means that optimizing the process of expansion could potentially eliminate cell collapse due to slow cooling.

Finally, microwaves can be guided, focused and confined easily assuring a safe and efficient work environment. In industry microwave heating is widely used both as a batch and a continuous process. The electrical impedance of the microwave source can easily be tuned to match the electrical impedance of the coupling liquid for maximizing efficiency [Leadbeater, 2006]. Electrical impedance (Z), describes a measure of opposition to a sinusoidal alternating current (AC) and in Cartesian form is expressed as

\[ Z = R + iX \] (4.31)

where the real part of impedance is the resistance (R) and the imaginary part is the reactance (X). Dimensionally, impedance is the same as resistance; the SI unit is the ohm. Merideth in his book emphasized the advantage of microwave heating. According to him “The overall efficiency of microwave heating systems is usually very high because of the exceptional efficiency of high-power magnetrons (85% at 900MHz, 80% at 2450MHz). “Very fast feedback control loops can be used to control process parameters accurately, leading to improved product quality”. Energy savings are expected in microwave heating, since a
microwave oven has instantaneous control of power, thus ensuring rapid startup and rapid establishment of equilibrium conditions after a change. With development in microwave technology it is expected that in years to follow the microwave heating applications shall become more efficient and easier to operate [Metaxas & Meredith, 1983]. It should be noted that although microwave heating is fundamentally different than conventional means, the cooling of a material that had been subjected to microwave heating is due to heat loss following conventional heat transfer modes of radiation, conduction and convection.

4.3 Experimental

4.3.1 Free radical bulk polymerization

Materials

Styrene monomer of high purity (≥ 99%), containing 10-15 ppm 4-tert-butylcatechol as inhibitor, supplied by Sigma-Aldrich was filtered through a column of Alumina powder in order to remove inhibitors. 2-butanol with high purity (≥ 99%) was supplied by Fischer scientific. Azobisisobutyronitrile (AIBN) (98% purity) supplied by Sigma-Aldrich was used as the free radical initiator.

Polymerization process

Calculated amount of AIBN initiator (240mg in 20ml styrene) was
dissolved in styrene by ultrasonication for 15 minutes. Monomer with initiator was then carefully dispensed in 2 ml capacity airtight vials using micropipette. Batch of 5 solution samples were prepared with varying concentrations of 2-butanol in the monomer/ initiator system using ultrasonication for 15 minutes.

Generally, laboratory scale bulk polymerization is performed in a closed flask with condensers attached and continuous stirring and heating on a hot plate. The mechanical stirring is required in order to maintain a thermal equilibrium throughout the monomer bulk and to provide a homogeneous distribution of growing chains. However, the purpose of this polymerization was to obtain cast polymer pellets in the cylindrical shape of the 2ml reaction vial. In order to achieve thermal equilibrium in the reaction vials without mechanical stirring, the vials were heated by radiation in a precision furnace with a PID feedback control system. The Furnace (Fig 4.6) was manufactured by Vector Furnaces Ltd. The samples were heated at 90ºC for 24 hours and annealed in the furnace for 2 hours at 50ºC to achieve polymerization and induced phase separation. After polymerization the polystyrene was obtained in intact pellet form by breaking the sample vial by a sharp impact.

Bulk polymerization of styrene and 2-butanol is carried out to obtain pellets of substantially larger size than commercially used beads (Fig.4.7). It should be noted that the commercial process involves
Figure 4.6 Precision furnace used for polymerization and determination of phase diagram experiments. Inset shows phase separation in 10% concentration sample while lower concentration samples are clear.

Figure 4.7 Reaction vial dimensions, b. pellet dimensions
convection heating by steam. Convection heat transfer is a surface
dependant process and thus a high surface to volume ratio is required. The
novel method studied in this research uses electromagnetic radiation,
which is a volumetric process. Thus, larger individual volumes (pellets)
are acceptable. It should also be noted that the samples were annealed and
Scanning electron microscopy (SEM) and Thermo Gravimetric Analysis
(TGA) was used to verify uniformity of phase distribution throughout the
matrix.

