Temperature Gradients in Molten Polymers During the Cooling Process

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ABSTRACT: Temperature gradients of various molten polymers during the cooling process were examined using a cooling jacket apparatus coupled with a novel temperature sensor. The temperature gradients appeared to be influenced by the heat transfer between the cooling medium and the polymer, the melt temperature, and crystallization temperature of the polymers. The results were then compared with theoretically generated data. The simple theoretical model yields a good comparison with the experimental data at the center of the duct but the accuracy is more limited at other radial positions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3268–3274, 1999

Key words: molten polymers; temperature gradient; crystallization temperature; melt temperature; cooling process

INTRODUCTION

The manufacture of an article from polymer involves heating, shaping, and cooling processes. As a result of these processes, the polymer melt in the processing equipment can be subject to large temperature distributions. The rate of cooling usually is a main parameter in determining the rate of polymer production and the degree of crystallinity of the polymer products, thus determining their physical properties. In the case of injection molding, cooling time not only determines the cycle time of the process but also influences the properties of the end products such as degree of crystallinity, residual stress, molecular orientation, and shrinkages.[1] Since thermal conductivity of polymer is generally low, cooling is not instantaneous. Changes in the size and thickness of the product also result in changes to the cooling time and thus the properties of the product.

It is essential to determine the effect of cooling and crystallization on the temperature gradients of polymer melts during the cooling process. This present work was carried out by designing a cooling jacket apparatus that, with the use of a novel temperature sensor,[3,4] allowed a cooling process of various thermoplastic melts to be followed. In addition, the effect of cooling rate was also examined using DSC. The experimental results were then directly compared with theoretically generated data.
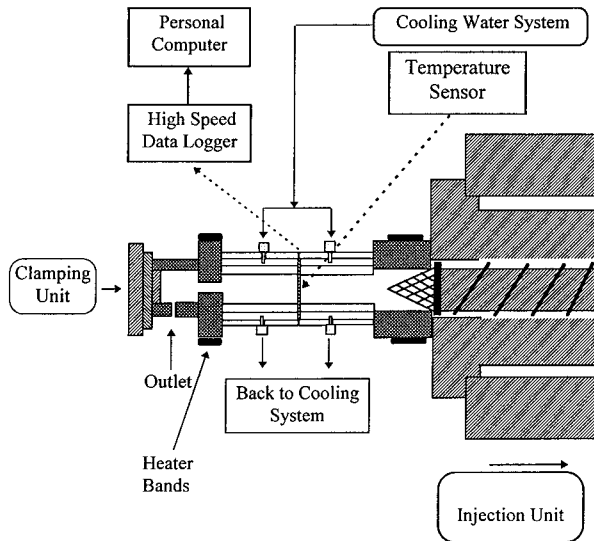
EXPERIMENTAL

Apparatus Design

Figure 1 shows an arrangement of the cooling jacket apparatus used to measure the temperature gradient of various polymers during rapid cooling process. The apparatus was attached be-

Figure 1 An experimental arrangement of the cooling jacket apparatus.

tween the injection and clamping units of the injection molding machine (Negri Bossi NB60, Italy). The jacket was made of stainless steel with a water channel. A novel temperature sensor was inserted between the front and rear sections of the jacket. The novel temperature sensor involved the construction of thermocouple mesh originally designed by Wood et al.[4] The sensor used consists of series of thermocouples forming an interconnected mesh, perpendicular wires that were made of two dissimilar materials, a Chromel–Alumel mesh constructed from wires of 0.25 mm used in this work. The electromotive force at each junction, and hence the temperature at the junctions, can be determined by measuring the voltages around the periphery of the mesh and using Kirchhoff's Law to analyze the network of junctions. The mesh is typically supported around its periphery using a suitable nonmetallic supporting frame. More detail of the temperature sensor can be obtained elsewhere.[3–4] The temperature measurement was taken at different points across the duct radius (10 mm), the measured points being 0.5, 1.5, 2.8, 5.9, and 8.8 mm away from the duct center, which corresponded to reduced radius (r/R) of 0.05, 0.15, 0.28, 0.59, and 0.88, respectively. The temperature measurement was taken using a high-speed data logger that was connected to a personal computer. The cooling unit was supplied with chilled water at approximately 15°C at the inlet and at the outlet, the temperature was between 60 and 15°C, at the

start of each test and at the end of the test, respectively. Four commercial polymers were used, including a low-density polyethylene (LDPE, Exxon LD100BW), a high-density polyethylene (HDPE, HOSTALEN GA7260), a polypropylene (PP, MOPLEN 3400MN1), and a polystyrene (PS, LACQRENE 1540/1), all being supplied by Exxon Chemical (Belgium).

