The Application of Multiple Regression Analysis to the Property–Structure–Processing Relationship on Forging of Isotactic Polypropylene

SATOSHI OSAWA,[1] HIROAKI MUKAI,[1] TOSHIO OGAWA,[1] ROGER S. PORTER[2]

[1] Department of Applied Material Science, Kanazawa Institute of Technology, Nonoichi, Ishikawa 921, Japan

[2] Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

Received 16 April 1997; accepted 31 July 1997

ABSTRACT: The property–structure–processing relationship on the forging of isotactic polypropylene (iPP) has been investigated by applying multiple regression analysis. The analysis showed that the optical and mechanical properties of forged iPP can be described quantitatively by phase structures and the compression draw ratio (CR). For optical clarity, appropriate variables to explain the property are the smectic fraction (X_s), the amorphous fraction (X_a) and CR^{-1}. The increase in the smectic fraction and CR reduced the turbidity (for example, the increase in optical clarity) of the sample. The contribution of smectic phase estimated by the analysis was about one-third of the compression draw, as revealed by CR^{-1}. For mechanical properties, X_s, X_a, and $CR^{1/2}$ were the appropriate variables. The existence of the smectic phase reduced the tensile mechanical properties. The effect of X_s is 12 times higher in modulus than that in strength. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1297–1302, 1998

Key words: multivariate analysis; multiple regression analysis; polypropylene; forging; mechanical properties

INTRODUCTION

In any solid-state deformation of polymers, the resultant physical property is correlated to morphologies, such as molecular orientations, and phase structures. The processing variables, such as draw ratio, compression ratio, and temperature, also affect the morphologies.[1–3] Therefore, it is important to understand the quantitative contribution of the morphology or the processing variable to the resultant property.

The multiple regression analysis is one of the statistical methods for describing the characteristic of the subject as a function of many factors.[4,5]

Correspondence to: S. Osawa.

Journal of Applied Polymer Science, Vol. 68, 1297–1302 (1998)
 CCC 0021-8995/98/081297-06

The basic equation for linear multiple regression analysis is

$$Y = a_0 + \sum_j a_j X_j \qquad (1)$$

where Y is a criterion variable and X_1, $X_2 \cdots X_j$ are explanatory variables; a_0 is a constant; and a_1, $a_2 \cdots a_j$ are the regression coefficients, which means the rate of contribution of each variables. The method is used to describe analyses of data that are multivariate in the sense that numerous observations or variables are obtained for each individual or unit.[6] For example, appropriate amounts of fillers, such as glass and talc, on improving mechanical properties of polypropylene are controlled based on the results of multiple regression analysis.[7,8] The analysis is also applied

to optimization of the injection molding process with multicavity molds.[9]

In this study, the method is applied to understand the property–structure–processing relationship of planar deformation of isotactic polypropylene (iPP). The quantitative contributions of draw ratio and phase structures to the optical clarity and mechanical properties of forged iPP are compared to each other.

EXPERIMENTAL

The isotactic polypropylene (iPP) for study (supplied by the Phillips Co., Bartlesville, OK) had a melt index of 4.0 corresponding to a molecular weight (M_w) = 2.9×10^5. The original pellets were molded into 5.6-mm-thick sheet in a vacuum press at 220°C. The molded sheets were uniaxially compressed under isothermal conditions, at 50 and 140°C. The forging experiment consists of squeezing the polymer out of the compression zone. The compression area (1.0-inch-diameter cylinder) remains unchanged during forging. The compression draw ratio (CR) is defined by the sample thickness ratio before (d_0) and after (d) compression, that is, CR = d_0/d. The range prepared in this study is up to CR of 42. A detailed description of the method has been given.[10,11]

The optical transmission of forged iPP was measured using a micron photosizer (Seishin Enterprise Co., SKN-1000). The transmittance (T) is a ratio of beam intensity transmitted through the sample to the intensity incident on the sample. The turbidity τ was calculated by

$$\tau = -(\log T)/d \tag{2}$$

where d is sample thickness.

Wide-angle X-ray (WAX) analysis was made with a Rigaku RAD system X-ray generator using Ni-filtered Cu Kα radiation. From diffraction profiles of the 040 and 110 plane, the crystallite size was obtained by using Scherrer's equation, as follows:

$$D = K\lambda/b \cos \theta \tag{3}$$

where K is a constant, $b = (B^2 - b_0^2)^{1/2}$, B is measured half-width of the experimental profile, b_0 is the instrument resolution, and λ is X-ray wavelength. The instrumental resolution was obtained from scans of single crystal silicon.

