JOURNAL OF MATERIALS SCIENCE **38** (2003) 2233–2239

EPS molecular weight and foam density effects in the lost foam process

M. SANDS, S. SHIVKUMAR
Department of Mechanical Engineering, Worcester Polytechnic Institute, Worcester, MA 01609
E-mail: shivkuma@wpi.edu

The effects of pattern molecular weight and density on casting formation in the lost foam process have been studied. The tensile properties of injection molded ASTM D638 tensile rods have been measured for various densities and molecular weights. Thermogravimetry, differential scanning calorimetry and other techniques have been used to study the thermal degradation characteristics of the pattern. A thermometric technique has been used to study the mold filling behavior with aluminum alloy A356. The results indicate that the tensile properties in the foam generally improve with increasing molecular weight and density. The structural characteristics of the foam may have a greater influence on mechanical properties than molecular weight. The rate of volatilization of the polymer increases as the weight average molecular weight, M_w, is lowered from 304,000 g/mol to 152,000 g/mol. The mold fill time increases with pattern density and M_w. The data suggest that pattern density and molecular weight may have a significant effect on the quality of the casting. © *2003 Kluwer Academic Publishers*

1. Introduction

Linear polystyrene with a weight average molecular weight (M_w) of about 300,000 g/mol and that is expanded to a bulk density between 20 and 30 kg/m^3 is typically used for casting production in the lost foam process [1]. During casting formation, the expanded polystyrene (EPS) undergoes thermal degradation by random chain scission through a series of complex physico-chemical transitions [2]. The types of degradation products formed, the kinetics of degradation and the associated endothermic losses in the liquid metal are all influenced by the characteristics of the foam. The primary factors controlling the properties of the foam are the bulk density, cell size and orientation, degree of bead fusion and molecular distribution (i.e., molecular weight and polydispersity index). Various other parameters that are specific to certain machines, resins and/or molding conditions may also affect the properties of the foam. The molecular weight can be expected to have a significant influence on the injection molding characteristics of the foam. Variations in the molecular weight distribution may change the glass transition temperature (T_g) and the tensile and viscoelastic properties of the polymer [3]. These changes may influence the expansion of the bead during molding and also the shrinkage in the pattern after production [4]. Further, molecular weight can also influence the rate of degradation of the polymer. Thermal degradation experiments with polystyrene have shown that the dynamics of polymer degradation and the nature of the products formed depend on the macromolecular chain length (i.e., molecular weight) [5]. Consequently, it can be expected that the molecular characteristics of the polymer pattern will have a significant effect on casting formation in the lost foam process. The purpose of this contribution is to examine the effects of molecular weight and pattern density on mold filling of aluminum alloys in the lost foam process. The effects of polymer bead fusion on casting characteristics have been described elsewhere [6].

2. Experimental procedure

Two batches of raw beads of polystyrene were obtained from StyroChem International, Fort Worth, Texas. Gel Permeation Chromotography (GPC) on the raw beads yielded the following molecular weight characteristics in the two batches a) Weight average molecular weight, $M_w = 304{,}000$ g/mol, Number average molecular weight, $M_n = 135{,}000$ g/mol, Polydispersity $= 2.23$ b) $M_w = 152{,}000$ g/mol, $M_n = 74{,}000$ g/mol, Polydispersity $= 2.02$. The raw beads were expanded and molded at General Motors Corp., Saginaw, MI to produce ASTM D638 tensile specimens. The ASTM D638 tensile specimens were molded with T beads to achieve the required density. Experiments were conducted at nominal pattern densities of 19.5, 20.8, 22.4 and 32 kg/m^3. The molding conditions were controlled to produce samples with similar levels of bead fusion in the foam. The extent of bead fusion (measured as the fraction of *transbead* fracture) was between 40 and 60% [6]. The tensile properties in the polymer pattern were measured with an IMS mechanical testing machine according to ASTM D638 Tensile Test Standards

0022–2461

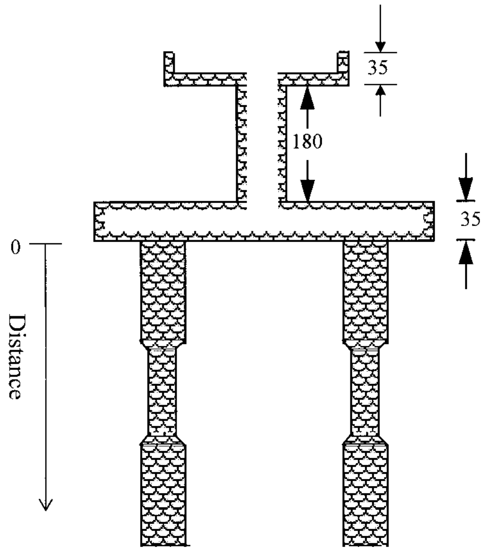

Figure 1 Schematic of the test patterns used to study the flow behavior. Up to 12 thermocouples were placed in each tensile bar along its length. The distance of flow was measured as indicated in the figure. (All dimensions in mm).