Procedure

The experimental procedure was as follows:

1. Having assembled the apparatus shown in Figure 1, the apparatus was filled with polymer melt by screw rotation and left to achieve a thermal equilibrium, which took about 30 min.[3] The apparatus temperature was 170°C.
2. The chilled water supply was turned on, and the water passed through the cooling jacket of the apparatus. After approximately 5 s, temperature measurement was initiated, after which the radial melt temperatures were taken as a function of time. Note that the chilled water was continuously flowing through the apparatus during this period.
3. After 30 min the chilled water was turned off and the cooling unit was disassembled.
4. The apparatus was heated up again until the polymer was melted in order to facilitate disassembly. The experiment was then repeated from steps 1 to 3 using different polymers.

RESULTS AND DISCUSSION
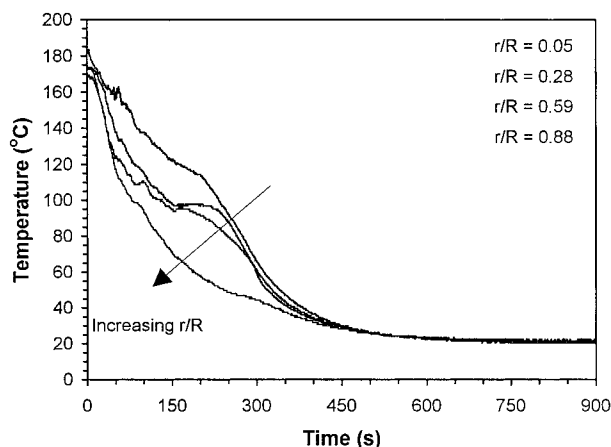
Discussion of Experimental Results

Semicrystalline Polymers

Figures 2 and 3 show the results of the temperature gradients as a function of cooling time at various points in the circular duct for the LDPE and HDPE, respectively. It was found that the temperature gradients were different. The slope of each curve represented the local rate of cooling of the polymer layers. Near the duct wall (r/R of 0.88), the local rate of cooling was relatively rapid compared to that at the duct center. This was expected due to the low thermal conductivity of the polymer melts. With the LDPE, plateau values of temperature were seen around 95 to 100°C,
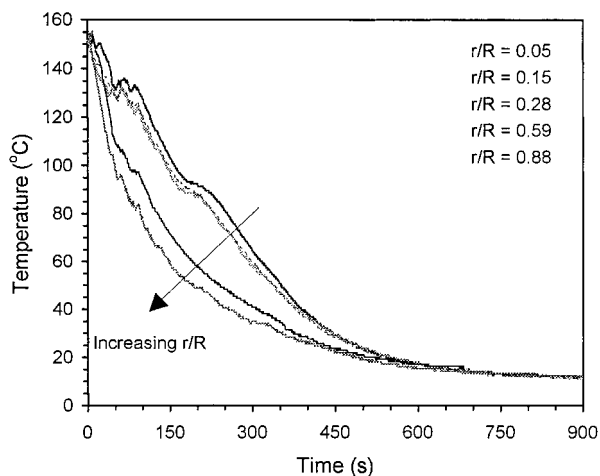
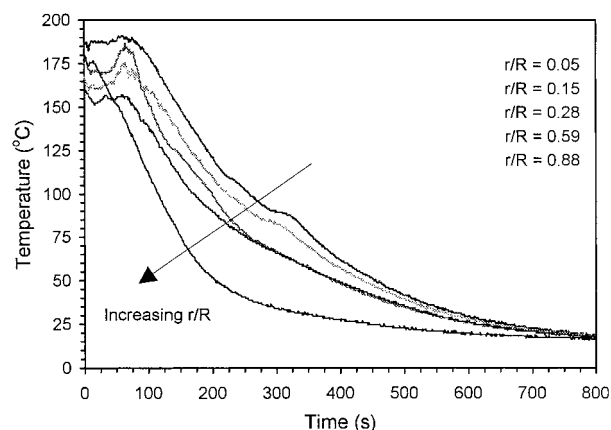**Figure 2** Temperature gradients of the LDPE during cooling.

