Korea-Australia Rheology Journal
Vol. 16, No. 4, December 2004 pp. 163-168

Investigation of pressure-volume-temperature relationship by ultrasonic technique and its application for the quality prediction of injection molded parts

Jung Gon Kim[1], Hyungsu Kim[2], Han Soo Kim and Jae Wook Lee*
Applied Rheology Center, Department of Chemical and Biomolecular Engineering, Sogang University, 1 Shinsoo-dong, Mapo-gu, Seoul 121-742, Korea
[1]Hyosung Corporation, R&D Center for Chemical Technology, Bottle Process Team, Hogye-dong, Dongan-gu, Anyang 431-080, Korea
[2]Applied Rheology Center, Department of Chemical Engineering, Dankook University, 147, Hannam-ro, Yongsan-gu, Seoul 140-714, Korea

(Received October 15, 2004; final revision received November 25, 2004)

Abstract

In this study, an ultrasonic technique was employed to obtain pressure-volume-temperature (PVT) relationship of polymer melt by measuring ultrasonic velocities under various temperatures and pressures. The proposed technique was applied to on-line monitoring of injection molding process as an attempt to predict quality of molded parts. From the comparison based on Tait equation, it was confirmed that the PVT behavior of a polymer is well described by the variation of ultrasonic velocities measured within the polymer medium. In addition, the changes in part weight and moduli were successfully predicted by combining the data collected from ultrasonic technique and artificial neural network algorithm. The results found from this study suggest that the proposed technique can be effectively utilized to monitor the evolution of solidification within the mold by measuring ultrasonic responses of various polymers during injection molding process. Such data are expected to provide a critical basis for the accurate prediction of final performance of molded parts.

Keywords **:** injection molding, PVT, quality prediction, ultrasonic technique

1. Introduction

Injection molding can be characterized as a single-stage polymer processing operation for manufacturing finished plastic parts with a low labor per unit ratio. The ultimate properties and overall quality of the part are highly dependent on process variables that are essentially controlled by hydraulic pressure. Although this process allows rapid, automated production of a wide variety of complicated three-dimensional parts, injection molded parts are different from each other in their quantities and qualities, even if they were molded under the fixed condition. Because of this, it is difficult to accurately predict the properties of molded part such as part weight, part thickness, modulus and impact strength.

In general, the microstructure developed during injection molding of polymers is closely related to the physical properties of the final products. The structural features of injection molded parts are quite anisotropic and heterogeneous; they vary with position through the cross-direction and flow-direction of the molded parts. This is particularly true for semi-crystalline polymers, since rapid cooling can cause different degree of crystallization throughout the part. Among numerous factors, the pressure-volume-temperature (PVT) relationship within the mold has a critical influence on the quality of the parts. Accordingly, it is of paramount importance to thoroughly measure PVT relationship for the effective quality control in injection molding process.

There have been a number of studies concerning the microstructure gradients developed in injection molded semi-crystalline polymers (Fujiyama *et al.*, 1988; Hobbs and Pratt, 1975; Hsiung *et al.*, 1990; Tan and Kamal, 1978). Most of these studies were concentrated on the off-line tests for final products by using optical microscopy, differential scanning calorimetry, and wide angle X-ray diffraction techniques. These methods, however, are somewhat time-consuming and on-line evaluation with such techniques is difficult to be practiced. In order to overcome the problems stated above, a new sensor system enabling direct assessment of PVT relationship of polymer needs to be introduced.

As is well known, ultrasonic velocity is related to the

*Corresponding author: jwlee@ccs.sogang.ac.kr

modulus and the density of the materials. Based on that relation, there have been a number of studies in which a correlation between the ultrasonic velocity and modulus for polymers was found (Moseley *et al.*, 1960; Leung *et al.*, 1984). Most of those studies, to our knowledge, were concerned with materials in solid state. Final performance of polymer based parts, however, should be dependent on the history of solidification starting from the molten state. Thus, for the rigorous evaluation and prediction of the properties of molded parts, it is necessary to trace the evolution of phase change within the mold. As noted in our previous paper (Kim *et al.*, 2000), it was not possible to properly predict the modulus and strength of the parts by measuring the cavity pressure data, which is mainly due to the lack of information on the interior molecular status. In this study, an attempt has been made to investigate PVT behavior of a polymer by measuring ultrasonic velocities during injection molding process. By combining this method and artificial neural network technique, the weight and modulus of the molded part were predicted.