[7]. At least 5 and up to 10 specimens were measured under each condition. The thermal degradation characteristics of the polymers were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) with Perkin Elmer instruments, DSC7 and TGA7 respectively. Data were obtained for heating rates of 10°K/min and 200°K/min. The thermogravimetric analysis was conducted in the normal mode, where the sample was placed in the crucible and the unit was heated to increase the temperature at the desired heating rate. In addition, kinetic data on the degradation behavior were obtained from isothermal experiments, designed to simulate the large heating rates encountered under casting conditions. In this case, the furnace in the TGA apparatus was heated to the desired temperature. Subsequently, the crucible with the polymer sample was rapidly raised into the furnace chamber and the weight loss was monitored as a function of time at constant temperature. Experiments were conducted at temperatures between 450 and 1200°K.

Castings were produced with the pattern shown in Fig. 1. Two tensile bars with varying densities and molecular weights were attached on opposite ends of a runner. The assembled pattern was then coated with a commercial coating slurry so as to obtain a dried coating thickness of 0.2 mm. The coated pattern was instrumented with several chromel-alumel thermocouples and buried in unbonded silica sand (AFS 55). The sand was compacted with a pneumatic compactor at 0.65 MPa for 45 s. Aluminum alloy A356 at $1040 \pm 5°$K was then poured onto the pattern to produce the casting. A data acquisition system was used to record the temperature histories during casting formation.

3. Results and discussion

The molecular weight and its distribution may have a significant effect on the properties of polystyrene. In general, the tensile strength of bulk polystyrene increases with molecular weight [8]. This increase is often attributed to additional entanglements produced at higher molecular weights [9]. Various empirical equations have been used to describe the relationship between tensile strength and molecular weight, with the following equation, attributed to Flory [10], commonly reported in the literature for broad and narrow molecular distributions:

$$\sigma_{\mathrm{UTS}} = A + \frac{B}{\bar{M}_{\mathrm{n}}} \qquad (1)$$

where, A and B are empirical constants. In addition, it has also been shown that the contributions of molecular weight to the strength become significant at $M_{\mathrm{w}} > 60{,}000$ g/mol [11]. The data of Bersted *et al.* [11] indicate that Equation 1 may describe the relationship between strength and molecular weight adequately for low values of polydispersity index (i.e., narrow molecular distribution). However, Equation 1 cannot be used to correlate the strength with molecular weight for high polydispersity index (i.e., broad molecular weight distribution). Other molecular parameters have been developed by Bersted *et al.* [11] and Fellers and Chapman [12] to correlate the mechanical properties with molecular characteristics for narrow and broad distributions. It is clear however, that molecular weight and its distribution play a vital role in controlling the mechanical properties of amorphous polystyrene.

The properties of the parent polymer clearly will influence the properties of expanded polystyrene. In this respect, the effects of molecular weight distribution described above for polystyrene are also important in EPS. The effects of molecular weight on tensile properties of EPS such as elastic modulus and %elongation are clearly evident from the data shown in Table I. The tensile modulus increases and the %elongation decreases as M_{w} changes from 152,000 g/mol to 304,000 g/mol. This behavior is observed for all the four foam densities shown in Table I. The effects

TABLE I Tensile properties in ASTM D638 tensile specimens as a function of pattern density and weight average molecular weight (M_{w}). (E: Tensile Modulus, UTS: Tensile Strength and %El: %elongation)

	$M_{\mathrm{w}} = 152{,}000$ g/mol			$M_{\mathrm{w}} = 304{,}000$ g/mol		
Density (kg/m^3)	E (MPa)	UTS (MPa)	%El	E (MPa)	UTS (MPa)	%El
19.5	1.66 ± 0.32	0.138 ± 0.02	7.8 ± 1.7	2.78 ± 0.20	0.152 ± 0.04	4.9 ± 1.4
20.8	2.29 ± 0.09	0.152 ± 0.02	7.7 ± 1.7	3.83 ± 0.12	0.162 ± 0.02	4.8 ± 1.6
22.4	2.21 ± 0.10	0.193 ± 0.02	8.3 ± 1.4	4.07 ± 0.19	0.172 ± 0.03	5.2 ± 0.7
32.0	4.21 ± 0.24	0.271 ± 0.01	7.1 ± 0.2	4.48 ± 0.09	0.221 ± 0.01	6.1 ± 0.3

of molecular weight on tensile strength are not readily evident from the data shown in Table I. For low pattern densities (19.5 and 20.8 kg/m^3), the tensile strength increases slightly (~10%) as M_w changes from 152,000 g/mol to 304,000 g/mol. For high pattern densities (22.4 and 32 kg/m^3), however, there is a decrease in tensile strength for similar changes in M_w. Tensile fracture in cellular foams is influenced strongly by various defects in the foams such as cracks, cluster of cells and damaged cells [13]. The breakage of cell walls and reorientation of neighboring cells during crack propagation has a strong influence on fracture and therefore the tensile strength is likely to be governed by microstructural parameters. It has been shown that in many cellular foams, the tensile strength may be strongly affected by variations in cell size, geometry, and number resulting from the deformation under load. Hence, in Table I, the variability in the local cellular structures may have obscured any discernable effect of M_w on tensile strength. By comparison, elastic modulus, is relatively unaffected by microstructural variability [13]. The elastic deformation is determined primarily by cell wall extension and bending, so properties of the base material have a strong effect on E. Hence, the data shown in Table I indicate that for all 4 pattern densities, E increases as M_w increases.