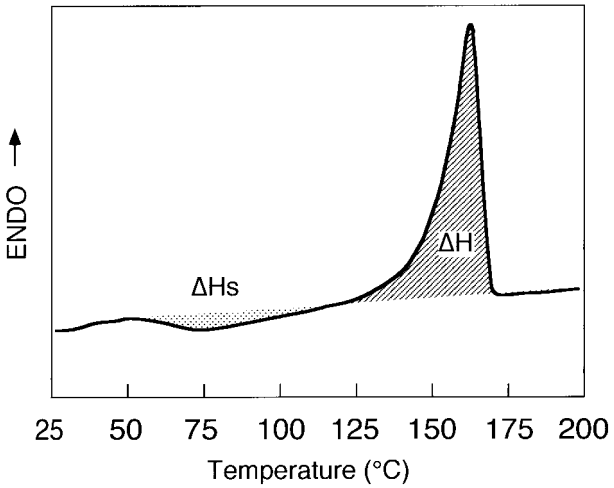

Figure 1 Typical DSC thermogram of iPP forged at 50°C.

In the forging experiment, iPP samples deformed at 140°C are composed of α-crystal only, plus amorphous; on the other hand, the sample forged at 50°C contains draw-generated smectic, α-crystal, and amorphous phases.[10,11] To estimate the phase fractions of α-crystal (X_c), smectic (X_s), and amorphous (X_a), thermal analyses were performed on the forged samples with a Perkin–Elmer DSC 7 calorimeter. All scans were recorded at a heating rate of 20°C/min. Figure 1 shows the typical differential scanning calorimetry (DSC) thermogram for the samples forged at 50°C. The exotherms for formation of the smectic phase (ΔH_s) was observed at around 80°C. The smectic phase reverts back to the α-crystal after the exotherms (since the exothermic process is a transition from smectic to α-crystal),[12] followed by the crystal-to-melt transition. Therefore, the heat of fusion (ΔH) indicated in Figure 1 consists of X_c plus X_s; that is, $\Delta H = (X_c + X_s)\Delta H_c^\circ$, where ΔH_c° is heat of fusion for α-crystal (33 cal/g).[13,14] The transition energy for smectic to crystals (ΔH_s°) estimated in our prior study was 5.5 cal/g.[12] Then the X_s, X_c, and X_a can be calculated as follows:

$$X_s = \Delta H_s/\Delta H_s^\circ \tag{4}$$

$$X_c = \Delta H/\Delta H_c^\circ - X_s \tag{5}$$

$$X_a = 1 - X_c - X_s \tag{6}$$

For the sample forged at 140°C, there is no exthotherms on DSC profile. Therefore, $X_s = 0$ for the calculation of X_c and X_a in eqs. (5) and (6).

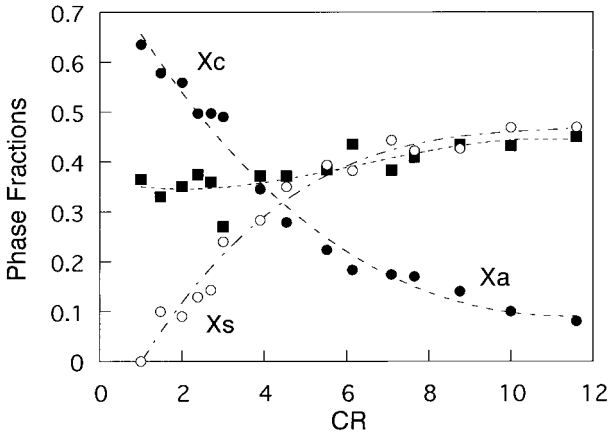

Figure 2 The phase fractions of X_c (●), X_s (○), and X_a (■) as a function of the CR for samples forged at 50°C.

The modulus and strength of forged samples were measured by a conventional tensile tester at room temperature. The strain rate for the measurement of tensile modulus was 10^{-3} (s^{-1}).

RESULTS AND DISCUSSION

The phase structures of forged iPP are as functions of draw temperature and compression draw ratio (CR). Figure 2 shows the phase fractions of forged iPP at 50°C. A large amount of α-crystal (X_c) transform to smectic phase (X_s) by a CR of 10. For samples forged at 140°C, on the other hand, there was no smectic fraction. These change in phase fractions, especially the formation of smectic with draw, greatly affects the optical and mechanical properties. Therefore, the fraction and the CR are important explanatory variables to explain the properties (criterion variables) in the multiple regression analysis.

