

Effects of Glass-Fiber Content and Coolant Temperature on Temperature and Crystallinity Profiles of PP Melt During Cooling

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ABSTRACT: This investigation studied the temperature gradients and degree of crystallinity of polypropylene melt across a circular duct during the cooling process, where the coolant used was chilled water. The effects of glass-fiber content, varying from 0 to 44 wt %, and coolant temperature, varying from 5 to 20°C, were our main interest. The results suggested that the rate of cooling of the polymer of each position across the duct was not significantly affected by the temperature of the coolant and glass-fiber contents, although the rate of cooling was influenced by the size of the duct. The crystallization temperature and degree of crystallinity of the polymer increased with increasing glass fiber contents and the coolant temperature. These phenomena were associated with the heat transfer between the coolant and the polymer, crystallization temperature, exothermic crystallization process, and thermal properties of the polymer. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2087–2097, 2001

Key words: temperature gradients; polymer melts; crystallization; cooling effects; degree of crystallinity; glass fibers

INTRODUCTION

One of the important factors that determines the quality of an injection-molded part is temperature during the cooling stage. As the first approximation, the cooling stage is regarded as the longest cycle, whereas the injection stage usually accounts for only a small portion of the molding cycle.¹ An effective heat extraction is importantly required under

the cooling stage because it reduces the cycle time. The effective cooling is normally achieved using chilled water as a coolant. Generally the temperatures of the mold surface are in the range of 5–10°C up to 40–50°C for most thermoplastics.² In injection molding, the rate of cooling is a main parameter in determining not only the production rate but also the properties of the end products, such as degree of crystallinity, residual stress, molecular orientation, and shrinkage.³ The most desirable cooling is to obtain a rapid rate of cooling with uniform temperature across the face of the mold.

There are many researchers^{4–6} investigating the cooling behavior of molten polymers during the cooling stage in injection molding, carried out using various computer-aided design (CAD) sys-

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tems. Hu et al.⁴ investigated the effect of cooling system design and process parameters (such as part thickness, mold thermal properties, coolant temperature, cycle time) on cyclic variation of mold temperatures using the dual reciprocity boundary element method (DRBEM) in the injection-molding process. Higher temperature fluctuation was found near the mold surface, which was dependent on the distances to the cooling channel. The mold thermal property (thermal conductivity) and coolant temperature were observed to have a considerable effect on the variations in mold temperature values, whereas the effects of cycle time and part thickness were not significant. More details on the influence of mold temperature on the properties of the end products were summarized by Friel.⁵ Opolski and Kwon⁶ developed and redesigned a CAD system for cooling analysis of molten polymers during the cooling process in injection molding, aiming to achieve balanced cooling between the core and cavity parts of a mold. The results showed that the modified version of the CAD system gave more effective cooling performance through the molding thickness.

Piorkowska⁷ studied the thermal effects such as thermal conductivity and diffusivity of a polymer during crystallization. It was shown that the liberation of latent heat of fusion caused the increase of the temperature inside the polymer and thus slowed down the rate of conversion of melt into spherulites. The work also indicated that the increase of the temperature resulted in the increase of thermal conductivity and diffusivity. Recent work by Sombatsompop et al.⁸ experimentally studied the temperature gradients of various types of thermoplastics during the cooling process using a cooling jacket apparatus coupled with a novel temperature-sensing device originally developed by Wood and colleagues,⁹ the experimental results of which were also compared with those obtained in theory. Their findings suggested that the temperature gradients were influenced by the heat transfer between the coolant and the polymer, the melt temperature, and crystallization temperature of the polymers. The crystallization process was found to slow down by the heat given out inside the polymer sample. In addition, the simple theoretical model yielded a good comparison with the experimental data only at the core part of the molding, the accuracy of which was more limited at distances away from the center of the mold.

Although the literature^{4–6,8} has many references to the temperature gradients of unfilled homopolymers during the cooling process, little attention has been given to filled polymers. Often, injection-molded products are not manufactured from one polymeric material, but blended with other types of materials such as glass fibers.³ Data on the effect of cooling on the temperature gradients and degree of crystallinity of filled molten polymer during the cooling process are required. This study presents the temperature gradients and degree of crystallinity of glass fiber-filled polypropylene melt using a cooling jacket apparatus and an exposed junction-thermocouple temperature sensor, originally developed by Wood et al.^{8,9} The effects of fiber concentration added into the polymer and coolant temperature (chilled water was used as a coolant in this study) were our primary focus. Differential scanning calorimetry (DSC) was used to determine the degree of crystallinity.

