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Thermal degradation of foamed polystyrene

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The thermal degradation of foamed polystyrene patterns in the expendable pattern casting (EPC) process has been studied. Various physical transitions that may occur during the degradation of the polymer have been determined with scanning electron microscopy, differential scanning calorimetry and thermogravimetric analysis. The effects of polymer density and bead structure on the degradation characteristics have been investigated. The results indicate that, when exposed to elevated temperatures, the polymer beads collapse at about 110–120 °C. The collapsed beads melt at 160 °C, and start to vaporize at temperatures greater than about 275 °C. Complete volatilization occurs in the temperature range 460–500 °C. The heat of degradation of expanded polystyrene has been estimated to be at the order of 912 J g^{-1}.

1. Introduction

In a relatively new casting technique known as the expendable pattern casting (EPC) process, foamed polymer patterns are used for the production of metallic components [1]. The polymer material (polystyrene or polymethylmethacrylate) is initially injection moulded to the required shape. The moulded pattern is then coated with a ceramic slurry and buried in unbonded sand. Molten metal is directly poured onto the polymer pattern. The polymer undergoes thermal degradation through a series of complex transitions and is replaced by the molten metal to yield the casting after solidification. The operational and economic advantages of this innovative process have been summarized in the trade literature [1, 2].

The formation of the casting in the EPC process is strongly influenced by the thermal degradation characteristics of the polymer [3, 4]. The mould filling pattern and the solidification behaviour in the casting are governed by the degradation of the polymer. Further, many defects in the casting may originate by interaction between the polymer degradation products and the solidifying metal [5, 6]. Consequently, an investigation was initiated to study the degradation characteristics of polymers used in the EPC process. In this contribution, data on the thermal degradation of expanded polystyrene (EPS) are presented. Experiments have been conducted with typical polymers used in the EPC process. In addition, data have been acquired for various commercial grade polystyrene foams.

2. Experimental procedure

The effect of temperature on the initial polymer bead structure was studied by immersing samples of EPS into liquids between 50 to 170 °C. A hot wire cutter was used to obtain 1.5 × 1.5 × 15 cm pieces from expanded polystyrene blocks provided by commercial suppliers. The sectioned piece was then fractured along the length by a simple bending action. This procedure was adopted in order to expose fresh beads within the polymer, which remain unaltered by the cutting process. The exposed surface was then dipped into a liquid at the desired temperature. Two different liquids were used in this study: water and a commercial wax. Water was used to obtain data for temperatures up to 100 °C and wax was used for temperatures between 100 to 170 °C. Initially, the dipping time was varied from 10 to 60 s. It was observed that increasing the dipping time did not have a significant effect on the physical structure of the polymer. An optimum dipping time of 30 s was used in all future experiments. During the experiments, the polymer piece was dipped in the liquid for 30 s, taken out and cooled to room temperature. Subsequently, the samples were coated with a thin layer of gold–palladium to facilitate examination in a scanning electron microscope. The coating was performed through a vacuum evaporator under a vacuum and the gold–palladium was evaporated onto the samples by passing a current of about 25 A through a tungsten basket holding the gold–palladium wire. The coated samples were then observed under a Jeol JSM-840 scanning electron microscope equipped with stage automated digital image analysis and a kevex delta system. The image of the beads was captured on a screen and the bead size was calculated through automated image analysis. At least 30–50 beads were selected randomly, and their sizes were measured. Several samples were measured under each condition in order to obtain reproducible results. The beads were observed under magnifications of × 10– × 100. Data were acquired from 50 to 170 °C in intervals of 10 °C.

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Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to study the physico-chemical phenomena occurring during the thermal degradation of EPS in the temperature range 50–600 °C. The TGA apparatus consisted of a Mettler TC10A processor, in conjunction with a Mettler TG50 thermobalance–furnace. Standard alumina crucibles with perforated lids and a volume of 0.07 cm^3 were used to weigh and heat the polymer samples. Approximately 3 mg of EPS was then placed inside the crucible and weighed with an accuracy of $\pm$ 0.001 mg. In order to purge the gases evolved during degradation, a constant air flow of 100 $ml\,min^{-1}$ was maintained during the experiments. The temperature was measured by a Pt-100 temperature sensor, with display accuracy of $\pm$ 0.1 °C. Experiments were conducted for heating rates between 10 to 30 $°C\,min^{-1}$. The degradation behaviour in the temperature range 50–600 °C was studied. The DSC instrument consisted of a Mettler TC10A processor in conjunction with a Mettler DSC20 cell. Approximately 3–4 mg of EPS was heated at a rate of 10 $°C\,min^{-1}$.

