

Thermal Degradation of Foamed Polymethyl Methacrylate in the Expendable Pattern Casting Process

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The thermal degradation of foamed polymethyl methacrylate (PMMA) patterns in the expendable pattern casting process has been studied. Various physical transitions that may occur during the degradation of PMMA have been determined using scanning electron microscopy, differential scanning calorimetry, and thermogravimetric analysis, and the effects of polymer density on the degradation characteristics have been investigated. The results indicate that, when exposed to elevated temperatures, the polymer beads collapse at about 140 to 200 °C. The collapsed beads melt at 260 °C and begin to volatilize. Peak volatilization temperatures are on the order of 370 °C. The end temperature for volatilization is between 420 and 430 °C. The initial density of the polymer does not have a significant effect on the transition temperatures associated with degradation.

Keywords

EPC process, full mold process, lost foam process, PMMA, polymethyl methacrylate, thermal degradation

1. Introduction

THE expendable pattern casting (EPC) process utilizes foamed polymer patterns for the production of metallic components (Ref 1). The polymer material (polystyrene or polymethyl methacrylate, PMMA) is initially injection molded to the required shape. The molded pattern is then coated with a ceramic slurry and buried in unbonded sand. Molten metal is poured directly 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 (Ref 1, 2).

Expanded polystyrene (EPS) is the principal pattern material used in commercial practice. During the filling of the mold, EPS undergoes degradation through a series of complex transitions, the extent of which depends on the melt temperature (Ref 3). The interaction of the degradation products with the solidifying metal may lead to defects in the casting unique to the EPC process (Ref 4). When EPS patterns are used for producing ferrous castings, several carbon defects may form in the cast component (Ref 5). In order to overcome these problems, a new moldable foam based on PMMA has been developed (Ref 6).

This paper describes a study of the thermal degradation characteristics of PMMA foams used in the EPC process. Various physical transitions that may occur during the thermal degradation of foamed PMMA patterns have been determined. Data have been acquired for polymers of two different densities.

2. Experimental Procedure

The effect of temperature on the initial polymer bead structure was studied by immersing samples of PMMA in liquids heated between 50 and 270 °C. A hot wire cutter was used to obtain 1.5 by 1.5 by 15 cm pieces from PMMA blocks supplied by Dow Chemical (Ref 7). 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 and 270 °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 subsequent experiments.

During the experiments, the polymer piece was dipped in the liquid for 30 s, removed, 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 (SEM). The coating was performed in a vacuum evaporator 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 SEM equipped with stage-automated digital image analysis and a Kevex (Kevex X-Ray Inc., Scotts Valley, CA) delta system. The image of the beads was captured on a screen, and the bead size was calculated using automated image analysis. At least 40 to 60 beads were selected randomly and their sizes measured. Several samples were measured under each condition in order to obtain reproducible results. The beads were observed under magnifications of 10 to 100 \times . Data were acquired from 50 °C to about 270 °C in intervals of 10 °C.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to study the physicochemical phenomena occurring during the thermal degradation of PMMA in the temperature range of 50 to 600 °C. The TGA apparatus consisted of a Mettler TC10A (Mettler Toledo, Worthington, OH) processor in conjunction with a Mettler

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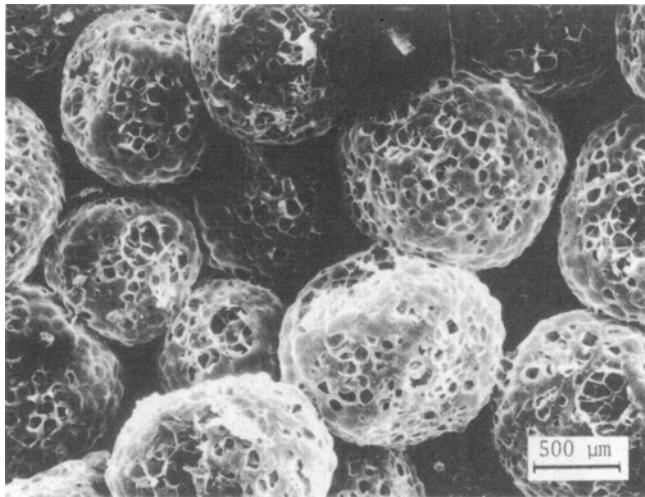


Fig. 1 Micrograph showing the bead structure in the foamed polymer (initial density, 0.024 g/cm³)