In order to study the effect of microwave heating by ionic conduction,
special samples were prepared using organic salt lithium per-chlorate. 9% 
by volume of 2-butanol was selected as an appropriate concentration of
expansion agent for this study. Four samples were prepared, two
containing 0.1% by weight of lithium per chlorate (w.r.t. 2-butanol)
dissolved in 2-butanol while the other two were regular 2-butanol phase in
polystyrene matrix. The objective was to subject all these samples to the
same microwave conditions and study the temperature feedback response
of the ionic conduction in comparison to dipole rotation heating effect in
microwave.

**Characterization techniques:**

**Gel permeation chromatography (GPC)**

Gel permeation chromatography was used to determine the number
average molar mass (Mn), the weight average molar mass (Mw), and the molar mass distribution (Mw/Mn) of the PS. The samples were measured on a Waters Modular GPC. Temperature of column and detector were kept at 40°C. Solvent was THF at 1ml/minute with an injection volume of 50ml and a sample concentration of 2 mg/ml. The columns were calibrated with Toyo Soda polystyrene standards.

**Thermogravimetric analysis (TGA)**

In order to verify the 2-butanol content of the pellets, the weight loss of PS samples containing different concentration of 2-butanol was measured using TGA under Nitrogen flow of 100ml/min. The temperature sequence started at 30°C at a heating rate of 5K/min to 180°C and was followed by an isotherm at 180°C for 20 min. The instrument used was a TA instrument with model name TGA Q50 V6.7 Build 203.

**Differential Scanning Calorimetry (DSC)**

The glass transition temperature (Tg) of PS samples and approximate temperature range of expansion was determined using a Mettler DSC 821. The heating rate was 5°C/min and for each sample two heating runs from 30°C to 180°C were recorded with 100 ml/min N₂ as the purge gas. An isotherm at 30°C was run for 15 minutes to obtain thermal equilibrium within the sample. Indium was used for temperature and heat of fusion calibration.
For verification purpose a modulated test was also run. The operating parameters were

Isotherm at 25 °C for 10min

Temperature ramp from 25 °C to 75 °C at 5 °C/min

Isotherm at 75 °C for 5 min

Temperature drop from 75 °C to 25 °C at -5 °C/min

Isotherm at 25 °C for 5 min

Temperature ramp from 25 °C to 75 °C at 5 °C/min

Each test was run two times to check for repeatability.

**Scanning electron microscopy (SEM)**

SEM was performed on all samples to visualize the 2-butanol phase separation droplet size and dispersion. The high vacuum inside the SEM chamber creates evaporation of the 2-butanol liquid phases and exposes the separated phases as holes on the surface. Fractured surfaces of PS pellets were imaged after coating with gold. A LEO 1525 Field Emission scanning electron microscope was used. Two image processing programs were used for analysis for the SEM images. ImageJ image processing program was used to establish binary contrast between the 2-butanol phases from the matrix by threshold function. (Fig 4.8) ImagePro Plus 4.5.0.19 was used to determine the mean diameter, standard deviation, and size distribution of the holes.
4.3.2 Determination of phase diagram for PS, 2-butanol system

Styrene samples with varying concentrations of 2-butanol and calculated amount of free radical initiator were prepared in a batch of airtight vials of 2ml capacity. The vials were heated in the programmable precision furnace at 90ºC for 24 hours. After completion of polymerization the furnace temperature was allowed to drop by 1 degree and maintain steady state for 1 hour. The vials at 89ºC were visually checked for signs of turbidity (cloud point). At cloud point, a sharp alteration of light transmission takes place due to scattering of light at separated phases and the entire sample turns opaque/translucent. This process was repeated at intervals of 1ºC until 27ºC and subsequent cloud points were plotted as concentration versus temperature to obtain a phase diagram at a specific molecular weight. The molecular weight and distribution of the samples were determined by GPC. See Table 4.6.
Table 4.6 Sample ID with concentration of expansion agent for determination of phase diagram experiment.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-butanol% volume</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>10</td>
<td>12</td>
<td>14</td>
<td>16</td>
<td>18</td>
<td>20</td>
<td>22</td>
<td>24</td>
</tr>
</tbody>
</table>

