

Effects of Molding Conditions on Properties of Injection-Molded Polycarbonates

HIROYUKI KODA, *Research Laboratory, Plastics Department, Mitsubishi Edogawa Chemical Company, Toyonaka, Japan*

Synopsis

Statistically designed experiments were carried out to study the effects of molding conditions on the properties of two types of polycarbonate, which were synthesized by the solvent process and the melt process, respectively. The properties tested in this study were classified into two groups with respect to the effect of molding conditions. One, which included birefringence, heat shrinkage at 180°C, and surface resistance to Taber abrasion, was mainly affected by stock temperature and was slightly affected by holding pressure. The other, which included resistance to solvent crack, Rockwell hardness, density, and heat shrinkage at 120°C, was affected by mold temperature and holding pressure. Mechanically isotropic moldings with a low degree of frozen orientation could be molded at a high stock temperature and at a low holding pressure, where stock temperature was more effective than holding pressure. Moldings with low residual stresses could be molded at a high mold temperature and at a low holding pressure. Essentially there was no difference in the molding conditions and properties by the method of synthesis. However, under the same molding conditions polycarbonate synthesized by the melt process gave a higher degree of frozen orientation and somewhat more rigid moldings.

Introduction

Data on the effects of molding conditions on properties of injection-molded articles are valued not only for their practical applicability but also for their rheological information.

Such data have been reported by many investigators, and it appears that there are two currents of such work. One of these deals with the effects of molding conditions on mechanical strengths;¹⁻³ the other, on residual strains.^{4,5} However, all of these studies were limited to information on the rheological role of the molding conditions with the exception of one.⁴ There are very few data on polycarbonate.^{6,7}

In this study an attempt was made to obtain overall information on the rheological role of molding conditions by using polycarbonates. A simple scheme on the effect of molding conditions on the properties of molded articles was obtained.

Experimental

Two types of Iupilon polycarbonate (Mitsubishi Edogawa Chemical Co.), one of which (S-PC) was synthesized by the solvent process and the other

(M-PC) by the melt process, were used in this study. The molecular weights of both PC were 2.5×10^4 . Care was taken not to allow any contamination or appreciable moisture absorption to occur before and during the injection molding.

Disks ($4 \times \frac{1}{8}$ in.) were molded with a reciprocating screw injection machine (Nikko-Ankerwerk, 5 oz). Molding conditions were statistically designed as shown in Table I, and two runs were carried out, one (series S) for S-PC and the other (series M) for M-PC.

TABLE I
Experimental Conditions

Expt. no.	Stock temp., °C	Mold temp., °C	Holding press., kg/cm ²	Inject. rate, cm ³ /sec
1	280	60	530	65
2	280	90	890	90
3	280	120	1250	115
4	300	60	890	115
5	300	90	1250	65
6	300	120	530	90
7	320	60	1250	90
8	320	90	530	115
9	320	120	890	65

Birefringence value was measured along the disk diameter across the gate. Mean birefringence value, $\bar{\Delta n}$, of the disk was calculated by the method shown in Figure 1, in which the area of the rectangle AEFD was equal to the integrated value of birefringence (area ABCD).

The Taber abrasion test was carried out in accordance with ASTM Designation D 1044-56. The resistance to abrasion of the disk was determined by measurement of weight loss after abrasion of 1000 cycles with a 1000 g load by using CS-17 wheels.

Heat shrinkage of the disk was measured on the disk diameter in the flow direction after treatment at 180°C for 1 hr or 120°C for 200 hr in an air-circulating oven.

The resistance to solvent crack of the disk was determined by measurement of time to initiate a crack when a disk was immersed in carbon tetrachloride kept at 30°C, and the amount of crack formed was classified.

The Rockwell hardness test was carried out in accordance with Procedure A in ASTM Designation D 785-60T. The disks were tested without pile-up.

Specimen density was measured at 25°C according to ASTM Designation D 792-60T, in which distilled water was used as the immersion liquid. The density was calculated with 0.99707 as the density of distilled water at 25°C as reference. Test specimens used were cut from the disks as shown in Figure 2, and ten pieces (about 15 g) of location 1 in Figure 2 were

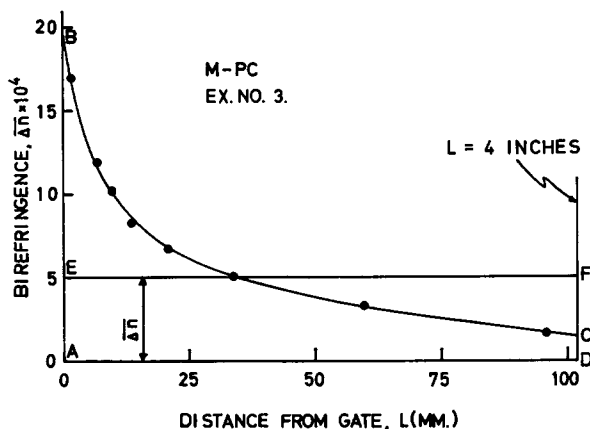


Fig. 1. Birefringence along disk diameter across gate, and mean birefringence.