Foamed polymer patterns containing “T” beads and having densities between 0.02 to 0.026 $g\,cm^3$ are typically used in the EPC process. Most of the experiments were conducted with these polymers. In addition, the degradation behaviour of commercial grade polystyrene containing “B” and “C” beads was also studied. In this case, data were acquired for polymers with densities between 0.02 and 0.05 $g\,cm^{-3}$. In all of the above experiments, several tests were conducted under similar conditions in order to obtain reproducible results.

3. Results and discussion

Expanded polystyrene used in the EPC process is an amorphous, linear polymer with molecular weights ranging from 300 000 to 500 000. The bead structure in a polymer with “T” beads and a density of 0.024 $g\,cm^{-3}$ is shown in Fig. 1. The polymer consists of nearly spherical beads with an average bead size of 1.5 mm (Table I). Increasing the density of the polymer from 0.024 to 0.026 $g\,cm^{-3}$ does not have a significant effect on the average bead size. In many cases, the beads also exhibit facets, as shown in Fig. 2.

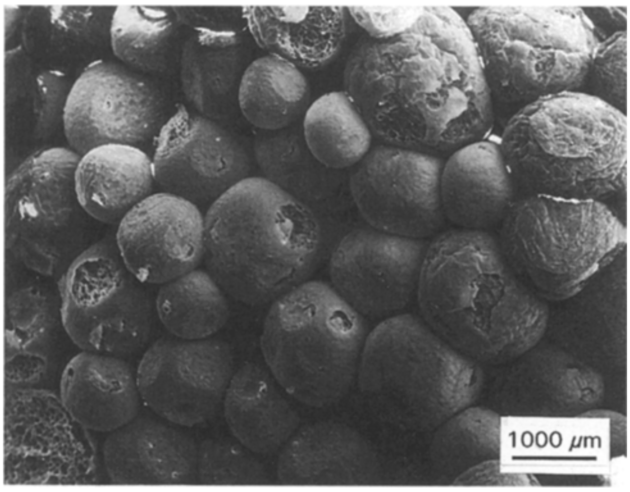

Figure 1 Photograph showing the bead structure in EPS with a density of 0.024 $g\,cm^{-3}$ (“T” beads). Expanded polystyrene consisting of “T” beads is typically used in the EPC process.

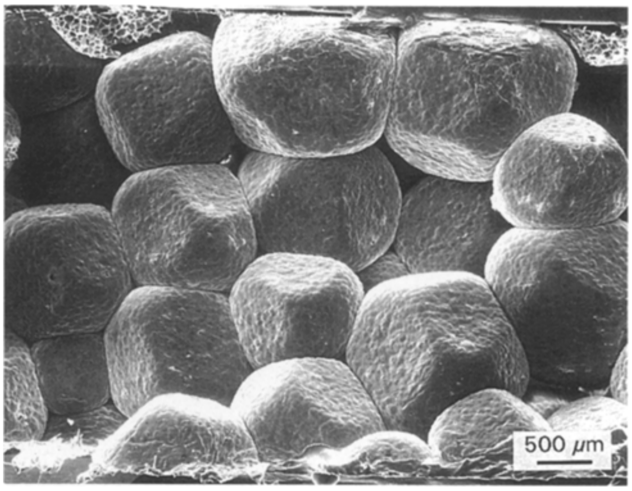

Figure 2 Photograph showing faceted beads in EPS (density = 0.024 $g\,cm^{-3}$, “T” beads).