4.3.3 Expansion and molding of novel expandable polystyrene

Laboratory scale microwave oven was used to expand polystyrene pellets of different 2-butanol concentration. The oven used was model CEM Discover. The microwave unit operates at 2.45 GHz and produces continuous waves at maximum power of 300W. The oven consists of a cylindrical chamber designed to fit one factory standard test tube as reaction chamber. The test tubes are supplied with a special cap that acts as a safety pressure seal. In case of evolution of gases from the reactor, a purge gas system can be used by inserting inlet and outlet needles through the safety cap (Fig 4.9). The purged gas argon is passed through a room temperature trap with silicone oil. The temperature inside the chamber is measured and controlled by an infrared temperature measuring feedback system (Fig. 4.10). A PID system controls the microwave power supplied to the reactor by reading the temperature feedback. Factory supplied application software is used to control and measure the transient temperature and power profile. After trial and error experiments the experimental conditions for expansion of polystyrene pellets were determined as the following:
Figure 4.9 Standard microwave reaction vessel with sample inside.
b. Microwave experimental setup

Figure 4.10 Typical feedback control results for microwave expansion process
• Temperature Ramp Time: 10 seconds
• Temperature Hold Time: 60 seconds
• Maximum Power: 300W
• Purge Gas: Argon

4.4 Results and Discussion

4.4.1 Free radical polymerization

Polymerized samples (Fig.4.11) were obtained with varying concentrations of 2-butanol in polystyrene matrix as cylindrical pellets. At room temperature a critical volumetric concentration of 8% 2-butanol was identified as the cloud point for the samples obtained.

GPC results for three samples with varying 2-butanol concentration along with commercial expandable polystyrene bead (T170B) supplied by Styrochem are tabulated below in Table 4.7.

It should be noted that although all samples were prepared from the same initiator concentration, the volumes of the samples were a little different in order to obtain accurate volumetric concentrations of 2-butanol. Also, an oxygen free environment to reduce free radical scavenging was not provided for polymerization. Although, a very close molecular weight and distribution was obtained as compared to commercial samples, the
Figure 4.11 Image shows phase separation in 8% sample at room temperature. 7% and 6% samples are clear.

Table 4.7 GPC results for polystyrene samples

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Alcohol %</th>
<th>Mw</th>
<th>Mn</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>T170B</td>
<td>7.5%</td>
<td>260,300</td>
<td>120,200</td>
<td>2.16</td>
</tr>
<tr>
<td>A</td>
<td>8%</td>
<td>204,700</td>
<td>92,180</td>
<td>2.221</td>
</tr>
<tr>
<td>B</td>
<td>7%</td>
<td>198,500</td>
<td>103,600</td>
<td>1.972</td>
</tr>
<tr>
<td>C</td>
<td>6%</td>
<td>263,700</td>
<td>122,200</td>
<td>2.158</td>
</tr>
<tr>
<td>Mean</td>
<td>N/A</td>
<td>222,300</td>
<td>105,993</td>
<td>2.117</td>
</tr>
<tr>
<td>(Excluding T170B)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
deviation among the individual samples can be attributed to the above-mentioned causes. It should also be noted that the negligible difference in values of molecular weight and PDI of the samples A and B allows the conclusion that maximum solubility of 2-butanol at room temperature in PS of Mw = 200,000 and PDI = 2 is in between 7% and 8% by volume.