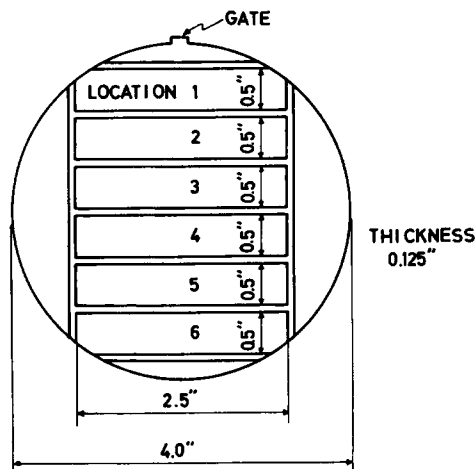


Fig. 2. Diagram of test pieces for measurement of density, showing how pieces were cut.

used for one measurement and tested after conditioning in a CaCl_2 desiccator for several days.

The data were statistically analyzed in order to obtain significant information. The variances of the data were calculated, and their significance was evaluated by the F test. Then the contributions of molding conditions to the properties of PC were calculated.

Results and Discussion

The frozen orientation of polymer chains in a molded article can be detected by measuring heat shrinkage at a temperature above the glass transition temperature, which is 149°C in case of PC,⁸ and the birefringence values, which are related to the molecular orientation. By this means it is

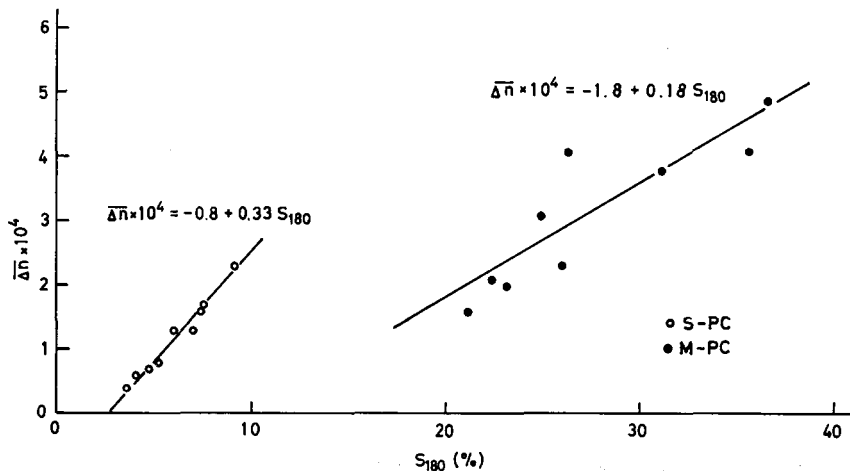


Fig. 3. Dependence of mean birefringence on heat shrinkage at 180°C.

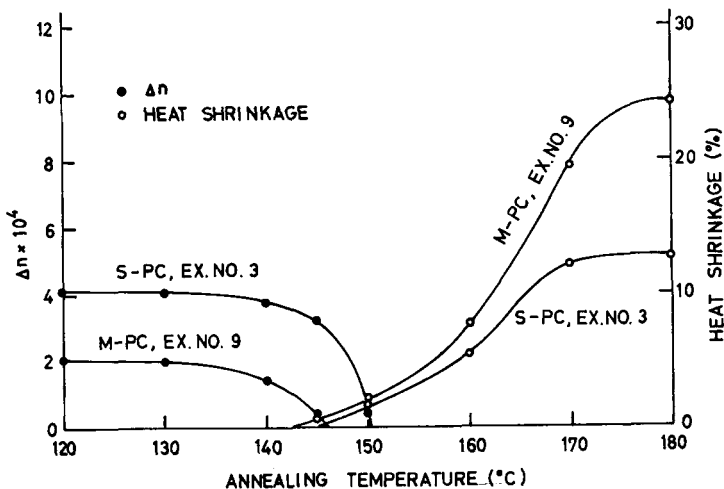


Fig. 4. Heat shrinkage and change in birefringence after annealing at indicated temperature for 2 hr.

possible to obtain an analogous correlation between birefringence value and heat shrinkage (i.e., elongation ratio) to that of the orientational birefringence of polymer in a rubbery state.⁹ Figure 3 shows the good correlation between $\Delta\bar{n}$ and heat shrinkage at 180°C, S_{180} (%), although the fact that S_{180} does not become zero when $\Delta\bar{n}$ is extrapolated to zero is unusual.