2. Background

2.1. Artificial neural network (ANN)

The development of ANN has been inspired by the biological neural network, which does not operate digitally. ANN consists of many single neurons in one layer, each of which is connected to each neuron of other layer using weighted links. In ANN, a neuron takes its inputs multiplied by their respective weights, and summed together, then performs some mathematical operations by sigmoid function, and passes the result along the output. This output may then be picked up by other neurons as part of their input pattern.

The training begins by initializing all weights to small but non-zero values. Then, a subset of the collection of training samples is presented to the network, one at a time. A measure of the error incurred by the network is made, and the weights are updated in a way that reduces the error known as the back propagation. Details of utilizing ANN technique can be found elsewhere (Kim, 2000).

2.2. Acoustic parameters

Ultrasound is defined as a sound wave whose frequencies are above 20 KHz. Measurements of ultrasonic velocity and absorption provide useful basis for probing molecular structure and mechanical properties of polymers. As a molecular probe, acoustic properties are related to structural factors such as glass transition, cross-link density, morphology, and chemical composition. Thus, acoustic measurements can be used to assess any of these factors, or at least to monitor changes that may occur as a function of time, temperature, pressure, etc.

Longitudinal ultrasonic velocity responds to changes in bulk modulus and density, which are obviously dependent on pressure (P) and temperature (T). The velocity of propagation of an ultrasonic wave is a characteristic of a given material and can be calculated using the elastic constants of the material. Longitudinal ultrasonic velocity (v_l) is related to the elastic constants and density by the following equation (McSkimin, 1964):

$$v_l = [(K_A + 4G/3)/\rho]^{1/2} \quad (1)$$

where K_A is the adiabatic bulk modulus (equal to the reciprocal of the adiabatic compressibility), G is the shear modulus, and ρ is the polymer density.

Since shear modulus is relatively small for polymer melts in comparison with their bulk modulus, Eq.(1) is normally simplified for melts to:

$$v_l = [K_A/\rho]^{1/2} \quad (2)$$

As expressed in these equations, a relationship can be established between ultrasonic velocity and density of polymer, which can be obtained by identifying the relation between $K_A(P,T)$ and $G(P,T)$ based on the PVT relationship of polymers.

3. Experimental

3.1. PVT measurement

The controlled cooling rate measurements of polymeric volumetric data were taken by the PVT-100 apparatus (SWO, Germany), which provides two optional modes: isobaric and isothermal operations. In this work, the isobaric operation was carried out under seven different pressures and three different cooling rates of 5, 10, and 20°C/min. The pellets of polypropylene (PP, Honam Petrochemicals, SFR-170G) were first weighed and then melted in the cylindrical chamber at a temperature of 230°C for 5 min and subsequently cooled under three different cooling rates for each pressure. The temperatures of the chamber were changed from 50°C to 230°C.

3.2. Ultrasonic measurement

Ultrasonic signals were obtained by using Panametric 5072PR pulser/receiver system having a bandwidth of 35 MHz with two ultrasonic transducers (10 MHz). Wave forms were sampled and displayed using a GAGE CS 2150 digital oscilloscope board with a sampled frequency of up to 250 MHz. The signal exhibited a peak in voltage when the ultrasonic wave was received, having passed through a sample of polymer melt. The measured time upon the receipt of the signal is a time taken for a longitudinal ultrasonic wave to pass through the entire cell including sample which is bound with two transducers (one to transmit and the other to receive). This is termed as ultrasonic transit time, and the ultrasonic velocity through the melt may be directly obtained from its value. The trans-

ducers comprise a delay line material onto which a piezoelectric sensor is mounted.