Table I Crystallization Temperature of the Polymers for a Cooling Rate of 5°C/min Using DSC

Polymers	Crystallization Temperature, T_c (°C)
LDPE	98
HDPE	118
PP	125

whereas that of the HDPE was about 115 to 120°C. These temperatures were observed to be the crystallization temperatures (T_c), experimentally measured using the DSC technique; the results are listed in Table I. T_c was taken as the temperature at which the peak of the exotherm occurred. T_c of the LDPE and HDPE were 97 and 118°C, respectively. It is widely accepted that at the crystallization temperature a semicrystalline polymer undergoes an exothermic transformation, during which heat is conducted out due to the change of state.[5] Therefore at this temperature, while heat is still being conducted away, the energy released by the transformation is the dominant factor. It should be noted that the cooling rates of the melts before and after the crystalli-

zation temperature were different. The rate of cooling before crystallization occurred seemed to be higher due to the fact that the temperature gradient between the melts and the cooling medium were relatively high.

Another significant feature was the temperature step seen around temperatures of 135°C with the LDPE and 160°C with the HDPE. These are in the range of their crystallization temperatures. The crystallization process is progressive. As the outer layers crystallize, the inner layers are still molten. The exotherm associated with crystallization disturbs the temperature gradient in the system and so, temporarily, heat losses from the inner layers are slow and may possibly stop.

Figure 4 shows the temperature gradients of the PP at different points in the duct as a function of time. Similar results were obtained as for the LDPE, such that the temperature decreased with time, a step that was present around the crystallization temperature ($T_c = 125$°C for PP). It should be noted that the times taken to reach the uniform temperature (temperature of the chilled

Figure 3 Temperature gradients for the HDPE during cooling.

Figure 4 Temperature gradients of the PP during cooling.

**Table II   Effect of Cooling Rate on Crystallization Temperature of the LDPE**

Run No.	Cooling Rate (°C/min)	Crystallization Temperature (°C)
1	5	94
2	10	90
3	15	86
4	20	84

water) were different for the three polymers. This was due to: (1) the low thermal conductivity of the PP as compared to the LDPE,[6] and (2) the higher heat of fusion of the PP as compared to the LDPE.[5,7]

Table II shows the crystallization temperature of the LDPE with different cooling rates obtained by the DSC technique. It was found that the crystallization temperature increased with decreasing rate of cooling.

Amorphous Polymer

Polystyrene was used as an amorphous polymer for comparison purposes. The temperature of the polymer at different positions in the duct radius is shown in Figure 5. No obvious step change in the melt temperature was seen, due to the fact that the polymer does not crystallize. It was interesting to note that, although the thermal conductivity of the PS was less than those found with the semicrystalline polymers (such as LDPE and PP), the time taken to reach the uniform temperature was faster. This arose due to the absence of a
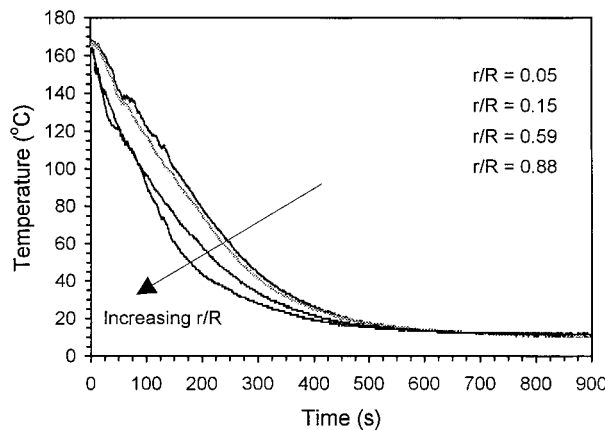
Figure 5 Temperature gradients of the PS during cooling.
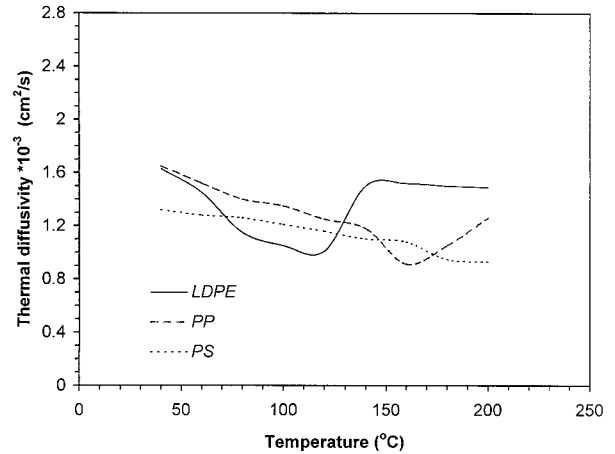
Figure 6 Thermal diffusivity of various polymers as a function of temperature.

crystallization exotherm found with the semicrystalline polymers.