TGA results were used to check the weight percentage of 2-butanol samples. The results are illustrated below in Table 4.8 and Figure 4.12 showing three sample TGA graphs.

DSC results for 0%, 10%, 12%, 16% and 18% concentration of 2-butanol+PS are presented in the figure 4.13 below.

For the pure PS sample the glass transition is obtained at 96.16°C, which falls in the acceptable range of glass transition for polystyrene. However for all other samples containing 2-butanol the Tg coincides with the boiling point of 2-butanol (99°C) and cannot be separately distinguished since a substantial DSC peak is encountered due to evaporation of 2-butanol phase. The DSC data correlates well with the TGA data and both show the temperature range for liberation of the 2-butanol to be between 90°C to 120°C. The TGA data also shows mass loss due to evaporation between the temperatures of 55°C to 90°C increasing with increase in concentration of 2-butanol. This also correlates with the DSC data,
Figure 4.12 Thermo gravimetric analysis results showing weight loss of 2-butanol a. Sample containing 12% by vol. b. 16% by vol. and c. 18% by vol. of 2-butanol
Table 4.8 TGA report of 2-Butanol weight percentage (samples same as Table 4.7)

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Volumetric % of 2-butanol added to styrene monomer</th>
<th>Weight % composition of 2-butanol in PS obtained by TGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>5.2</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>7.8</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>9.1</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>11.71</td>
</tr>
<tr>
<td>7</td>
<td>16</td>
<td>14.79</td>
</tr>
<tr>
<td>8</td>
<td>18</td>
<td>18.31</td>
</tr>
</tbody>
</table>

Figure 4.13 DSC results for expandable PS with varying concentration of 2-Butanol
particularly with the 18% sample showing signs of gas evolution through constant fluctuation of the baseline between 55°C to 90°C. For each polymer sample containing 2-butanol phase, a change in specific heat capacity was noted with peak in the range of 44°C to 49°C. The endothermic and exothermic changes are collectively attributed to latent heat of evaporation of 2-butanol from the surface and diffusion through porous media and mass loss, since the experiments were run using open type pans. The irreversible nature of this curve was verified by modulating the temperature in the ranges of 25°C to 75°C and a typical result is illustrated in Fig. 4.14. This DSC experiment shows that the initial peak observed at approximately 48°C cannot be a relaxation peak since it is irreversible. Thus it is attributed to evaporative mass loss, which also agrees with the TGA results.

For Scanning Electron Microscopy Results, see fig. 4.15 and 4.16. For Image Analysis Results, see Table 4.9.

The SEM image analysis results (Table 4.10) of samples prepared for determination of phase diagram (Table 4.7) provide a correlation between the phase concentrations and morphology and distribution of phase separation. For sample containing 8% by volume of 2-butanol, PIPS produced morphology of distributed spherical alcohol phase (droplets) within the polymer matrix with an average diameter of 2.3 m.
Figure 4.14. (a) Modulated DSC results showing irreversible nature of peak at 48 °C (b) Time-temperature programming for modulated DSC.
Scanning Electron Microscopy Results:

Figure 4.15 SEM images showing PIPS of varying concentrations of 2-butanol in PS

4.15.a. 6% by volume of 2-butanol

4.15.b. 8% by volume of 2-butanol

4.15.c. 10% by volume concentration of 2-butanol
Figure 4.16 SEM images showing PIPS of varying concentrations of 2-Butanol in PS
**Image analysis results:**