In order to find the cause of these phenomena, the changes in birefringence value and heat shrinkage after successively annealing for 2 hr at each temperature from below to above the glass transition temperature were investigated with specimens cut from the disks. The data obtained

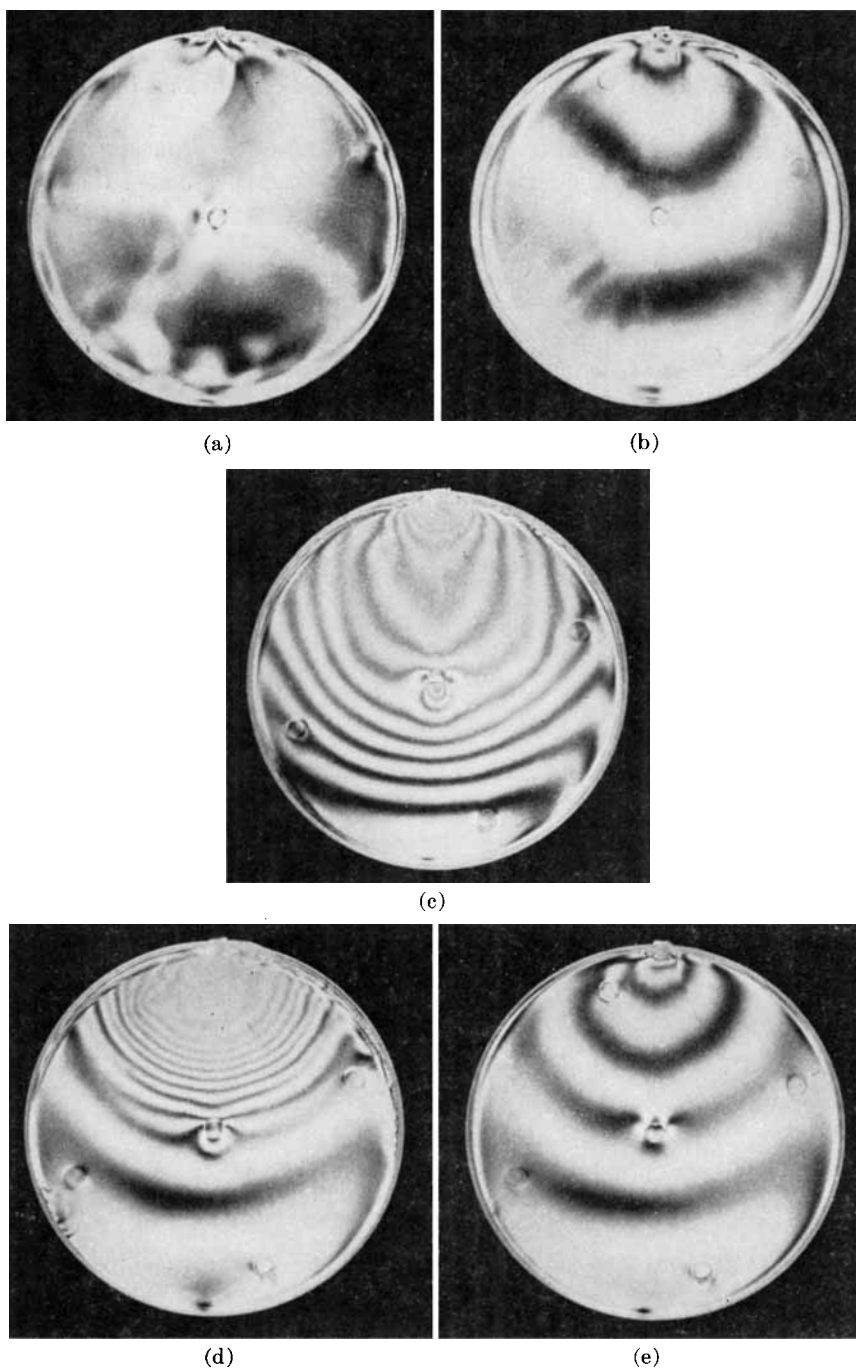


Fig. 5. Effect of holding time on birefringence pattern; viewed between circular polariscope. Holding time: (a) 0.8 sec.; (b) 1.8 sec.; (c) 4.8 sec.; (d) 7.3 sec.; (e) 9.8. Sample M-PC, experiment 5.

are given in Figure 4, which shows that birefringence disappears at a temperature range up to the glass transition temperature, while heat shrinkage due to segmental motion of the polymer chains is very small in the same temperature range.