TABLE I Effect of temperature on average bead size (mm)

	Foam density ($g\,cm^{-3}$)			
	“T” beads		“C” beads	
Temperature (°C)	0.024	0.026	0.024	0.048
20	1.50 ± 0.09	1.48 ± 0.10	3.23 ± 0.44	1.84 ± 0.33
80	1.48 ± 0.09	1.48 ± 0.08	3.05 ± 0.48	2.01 ± 0.27
90	1.46 ± 0.07	1.47 ± 0.06	3.29 ± 0.60	2.05 ± 0.43
100	1.49 ± 0.07	1.49 ± 0.06	3.45 ± 0.44	2.08 ± 0.46
110	1.05 ± 0.08	1.07 ± 0.06	2.34 ± 0.25	1.53 ± 0.22
115	1.01 ± 0.07	0.98 ± 0.06	2.52 ± 0.27	1.42 ± 0.26
120	0.55 ± 0.05	0.65 ± 0.05	1.18 ± 0.12	1.13 ± 0.15
130	0.52 ± 0.03	0.54 ± 0.04	1.05 ± 0.10	0.99 ± 0.12
140	0.44 ± 0.03	0.50 ± 0.03	0.96 ± 0.13	0.88 ± 0.15
150	0.42 ± 0.02	0.50 ± 0.02	0.89 ± 0.09	0.88 ± 0.12

The surface that results from the fracturing of the polymer specimen is an indication of the degree of fusion between the beads. When the degree of fusion

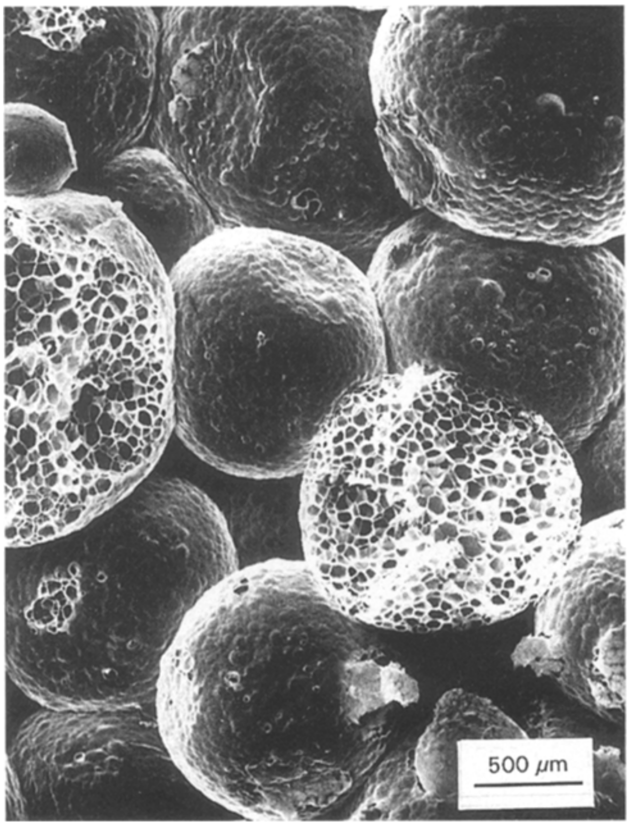

Figure 3 Photograph showing the bead structure in the polymer. The extent of fracture across the beads (transbead fracture) is an indication of the degree of fusion between the beads.

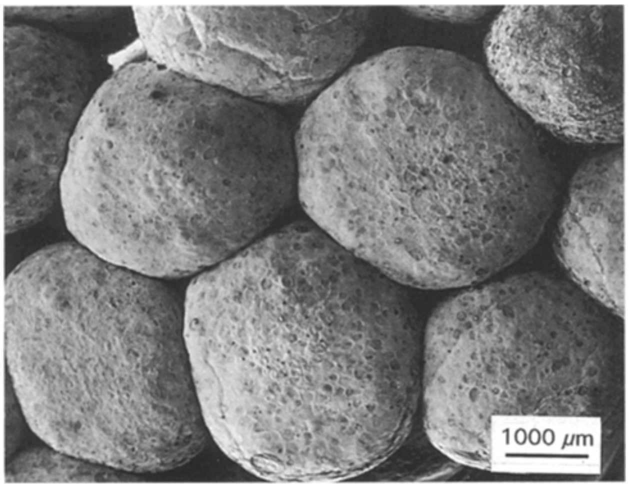

Figure 4 Photograph showing the bead structure in commercial grade EPS with a density of 0.024 g cm^{-3} ("C" beads).

indicates a low degree of fusion. The extent of transbead fracture in the polymer is estimated to be between 40 to 70%.