EXPERIMENTAL

Materials and Experimental Apparatus Design

The polymer used in this investigation was a polypropylene (PP, P-700-J) supplied in granular form by Thai Polymer Propylene Co. Ltd. The as-received glass fibers were supplied by Thai Retrotech Co. Ltd in the form of chopped strands. Fiber dimensions were 4.5 mm long and 13 μm in diameter. The glass fibers were added into polypropylene melt at various concentrations, ranging from 0 to 44 wt %, using a twin-screw extruder (Haake PolyLab Rheomix CTW100P, Germany). The blending conditions of glass fibers and the polymer were as used in previous work.¹⁰

An arrangement of the cooling jacket apparatus used to measure the temperature gradient of molten polymers during the cooling process is shown in Figure 1, in which the apparatus is attached at the end of the injection unit of an injection-molding machine (Elite E-80, Italy) using M12 bolts to tightly clamp the components together. The jacket was made of stainless steel with a water channel. The temperature-sensing array used, originally invented by Wood et al.,⁹ based on the use of Type K thermocouple wires, was inserted between the front and rear sections of the jacket. Because the thermocouple junctions were exposed directly to the polymer melt, there

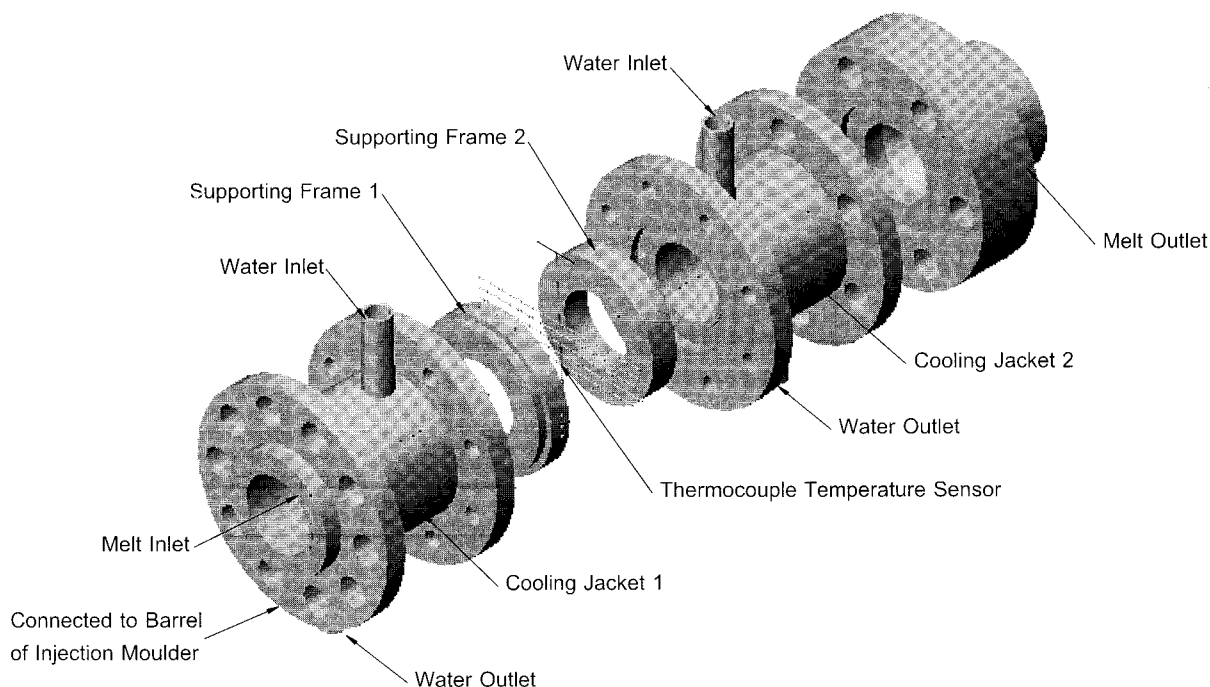


Figure 1 An experimental arrangement of cooling jacket apparatus.

were only relatively minor errors resulting from the heat-conduction and shear-heating effects during the temperature measurements. The accuracy of the temperature measurement was on the order of 2.5%. (More details concerning the temperature sensor may be obtained elsewhere.^{9,11}) The temperature measurement was taken at different points across the duct diameter (35 mm), the measured points of which were 0.0, 3.5, 7.0, 10.5, and 14.0 mm away from the center of the duct, which corresponded to reduced radius (r/R) values of 0.0, 0.2, 0.4, 0.6, and 0.8, respectively. The temperature measurements were taken using a high-speed data logger, which was connected to a personal computer. The cooling unit was supplied with chilled water whose temperatures can be varied from 5 to 20°C.