This disappearance of birefringence must be caused by some kind of local mode motion of the polymer molecule. It has been postulated that bire-

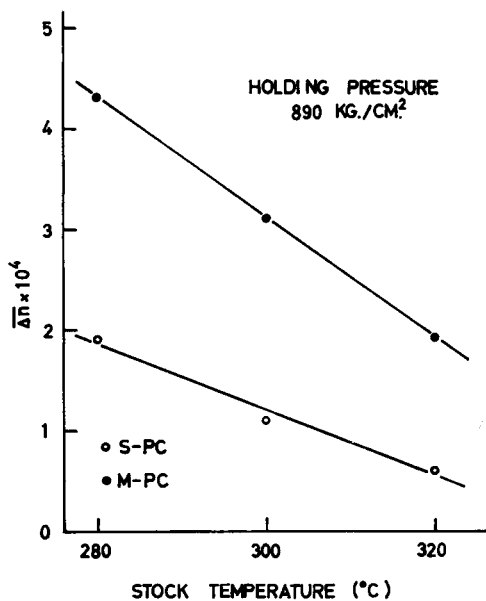


Fig. 6. Dependence of mean birefringence on stock temperature.

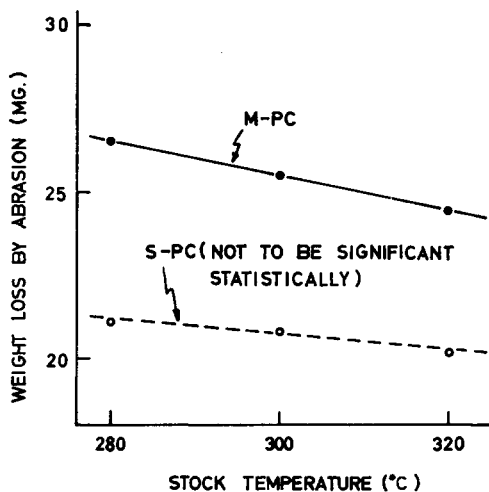


Fig. 7. Dependence of resistance to Tabor abrasion on stock temperature.

fringence is due to orientation of molecular groups having polarizability anisotropy.¹⁰ It has also been reported that in some polymers the sign of the birefringence changes from negative to positive near the glass transition temperature, owing to the thermal motion of the molecular groups. In view of these facts the most reasonable explanation of the unusual correlation between $\overline{\Delta n}$ and S_{180} is that during the cooling process of the molded piece the orientation of molecular groups from which birefringence arises are frozen in a more disordered state than that of the orientation of molecular chains. There is a difference in these unusual correlations between S-PC and M-PC, as shown in Figure 3, although the difference in the molecular structure between them is not obvious.

As pointed out by Spencer and Gilmore,⁴ frozen orientation is formed during the packing process, but it was found that the contribution of discharge of polymer melt to frozen orientation was very large, as shown in Figure 5, if the packing or holding time was too short. In the early stage of packing period discharge flow takes place over the entire disk area, but the melt temperature is still so high that the molecular orientation caused by it cannot freeze at all. Then the degree of frozen orientation increases with increase in holding time. A further increase in the holding time restricts the discharge flow and results in high birefringence patterns near the gate only. Thus, the gate-sealing time can be determined by utilizing this phenomenon. In Figure 5 the gate-sealing time lies between 7.3 and 9.8 sec.

Stock temperature and holding pressure were significant at the 1% level for $\overline{\Delta n}$ and S_{180} . The contribution of stock temperature to these properties was about 80%, whereas it was only about 10% for holding pressure. Mold temperature was not significant, and injection rate was significant at the 1% level, but its contribution was negligible. In Figure 6 it can be seen that the value of $\overline{\Delta n}$ shows a large decrease with increase in the stock temperature. Therefore, it can be concluded that, the higher the stock temperature is, the more the molecular orientation caused by the holding pressure is relaxed during the cooling process.

Mechanical strength and its anisotropy has been related to the extent of frozen orientation.¹⁻³ Therefore, the mechanical strength and stress craze, or crack, which is induced by thermal or mechanical two-dimensional tension,⁴ must be affected by stock temperature. The degree of frozen orientation of M-PC is higher than that of S-PC under the same molding conditions.