### Table 4.9 Morphological characterizations of 2-Butanol phases in PS matrix at room temperature

<table>
<thead>
<tr>
<th>2-Butanol %</th>
<th>Mean Dia. μm</th>
<th>SD μm</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2-butanol does not show any phase separation and remain in solution in the PS matrix.</td>
</tr>
<tr>
<td>2</td>
<td>2.3</td>
<td>0.2</td>
<td>Phase separated spherical domains are observed at 8% by volume concentration of 2-butanol</td>
</tr>
<tr>
<td>3</td>
<td>1.6</td>
<td>0.2</td>
<td>Phase separated domain dimensions and distribution increase are observed at 10% by volume concentration of 2-butanol</td>
</tr>
<tr>
<td>4*</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>5</td>
<td>1.3</td>
<td>0.4</td>
<td>Bimodal distribution of phase dimensions is observed</td>
</tr>
<tr>
<td>6</td>
<td>3.3</td>
<td>0.3</td>
<td>The phase dimensions and distribution increase further and seem to saturate the matrix. The diameter becomes larger than the separation distance between 2 spherical 2-butanol phases.</td>
</tr>
</tbody>
</table>

*Could not be determined accurately by image analysis.*

### Table 4.10 Temperature dependence of binodal and spinodal compositions for PS-2-Butanol system

<table>
<thead>
<tr>
<th>Temperature</th>
<th>27°C</th>
<th>40°C</th>
<th>50°C</th>
<th>65°C</th>
<th>75°C</th>
<th>85°C</th>
<th>95°C</th>
<th>105°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binodal composition</td>
<td>0.94</td>
<td>0.93</td>
<td>0.92</td>
<td>0.89</td>
<td>0.87</td>
<td>0.81</td>
<td>0.75</td>
<td>0.71</td>
</tr>
<tr>
<td>Spinodal composition</td>
<td>0.785</td>
<td>0.737</td>
<td>0.697</td>
<td>0.641</td>
<td>0.606</td>
<td>0.573</td>
<td>0.526</td>
<td>0.486</td>
</tr>
</tbody>
</table>
Uniformity in distribution of separated 2-butanol phases were found to increase with increasing volumetric concentration and a bimodal distribution was observed at 14% of alcohol concentration. As discussed earlier in section 4.2.1, this bimodal distribution may result from formation of smaller phase separated domains at an early stage of PIPS and cannot be considered as an indication of NISD. It should also be noted that in all the samples the standard deviation in phase diameter is nontrivial. Generally a large standard deviation in the diameter of separated phases indicates NG mechanism since it involves random nucleation and is a relatively slower process than SD [Moschiar, 1991]. However, as discussed in section 4.2.1 from the SEM images alone a conclusion about the mechanism of PIPS cannot be reached.

4.4.2 Determination of Phase Diagram

The cloud points are plotted as illustrated in Fig.4.17 to obtain the phase diagram for 2-butanol in PS matrix. Since the experiment was performed at a temperature resolution of 1°C, an error bar of ±1°C has been used. From TGA data the concentrations were verified to be fairly accurate and ±0.5 % concentration error bar was used in the abscissa. Literature values obtained for solubility of 1-butanol in Polystyrene is included in Fig.4.17 for comparison [Bernardo, 2007]. The PS used in the literature had Mn =140,000 with PD = 1.64 while PS used in experiment had mean Mn = 105,993 with mean PD = 2.117. The lower solubility in the literature case
Figure 4.17 Plot of phase diagram (cloud point) for 2-butanol in PS matrix at constant molecular weight $M_n = 105,993$ (avg.) and $PD = 2.117$

Figure 4.18 Estimation of interaction parameter for PS-2-butanol system
of 1-butanol may be attributed to its longer chain length and higher molecular weight of the matrix.