In EPS, the structural factors associated with the foam such as density and cell size and geometry, and the extent of bead fusion have a greater influence on mechanical properties than M_w [4]. In particular, the density of the foam plays a major role in controlling the mechanical properties of the foam as shown in Table I. The effects of density on mechanical properties of EPS have been studied extensively and various empirical equations have been developed to describe this dependence [14]. In general, the following power law equation has been used by several investigators to describe the dependence of tensile modulus (E) or tensile strength (σ_UTS) on foam density (ρ_S) [4]:

$$E \quad \text{or} \quad \sigma_\mathrm{UTS} = K(\rho_\mathrm{S})^n \tag{2}$$

where K and n are constants. In closed cell foams such as EPS, the nature of the cells (i.e., cell size, cell wall thickness, cell geometry and orientation) within each bead may have an appreciable effect on mechanical properties [15]. Depending on the final density of the foam, the cells can be in the shape of packed dodecahedra. The average cell size may vary with the molding conditions. The model of Gibson and Ashby [13], based on a combination of stretching lamellae and bending of struts, can be used to develop a mathematical relationship between strength and density in cellular foams that includes the cellular characteristics:

$$\frac{E_\mathrm{S}}{E_\mathrm{M}} = \phi^2\left(\frac{\rho_\mathrm{S}}{\rho_\mathrm{M}}\right)^2 + (1-\phi)\left(\frac{\rho_\mathrm{S}}{\rho_\mathrm{M}}\right) \tag{3}$$

$$\frac{\sigma_\mathrm{S}}{\sigma_\mathrm{M}} = 0.65\left(\frac{\phi\rho_\mathrm{S}}{\rho_\mathrm{M}}\right)^{3/2} + (1-\phi)\left(\frac{\rho_\mathrm{S}}{\rho_\mathrm{M}}\right) \tag{4}$$

where E is the modulus and σ is the strength. The subscripts S and M refer to the foam and matrix polymer. Gibson and Ashby [13] used a fitting parameter Φ in their model to describe the fraction of the material acting as struts. Best fits for the present data were obtained with $\Phi = 0.95$ (Fig. 2).

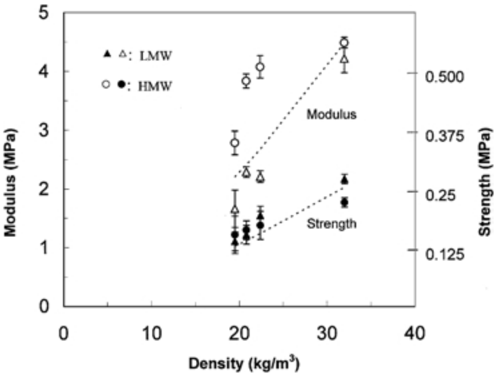

Figure 2 Tensile modulus and strength as a function of density. Symbols correspond to measured values. The dotted lines are calculated using Equations 3 and 4 obtained from the model of Gibson and Ashby [13]. LMW: $M_\mathrm{w} = 152{,}000$ g/mol HMW: $M_\mathrm{w} = 304{,}000$ g/mol.

The extent of bead fusion obtained during the molding of the pattern is an important structural parameter in EPS [6, 16]. The tensile strength improves significantly with increased bead fusion [6, 17,18]. For example, the tensile strength in EPS patterns has been measured to be on the order of 0.17 MPa and 0.42 MPa for low (<1%) and high (>90%) degree of bead fusion.

The molecular weight distribution may play an important role in the molding of the foam [4]. The results of Stafford *et al.* [19] suggest that the cell size in the foam is affected by the molecular weight distribution. A narrow molecular weight distribution may lead to smaller cell sizes in the foam. Stafford *et al.* [19] indicate that high and low molecular fragments may be necessary to support the cell structure. The high molecular weight component may stabilize the cells by promoting enhanced intermolecular entanglements, while low molecular weight component may enhance rapid cell growth. The shrinkage of the polymer after molding is influenced by the molecular weight distribution. In general, a higher molecular weight and a higher polydispersity may lower the amount of residual shrinkage [20, 21].

The thermal degradation characteristics of polystyrene have been studied extensively [22–24]. Most of these investigations were performed primarily by means of thermogravimetry and molecular weight characterization. Generally, the degradation behavior is studied in isothermal experiments by exposing the polymer over times from minutes to hours in the temperature range 550 to 700°K. The polymer is heated to the desired temperature at relatively low heating rates (typically less than 10°K/min). The products of degradation have been identified to be styrene monomer, styrene oligomers up to hexamer but mostly dimer and trimer, benzene, toluene and several light hydrocarbons [5, 23].

Based on these experiments, it is generally believed that polystyrene degrades primarily by random-chain scission and that chain-end scission is much less significant [24]. The potential reaction pathways that have been identified are bond scission, depolymerization (direct β scission), intramolecular hydrogen transfer (backbiting) followed by β scission, chain stripping, intramolecular cyclization, intermolecular crosslinking and radical recombination reactions [25]. Among these reactions, β scission, leads to the formation of styrene monomer, while random scission leading to backbiting and β scission, may result in the formation of styrene oligomers. The remaining reaction pathways listed above may lead to the formation of other compounds such as benzene, toluene and other hydrocarbons.