In series M the resistance to abrasion was also affected by stock temperature, which was significant at the 1% level. Its contribution was about 40%. Holding pressure, mold temperature, and injection rate did not affect the resistance to abrasion. Figure 7 shows that the resistance to abrasion becomes high with increase in stock temperature, i.e., with decrease in frozen orientation. In the measurement of abrasion resistance the frozen orientation layer of a test specimen was placed parallel to the abrasion surface. The intermolecular forces are weakened in a direction

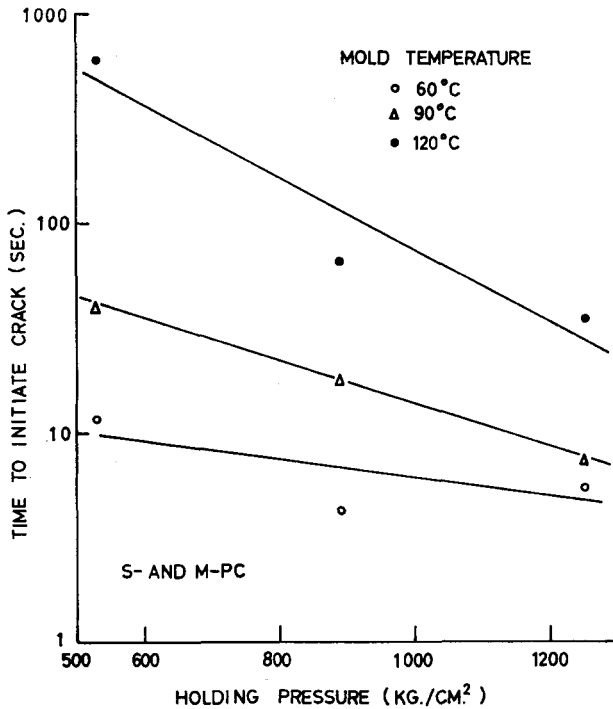


Fig. 8. Dependence of resistance to solvent crack on holding pressure and mold temperature.

perpendicular to the orientation layer. Therefore, the above-mentioned experimental results are reasonable.

In Taber abrasion the abrasion area is about 30 cm²; hence, 25 mg in weight loss after abrasion corresponds to 7 μ in thickness loss, provided the density of PC is 1.2 g/cm³. It is assumed that frozen orientation is also present in the surface layer of 7 μ .

The resistance to abrasion of S-PC was higher than that of M-PC under the same molding conditions.

As mentioned above, the frozen orientation and resistance to abrasion were mainly affected by stock temperature. Now let us consider the resistance to solvent crack, Rockwell hardness, density, and heat shrinkage at 120°C. These were affected by mold temperature and holding pressure. The mold temperature and holding pressure were significant at the 1% level for resistance to solvent crack, and their contributions amounted to a total of about 60%. Figure 8 shows that the resistance to solvent crack becomes higher with increase in the mold temperature and with decrease in the holding pressure. Interaction between them was also observed; that is, the resistance to solvent crack at a low mold temperature is less dependent on the holding pressure than the resistance to solvent crack at a high mold temperature. The stock temperature and injection rate were signifi-

cant at the 1% level, and their contributions amounted to a total of about 40%. However, their effects were intermingled with the interaction between mold temperature and holding pressure. It probably can be said that this interaction is dominant and the effects of stock temperature and injection rate on the time of crack formation are negligible, by analogy with the results given in Table II, which shows no effect of stock temperature and injection rate on the amount of crack produced.

TABLE II
Effects of Molding Conditions on Resistance to Solvent Crack^a

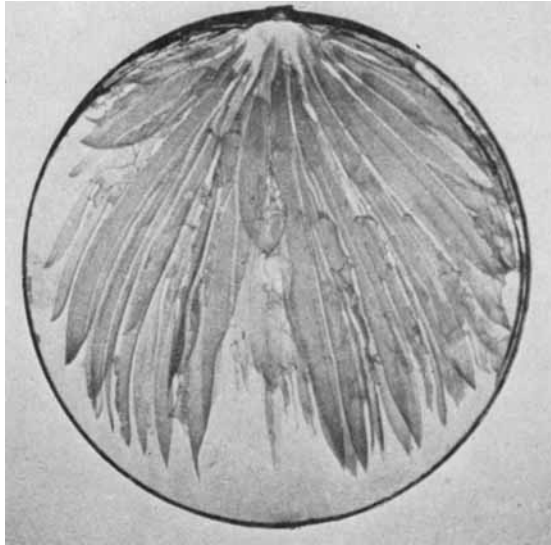
Factor	None	Very little	Little	Much	Very much
Stock temp.:					
Low		2	4		
Middle	2		2	2	
High		4		1	1
Mold temp.:					
Low			4	1	1
Middle		2	2	2	
High	2	4			
Holding press.:					
Low	2	2	2		
Middle		2	4		
High		2		3	1
Inject. rate:					
Low		2	2	2	
Middle	2	1	1	1	1
High		4	2		

^a Frequency distribution, in which the expt. no. 1-9 of S-PC and M-PC were classified according to the amount of crack occurring.