TG50 thermobalance/furnace. Standard alumina crucibles with perforated lids and a volume of 0.07 cm³ were used. Approximately 3 mg of PMMA was placed inside the crucible and weighed with an accuracy of ±0.001 mg. In order to purge the gases evolved during degradation, a constant air flow of 100 mL/min was maintained during the experiments. The temperature was measured with a Pt-100 temperature sensor with an accuracy of ±0.1 °C. Experiments were conducted for heating rates between 10 and 30 °C/min. The DSC instrument consisted of a Mettler TC10A processor in conjunction with a Mettler DSC20 cell. Approximately 3 to 4 mg of PMMA was heated at a rate of 10 °C/min.

Foamed polymer patterns containing T-beads and having effective densities between 0.02 and 0.03 g/cm³ are typically used in the EPC process. Consequently, experiments were conducted with foamed polymers containing T-beads. Data were acquired for two values of initial density: 0.021 and 0.024 g/cm³. In all the experiments, several tests were conducted under similar conditions in order to obtain reproducible results.

3. Results and Discussion

Foamed PMMA patterns used in the EPC process are amorphous, linear polymers with a chemical formula of (C₅H₈O₂)_n and with molecular weights ranging from 300,000 to 500,000. The typical bead structure in the polymer pattern is shown in Fig. 1. The polymer consists of nearly spherical beads with an average bead size of 1.5 mm (Table 1). 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 is high, fracture occurs across the beads (transbead fracture), as shown in Fig. 1. Fracture predominantly along the beads (interbead fracture) indicates a low degree of fusion. The extent of transbead fracture in the polymer was measured to be between 20 and 90%. Samples obtained from different polymer blocks exhibited large variations in the degree of fusion. The average bead size varies inversely with polymer density. As the initial density of the polymer increases from 0.021 to 0.024

Table 1 Effect of temperature on average bead size

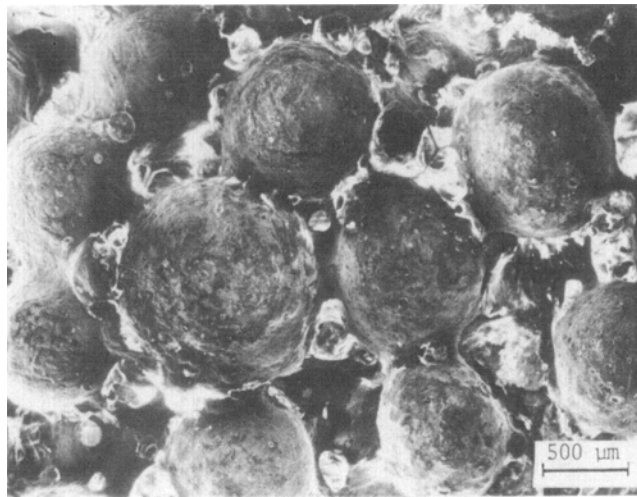
Temperature, °C	Average bead size, mm, at a polymer density of:	
	0.021 g/cm ³	0.024 g/cm ³
25	1.47 ± 0.10	1.32 ± 0.07
50	1.46 ± 0.08	1.31 ± 0.08
60	1.47 ± 0.08	1.32 ± 0.08
70	1.48 ± 0.09	1.31 ± 0.08
80	1.49 ± 0.07	1.30 ± 0.09
90	1.46 ± 0.08	1.32 ± 0.07
100	1.49 ± 0.08	1.31 ± 0.08
110	1.47 ± 0.07	1.29 ± 0.08
120	1.48 ± 0.09	1.28 ± 0.10
130	1.47 ± 0.08	1.30 ± 0.05
140	1.39 ± 0.09	1.31 ± 0.07
150	1.01 ± 0.08	1.31 ± 0.09
160	1.01 ± 0.07	1.25 ± 0.09
170	0.97 ± 0.10	1.16 ± 0.08
180	0.94 ± 0.08	0.98 ± 0.07
190	0.96 ± 0.08	0.77 ± 0.06
200	0.53 ± 0.04	0.66 ± 0.04
210	0.51 ± 0.03	0.66 ± 0.04
220	0.50 ± 0.03	0.48 ± 0.04
230	0.47 ± 0.04	0.46 ± 0.03
240	0.44 ± 0.03	0.44 ± 0.02
250	0.42 ± 0.02	0.44 ± 0.02

g/cm³, the average bead size decreases from about 1.5 to 1.3 mm.