Several investigators have used flash pyrolysis to study the kinetics of degradation at high heating rates [23, 26–29]. In flash pyrolysis of vinyl polymers, the fraction of volatile matter increases when compared to the value in slow heating, because the ratio of the random scission of main chain and depolymerization changes. Flash pyrolysis of polystyrene has shown that nearly 60 to 80% of the monomer units in the sample may be transformed into monomer molecules, while the remaining 20 to 40% may be converted in dimer, trimer and higher oligomers [30, 31]. De Amorim *et al.* [27] exposed polystyrene to temperatures between 773°K and 1073°K for 1 s under flash pyrolysis conditions. Their experiments provide degradation data for conditions closest to the lost foam process. Their data show that the styrene monomer yield increases from about 60% at 773°K and peaks at 80% at about 1073°K. The fraction of dimer and trimer decrease with increasing temperature. This effect of temperature has been attributed to variations in kinetic parameters. The activation energy (Q) for the depolymerization reaction leading to styrene monomer is estimated to be 100 KJ/mol, while Q for the transfer reactions resulting in the formation of dimer and trimer is 55 kJ/mol. In their experiments, flash pyrolysis at 1073°K for 2 s yielded oligomers (up to $n = 5$) that represent 20 to 50% of the initial mass of the sample. The fraction of secondary products such as benzene, toluene, etc., is relatively constant up to about 1073°K and starts to increase beyond 1123°K as the styrene molecules start to fragment. Similar data have been obtained by Bouster *et al.* [23], Yang and Shibaski [29] and Karaduman *et al.* [28]. Flash pyrolysis of polystyrene at 973°K results in nearly 2 to 3% and 3 to 5% of the polymer being converted to dimer and trimer respectively [23]. The corresponding values for both dimer and trimer at 1073°K are on the order of 1 to 2%. Further, in this temperature range, nearly 10% of the polymer does not decompose completely indicating compounds higher than trimers. De Amorim *et al.* [27] have shown that oligomers up to hexamers can be produced during the degradation of polystyrene. All these results are consistent with the data from numerous investigations of the polymer degradation in the lost foam process which indicate that a large fraction of the polymer (>60%) is converted to a viscous residue at the metal front [2].

The effects of degradation on the molecular weight distribution in the polymer have been studied by several investigators [5, 23]. As the polymer degrades, the molecular weight decreases rapidly initially [32]. Several investigators have proposed the presence of "weak links" in the polymer to initiate the rapid drop in molecular weight at low reaction times [33, 34]. This initial decrease in molecular weight through random chain scission has been shown to exhibit first order kinetics [34, 35]. When the conversion rate is high (i.e., M_n changes substantially during degradation), polydispersity index may also decrease during this initial stage indicating that the larger molecules may undergo a greater number of scissions [33, 36]. A possible explanation for this behavior is that larger molecules have a greater number of bonds and, hence, there is a higher statistical probability of breaking a bond. In addition, long chains have a stronger tendency to form kinks than short chains. The resulting bond angle strain may weaken the C—C bond, thereby leading to a higher C—C scission rate [36].

The initial molecular weight distribution of the sample has a significant effect on the kinetics of degradation and on the products of decomposition. As the molecular weight increases, the styrene monomer yield increases, and the fraction of dimers, trimers and other minor products decreases [5, 23, 37–39]. For example, styrene yields at 1073°K are on the order of 60% and 79% for M_w of 2200 and 100,000 g/mol respectively [23]. Madras *et al.* [34] have shown that the chain scission rate coefficient is a function of M_w. It varies linearly with M_w at low M_w, but exhibits a second order dependence at higher M_w. The polydispersity index also influences the degradation behavior. In polymers with long molecules, the greater molecular entanglement leads to increased probability of oligomer formation through intermolecular transfer [5].

Thermal degradation of EPS begins with the collapse of the expanded beads [2] This collapse is determined by the glass transition temperature in the base polymer. It has been shown that the glass transition temperature for polystyrene increases with M_n [40]. This dependence may be expressed as follows for normal heating rates [41]:

$$T_\mathrm{g} = 100^\circ\mathrm{C} - \frac{1.8 \times 10^5}{M_\mathrm{n}} \tag{5}$$

The following values were obtained in this study: $T_\mathrm{g} = 370^\circ\mathrm{K}$ for $M_\mathrm{n} = 74{,}000$ g/mol and $T_\mathrm{g} = 379^\circ\mathrm{K}$ for $M_\mathrm{n} = 135{,}000$ g/mol. The preceding values of T_g were obtained from DSC experiments conducted at 200°K/min. The measured T_g data compare well with the values predicted from Equation 5, 371°K for $M_\mathrm{n} = 74{,}000$ g/mol and 372°K for $M_\mathrm{n} = 135{,}000$ g/mol. This difference in glass transition temperature for the two base polymers is reflected in the bead collapse temperature of the foams: $M_\mathrm{n} = 74{,}000$ g/mol, Collapse temperature = 383°K, $M_\mathrm{n} = 135{,}000$ g/mol, Collapse temperature = 388°K. The bead collapse temperatures were measured by monitoring the diameter of the bead as a function of temperature [42]. The temperature at which there is a measurable decrease in the diameter of the expanded beads is defined as the collapse temperature. Beyond a critical temperature, the white beads disappear completely and form a transparent viscous residue. This temperature for both values of M_n was typically around 438°K. The density of the polymer did not have any significant effect on the glass transition temperature or the collapse temperature.