Experimental Procedure for Temperature Gradient Measurements

The experimental procedure started when the apparatus was filled with polymer melt by screw rotation and was left to achieve a thermal equilibrium, which took about 30 min.¹² The apparatus temperature used was 190°C. 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. Following that, the radial melt temperatures were taken as a function of time. The chilled water was continuously flowing through the apparatus during this period. After 45 min the chilled water was turned off and the cooling unit was disassembled. The apparatus was heated up again until the polymer was melted to facilitate disassembly. The experiment was then repeated using different chilled water temperatures and glass-fiber concentrations.

Measurement of Degree of Crystallinity

Differential scanning calorimetry (DSC) was used to determine the degree of crystallinity of the polymer, which was based on the amount of energy required to melt a specific mass of the polymer that is measured by integrating the area under the melting peaks, regarded as the heat of fusion of the sample, the details of which are found elsewhere.¹² The degree of crystallinity was measured for various radial points across the flow channel and thus the radial crystallinity profiles were determined. The experimental procedure was similar to that used for the temperature gra-

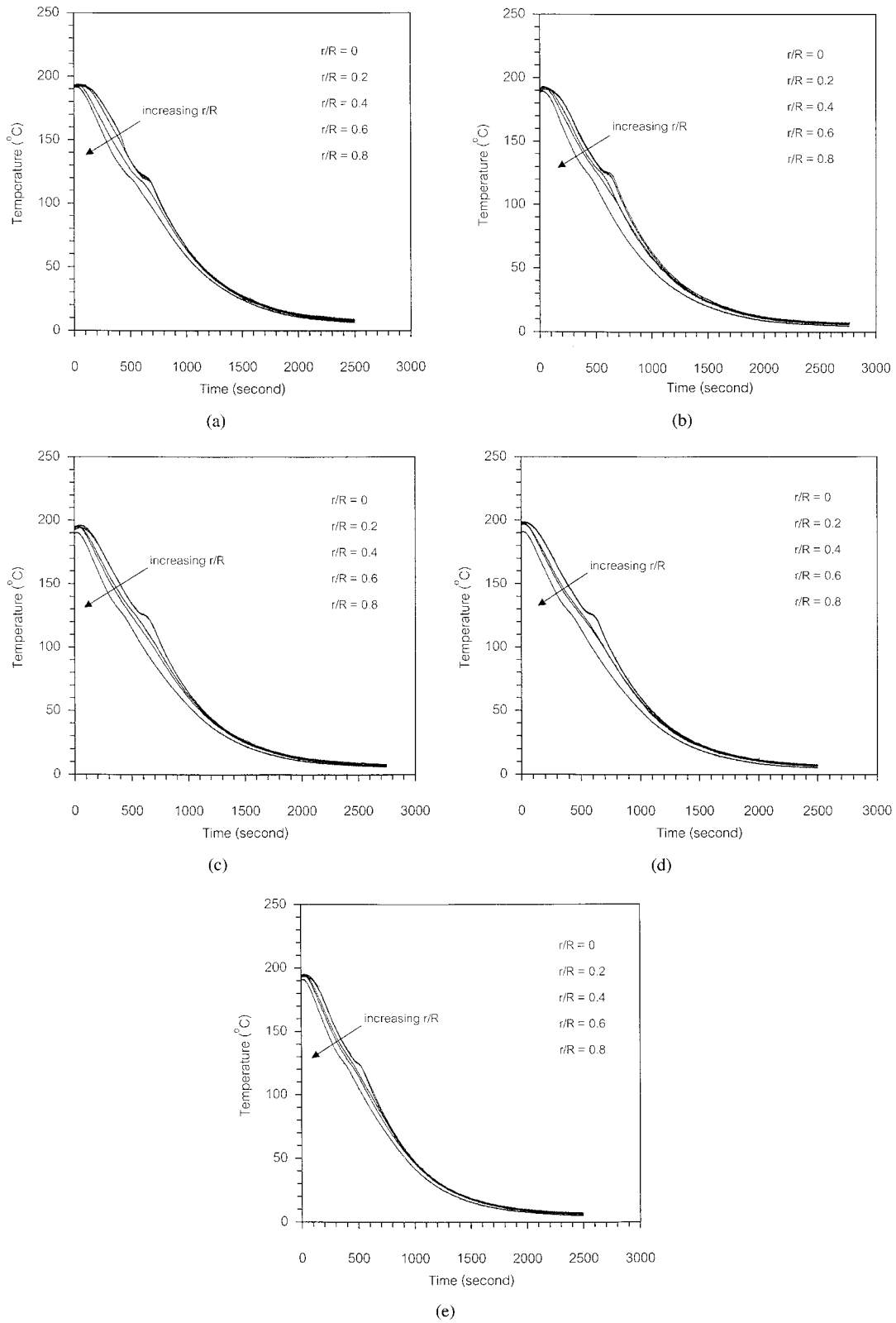


Figure 2 (a) Temperature gradients of the unfilled PP during cooling. (b) Temperature gradients of the PP filled with 17 wt % glass fibers during cooling. (c) Temperature gradients of the PP filled with 29 wt % glass fibers during cooling. (d) Temperature gradients of the PP filled with 38 wt % glass fibers during cooling. (e) Temperature gradients of the PP filled with 44 wt % glass fibers during cooling.