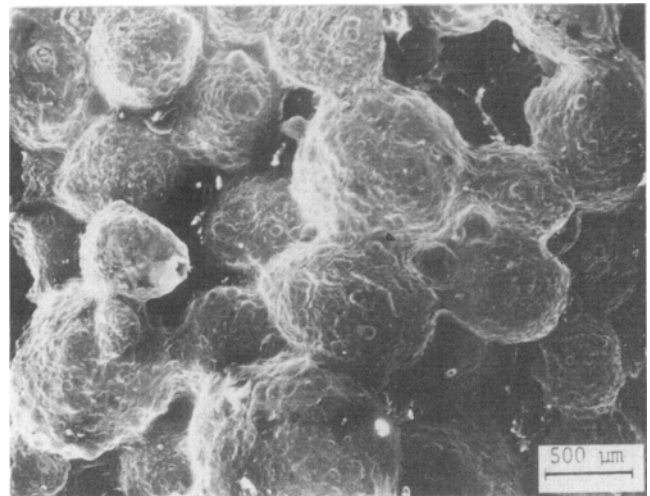
The polymer beads collapse rapidly upon exposure to elevated temperatures (Fig. 2). The overall bead structure in the polymer does not change significantly up to about 140 to 150 °C (Table 1). As the temperature is increased beyond this value, the expanded beads begin to collapse rapidly and the average bead size decreases (Fig. 3). The average bead size in a polymer with a density of 0.021 g/cm³ decreases from about 1.4 mm at 140 °C to 0.5 mm at 200 °C. Thus, the collapse temperature for PMMA patterns is between 140 and 200 °C. By comparison, the glass transition temperature of PMMA has been reported to be on the order of 105 °C (Ref 8). The average bead size continues to decrease up to about 250 °C as the beads return to their unexpanded size (Fig. 3). At 260 °C, the beads melt to produce a viscous residue (Fig. 4). The polymer density does not have a significant effect on the collapse or melting temperatures.

The melted beads degrade in a fashion similar to that of bulk PMMA. The polymer starts to volatilize at temperatures between 250 and 260 °C (Table 2), as shown in the TGA curve plotted in Fig. 5. Peak volatilization temperatures are on the order of 370 °C. The end temperature for volatilization is between 420 and 430 °C. A weight loss of about 95% is measured at 430 °C. The remaining residue continues to vaporize gradually as the temperature is increased above 430 °C. The residue remaining at 600 °C was typically between 0.5 and 1.2%. Increasing the heating rate from 10 to 30 °C/min did not significantly affect the volatilization temperatures.

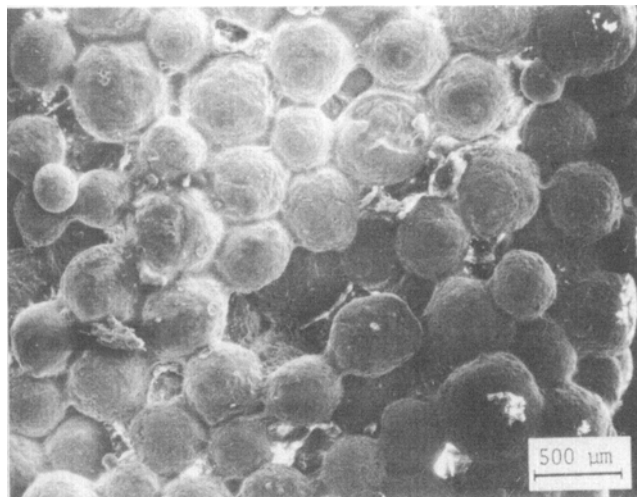
The DSC data for PMMA typically indicate a large endothermic peak between 260 and 430 °C (Fig. 5). This endothermic peak is associated with the volatilization of the polymer sample. The heat of degradation calculated from this endothermic peak is on the order of 842 J/g. By comparison, the heat of polymerization for PMMA has been reported to be 578 J/g (Ref 8). Some samples exhibited a small endothermic peak between