After the beads collapse completely, the degradation of EPS is similar to that of bulk polystyrene. As indicated above, the rates of degradation are strongly influenced by temperature (Fig. 3). In addition, at all temperatures, the polymer with a M_n of 74,000 g/mol has a higher rate of overall degradation than the polymer with a M_n of 135,000 g/mol (Fig. 4). The activation energy for the whole degradation process has been calculated from the data in Fig. 3 to be on the order of 40 kJ/mol. This energy is close to the activation energy for the termination reactions (55 kJ/mol) described above. Thus, it can be expected that a large fraction of the polymer initially transforms to dimer, trimer and other oligomers. The fraction of EPS transformed to a viscous non-volatile residue after exposure to 1020°K for short times (<5 s) has been measured to be on the order of 60 ± 15% and 70 ± 12% for M_n of 74,000 g/mol and 135,000 g/mol respectively.

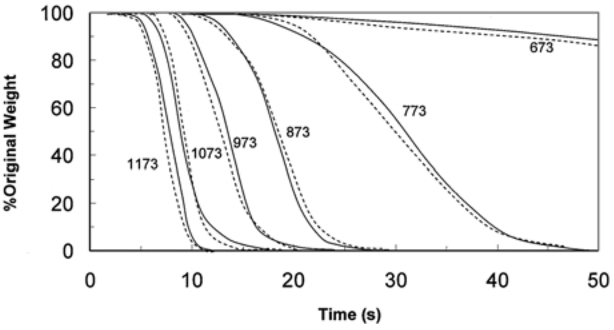

Figure 3 Kinetic data on the thermal degradation of EPS obtained from isothermal experiments. During the experiment, the furnace in the TGA apparatus was heated to the desired temperature and the crucible with the EPS sample was rapidly raised into the furnace chamber. The weight loss was monitored as a function of time at constant temperature. (——): $M_w = 304{,}000$ g/mol (-----): $M_w = 152{,}000$ g/mol.

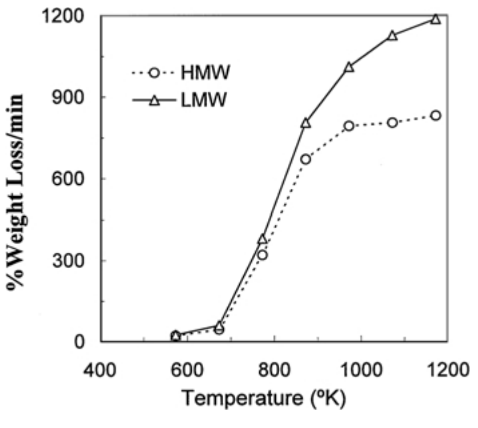

Figure 4 Maximum rate of weight loss as a function of temperature. The maximum rate of weight loss was measured as the maximum slope on the curves shown in Fig. 3. (HMW: $M_w = 304{,}000$ g/mol LMW: $M_w = 152{,}000$ g/mol).

The flow behavior of an aluminum alloy, for the different conditions used in this study, are plotted in Figs 5 and 6. As can be expected, the fill times increase with the density of the polymer. For example, at a M_n of 74,000 g/mol, the fill times are measured to be 1.6 s and 4.8 s for densities of 19.5 kg/m^3 and 32 kg/m^3 respectively. Also, the fill time for a M_n of 74,000 g/mol is generally less than the fill time for a M_n of 135,000 g/mol (Fig. 7).

The experiments with polystyrene indicate that in order to maximize the monomer yield a temperature of about 1073°K and a $M_w > 50{,}000$ g/mol may be necessary. These conditions are already attained in the lost foam process where the typical M_w is on the order 300,000 g/mol and the pouring temperature is 1023°K. However, it appears that a change in molecular weight from 300,000 g/mol to about 150,000 g/mol may affect the nature of degradation and the kinetics of the degradation process. The average flow velocity in patterns with M_w of 152,000 g/mol was slightly greater

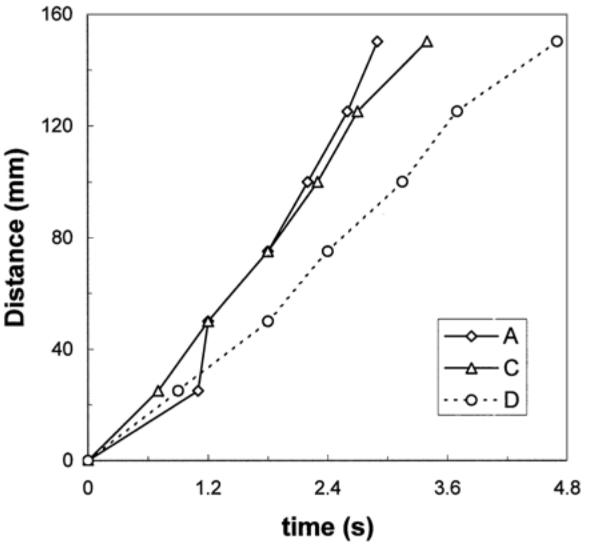

Figure 5 Distance of flow as a function of time for $M_w = 304{,}000$ g/mol. (A: Density = 19.5 kg/m^3, B: Density = 20.8 kg/m^3, C: Density = 22.4 kg/m^3, and D: Density = 32 kg/m^3.