Optical Property

Figure 3 shows the turbidity τ of forged iPP as a function of the CR. The turbidity τ seems to be functions of smectic phase fraction and the CR. The τ of both samples forged at 50 and 140°C decrease rapidly with increasing CR. Further, the τ of smectic generated sample (50°C) is lower than that of α-crystal sample (140°C) at a comparable CR. These results suggest that at least two factors provide optical clarity for forged iPP: One is directly related to generation of the smectic phase shown in Figure 2, and one is related to common structural changes in both samples induced by the forging. In semicrystalline polymers, there are several factors that influence optical clarity, such as the refractive index of phases, the shape, and the size of spherulite. Among the factors, the refractive index would be directly related to the phase fraction. The densities of smectic, α-crystal, and amorphous are 0.916, 0.936, and 0.85 g/cm^3, respectively.[15] The density is proportional to the refractive index. By the forging, α-crystal transforms to smectic, which minimizes the difference in the refractive indices between crystal (smectic is a disordered crystal form of iPP) and amorphous phases, leading to higher transparency, that is, a decrease in τ of the sample.

The transparency of semicrystalline polymer film is also affected by the shape and size of spherulites. We have shown that the spherulite is pancaked as deformation proceeds.[16] At a high CR, the layer structure is seen to be composed of a stacking of deformed spherulite planes. Takahashi et al. have studied the structure of highly transparent polypropylene (called PURELAY).[17] They suggested that the origin of the high transparency is to have sheaf-like crystalline superstructures instead of spherulite and to have smaller radii of spherulites. The radii of spherulite along the compression direction decrease rapidly by the forging because the radius is expressed by $D = D_0/\mathrm{CR}$ (D_0 is radius of spherulite of undeformed iPP) if the deformation is affine. D is evaluated as an average of 50 spherulites in the microphotograph. Figure 4 shows the D of forged iPP used in this study as a function of CR^{-1}. The relation between D and CR^{-1} is almost linear, implying an affine deformation. In the deformed

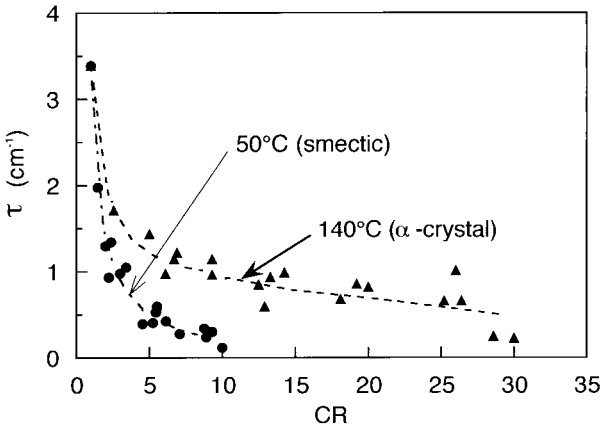

Figure 3 The turbidity τ of iPP forged at 50 (●) and 140°C (▲) as a function of the CR.

spherulite, the crystalline size D_c also decreases with draw. Figure 5 shows the relation between the D_c (for 040 and 110 planes) and CR. The results indicate a linear relation between D_c^2 and CR^{-1}, though the data is scattered. The decrease in the size of scatters would lead to the high transparency and the structural change in the size is closely related to CR^{-1}. Thus, CR^{-1} might be also an important explanatory variable for linear multiple regression analysis expressed by eq. (1).

Let τ be the criterion variable Y for the multiple regression analysis. Then the phase fractions of smectic (X_s), amorphous (X_a), and CR^{-1} are taken for this analysis as explanatory variables of X_j because these variables are closely related to τ, as mentioned in Figures 3–5. The sum of phase fractions $X_s + X_a + X_c = 1$. Therefore, two of the three fractions are chosen for the analysis. To compare each contribution of the explanatory variable to τ, by comparison of each regression coefficient, data must be normalized as Y_j' and X_j':

$$Y_j' = \frac{Y_j - \bar{Y}_j}{\sqrt{S_{xx}}} \quad (7)$$

$$X_j' = \frac{X_j - \bar{X}_j}{\sqrt{S_{xx}}} \quad (8)$$

where Y_j and X_j are data of each variable, and $\bar{Y}_i$ and $\bar{X}_i$ are the average of Y_j and X_j, respectively.