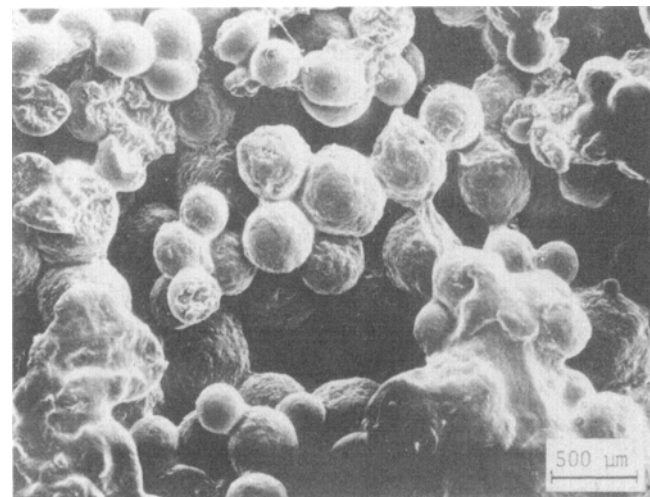
(a)



(b)



(c)



(d)

Fig. 2 Effect of temperature on polymer bead structure (initial density, 0.024 g/cm^3). (a) $110 \text{ }^\circ\text{C}$. (b) $180 \text{ }^\circ\text{C}$. (c) $210 \text{ }^\circ\text{C}$. (d) $240 \text{ }^\circ\text{C}$

Table 2 TGA and DSC data as a function of polymer density

Temperature, $^\circ\text{C}$	TGA		DSC	
	0.021 g/cm^3	0.024 g/cm^3	0.021 g/cm^3	0.024 g/cm^3
Start	255 ± 8	264 ± 4	261	269
Peak	373 ± 4	368 ± 6	374	375
End	428 ± 5	429 ± 7	432	421

90 and $120 \text{ }^\circ\text{C}$. This endothermic peak corresponds to the glass transition within the polymer. The transition temperatures obtained from the DSC experiments compare well with the TGA results, as shown in Table 2. The initial polymer density does not have a significant effect on the transition temperatures.

The preceding data indicate that the collapse and melting temperatures for PMMA are higher than the corresponding values for EPS (Table 3). The volatilization of PMMA patterns, however, begins at a lower temperature than EPS patterns. The

start temperature for volatilization of PMMA is about 25 to $50 \text{ }^\circ\text{C}$ lower than the value for EPS. In addition, the end temperature for volatilization of PMMA is about 40 to $70 \text{ }^\circ\text{C}$ lower than the value for EPS.

The thermal degradation of PMMA is significantly different from other polymers and, consequently, has been investigated extensively (Ref 11, 12). Madorsky (Ref 11) has studied the pyrolysis of bulk PMMA in vacuum at elevated temperatures. The data obtained indicate that the degradation process begins at

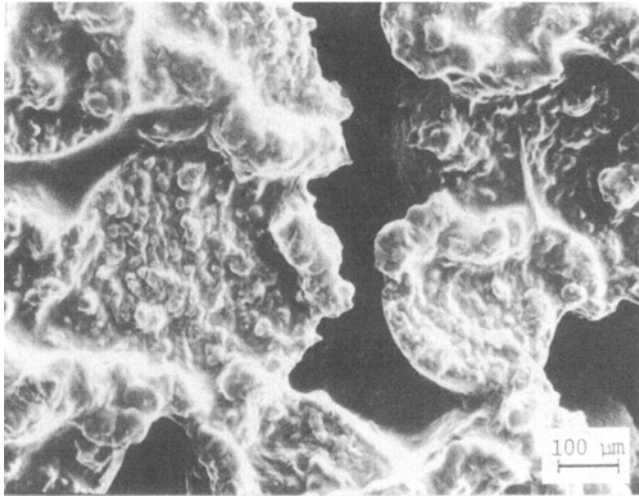


Fig. 3 Micrograph showing the melted beads at 260 °C (initial density, 0.024 g/cm³)