The bead structure in a commercial grade EPS consisting of "C" beads and with a density of 0.024 g cm^{-3} is shown in Fig. 4. The corresponding structure in a polymer with "B" beads is shown in Fig. 5. The average bead sizes for "C" and "B" beads are measured to be on the order of 3.2 and 3.4 mm, respectively. The bead structure in a polymer consisting of "C" beads and with a density of 0.048 g cm^{-3} is shown in Fig. 6. As the density of the polymer is increased from 0.024 to 0.048 g cm^{-3}, the average bead size decreases from 3.2 to 1.8 mm.

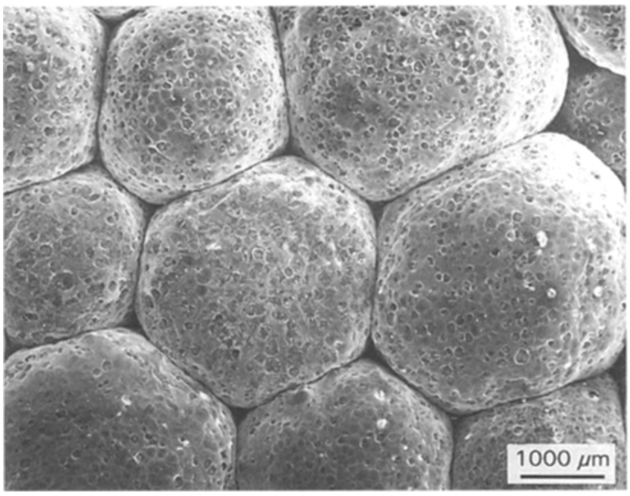

Figure 5 Photograph showing the bead structure in commercial grade EPS with a density of 0.024 g cm^{-3} ("B" beads).

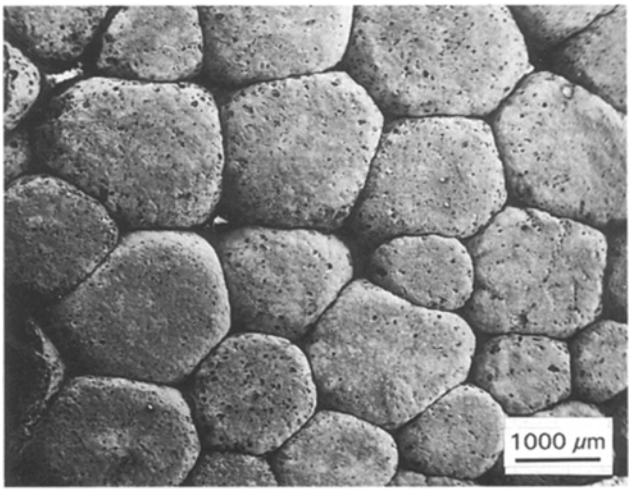

Figure 6 Photograph showing the bead structure in commercial grade EPS with a density of 0.048 g cm^{-3} ("C" beads).

When exposed to elevated temperatures, EPS collapses rapidly. The photographs shown in Figs 7 and 8 illustrate the variation of bead size with temperature in polymers with "T" beads. The overall bead structure does not change significantly up to temperatures of 100 °C (Table I). As the temperature is increased beyond 110 °C, the expanded beads begin to collapse rapidly and the average bead size decreases substantially (Fig. 8). At 120 °C, the average bead size has decreased from about 1.5 to 0.55 mm. Thus, the collapse temperature for EPS is between 110 to 120 °C. This collapse temperature compares well with the glass transition temperature of polystyrene, which has been reported to range from 80 to 120 °C [7, 8]. The average bead size continues to decrease further up to about 150 °C as the beads return to their unexpanded size (Fig. 9). At 160 °C, the beads completely melt to produce a viscous residue. A similar behaviour is observed with polymers containing "C" beads (Fig. 9). The bead size does not change significantly up to about 110 °C. A sharp decrease in the bead size is