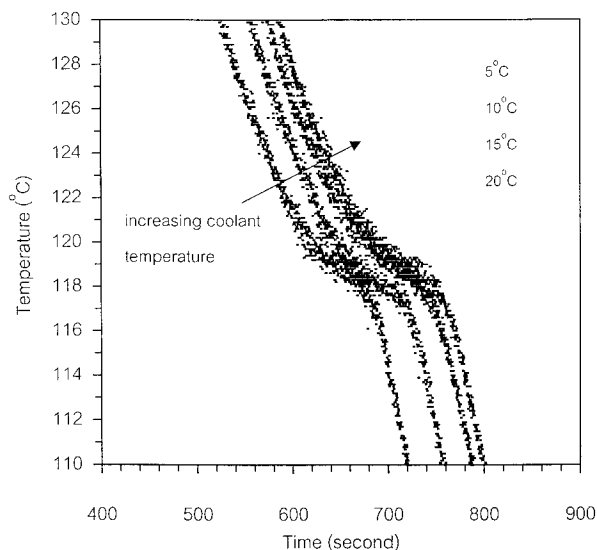


Figure 3 Temperature gradients of the unfilled PP at the duct center (r/R of 0.0) for different coolant temperatures.

dient measurement, but in this case, no temperature sensor was required. After the chilled water was turned off and the cooling unit was disassembled, the polymer rod was then taken from the apparatus. This was possible because the polymer contracted under the cooling. Small pieces of the polymer at various points across the diameter of the polymer rod were taken and the measurement of degree of crystallinity was performed. The experiment was then repeated using different chilled water (or coolant) temperatures and glass-fiber contents.

RESULTS AND DISCUSSION

Temperature Gradients

General Observations

The results of the temperature gradients as a function of time at various points across the duct, using a coolant temperature of 5°C, for the PP filled with different glass-fiber contents (ranging from 0 to 44 wt %) are shown in Figure 2(a)–(e). It was found that the glass-fiber contents did not affect the general trend of the results, in that the temperature of the polymer decreased with time. The slope of each curve represented the local rate of cooling of the polymer layers. Near the duct wall the cooling rate was relatively rapid com-

pared to that at the duct center. This was expected because of the low thermal conductivity of the polymer melt, which type of behavior was also found in previous work.⁷ In all cases, plateau values of temperature, seen around 120 to 130°C, were more pronounced around the duct center. These temperatures were observed to be the crystallization temperatures. These plateau values of temperature were caused by an exothermic transformation of the polymer melt, during which heat was conducted out because of the change of state²; the energy released by the transformation was the dominant factor while heat was still being conducted away.

Effects of Coolant Temperature and Glass Fibers

From the manufacturer's point of view the molder is often interested in the time taken for a product to solidify to a point at which it can be removed from the mold, and how long the actual cooling time of the molding process is. These are usually associated with the solidification of the melt around the duct center. Therefore, we were interested in the temperature gradients of the polymer around the duct center ($r/R = 0.0$), which were affected by coolant temperature.

Figures 3, 4, and 5 show the selected results of the temperature gradients at the duct center ($r/R = 0.0$) as a function of time, at the temperature range of 110 to 130°C, for the PP melts filled with

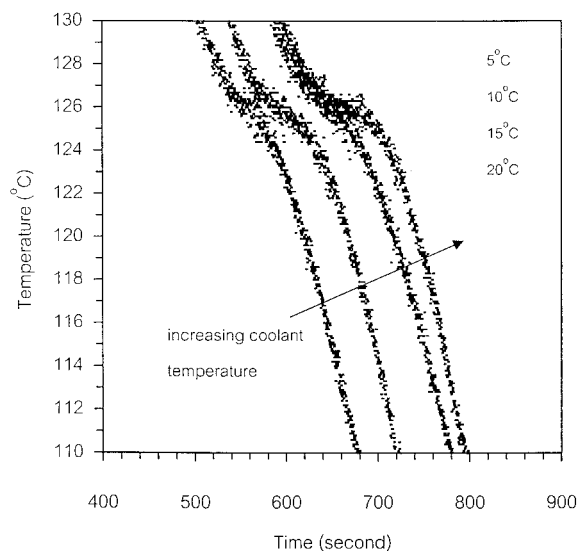


Figure 4 Temperature gradients of the PP filled with 29 wt % glass fibers at r/R of 0.0 for different coolant temperatures.