3.3. Interrelation of PVT and ultrasonic velocity

An ultrasonic measuring cell was built so that measurement of the velocity of transmission could be carried out under the isobaric and isothermal conditions. The cell was located in one barrel of a Geoffert capillary rheometer, where the rheometer piston was used to compress and decompress a sample to facilitate pressure changes. Band heater was attached outside the cell and temperature was controlled by means of a PID controller with J-type thermocouple. A pair of transducer ports was located in the cell walls, in which two ultrasonic transducers were positioned in opposite direction to operate under transmission mode with piezoelectric pressure transducer (Dynisco). This arrangement allows the polymer melt to be heated and accurately pressurized and the ultrasonic transit time, melt pressure, and melt temperature can be monitored.

3.4. Measurement of ultrasonic velocity during injection molding

The experimental trials were carried out on an injection molding machine from Arburg company (Allrounder 220M 75). The machine was equipped with computer-based controller, as well as external mold temperature controller (Regloplas RG-150).

The mold used for this experiment basically produces plate-type pieces. The mold cavity was 2.5 mm thick and was equipped with three pressure sensors. Two ultrasonic transducers were positioned facing each other on opposite sides of the mold cavity so that one transducer can receive pulses generated by the other. Using this configuration, it was possible to measure the ultrasonic velocity through the polymer phase. The ultrasonic pulses were generated and amplified using Panametric 5072 PR system. These signals were digitized with a GAGE CS 2125 analog to digital converter, and then transmitted to the computer using a direct memory access card.

4. Results and discussion

4.1. Analysis of PVT relationship and ultrasonic velocity

The volumetric data of polypropylene(PP) were measured for various pressures at a cooling rate of 5°C/min to confirm the validity of the Tait model (Hirschfelder *et al.*, 1954) which is purely empirical and describes the volume along an isothermal line in terms of the volume at zero pressure and Tait parameters. As shown in Fig. 1, the experimental data are in excellent agreement with the proposed model, which offered a rational basis for the further analysis throughout this study.

The typical pattern of ultrasonic wave through PVT cell

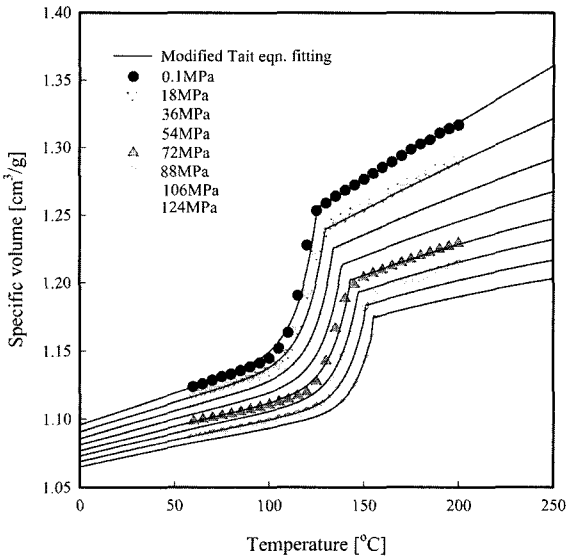

Fig. 1. The PVT relationship of polypropylene with Tait equation at a cooling rate of 5°C/min.