Comparison of Experimental and Theoretical Results

The theoretical analysis was based on the Fourier equation for nonsteady heat transfer in one dimension x, shown in eq. 1[8]:

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha}\frac{\partial T}{\partial t} \tag{1}$$

where T is temperature and α is the thermal diffusivity.

The solution to the preceding partial differential equation is conveniently expressed in graphical form, which is the plot of the dimensionless temperature gradient (T^*) against the Fourier Number (F_o). These two dimensionless parameters can be obtained by eqs. 2 and 3:

$$T^* = \frac{T_3 - T_2}{T_1 - T_2} \tag{2}$$

$$F_o = \frac{\alpha t}{x^2} \tag{3}$$

where T_1 = initial uniform melt temperature
T_2 = temperature of cooling medium
T_3 = temperature at time t
x = radius of the cylinder

It should be noted that α values in eq. 3 are found to change with temperature.[7] In this analysis, the
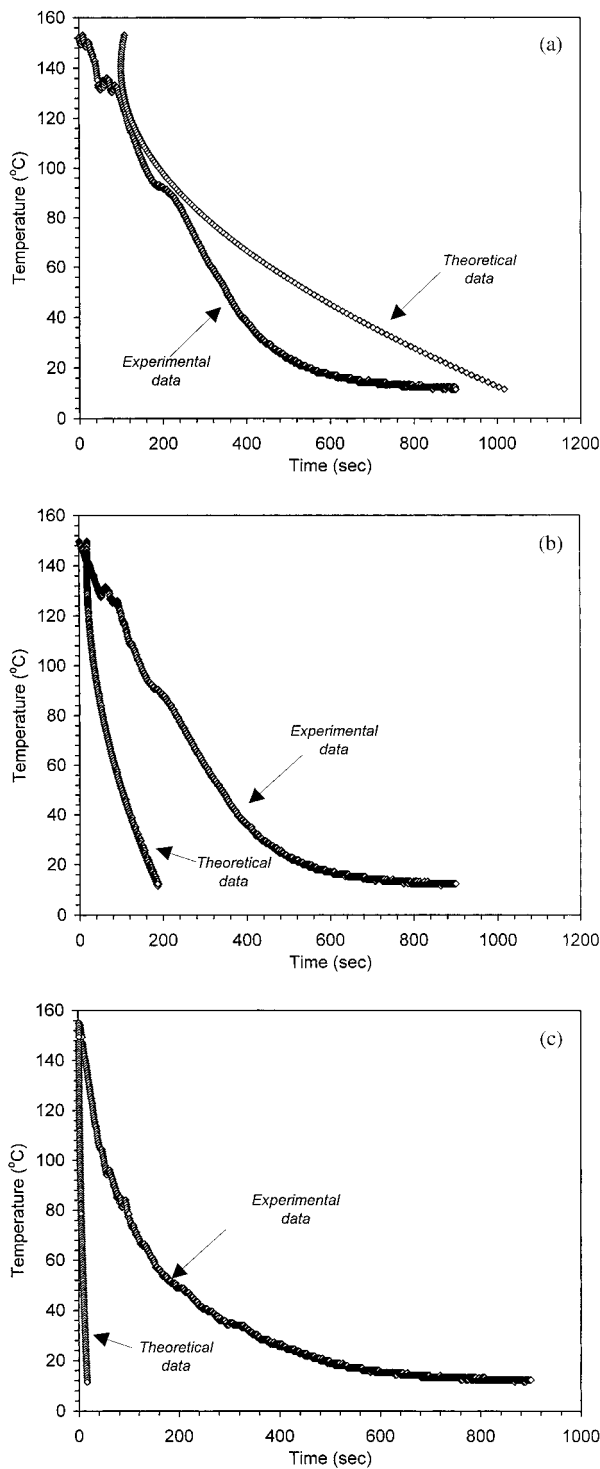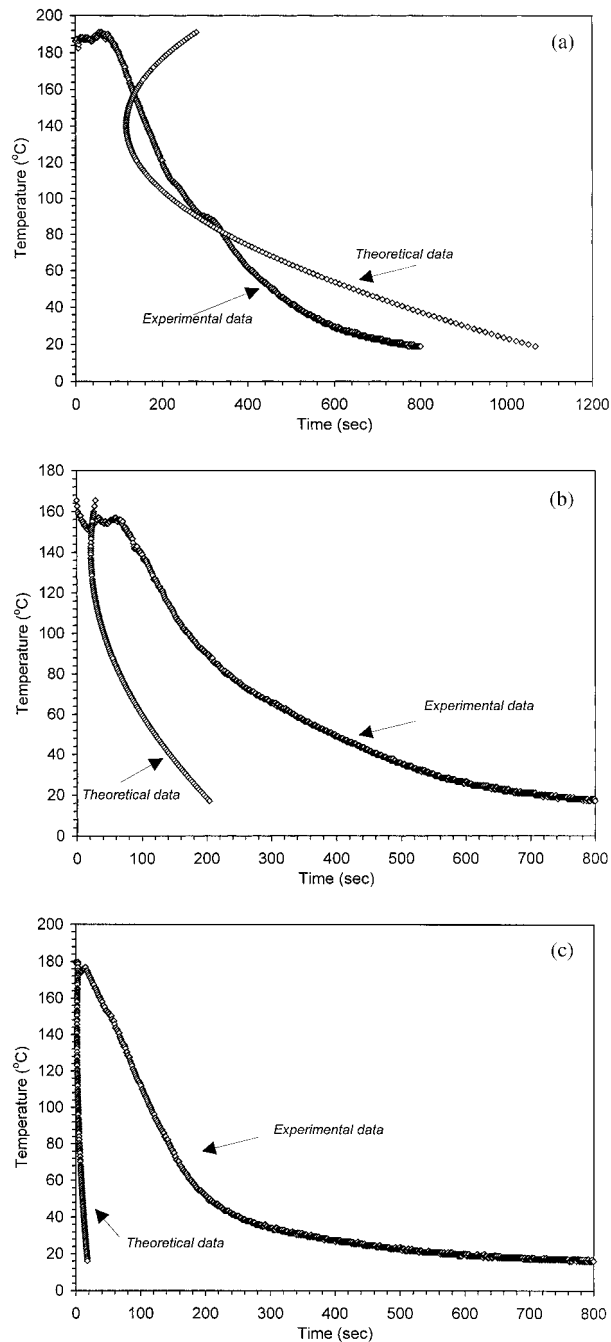
Figure 7 Comparison of theoretical and experimental temperature gradients for the LDPE during cooling. (a) r/R = 0.05; (b) r/R = 0.59; (c) r/R = 0.88.