The Flory-Huggins free energy of mixing Equation 4.2 is used to generate the composition dependence of free energy of mixing in PS-2-butanol system (Fig.4.19). Values of interaction parameter for 2-butanol were taken from Table 4.4 and extrapolated to obtain values between room temperature and 105°C (Fig.4.18) Equilibrium positions were found by the common tangent rule (position of a tangent that also passes through the point 0,0). The two equilibrium positions at 300K were found to be at compositions \( \phi' = 0 \) and \( \phi'' = 0.94 \). This result is in agreement with experimental observations where up to 7% by volume of 2-butanol was found to be soluble in PS. Inflection points \( \phi_{sp} \) at different temperatures were determined by setting the second derivative of the FH equation to zero (Table 4.10). With increase in temperature the equilibrium position \( \phi'' \) shifted to lower values while \( \phi' \) stayed constant at the origin (0). It is evident from the phase diagram that at compositions in the range of 8% by volume of 2-butanol (\( \phi_1 = 0.92 \)) the metastable region is significant and phase separation of 2-butanol by NG mechanism can be expected at near room temperature. To further support this point the spinodal and binodal curves were plotted and compared with the cloud point results obtained by experiments.
Figure 4.19 Composition dependence of free energy of mixing for PS-2-butanol system
The binodal points were fitted with a logarithmic trendline while the spinodal points were fitted with a linear trendline. The cloud point data lied within the spinodal and binodal curves and was fitted well with a logarithmic trendline. From analyzing Fig. 4.20 it can be concluded that the probability of phase separation by NG mechanism is much higher than by SD in PS-2-butanol system. However, the curves were generated considering FH equations that presents a simplistic model, neglecting surface conformational entropy. The other major assumptions in the FH equation are that there are no volume changes upon mixing, and that the interaction parameter is assumed to be

![Graph showing comparison of cloud point composition with calculated binodal and spinodal compositions as a function of temperature.](image)

**Figure 4.20** Comparison of the cloud point composition with calculated binodal and spinodal compositions as a function of temperature
independent of concentration. The theory also neglects free volume effects and thus effects of temperature over free volume.

4.4.3 Expansion results from microwave experiments

Polystyrene pellets with varying concentration of 2-butanol were synthesized by bulk polymerization and PIPS technique. 7.8% by weight of 2-butanol (Sample 3 in Table 4.8) was found to be a critical concentration where phase separation occurred. Characterized microwave radiation was then successfully used to expand solid polymer pellets into expanded polystyrene inside glass test tube molds (Fig. 4.21).

From microwave expansion experiments of PS pellets containing 2-butanol, uniform foam formation was only observed for those samples with phase separation. The 4% sample did not expand under the

Figure 4.21 a. PS pellet in glass tube mold; b. Pellet expanded into foam taking up shape of mold.
experimental conditions, although void spaces were formed inside the sample due to phase change of 2-butanol. (Fig. 4.23.a, b) The 6% sample expanded but had high density and non-uniformity in its foam structure. (Fig. 4.23.c, d) An overall volumetric increase of approximately 200% was observed in the sample containing 8% by volume of 2-butanol. The open cellular structures in 8% sample were found to be macroscopic in dimensions without characteristic uniformity (Fig 4.23.e, f). This was probably due to non uniform diffusion rates and temperature gradient within the sample. The surface to volume ratio of the expandable pellets was identified as the control parameter for generating cellular foam with uniform density and further experiments were carried out for size optimization of the expandable PS resin (Sec. 4.5).

Using ionic conduction with 0.1% weight fraction of lithium per chlorate (w.r.t 2-butanol), a significant increase in microwave coupling efficiency was observed. In order to reach the target temperature of 93°C a much lower average power of 80W was required compared to average power of 175W in case of heating by dipole rotation. The target temperature of 93°C was reached and steady state was obtained after 40 seconds of hold time compared to 60 seconds required for the case of heating by dipole rotation alone (Fig 4.24 a, b). The area under the power-time curve was calculated to be approximately 9,000 Joules in case of heating by dipole
**Figure 4.22** Image showing expansion of PS with varying concentrations of 2-butanol in cylindrical shape. 

- a. expandable pellets, 
- b. pellets expanded into foam.