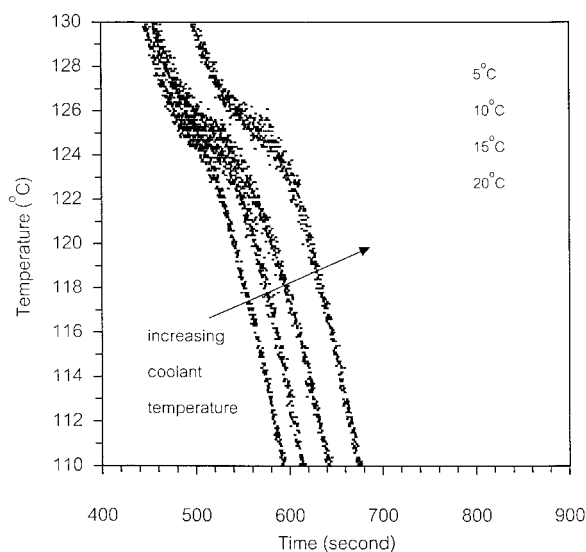


Figure 5 Temperature gradients of the PP filled with 44 wt % glass fibers at r/R of 0.0 for different coolant temperatures.

0, 29, and 44 wt % of glass fibers, respectively, for different coolant temperatures. Generally, it was found that the temperature gradients for each coolant temperature were slightly different. For the unfilled PP melt (Fig. 3), the greater the coolant temperature, the higher the crystallization temperature (this was observed by the temperature steps). This effect was more pronounced when adding the glass fibers (Figs. 4 and 5). It was also seen that the temperature steps for the unfilled PP melt were more pronounced (wider) than those for the filled PP. This may probably be attributed to an increase in the thermal conduc-

Table I Degree of Crystallinity of the Unfilled PP for Various Coolant Temperatures at 10°C Heating Rate Using the DSC Technique

r/R	Degree of Crystallinity (%) for Various Coolant Temperatures (°C)			
	5	10	15	20
0.0	39	39	39	38
0.2	39	38	38	37
0.4	38	38	37	37
0.6	36	36	36	36
0.8	34	35	35	36

Table II Uncorrected Values of Degree of Crystallinity of the PP for Various Glass-Fiber Contents at 10°C Heating Rate Using the DSC Technique

r/R	Degree of Crystallinity (%) for Various Glass-Fiber Contents (wt %)				
	0	17	29	38	44
0.0	39	34	30	27	25
0.2	38	33	29	26	24
0.4	38	32	28	25	23
0.6	36	32	27	25	23
0.8	35	31	27	24	22

tivity of the polymer that has glass fibers.¹³ The increase in crystallization temperature was observed when adding the glass fibers and the crystallization temperatures of the PP melt filled with 29 and 44 wt % glass fibers were around 124–127°C, whereas those of the unfilled PP melt were around 118–121°C. The increased crystallization temperatures attributed to the glass fibers may result from the shear caused by a difference in the thermal expansion coefficients of the polymer and the fiber during cooling.¹⁴ In this case, the glass fibers acted as foreign particles within the polymer melt, which formed a number of nuclei during cooling, thus increasing the crystallization temperature of the polymer.¹⁵

Another significant aspect to point out was the rate of cooling of the polymer. Although the polymer melt experienced different coolant tempera-

Table III Corrected Values of Degree of Crystallinity of the PP for Various Glass-Fiber Contents at 10°C Heating Rate Using the DSC Technique

r/R	Degree of Crystallinity (%) for Various Glass-Fiber Contents (wt %)				
	0	17	29	38	44
0.0	39	41	42	44	45
0.2	38	40	41	42	43
0.4	38	39	40	40	42
0.6	36	39	38	40	41
0.8	35	37	38	39	40