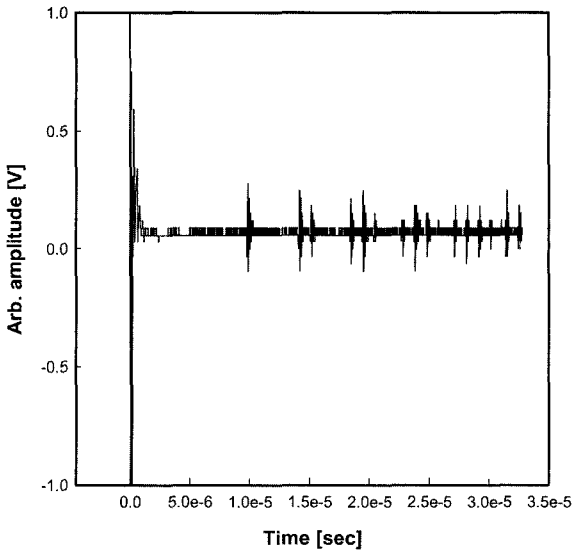

Fig. 2. The general pattern of ultrasonic wave through the PVT measurement cell.

is shown in Fig. 2, where ultrasonic velocities were determined by measuring the time interval between the pulses. The first pulse designates the signal resulting from the transmission of ultrasonic wave traveling through buffer rods, cell walls and polymer sample. The following pulses are associated with successive reflections of the wave from the various interfaces existing within the cell. Here, ultrasonic velocities were changed depending on the distances between buffer rods which are mainly influenced by temperature due to different degree of thermal expansion. With a few steps of mathematical manipulation, an equation which correlates ultrasonic velocities with temperatures for a given pressure has been developed by combining equa-

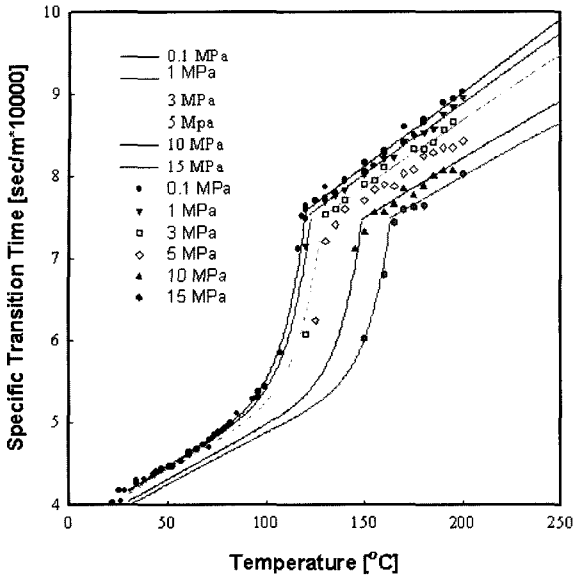

Fig. 3. Specific time as a function of temperature for various pressures.

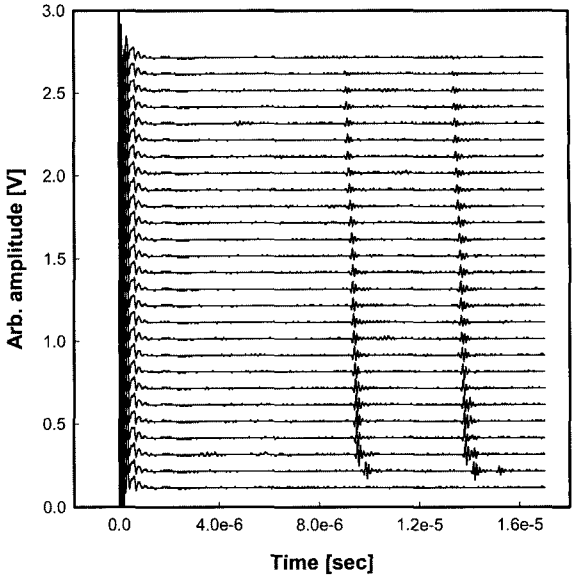

Fig. 4. Typical ultrasonic responses during injection molding process.

tion (1) with Tait equation (Kim, 2000). K_A and G of equation (1) was calculated by the thermo-mechanical meaning of Tait equation. By taking inverse of the ultrasonic velocity, the equation was expressed in terms of specific time (ST) and plotted as lines in Fig. 3 to compare with the experimentally measured values as dots. An excellent fitting of the measured ST data confirms the feasibility of the ultrasonic technique to the analysis of PVT behavior of polymer melt, as demonstrated in Fig. 3. The discontinuity observed at each data set corresponds to the crystallization temperature for the given pressure. This is a result of using two sets of constants included in Tait equation, one set for above the crystallization temperature and the other set for below the crystallization temperature.