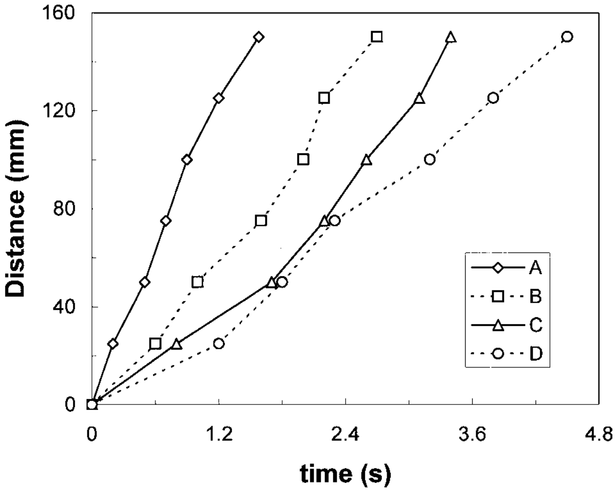

Figure 6 Distance of flow as a function of time for $M_w = 152{,}000$ g/mol. (A: Density = 19.5 kg/m^3, B: Density = 20.8 kg/m^3, C: Density = 22.4 kg/m^3, and D: Density = 32 kg/m^3).

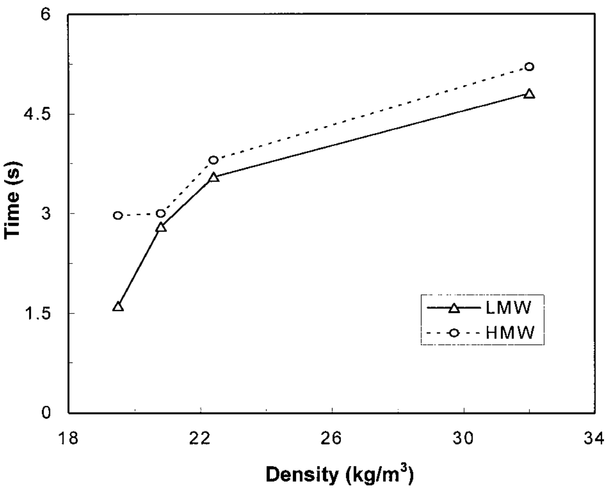

Figure 7 Mold fill time as a function of pattern density. (HMW: M_w = 304,000 g/mol, LMW: M_w = 152,000 g/mol).

than the velocity in patterns with a M_w of 304,000 g/mol (Fig. 8). A mass balance at the metal front yields [43]:

$$vA\rho_S\Delta t = R_V A\Delta t + R_L A\Delta t \tag{6}$$

or

$$v = \frac{1}{\rho_S}[R_V + R_L] \tag{7}$$

where v is the flow velocity, A is the cross sectional area, ρ_S is the density of the solid EPS, R_V is the rate of formation of gaseous products, R_L is an overall rate of oligomer formation. At any given temperature and M_w, R_V and R_L can be assumed to be constant, and hence, Equation 7 indicates that the flow velocity is inversely proportional to the density of the foam (Fig. 8). Furthermore, it was shown previously that the low M_w sample exhibits a slightly higher volatilization rate than the high M_w sample (Fig. 5). This result suggests that a greater fraction of the polymer is converted to oligomers as the M_w increases.

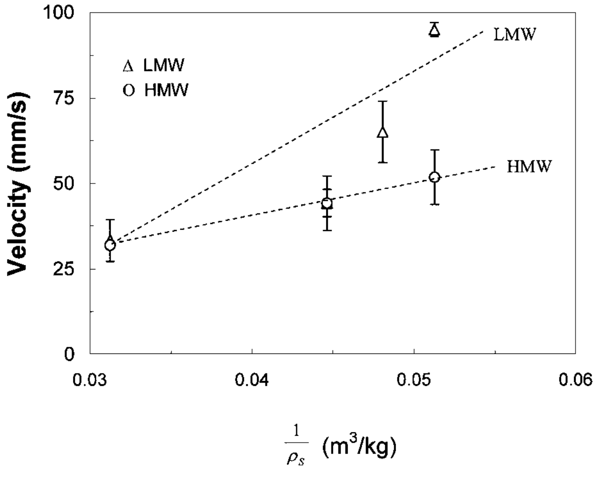

Figure 8 Average flow velocity as a function $1/\rho_S$. Symbols correspond to measured data while the dotted lines are best fit lines for the two sets of data. (ρ_S = Pattern density, HMW: M_w = 304,000 g/mol, LMW: M_w = 152,000 g/mol).