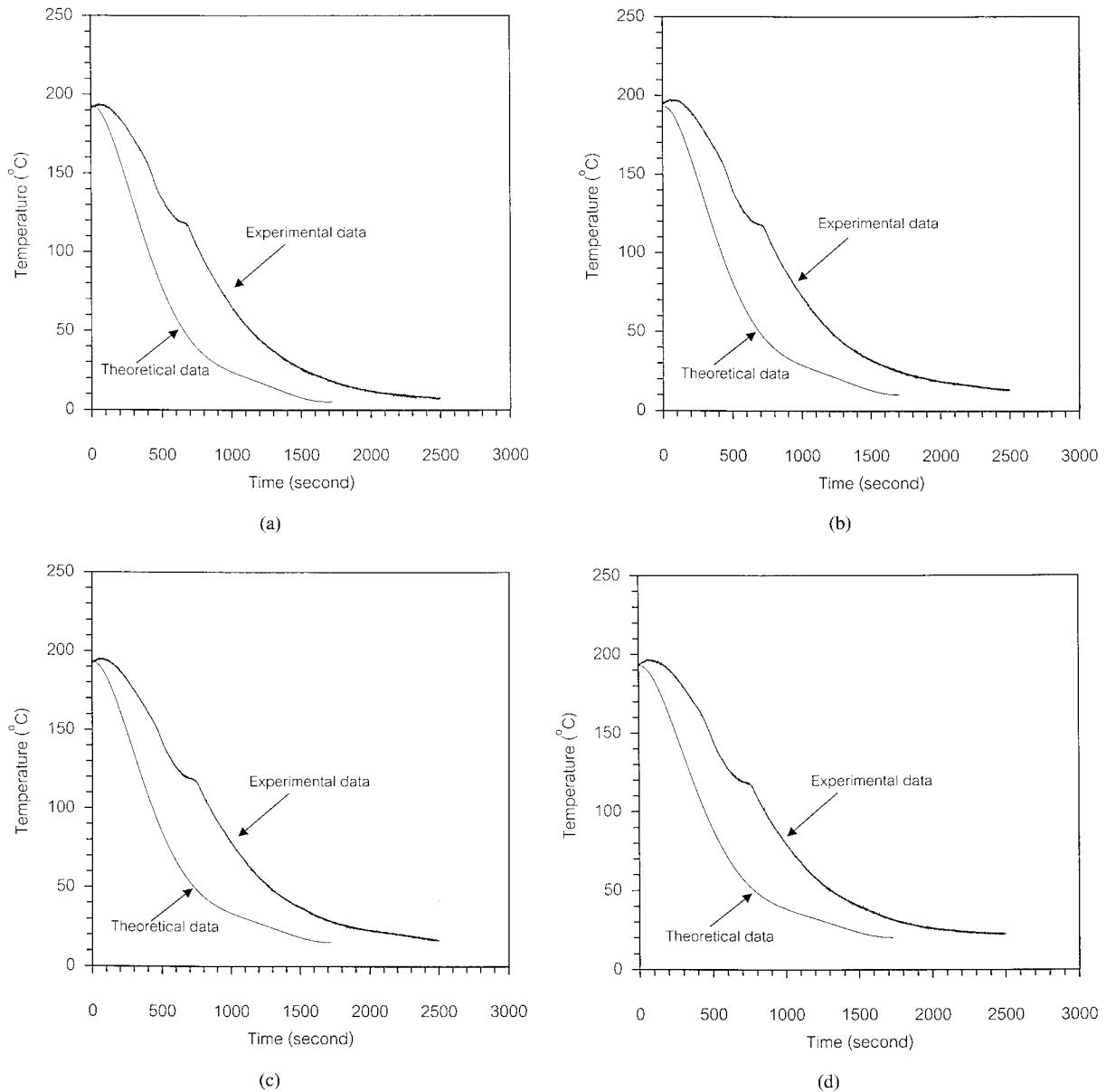


Figure 6 Comparison of theoretical and experimental temperature gradients during cooling for various coolant temperatures: (a) 5°C, (b) 10°C, (c) 15°C, and (d) 20°C.

tures, as shown in Figures 3 to 5, the rates of cooling were very similar, around 7–9°C/min (slope of the temperature gradients). This suggested that the coolant temperature had no significant effect on the rate of cooling. However, this was true exclusively when the size of the molding was large (duct diameter of 35 mm in this study). Previous work⁸ that used a duct with 20 mm in diameter showed that the rate of cooling of the PP melt of each point across the duct was different.

Near the duct wall, the local rate of cooling was relatively rapid compared to that at the duct center. With respect to the crystallization temperature, it can be observed from Figures 3 to 5 that the higher the coolant temperature, the higher the crystallization temperature, as one would expect. However, this effect was very small.