4.2. Ultrasonic velocity during injection molding process

By using the transmission echoes, the signal of interest can be amplified to augment the necessary sensitivity of measurement during molding process. The experimental setup employed in this study has been equipped by placing the transducer directly over the cavity and the second transducer was attached onto the opposite side of the mold. In this arrangement, no signal is received until the polymer fills the mold, since the ultrasonic wave will not pass through the air filled cavity.

Fig. 4 represents the resulting patterns of transmission and reflection for mold/polymer interface. The first echo seen is transmission through two molds and polymer melt. The second and following echoes are reflections from a bottom mold/polymer interface and a top mold/polymer interface. The amplitude slowly decays to zero as the part shrinks and is pulled away from the cavity surface.

The arrival time of a pulse traveling through the polymer will vary as either the density or the stiffness changes during injection molding process. The density of the polymer starts to increase immediately as the polymer melt is compressed after the injection step, and during the later stage, as the solidification proceeds, rate of change in density or modulus is decreased. Such behaviors are well described in Fig. 5 by the plotting ultrasonic velocities as a function of cycle time. It is also noted from Fig. 5 that as the injection temperature is raised, the velocities are decreased due to the lower modulus of polymer melt. Measurement of ultrasonic velocity was extended over longer cycle times as the

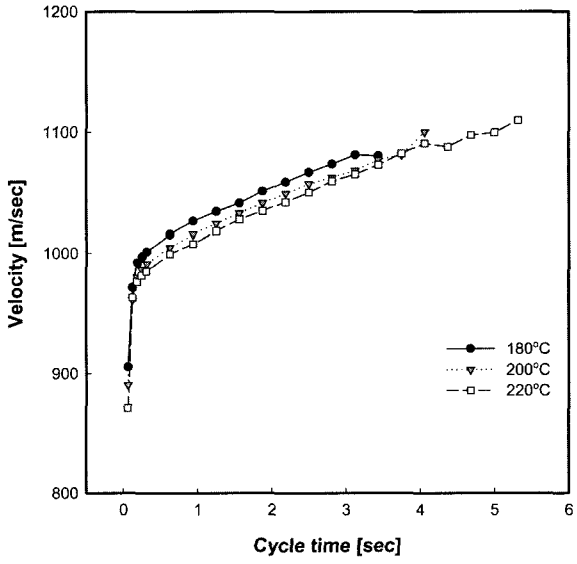

Fig. 5. Ultrasonic velocity vs. cycle time for injection temperatures of 180, 200 and 220°C.

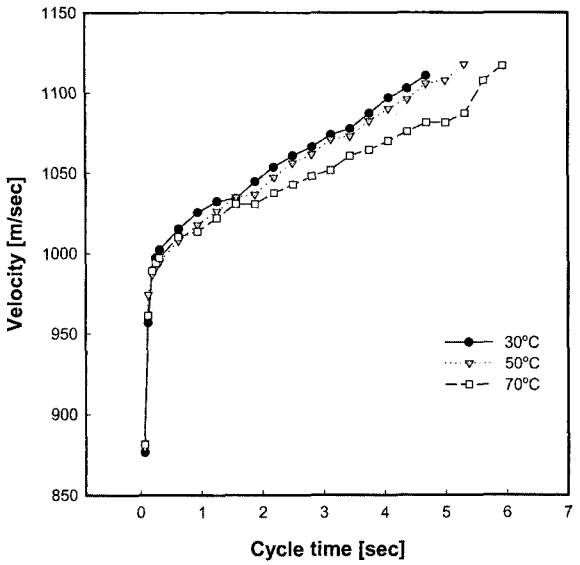

Fig. 6. Ultrasonic velocity vs. cycle time for mold temperatures of 30, 50 and 70°C.

injection temperature increases; this is simply because it takes longer to reach solidification in case of higher injection temperature.