The viscous residue formed during mold filling can contribute significantly to defect formation in the casting [2]. Preliminary experiments have shown that a greater number of defects were observed in patterns with a M_w = 304,000 g/mol than in patterns with a M_w of 152,000 g/mol [7]. Thus, a lowering of M_w from the typical value of 300,000 g/mol may be beneficial. However, this reduction in M_w may affect the strength and handling properties of the pattern. An appropriate combination of M_w and density may have to be designed based on the casting conditions, i.e., reduce M_w and increase density. For the patterns used in this study, E at a density of 20.8 kg/m^3 was 2.29 MPa and 3.83 MPa for M_w of 152,000 g/mol and 304,000 g/mol respectively. In order to achieve an E of 3.83 MPa at a M_w of 152,000 g/mol, the density has to be increased to about 26 kg/m^3 (based on Equation 2).

The principal goal of reducing the M_w of EPS for lost foam casting was to control the kinetics and products of degradation. Several other techniques have been reported in the literature to control the pyrolysis products of polystyrene. A suitable blending of low and high density fragments has been found to affect the composition of pyrolysis products [44]. The degradation process can be controlled through the use *para*-substitution with electron donating (CH_3, NH_2) or electron attracting substituents (Cl, Br) [45]. The degradation Poly(α-methyl styrene) results in almost 90% monomer conversion at 1073°K, compared to about 60% for polystyrene [22, 46]. Further, the nature of degradation can be controlled through the use of additives [4]. A variety of additives have been reported to affect the degradation, combustion and flame retardant properties of polystyrene [47]. For example, the hydrous pyrolysis of polystyrene increases the fraction of volatile products (i.e., monomer yield) and may lower the extent of oligomer formation [32]. Although, water is clearly not desirable for patterns used in lost foam casting, other additives may be considered to tailor the degradation process based on part geometry and casting conditions.

The results presented here indicate that the molecular characteristics of EPS may have a substantial effect on casting quality. It has been shown previously that bead fusion in the pattern is another important factor controlling mold filling and defect formation [7]. Casting formation in the lost foam process has been studied extensively. The influence of alloy composition, coating and sand properties and gating system design has been investigated [48–50]. The data shown above suggest that the pattern properties may play an equally important role in controlling casting soundness. Production of sound castings entails a proper control over polymer M_w and polydispersity and pattern density, cell size and bead fusion.

4. Conclusions

The molecular weight and density of the pattern play major roles in mold filling and casting formation. In EPS patterns, the major factors controlling the mechanical properties of the foam are density, molecular weight, cellular characteristics and bead fusion. In general, the modulus and strength increase with density, molecular weight and improved bead fusion. As the molecular weight increases, the styrene monomer yield increases, the fraction of dimers, trimers and other minor products decreases. The monomer yield reaches a peak at about 1073°K and M_w greater than 50,000 g/mol. These conditions are attained in the lost foam process where the typical M_w is on the order 300,000 g/mol and the pouring temperature is 1023°K. However, it appears that a lowering of M_w from the current value of 300,000 may be beneficial. A smaller bead collapse temperature, a higher volatilization rate and a lower mold fill time are observed as the M_w is reduced from 304,000 g/mol to 152,000 g/mol. The mold fill time is also proportional to the pattern density. As the M_w is reduced, the fraction of EPS transformed to oligomers decreases, and hence, the propensity for defect formation in the casting may be lowered. However, a reduction in polymer M_w may adversely impact the strength and dimensional stability of the foam. In addition, the molding and handling properties of the pattern may also be affected. It becomes imperative, therefore, to achieve a suitable balance between various parameters associated with the pattern such as M_w, polydispersity, density, cell size and bead fusion in order to control the quality of the casting. The optimum pattern properties needed for a given casting may depend on several factors including part geometry, gating system, alloy composition and the properties of the coating and the mold media.

Acknowledgements

A portion of this work was supported by General Motors Corp., Saginaw, MI. The authors gratefully acknowledge this support.