In consideration of the total cooling cycle time (the time taken for the polymer melt to reach the coolant temperature), from the results obtained

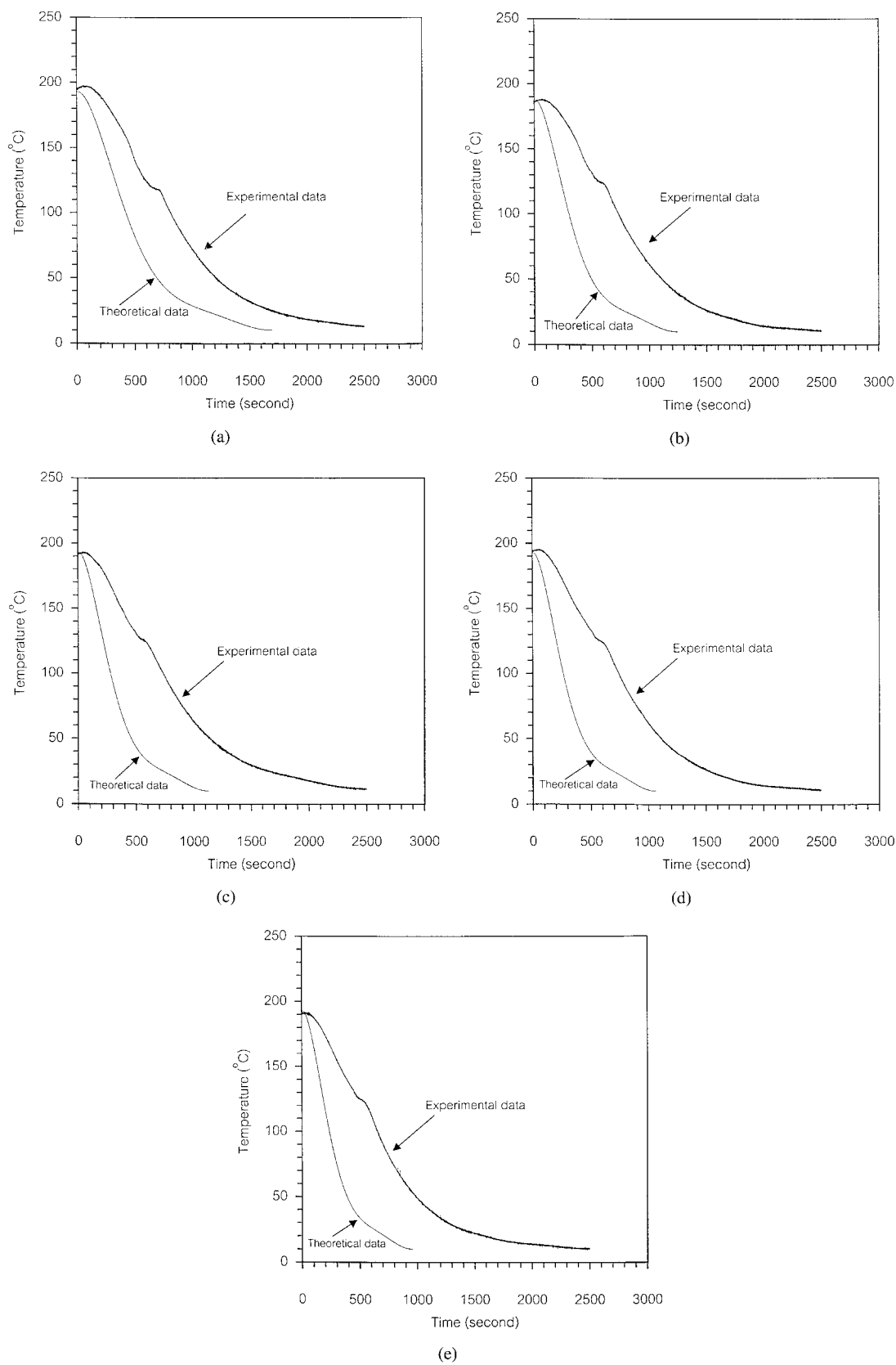


Figure 7 Comparison of theoretical and experimental temperature gradients during cooling for various glass-fiber contents: (a) 0 wt %, (b) 17 wt %, (c) 29 wt %, (d) 38 wt %, and (e) 44 wt %.

in this work, it was very difficult to specify a point at which the temperature of the melt had reached that of the coolant. For comparison purposes, the time taken for the melt that had reached a specified temperature of 110°C was used. As expected, the lower the coolant temperature, the faster the time to reach the specified temperature. In terms of the glass-fiber effect, the higher the fiber content, the faster the time to reach the specified temperature for a coolant temperature. This was associated with changes in thermal conductivity of the polymer with glass fibers.¹³

Degree of Crystallinity

Effect of Coolant Temperature

The results of changes in degree of crystallinity for the unfilled PP melt using different coolant temperatures were selected to examine the effect of coolant temperature, the values of which are listed in Table I. The results indicated that, with this type of apparatus, the coolant temperature had no significant effect on the changes in degree of crystallinity of the polymer resulting from the size of the duct, as stated. For a given coolant temperature, the values of degree of crystallinity were slightly different, probably attributed to small variations in cooling rates [comparison of the cooling curves in Fig. 2(a)–(e)]; at each point across the duct, the greater the r/R position, the less the degree of crystallinity, a result supported by the work of Kamal and Lafleur.¹⁶