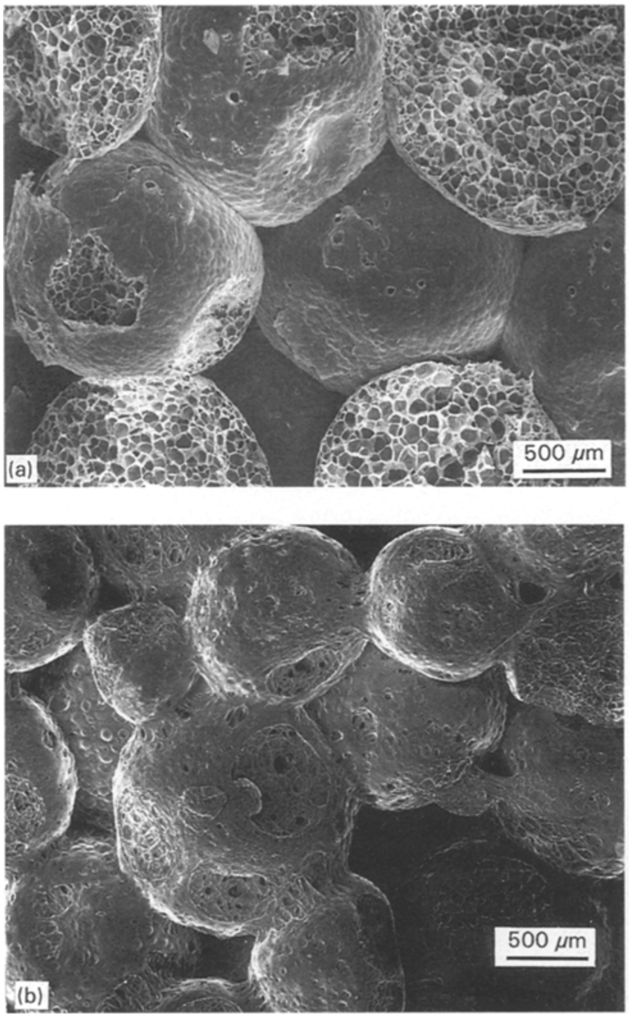

Figure 7 Photograph showing effect of temperature on bead structure ("T" beads, density = 0.024 g cm^{-3}): (a) 80 °C, (b) 110 °C.

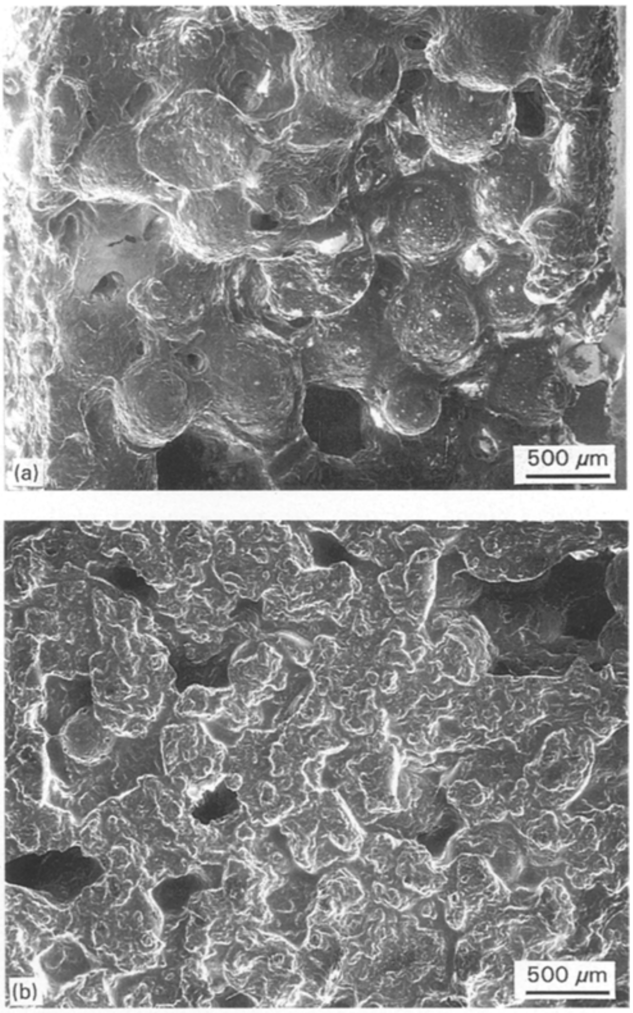

Figure 8 Photograph showing effect of temperature on bead structure ("T" beads, density = 0.024 g cm^{-3}): (a) 120 °C, (b) 160 °C.

observed between 110 to 120 °C. This polymer also melts at 160 °C. Increasing the density from 0.024 to 0.048 g cm^{-3} does not have a significant effect on the collapse or melting temperatures. Similar results were obtained for polymers with "B" beads. These results indicate that the polymer density and the initial bead structure do not have a significant effect on the collapse and melting temperatures.