- 8% volumetric concentration of 2-Butanol
- 7% volumetric concentration of 2-butanol
- 6% volumetric concentration of 2-butanol
Figure 4.23 Images of foam samples with varying 2-butanol concentration (a) 4% 2-butanol before microwave, (b) 4% sample after microwave showing internal void formation (c) 6% 2-butanol Top view after microwave (d) 6% 2-butanol side view showing non uniform expansion (e) 8% 2-butanol top surface of foam, (f) 8% 2-butanol cut surface of foam
Figure 4.24 (a) Microwave expansion by dipole rotation. (b) Microwave expansion by ionic conduction and dipole rotation
rotation while the energy required was reduced to approximately 4,575 Joules in case where salt was added (Fig. 4.25).

4.5 Synthesis and morphological characterization of cellular foam

4.5.1 Synthesis of expandable PS granules

PS pellets containing 8% by volume of 2-butanol are synthesized using free radical bulk polymerization (as described in section 4.3.1). 0.1% weight fraction of lithium per chlorate (w.r.t. 2-butanol), was added to the monomer-expansion agent system for better microwave coupling. The pellets were crushed using a mortar and pestle to obtain granules of varying size distribution. Standard sieves were then used to separate out granules of sizes ranging from (Fig 4.26)

a) Less than 225μm

b) 225μm to 450μm

c) 450μm and above

Sample granules were then weighed and filled inside glass test tube molds and subjected to microwave irradiation using following parameters

- Temperature Ramp Time: 10 seconds
- Temperature Hold Time: 60 seconds
- Maximum Power: 300W
- Purge Gas: Argon
Figure 4.25 Comparison of energy required for expansion in case of microwave heating without (a) and with (b) ionic salts

Figure 4.26 Granules of expandable PS separated using standard sieves
Among the samples only granules with 225μm to 450μm size range expanded to produce foam with characteristic morphology. Granule sizes above 450μm expanded to form highly non uniform cells similar to pellets. Granules lower in size than 225μm did not show any visible expansion.

After expansion the foam samples were collected and density was estimated from their volume and weight. The sample with granules in the range of 225μm to 450μm showed approximately 200% increase in volume and the density after expansion was calculated to be approximately 0.005gm/cc. The samples were then fractured and the fractured surfaces were characterized for morphology using SEM.

4.5.2 Morphological characterization of cellular foam using SEM

A LEO 1525 Field Emission scanning electron microscope was used for imaging. An open cellular structure with a characteristic morphology was observed for PS foam synthesized from granules (unlike from pellets). The cells were in the range of 100μm in dimension showing solid plate like rosette structures for walls (see Fig. 4.27) instead of thin porous cell walls found in commercially available foam (see Fig.2.5). Unlike commercial EPS foam neither a honeycomb intercellular structure nor distinct cellular boundaries were found in the microwave processed foam samples. Possible reasons for such non uniformity may be
Figure 4.27 SEM images of expanded foam showing cellular morphology at various magnifications
1. No plasticizers were used in the case of microwavable foam which can affect the flow behavior of the polymer during expansion.

2. The phase separated domain sizes for 2-butanol were in the range of 2.5 μm and this resulted in cell structures in the range of 100 μm instead of 30 μm characterized in commercial EPS foam (see Fig. 2.5). In commercial foam the expansion agent is more uniformly dispersed in a solution and there is no observable phase separation of pentane in PS matrix.

3. Individual granules were not treated with surface treatment agents as used in commercial process to keep the beads from sticking together. Thus in the microwave processed foam samples no distinct cellular boundaries were noticed due to coalescence of the granular boundaries during expansion of the polymer.

4.6 Conclusions and future recommendations

- Conclusions from the chapter can be summarized as follows:
- A novel concept of using microwaves to achieve expansion of polymeric foam was established using PS as a model polymer and 2-butanol as a model expansion agent.
- Synthesis of polystyrene with varying concentrations of 2-butanol was achieved in form of pellets.
• The polymer was characterized for molecular weight and distribution. The expansion agent was characterized for phase separation. Glass transition and temperature ranges of diffusion for 2-butanol was studied using characterization techniques like DSC and TGA. Solubility phase diagram was determined based on cloud point observations.