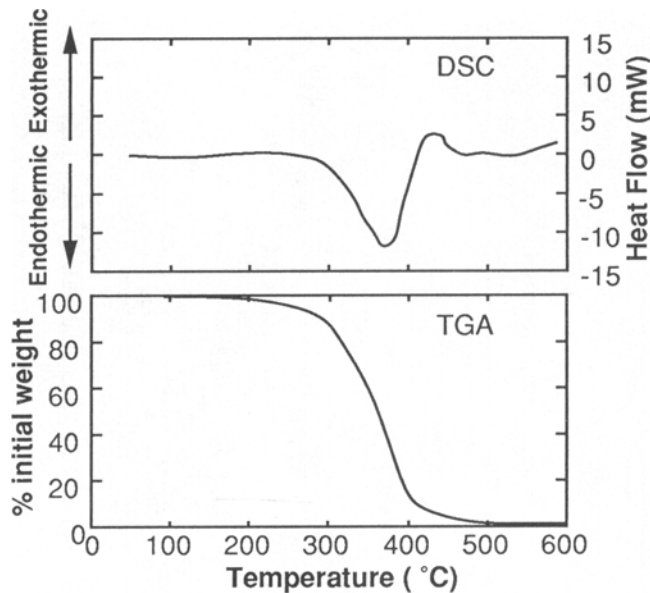


Fig. 4 Variation of polymer bead size with temperature for initial densities of 0.021 and 0.024 g/cm³

about 160 °C and that only limited amounts of volatile products are produced at this temperature. The fraction volatilized increases with temperature; complete volatilization is achieved at temperatures higher than 500 °C. The volatile products consist almost entirely of the monomer. As the temperature is increased above 500 °C, the yield of monomer is reduced and the gaseous products undergo additional fragmentation. At 1200 °C, the yield of monomer is as low as 10% and the gaseous products consist of lighter hydrocarbons (e.g., methane, ethane, ethylene, and propadiene) and large amounts of carbon monoxide and carbon dioxide. Due to the fragmentation of the monomer molecule at high temperatures, the volume of gases produced per unit mass of polymer (gas yield) increases with temperature (Fig. 6) (Ref 9).

The thermal degradation of PMMA occurs by a mechanism referred to as "unzipping." Monomer fragments may split off

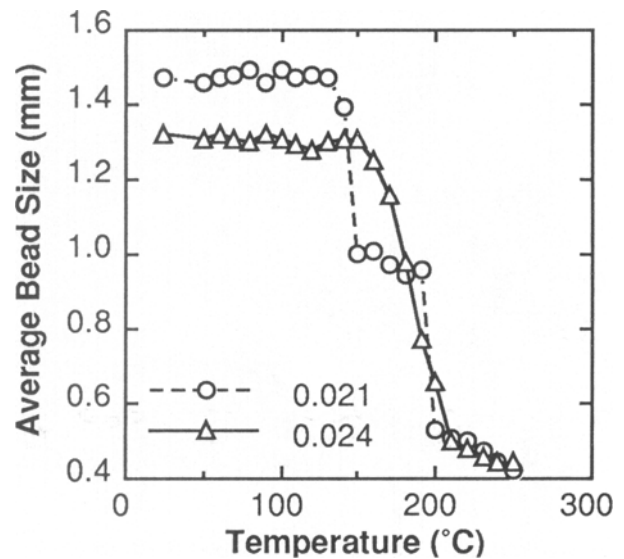


Fig. 5 Typical TGA and DSC plots for PMMA with an initial density of 0.024 g/cm³

Table 3 Thermal degradation characteristics of polymer patterns in the EPC process

Characteristic	EPS (Ref 10)	PMMA
Glass transition temperature, °C (Ref 8)	80-100	105
Collapse temperature, °C	110-120	140-200
Melting temperature for collapsed beads, °C	160	260
Temperature for start of volatilization, °C	275-300	250-260
Peak volatilization temperature, °C	400-420	370
End temperature for volatilization, °C	460-500	420-430
Heat of polymerization, J/g (Ref 8)	648	578
Heat of degradation, J/g(a)	912	842
Rate of vaporization at 750 °C, g/s·cm ² (Ref 9)	0.077	0.061
Rate of vaporization at 1300 °C, g/s·cm ² (Ref 9)	0.018	0.031
Gas yield at 750 °C, cm ³ (STP)/g (Ref 9)	230	273
Gas yield at 1300 °C, cm ³ (STP)/g (Ref 9)	760	804
Polymer transformed to viscous residue, % (Ref 9)	84	50
Nonvolatile residue at 1400 °C, % (Ref 6)	15	3