A sample curve obtained during a TGA experiment is shown in Fig. 10 for EPS with a density of 0.024 g cm^{-3} consisting of "T" beads. The EPS specimen starts to volatilize at 278 °C. The polymer is almost totally volatilized at 460 °C. Maximum volatilization rates are observed at about 420 °C. DSC data for EPS with "T" beads typically indicate a large endothermic peak between 320 to 490 °C (Fig. 10). This endothermic peak is associated with the volatilization of the polymer sample. The peak temperatures for "T" beads are between 395 to 415 °C. Many samples yield a small endothermic peak between 90 to 120 °C. This endothermic peak corresponds to the glass transition within the polymer. An exothermic peak that may have resulted from the oxidation of the sample is detected at about 540 °C. TGA data on volatilization for various polymers used in this study are summarized in Table II. It is observed that as the bead size increases, the volatilization of the polymer starts at a lower temperature. The temperature at which the volatilization is completed does not show any significant dependence on bead size [9]. For each bead size, the start temperature and the end temperature for volatilization increase with polymer density.

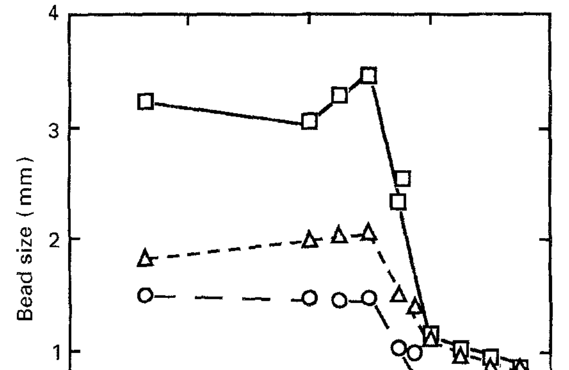

Figure 9 Variation of measured bead size with temperature for three different polymers: (○) "T" beads, 0.024 g cm^{-3}, (□) "C" beads, 0.048 g cm^{-3}, (△) "C" beads, 0.024 g cm^{-3}.

The thermal degradation of polystyrene is a radical chain process, which includes steps such as initiation, propagation, transfer and termination [10–12]. At temperatures below 300 °C, degradation takes place primarily through a decrease in the degree of polymerization. At temperatures greater than 300 °C, intermolecular transfer results in a decrease in the molecular weight. Further, depolymerization and intramolecular transfer lead to the evolution of monomer, oligomers and other low molecular fragments. The degradation process is controlled by these competing reactions. The thermal degradation products of polystyrene have been analysed under a variety of atmospheres. In all these cases, the major volatile product is styrene monomer. The degradation products may also contain oligomers of styrene, such as dimer and trimer, toluene, benzene, ethylbenzene and methylstyrene. The volume of gaseous degradation products produced per unit mass of the foamed polymer is a strong function of temperature as shown in Fig. 11 [13].

The thermal degradation of EPS is a highly endothermic process. The heat of degradation can be estimated by calculating the area under the endothermic peak in Fig. 10. The average heat of degradation was estimated to be 912 J g^{-1} for EPS with "T" beads. By comparison, the heat of depolymerization of polystyrene has been reported to be 709 J g^{-1}, if the depolymerized products consist entirely of the monomer [8]. The density of the polymer or the bead size did not have any significant effect on the heat of degradation. It should be noted that, in the EPC process, the endothermic degradation of the polymer at the metal front produces a chilling effect on the liquid metal. For example, if the heat losses at the metal front are neglected, the decrease in temperature in a unit volume of metal as a result of degradation of a unit volume of EPS can be calculated. In the case of aluminum alloys, the temperature in 1 cm^3 of molten aluminum would decrease by about 7 °C as a result of degradation of 1 cm^3 of EPS. Consequently, the pouring temperature for castings need to be increased in order to account for this temperature loss. In addition, the endothermic degradation of the polymer during the filling of the mould establishes steep thermal gradients in the casting. These thermal gradients promote directional solidification in the cast component.