Fig. 6 describes the effect of various mold temperatures on the ultrasonic velocity for a fixed injection temperature. Little difference was found in the initial velocities since the injection temperature was held constant. However, the ultrasonic velocity became slower owing to the delayed solidification as the mold temperature increases, as was consistently observed in Fig. 5. On the other hand, it was found throughout our investigation that ultrasonic velocity was little affected by injection speed and holding pressure.

The above experimental results suggest the utilization of the proposed technique to monitor the evolution of solidification by measuring ultrasonic responses of polymers during injection molding process.

4.3. Part quality prediction using ultrasonic wave

A standard feed-forward back propagation neural network was employed to directly investigate the interrelationship between parts qualities and the cavity variables. It is noted that eleven cavity variables including ultrasonic velocity and attenuation, were fed into the network for impartial performance evaluation concerning ANN of cavity pressures. As shown in Figs. 5 and 6, total ultrasonic pattern measured by ultrasonic devices during injection molding cycle time was put into the eleven input neurons for tracing total history of injection molded parts. The eleven input neurons consist of two parts. The one is cavity pressure pattern: the maximum cavity pressure, the area of cavity pressure and the total time of cavity pressure. The other is ultrasonic pattern: the initial ultrasonic velocity, the slope of initial ultrasonic velocity, the time of changing slope, the final ultrasonic velocity, the slope of final ultrasonic velocity, the initial attenuation, the maximum attenuation, and the final attenuation. The network was built with eleven input neurons, six hidden neurons, and a single output neuron. Adjustable training parameters, such as learning parameter, momentum factor, and noise factor were fixed at the optimum conditions of the analysis in order to prevent local minimum traps and improve convergence rate. Training continued for 10000 iterations and stopped when the error for the input pattern begins to be 10^{-4}.

Contrary to the previous prediction based on the cavity pressure data (Kim *et al.*, 2000), the proposed method in

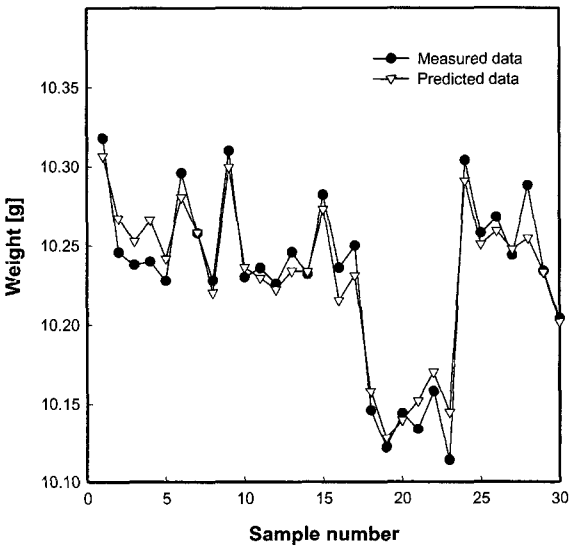

Fig. 7. Comparison of part weights between measured data and prediction made by ANN.

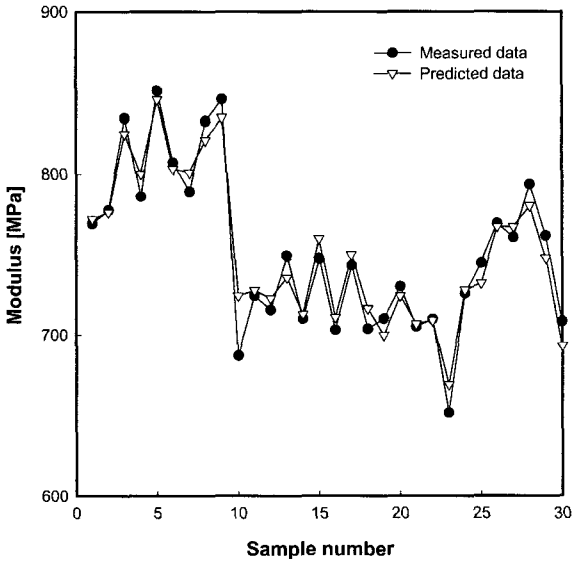

Fig. 8. Comparison of moduli between measured data and prediction made by ANN.