values of thermal diffusivity used were obtained experimentally for the specific temperature of interest; the results are shown in Figure 6. The

theoretically calculated results of the cooling curves for the LDPE at various radial positions across the duct are shown in Figures 7, 8, and 9, in which the selected experimental results are also used for comparisons.

The curves indicated that the theoretical cooling time for the polymer to reach the uniform

Figure 8 Comparison of theoretical and experimental temperature gradients for the PP during cooling. (a) r/R = 0.05; (b) r/R = 0.59; (c) r/R = 0.88.
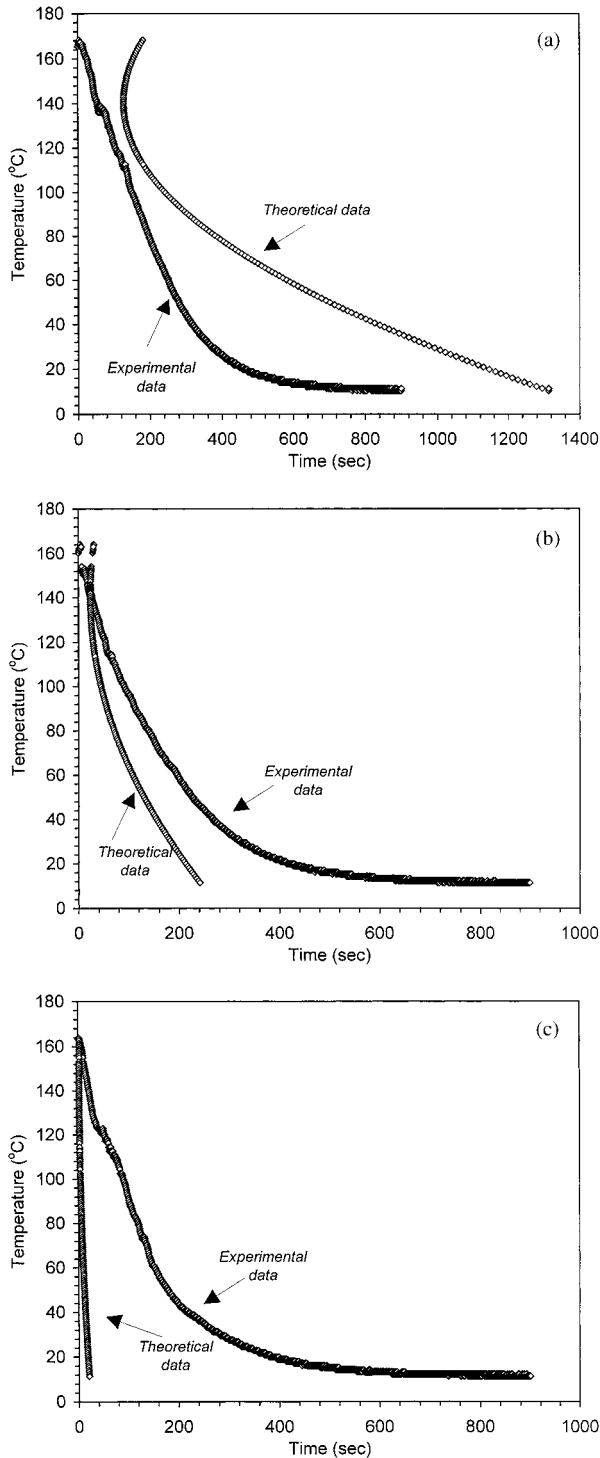
Figure 9 Comparison of theoretical and experimental temperature gradients for the PS during cooling. (a) r/R = 0.05; (b) r/R = 0.59; (c) r/R = 0.88.

temperature was much shorter than that found experimentally. In the case of the LDPE and PP at r/R of 0.05, the theory is in reasonable agree-

ment with the practical results until the crystallization exotherm occurs. It should be noted that the deviation in the theoretical curve for the PP at higher temperatures arises due to the changing thermal diffusivity of the polymer in that temperature region, which is in the crystalline melting range. After the crystallization temperature is reached, the differences between the theoretical and experimental sets of data become much greater. This is not surprising, as the theory does not take account of the exothermic crystallization process. Nearer the wall of the duct, at r/R of 0.88, the theoretical and the practical data are very different and it is thought that this arises due to the crystallization exotherm coupled with the boundary conditions at the wall/melt interface used in the derivation of the theory. It is noticeable that the deviation from the theory at higher values of r/R is greater with PP than with LDPE. It is thought that this difference arises due to the slightly higher energy of crystallization found in the case of the polypropylene coupled with its lower thermal conductivity.[6,7] In the case of the crystallization process, the energy released is very significant, being the equivalent of an approximate rise in the temperature of the melts of 20 to 30°C.[6,7] Thus the energy released on the crystallization of the polypropylene is slightly higher than that found with the LDPE; this heat is being conducted away more slowly than is found with LDPE, and so the deviation from the theory is greater.

In the case of the polystyrene, again the theory provides a good fit to the experimental data at the center of the duct, with an increasing deviation at the T_g of the polymer. At r/R values closer to the wall, the deviation of the theoretical data from the experimental data is less than that found with LDPE, which was expected as there are no crystallization effects occurring.

In summary, the intention of this study was to highlight that the simple theory is, in fact, a good model only for the temperature at the center of a duct. This is of great practical significance from the manufacturer's point of view as solidification at this point represents an end point to the effective molding cycle. This work also illustrates just how long the actual cooling time to around room temperature is, in practice, and the extent to which this deviates from the simple theory.

CONCLUSIONS

The cooling time for polymer melts during the cooling process can be accurately determined only

by using the Fourier equation at the core section of the moldings. The temperature gradients appeared to be influenced by the heat transfer between the cooling medium and the polymer, the melt temperature, and crystallization temperature of the polymers. The temperature gradients and the time taken to reach the uniform temperature of the PS were simpler and faster, respectively, than those observed with the LDPE and PP. In all polymers used, the simple theoretical model yields a good comparison with the experimental data at the center of the duct, but the accuracy is more limited at other radial positions.

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