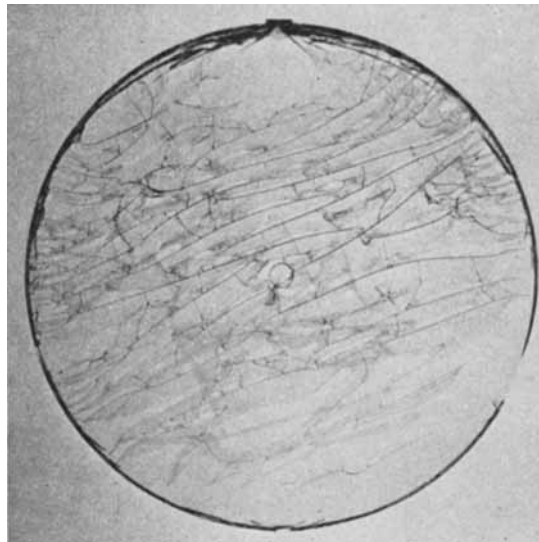
The resistance to solvent crack described in this study probably is related to the extent of residual stress that is frozen into the molded article. It has been pointed out that this residual stress is related to the elastic contribution of the polymer melt during processing.¹¹ Since the extent of elastic contribution becomes larger with increase in the force applied, decrease in the resistance to solvent crack with increase in the holding pressure is reasonable. The highest holding pressure produces peeled cracks, which are propagated in the flow direction when frozen orientation exists but are propagated at random when frozen orientation is absent, as shown in Figure 9. Increase in the mold temperature decreased the residual stress by means of its annealing effect, and high resistance to solvent crack resulted. In this connection, cracks were not formed in any of the test pieces by annealing at 120°C for only 30 min, when they were immersed in carbon tetrachloride kept at 30°C.

In series S, the Rockwell hardness in M scale was affected by the mold temperature, which was significant at the 1% level. Its contribution was about 50%. Holding pressure was not significant statistically. Figure 10

shows that the Rockwell hardness increases with increase in the mold temperature. In series M, the mold temperature and holding pressure were significant at the 1% level, and their contributions amounted to total of about 50%. Interaction was observed between these; that is, the Rockwell hardness at a high mold temperature was less dependent on the holding pressure than that at low mold temperature. The Rockwell hardness



(a)



(b)

Fig. 9. Typical views of peeled cracks. Propagation in: (a) flow direction; (b) at random.

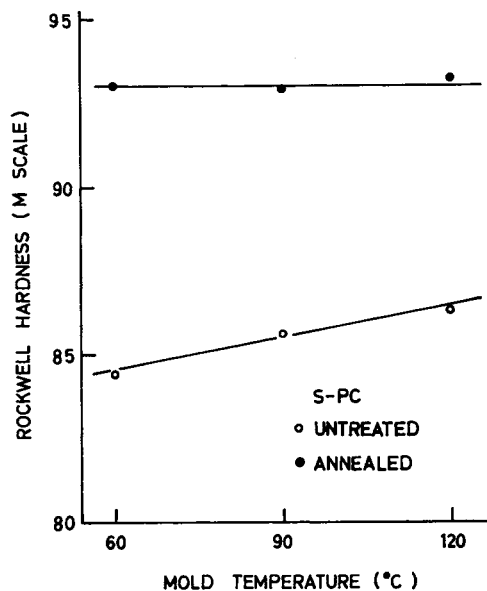


Fig. 10. Dependence of Rockwell hardness on mold temperature before and after annealing at 120°C for 2 hr.

became higher with increase in the holding pressure. In both series the effects of stock temperature and injection rate were not significant statistically, or their contributions were negligible.

The surface hardness of M-PC was higher by about 1 point on the Rockwell M scale than that of S-PC.

The surface hardness of disk increased by about 4 points on the average on the Rockwell M scale after treatment at 120°C for 2 hr and increased further by an additional 4 points after treatment for 100 hr. This increase in surface hardness is the same phenomenon reported by Goldblum¹² and has been interpreted as a rearrangement of the already existing state of short-range order or as a so-called physical crosslinking.¹³ This interpretation was based on the observation of a steep and narrow dispersion range in the temperature range above 110°C when damping was measured, which indicated a certain loosening with the bisphenol groups in the PC molecules. After the heat treatment the molding conditions were no longer significant statistically with respect to Rockwell hardness. It is noteworthy that the effects of mold temperature and holding pressure on the surface hardness were lost by annealing at 120°C. This fact is shown in Figure 10. The annealing effects of high mold temperature can also be pointed out as the reason for the increase in surface hardness with increase in the mold temperature.