References

1. E. H. NIEMANN, *AFS Trans.* **95** (1988) 793.
2. S. SHIVKUMAR and X. YAO, *Scr. Metall. Mater.* **33** (1995) 39.
3. L. BU, Y. WAN, H. LITTLETON and J. MAYS, *Ameri. Chem. Soc., Polym. Prep.* **40**(2) (1999) 689.
4. D. KLEMPNER and K. FRISCH, "Handbook of Polymeric Foams and Foam Technology" (Hanser Publishers, New York, 1991).
5. T. FARAVELLI, M. PINCIROLI, F. PISANO, G. BOZZANO, M. DENTE and E. RANZI, *J. Anal. Appl. Pyrolysis* **60** (2001) 103.
6. J. ROSSACCI and S. SHIVKUMAR, *J. Mater. Sci.* **38**(2) (2003) 201.
7. M. SANDS, M.S. thesis, Worcester Polytechnic Institute, Worcester, MA, 1998.
8. N. NAKANO and S. HASEGAWA, *J. Soc. Mater. Sci. Jpn.* **33** (1984) 1206.
9. G. XUE, Y. LU, G. SHI and Q. DAI, *Polymer.* **35** (1994) 892.
10. P. J. FLORY, *J. Amer. Chem. Soc.* **67** (1945) 2048.
11. B. H. BERSTED and T. G. ANDERSON, *J. Appl. Polym. Sci.* **39** (1990) 499.
12. J. F. FELLERS and T. F. CHAPMAN, *ibid.* **22** (1978) 1029.
13. L. J. GIBSON and M. F. ASHBY, "Cellular Solids," (Cambridge University Press, Cambridge, 1997).
14. L. DI LANDRO, G. SALA and D. OLIVIERI, *Polym. Test.* **21** (2002) 217.
15. F. RAMSTEINER, N. FELL and S. FORSTER, *ibid.* **20** (2001) 661.
16. P. JARVELA, J. SARLIN, P. JARVELA and P. TORMALA, *J. Mater. Sci.* **20** (1986) 3139.
17. P. R. STUPAK, W. O. FRYE and J. A. DONOVAN, *J. Cell. Plast.* **27** (1991) 484.
18. P. R. STUPAK, W. RUSSELL and J. A. DONOVAN, "Microstructural Science," Vol. 18, edited by T. A. Place, J. D. Braun, W. E. White and G. F. Vander Voort (1990) 505.
19. C. STAFFORD, T. P. RUSSELL and T. J. MCCARTHY, *Macromolecules* **32** (1999) 7610.
20. T. FEN-CHONG, E. HERVE and A. ZAOUI, *Eur. J. Mech. A/Solids* **18** (1999) 201.
21. P. A. BERMAN, *Z Metallkd.* **29** (1973) 31.
22. S. L. Madorsky, "Thermal Degradation of Organic Polymers," (Interscience Publishers, New York, 1964).
23. C. BOUSTER, P. VERMANDE and J. VERON, *J. Anal. Appl. Pyrolysis.* **15** (1989) 249.
24. I. C. MCNEIL, M. ZULFIQUAR and T. KOUSAR, *Polym. Degradation. Stab.* **28** (1990) 131.
25. M. R. NYDEN, T. R. COLEY and S. MUMBY, *Polym. Eng. Sci.* **37** (1997) 1496.
26. P. T. WILLIAMS and E. A. WILLIAMS, *Environ. Tech.* **20** (1999) 1109.
27. M. T. SOUSA PESSOA DE AMORIM, C. BOUSTER, P. VERMANDE and J. VERON, *J. Anal. Appl. Pyrolysis.* **3** (1981) 19.
28. A. KARADUMAN, E. H. SIMSEK, B. CICEK and A. Y. BILGESU, *ibid.* **60** (2001) 179.
29. M. YANG and Y. SHIBASKI, *J. Polym. Sci. Part* A **36** (1998) 2315.
30. L. DEAN, S. GROVES, R. HANCOX, G. LAMB and R. S. LEHRLE, *Polym. Degradation Stab* **25** (1989) 143.
31. H. OHTANI, T. YUYAMA, S. TSUGE, B. PLAGE and R. H. SCHULTEN, *Eur. Polym. J.* **26** (1990) 893.
32. P. L. BELTRAME, L. BERGAMASCO, P. CARNITI, A. CASTELLI, F. BERTINI and G. AUDISIO, *J. Anal. Appl. Pyrolysis.* **40/41** (1997) 451.
33. J. KRSTINA, G. MOAD and D. SOLOMON, *Eur. Polym. J.* **25** (1989) 767.
34. G. MADRAS, G. Y. CHUNG, J. M. SMITH and B. J. MCCOY, *Ind. Eng. Chem. Res.* **36** (1997) 2019.
35. D. DONG, S. TASAKA and N. INAGAKI, *Polym. Degradation. Stab.* **72** (2001) 345.
36. T. SAWAGUCHI and M. SENO, *J. Polym. Sci. Part* A **36** (1998) 209.
37. M. SWISTEK, N. B. ISMAIL and D. NICOLE, *Polym. Recyc.* **3** (1997/98) 67.
38. D. DAOUST, S. BORMAN, R. LEGRAS and J. P. MERCIER, *Polym. Eng. Sci.* **21** (1981) 721.
39. M. GUAITA, *Br. Polym. J.* **18** (1985) 226.
40. J. RIEGER, *J. Therm. Anal.* **46**(3/4) (1996) 965.
41. L. H. SPERLING, "Introduction to Physical Polymer Science," 2nd ed. (John Wiley & Sons, Inc., New York, 1992).
42. S. MEHTA, M. S. thesis, Worcester Polytechnic Institute, Worcester, MA, 1992.
43. S. SHIVKUMAR and B. GALLOIS, *Trans. AFS.* **95** (1987) 801.
44. Z. DOLEZAL, V. PACAKOVA and J. KOVAROVA, *J. Anal. Appl. Pyrolysis.* **57** (2001) 177.
45. V. V. ZUEV, F. BERTINI and G. AUDISIO, *Polym. Degradation. Stab.* **71** (2001) 213.
46. O. S. WOO, T. M. KRUSE and L. J. BROADBELT, *ibid.* **70** (2000) 155.
47. G. BERTELLI, *ibid.* **20** (1988) 271.
48. S. BAKHTIYAROV and R. OVERFELT, *J. Elastomers Plast.* **32** (2000) 73.
49. E. N. PAN and K. Y. LIAO, *J. Chin. Soc. Mech. Eng. Trans. Chin. Inst. Eng. Ser.* C **21** (2000) 283.
50. Q. CHEN and C. RAVINDRAN, *J. Mater. Eng. Perform.* **9** (2000) 386.

Received 9 August 2002
and accepted 26 February 2003