(a) Estimated from the endothermic peak in the DSC curve

stepwise along the chain from the free radicals formed during scission. The unzipping reaction is the reverse of the propagation process encountered during addition polymerization. The methyl (CH₃) and the ester (COOCH₃) groups are electron donors and thus favor monomer formation. Consequently, gas yields with PMMA patterns are larger than with EPS patterns (Table 3). The degradation of EPS occurs by random scission, which results in the formation of large quantities of a viscous residue consisting of dimer, trimer, and tetramer (Ref 10). Almost 80 to 90% of the polymer may be transformed to the viscous residue during the formation of the casting (Table 3). This viscous residue can be pyrolyzed to a nonvolatile carbonaceous product. Moll and Johnson (Ref 6) have shown that nearly 15% of EPS may form a nonvolatile product during pyrolysis at 1400 °C. During their experiments, the polymer samples were

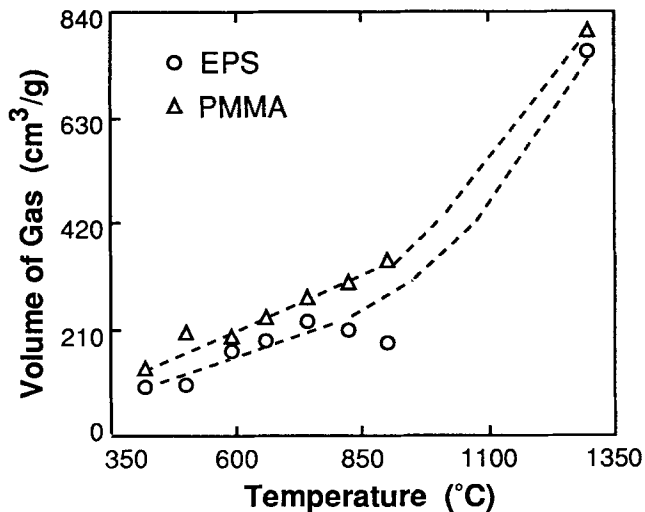


Fig. 6 Volume of gases (standard temperature and pressure) produced upon the degradation of a unit mass of PMMA as a function of temperature (initial density, 0.024 g/cm^3). Data for EPS are also shown for comparison (Ref 9).

heated rapidly (at a rate of $700 \text{ }^\circ\text{C/s}$) to $1400 \text{ }^\circ\text{C}$ and held for 18 s. The nonvolatile carbonaceous product may cause surface carbon defects in gray and nodular iron castings. In the case of PMMA, pyrolysis at $1400 \text{ }^\circ\text{C}$ yielded only about 3% residue. Consequently, carbon-related defects can be minimized with PMMA patterns. The manufacturers of the PMMA foam also indicate that the carbon pickup in steel castings can be reduced from 0.1 to 0.3% with EPS patterns to less than 0.05% with PMMA patterns (Ref 6). It should be noted that the presence of two oxygen atoms and the absence of an aromatic group in the methyl methacrylate molecule reduces the propensity for the formation of the nonvolatile residue. The carbonaceous degradation products may be oxidized to CO and CO_2 with PMMA patterns. Hence, PMMA patterns may be used to improve the quality of ferrous EPC castings. Because foamed PMMA is relatively expensive, copolymers of EPS and PMMA are also being developed for use with ferrous castings.

4. Conclusions

The thermal degradation of foamed PMMA patterns in the EPC process begins with the collapse of the initial bead structure in the temperature range of 140 to $200 \text{ }^\circ\text{C}$. The collapsed beads melt at $260 \text{ }^\circ\text{C}$. Volatile fragments begin to evolve at about 250 to $260 \text{ }^\circ\text{C}$. Peak volatilization temperatures are on

the order of $370 \text{ }^\circ\text{C}$. The end temperature for volatilization is between 420 and $430 \text{ }^\circ\text{C}$. The volatile fragments essentially consist of the monomer. The residue remaining at $600 \text{ }^\circ\text{C}$ is typically between 0.5 and 1.2%. Data obtained by DSC for PMMA indicate a large endothermic peak between 260 and $430 \text{ }^\circ\text{C}$. The heat of degradation calculated from this endothermic peak is on the order of 842 J/g . The initial density of the polymer does not have a significant effect on the transition temperatures associated with the degradation of the polymer. The collapse and melting temperatures for PMMA are higher than the corresponding values for EPS. The start temperature for volatilization of PMMA is about 25 to $50 \text{ }^\circ\text{C}$ lower than the value for EPS. In addition, the end temperature for volatilization of PMMA is about 40 to $70 \text{ }^\circ\text{C}$ lower than the value for EPS.

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