• Laboratory scale microwave technique was developed and successful expansion of synthesized pellets was achieved. Uniform foaming was observed in samples with phase separation while irregular or no foaming was observed below a critical concentration of 2-butanol in the PS matrix. Increase in microwave coupling efficiency was observed using ionic salt dissolved in 2-butanol.

• It was shown that glass could be successfully used as a molding material in order to achieve foam pattern in shape of the glass mold.

The study of novel expansion method for PS as discussed in this chapter is a proof of concept and has immense potential for further research and development. Future recommendations and scope of research are discussed as follows:

• The developed expansion process for PS can be used as a simple model for laboratory synthesis of different polymer cellular foam.

• As pointed out in section 4.2.2 many other alcohols are potential candidates for expansion agents for EPS besides 2-butanol, using
the novel process. Further research should be directed towards comparative study of dispersion for recommended alcohols (see Table 4.5), characterization of microwave coupling and expansion.

- Alcohols have a selective band for absorption for infrared (IR) radiation. Currently industrial IR sources are more efficient than microwave sources and the IR heating technology is well developed. Selective heating of alcohol phases and expansion using IR should also be studied.

- Mechanical engineering design, modeling and manufacturing of single component radiation based bead expander machine can be a stand-alone research project. Efficient recovery and recycling of the expansion agent should also be studied.

- Besides glass appropriate microwave transparent thermoset plastic molds can be synthesized in order to eliminate currently used expensive stainless steel molds and tooling. The whole process of pre-expansion may be eliminated if expandable beads can be maneuvered freely inside the microwave transparent mold, while being expanded. This may be achieved by providing gyroscopic motion to the mold during the expansion operation.

- Characterization of the raw polymer and the expanded foam obtained from the novel process is essential for mechanical, thermal properties and chemical compatibility for food grade and commercial applications.
• It has been reported in case of thermally induced phase separation of polymer blends, that the thermodynamics of phase separation is controlled by concentration fluctuations in the early stage and by diffusion and interfacial tension at a later stage [Luo, 2006]. The sample pellets of expandable polystyrene containing 2-butanol were synthesized by bulk polymerization in a precision furnace and annealed at 50°C for 2 hours. The thermal effects of the phase separation should be investigated by designing appropriate heat treatment experiments.

• In order to achieve uniform closed cellular structure in the foam, it is essential to obtain expandable beads [Snijders, 2003] Study of regular suspension polymerization of styrene with dissolved 2-butanol is recommended. Novel method for synthesis of the expandable polymer beads using UV photo suspension polymerization can also be valuable research. The research should be focused on obtaining different size expandable PS beads with varying concentrations of 2-butanol and characterizing for molecular weight and phase separation.

• Finally, modeling the expansion process using microwave heating may serve to understand and design complicated shapes and help in process optimization.
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**Vita**

Indraneel Sen was born in Calcutta, West Bengal, India on December 4th, 1975. He attended South Point High School and graduated in 1994. Following high school Indraneel attended Jadavpur University, Calcutta, India and graduated in 1999 with a bachelor of engineering degree in Mechanical Engineering. Upon completion of college he began his engineering career working first as an intern and then as a marketing executive in India’s leading electrical engineering company Crompton Greves Ltd. Indraneel resigned from office in February 2000 and started his business in assembly of room air conditioning units with his father. Realizing his dream to pursue research in technological field Indraneel applied for higher studies in the United States of America. In 2002 Indraneel accepted a Graduate Research Assistantship position at University of Tennessee at Knoxville and began his higher studies in Polymer Engineering under the advisory of Dr. Roberto Benson from Polymer Engineering department and later under co advisory of Dr. Dayakar Penumadu of Civil and Environmental Engineering department. Indraneel’s research was mainly focused on the study of degradation and characterization of polystyrene foam used in lost Foam Casting. Indraneel graduated as a Doctor of Philosophy in December 2007.