The density was affected by the holding pressure and the mold temperature, which were significant at the 1% level. Their contributions were about 70 and 10%, respectively. Stock temperature and injection rate

were not significant statistically, or their contributions were negligible. Figure 11 shows that the density increases with increase in the holding pressure. This is obviously due to the fact that the specific volume of polymer at a constant temperature decreases with increase in the pressure applied in accordance with the Spencer-Gilmore's equation for state of polymer.¹⁴ The density decreased slightly with increase in the mold temperature.

Change in density was observed after treatment at 120°C for 2 hr, and an additional small change in density was observed after a further treatment for 25 hr. After the heat treatment the molding conditions were no longer significant statistically for the density, as shown in Figure 11. These are the same phenomena observed in Rockwell hardness. In most of the cases

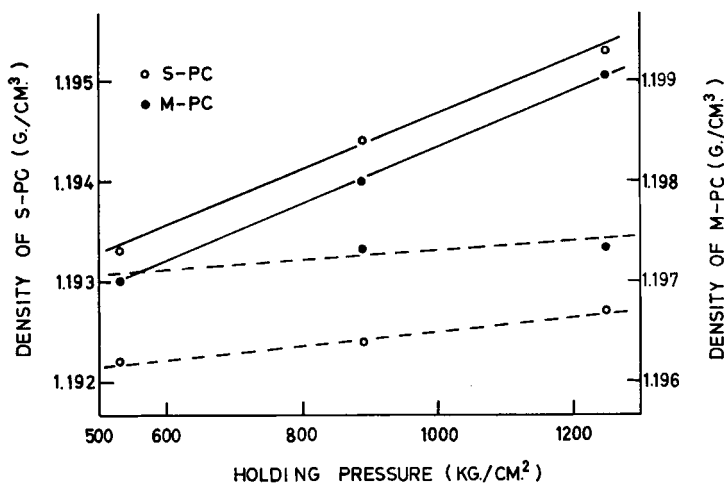


Fig. 11. Dependence of density on holding pressure: (—) before annealing; (---) after annealing at 120°C for 25 hr.

the density became lower by heat treatment, and the extent of the lowering became larger with increase in the holding pressure. Spencer and Gilmore⁴ have pointed out that the molded article contains quenching stress as a negative hydrostatic stress. If the holding pressure is sufficiently high, the positive hydrostatic stress will remain in the molded piece. The decrease in density by heat treatment is understandable if it is assumed that these residual, positive, hydrostatic stresses are relaxed at 120°C. The annealing effects of high mold temperature can also be pointed out as the reason for the lowering in density with increase in the mold temperature. However, the effect of mold temperature is small because this annealing effect, which gives rise to the volumetric expansion of disk, is restricted by the mold cavity.

The density of M-PC was higher than that of S-PC, both before and after heat treatment.

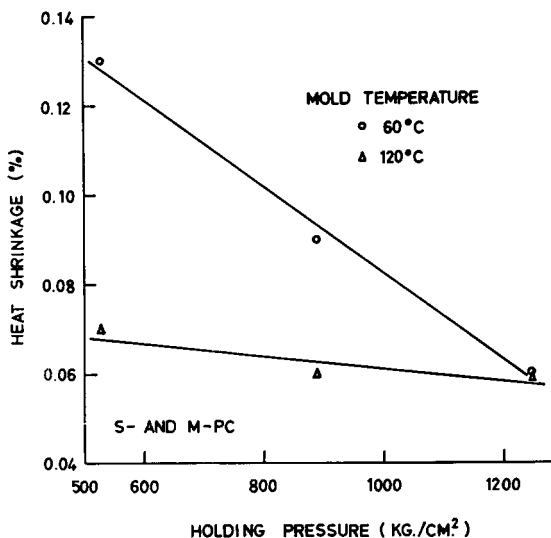


Fig. 12. Dependence of heat shrinkage at 120°C for 200 hr on holding pressure and mold temperature.

After relaxation of residual hydrostatic stress, i.e., change in density, the diameter of the disk shrunk gradually over a long time at 120°C. However, since a change in density was no longer observed, this shrinkage is probably compensated by an expansion in the thickness direction. The mechanism of this heat shrinkage probably differs from that of the change in density, because their relaxation time differs. However, this heat shrinkage may be due to some kind of a molecular motion of a short-range order, because the temperature concerned is below the glass transition temperature of PC.