this study represents an excellent agreement between the predicted and the measured values of part weight and modulus, as clearly seen in Figs. 7 and 8. The ANN analysis based on ultrasonic technique is able to more successfully trace the varying part weight, because ultrasonic wave has the relation with PVT that was obtained on shot-by-shot basis.

5. Conclusions

In order to trace the PVT behaviors of polymer melt, an ultrasonic technique was used to find the relationship between ultrasonic velocity and PVT data of a polymer. From the comparison with Tait model, the possibility of such correlation was confirmed. The proven feasibility of ultrasonic response in describing PVT behavior offered an important basis for monitoring the progress solidification within the mold after injection of polymer melt. Evolution of phase change in polymer sample was successfully characterized by the continuous measurement of ultrasonic velocities along with cycle times. By combining the data collected from ultrasonic technique and artificial neural network algorithm, the changes in part weight and modulus were successfully predicted. These results further emphasize the important aspect of ultrasonic technique, since ultrasonic responses directly reflects the changes in molecular status of the polymer under investigation. It is suggested that the proposed ultrasonic technique featured by on-line measurement of ultrasonic velocities can be utilized to monitor the evolution of molding process and to predict final properties of molded parts.

Nomenclature

G : shear modulus [Pa]
K_A : adiabatic bulk modulus [Pa]
P : pressure [Pa]
T : temperature [K]
V_l : longitudinal ultrasonic velocity [m/s]
ρ : polymer density [kg/m^3]

Acknowledgement

This study was supported by research grants from the Korea Science and Engineering Foundation (KOSEF) through Applied Rheology Center(ARC), an official KOSEF-created engineering center (ERC) at Korea University, Seoul, Korea.

References

Fujiyama, M., T. Wakino and Y. Kawasaki, 1988, Structure of skin layer in injection-molded polypropylene, *J. Appl. Polym. Sci.* **35**, 29-49.

Hirschfelder, J.O., C.F. Curtiss and R.B. Bird, 1954, Molecular theory of gases and liquids, Wiley, New York.

Hobbs, S.Y. and C.F. Pratt, 1975, The effect of skin-core morphology on the impact fracture of poly(butylene terephthalate), *J. Apply. Polym. Sci.* **19**, 1701-1722.

Hsiung, C.M., M. Cakmak and J.L.White, 1990, Crystallization phenomena in the injection molding of poly ether ether ketone and its influence on mechanical properties, *Polym. Eng. Sci.* **30**, 967-980.

Kim, J.G., I.H. Shin, W.H. Han and J.W. Lee, 2000, Injection molded part quality prediction using a new method of analysis, *J. Injection Molding Tech.* **4**, 201-210.

Kim, J.G., 2000, *Ph.D. Thesis*, Sogang University, Korea.

Leung, W.P., F.C. Chen, C.L. Choy, A. Richardson and I.M. Ward, 1984, Ultrasonic measurements of the mechanical relaxations and complex stiffness in oriented linear polyethylene, *Polymer* **25**, 447-451.

McSkimin, H.J., 1964, Physical acoustics, principles and methods, Mason, W.P., ed., Vol. 1, Chap 4, Academic Press, New York.

Moseley, W.W., 1960, The measurement of molecular orientation in fibers by acoustic methods, *J. Appl. Polym. Sci.* **3**, 266-276.

Tan, V. and M.R. Kamal, 1978, Morphological zones and orientation in injection-molded polyethylene, *J. Apply. Polym. Sci.* **22**, 2341-2355.