Effect of Glass Fibers

Table II shows the results of the degree of crystallinity at various points across the duct for the PP melt filled with glass fibers, ranging in content from 0 to 44 wt %. It can be seen that glass fibers had an effect on changes in the degree of crystallinity. It was mentioned earlier that addition of glass fibers resulted in an increase in the crystallization temperature of the polymer. One would then expect to obtain an increase in the degree of crystallinity of the polymer with the presence of glass fibers. However, Table II indicates that the degree of crystallinity decreased with glass fiber content. The explanation for this would be related to the way the measurement was carried out. In this work, the measurement of degree of crystallinity was performed by the DSC technique, which was based on the amount of energy re-

quired to melt a specific mass of the polymer. The mass of the sample used in the measurement was the sum of weights of the polymer and the glass fibers. Thus, the measured values of degree of crystallinity in Table II may be underestimated.

To obtain the correct values of degree of crystallinity, the real mass of the polymer had to be calculated, which was carried out by subtracting the weight of the glass fibers. The corrected values of degree of crystallinity are shown in Table III. It can be seen that the degree of crystallinity increased with increasing fiber content, as expected. The magnitude of the increase in degree of crystallinity attributed to the glass fibers corresponded well to that of the crystallization temperature as mentioned earlier. For a given fiber content, the value of degree of crystallinity of each polymer layer across the duct was slightly different. This could be the result of similar reasoning as stated earlier, that is, the small variations in cooling rates at each r/R position across the duct.

Comparison of Experimental and Theoretical Results

In this work, the theoretical analysis used was based on the Fourier equation for nonsteady heat transfer in one dimension x , shown in eq. (1)^{17,18}:

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (1)$$

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_0). These two dimensionless parameters can be obtained by eqs. (2) and (3):

$$T^* = \frac{T_3 - T_2}{T_1 - T_2} \quad (2)$$

$$F_0 = \frac{\alpha t}{x^2} \quad (3)$$

where T_1 is the initial uniform melt temperature, T_2 is the temperature of the coolant, T_3 is the temperature at time t , and x is the radius of the cylinder.

It should be noted that α values in eq. (3) are found to change with temperature. In this analysis the values of thermal diffusivity of the PP used were obtained experimentally for the specific temperature of interest, the values of which were obtained from a previously published study.⁸ According to previous work,⁸ this simple theoretical analysis yielded a good comparison with the experimental data only at the center point of the duct. Therefore, the comparison of the experimental and theoretical data in this work was restricted to the center position of the duct.

The theoretically calculated results of the cooling curves for the unfilled PP at the center position of the duct for different coolant temperatures are shown in Figure 6(a)–(d), where the selected experimental results are also used for comparisons. The differences between the theoretical and experimental cooling curves for all cases were the same, the greatest difference of which was around the crystallization temperature.¹⁶ This was not surprising, given that the theory did not take account of the exothermic crystallization process. In addition, the thermal diffusivity of the polymer changes significantly around the exothermic region.⁸ For a given time, the experimental temperatures were higher than the theoretical ones. The theoretical cooling time for the polymer to reach the coolant temperature was shorter. However, it seemed that the coolant temperature and fiber content had no effect on the differences in the experimental and theoretical data.

From Figure 7(a)–(e) it can also be seen that the differences between the theoretical and experimental sets of data became greater as the fiber content was increased. Following are some possible reasons for the discrepancies. First, the calculations of temperature values did not take account of the changing thermal diffusivity of the polymer filled with various concentrations of glass fibers. It was also noted that changes in the thermal diffusivity values did not produce major changes in the calculated results. Second, the theory did not take into consideration the exothermic crystallization process. Previous work⁸ showed that a good fit of the experimental data to the theoretical data was obtained when using polystyrene because no crystallization effects occurred. Finally, all the parameters, such as thermal diffusivity and temperature of the coolant, used in the calculations were obtained by various independent methods. Moreover, the conditions under which the polymer was being processed

may be different, which would lead to an error in the calculations.

CONCLUSIONS

Temperature gradients and degree of crystallinity of polypropylene melt during the cooling process were investigated using a cooling jacket apparatus coupled with a thermocouple temperature sensor. The results suggested that the rate of cooling of the polymer of each position across the duct was not significantly affected by the temperature of the coolant and glass-fiber contents, although the rate of cooling was influenced by the size of the duct. The crystallization temperature and degree of crystallinity of the polymer increased with increasing glass-fiber contents and the coolant temperature. These phenomena were associated with the heat transfer between the coolant and the polymer, crystallization temperature, exothermic crystallization process, and thermal properties of the polymer. The experimental temperature results were found to be different from the theoretical data.

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