Heat shrinkage after treatment at 120°C for 200 hr was affected by the mold temperature and the holding pressure, which were significant at the 1% level. Their contributions amounted to a total of more than 60%. The stock temperature was significant at the 1% level in series S and at the 5% level in series M. However, their effects are intermingled with the interaction between the mold temperature and the holding pressure, as shown in Figure 12. The injection rate was not significant in either series.

The annealing effect of high mold temperature can be observed again, because the heat shrinkage decreases with increase in the mold temperature. The reason for the decrease in heat shrinkage with increase in the holding pressure is probably as follows. Heat shrinkage is most likely canceled out by a volumetric expansion, which becomes larger with increase in the holding pressure as mentioned above.

A summary of the role of the molding conditions on the properties of injection-molded PC is as follows. Holding pressure is one of the stresses applied to a polymer melt and produces many kinds of strain, which can be frozen in the molded articles as residual strains or stresses, such as molecu-

lar orientation strain, hydrostatic stress, and some elastic strains. Strains caused by the holding pressure are relaxed to some extent by the thermal motion of the molecular chains or molecular groups during the cooling process. Consequently, the extent of its relaxation can be controlled by the temperature of the polymer melt or its cooling rate. Molecular orientation is relaxed by the segmental motion of PC molecules, which occurs in a temperature range above the glass transition temperature of PC; therefore, its extent of relaxation can be controlled mainly by the initial temperature of the PC melt, i.e., the stock temperature. On the other hand, hydrostatic stress and some elastic strains are relaxed by the local mode motion of PC molecules, which occurs in a temperature range below the glass transition temperature of PC; therefore, the extent of its relaxation can be finally controlled by the cooling rate or the residence time in the temperature range between 110 and 130°C, which is related to the mold temperature.

It has been reported that reduction in the amount of frozen orientation reduces mechanical anisotropy¹ and the tendency of the molded articles to stress craze.⁴ In this study it was considered that the effect of stock temperature on the resistance to Taber abrasion is due to the mechanical anisotropy, too. High stock temperature reduces the amount of frozen orientation in PC; thus, the mechanically isotropic PC moldings with a high resistance to stress craze can be molded at a high stock temperature and at a low holding pressure, where stock temperature is more effective than the holding pressure. PC moldings with low residual stresses, which are detected by carbon tetrachloride, can be molded at a high mold temperature and at a low holding pressure. However, it is more practical to consider that PC molded at a high mold temperature is somewhat more rigid, since it is annealed at 120°C, at which many properties of PC, such as Rockwell hardness, impact strength, tensile strength, and thermal deformation temperature, are changed, as stated elsewhere.^{12,13} These changes in properties are sometimes undesirable as, for example, when high impact strength is required.

It is possible to evaluate the practical optimum injection-molding conditions for PC by using certain criteria. These are the heat shrinkages at 180 and 120°C, which indicate characteristically how the properties of PC are affected by the molding conditions.

The effects of molding conditions on the properties of both S-PC and M-PC are essentially the same. However, M-PC gives a higher degree of frozen orientation and somewhat more rigid moldings at the same molding conditions.

The author wishes to thank K. Nakamura and K. Akabori for their assistance.

References

1. H. Keskkula and J. W. Norton, *J. Appl. Polymer Sci.*, **2**, 289 (1959).
2. R. Budesheim and W. Knappe, *Kunststoffe*, **49**, 257 (1959).
3. M. L. Collins and R. H. Whitefield, *Plastics*, **29**, 64 (1964).

4. R. S. Spencer and G. D. Gilmore, *Modern Plastics*, **28**, 97 (December, 1950).
5. L. I. Johnson, *Modern Plastics*, **40**, 111 (June, 1963).
6. R. B. Staub, *SPE J.*, **17**, 345 (1961).
7. Farbenfabriken Bayer AG, *Progressive Plastics*, **8**, 27 (December, 1966).
8. H. Schnell, *Angew. Chem.*, **68**, 633 (1956).
9. W. Kuhn and F. Gruen, *Kolloid-Z.*, **101**, 248 (1942).
10. R. D. Andrews and T. J. Hammack, in *Rheo-optics of Polymers (J. Polymer Sci. C, 5)*, R. S. Stein, Ed., Interscience, New York, 1964, p. 101.
11. C. J. Aloisio, S. Matsuoka, and B. Maxwell, *J. Polymer Sci. A-2*, **4**, 113 (1966).
12. K. B. Goldblum, *J. Appl. Polymer Sci.*, **8**, 111 (1964).
13. G. Peilstoecker, *Brit. Plastics*, **35**, 365 (1962).
14. R. S. Spencer and G. D. Gilmore, *J. Appl. Phys.*, **20**, 502 (1949).

Received November 14, 1967

Revised April 24, 1968