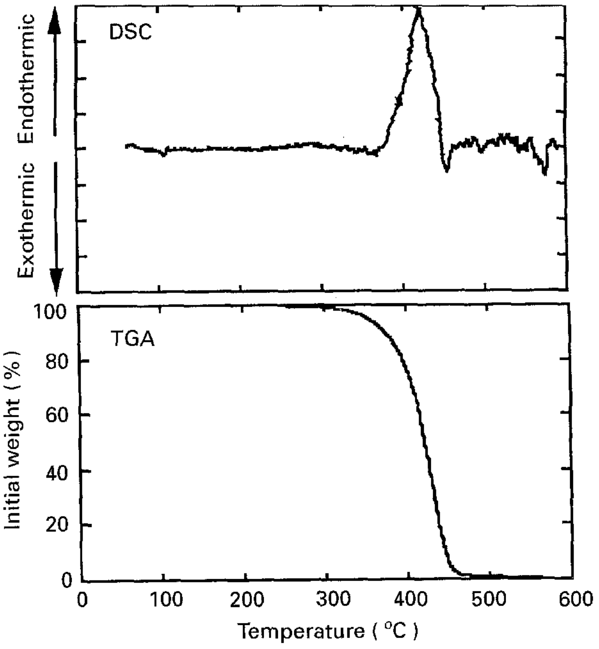

Figure 10 Typical thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) plots for EPS ("T" beads, density = 0.024 g cm^{-3}).

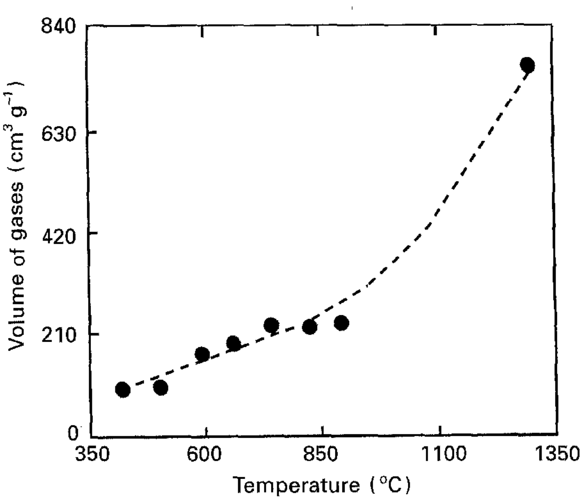

Figure 11 Volume of gases (STP) produced upon the degradation of a unit mass of EPS as a function of temperature ("T" beads, density = 0.024 g cm^{-3}) [13].

Conclusions

Several transitions may occur during the thermal degradation of foamed polystyrene. The beads collapse and decrease in volume substantially as the polymer is heated above 110–120 °C. This collapse

TABLE II Thermogravimetric analysis data obtained from test patterns

	Foam density (g cm^{-3})						
	0.024[a]	0.026[a]	0.024[b]	0.048[b]	0.020[c]	0.024[c]	0.028[c]
Start temperature (°C)	278	291	256	270	221	250	250
Peak temperature (°C)	417	419	403	426	401	403	418
End temperature (°C)	462	499	484	500	446	470	490

[a] "T" type beads.
[b] "C" type beads.
[c] "B" type beads.

temperature compares well with the glass transition temperature of polystyrene. The collapsed beads melt at 160 °C. The polymer density and the initial bead structure do not have a significant effect on the collapse and melting temperatures. Volatilization of the polymer used in the EPC process starts at about 275 °C. The polymer is almost totally volatilized between 460 to 500 °C. Maximum volatilization rates are observed at about 400–420 °C. As the bead size increases, volatilization of the polymer starts at a lower temperature. The start temperature and the end temperature for volatilization increase with polymer density. The average heat of degradation of EPS is estimated to be on the order of 912 J g^{-1}.

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