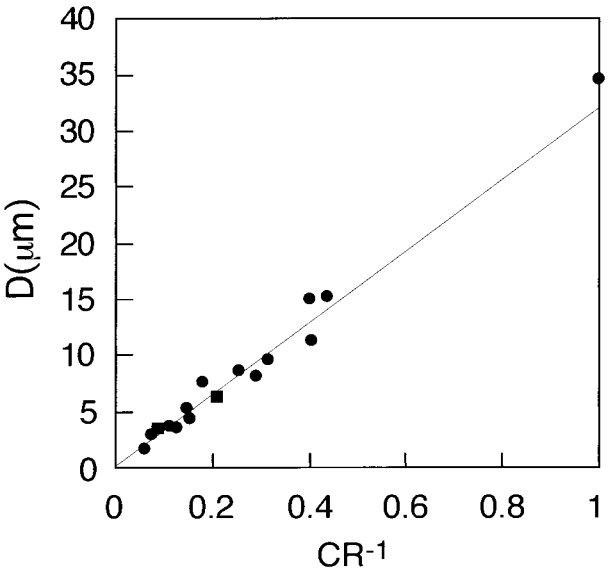

Figure 4 Relation between spherulite diameter (D) along the compression direction and CR^{-1} for samples forged at 50 (■) and 140°C (●).

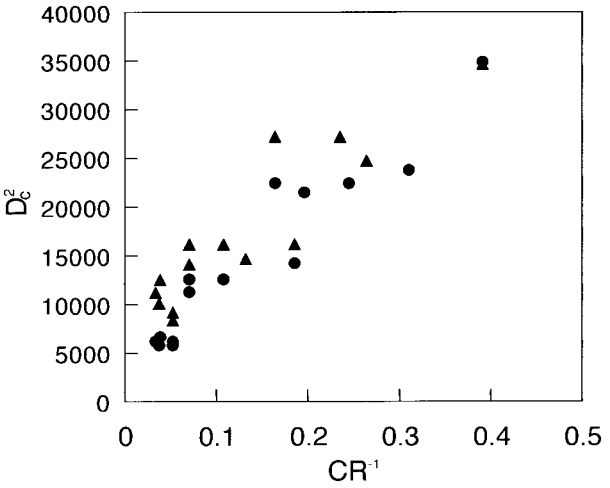

Figure 5 Relation between the crystallite size (D_c) of iPP forged at 140°C for (1, 1, 0) (▲) and (0, 4, 0) (●) planes.

S_{xx} is a variance of Y_j or X_j. Then, the following equation for τ as three functions of X_s, X_a, and CR^{-1} is obtained:

$$\tau = -0.0002 - 0.310X_s - 0.087X_a + 0.893CR^{-1} \quad (9)$$

This result demonstrates that the contribution of CR^{-1} ($a_{CR^{-1}} = +0.893$) and X_s ($a_{X_s} = -0.310$) to τ are large and that of X_a is minor. The adjusted R-square for the calculation is 0.994, indicating that τ can be well described by the sum of contributions of the three variables. An adjusted R^2 of 1 means that the criterion variable Y is completely expressed by the sum of contribution of each explanatory variable. The minus and plus for regression coefficients of X_s and CR^{-1} mean to reduce the τ and to increase τ, respectively. Namely, the increase in CR reduces the τ. The smectic contribution is about one-third of draw as revealed by CR^{-1}, judging from eq. (9). When CR is taken as a explanatory variable for this analysis, the adjusted R^2 drops to 0.64. This means that the CR^{-1} is an appropriate variable to describe the optical clarity of iPP rather than CR. This also suggests that the increase in clarity is directly related to the decrease of spherulite diameter D and/or crystallite size, D_c^2, since they correlate linearly to CR^{-1} (see Figs. 4 and 5).

Mechanical Properties

Another application of this analysis is for the tensile properties of forged iPP. Figures 6 and 7 show

the tensile modulus and strength of forged iPP as a function of CR. For samples forged at 140°C, both tensile modulus and strength parallel to the planar direction (perpendicular to compression direction) increased with CR. The smectic phase generated by forging at 50°C, however, reduced the tensile modulus with no significant effect on tensile strength. In planar deformation (forging), DR for the planar direction equals $CR^{1/2}$.[11] Therefore, the $CR^{1/2}$ is taken as a explanatory variable in the multiple regression analysis. The analytical equation obtained from the normalized data of X_s, X_a, and $CR^{1/2}$ for strength and modulus are expressed by eqs. (10) and (11), respectively.

$$\text{Modulus} = 0.00001 - 0.509X_s - 0.009X_a + 0.728CR^{1/2} \quad (10)$$

$$\text{Strength} = 0.00002 - 0.043X_s - 0.056X_a + 0.953CR^{1/2} \quad (11)$$

The adjusted R^2 are 0.982 and 0.995 for eqs. (10) and (11), respectively. The contribution (refer to the regression coefficient) of the smectic fraction X_s is 12 times higher in modulus than that in strength. Equations (10) and (11) indicate that $CR^{1/2}$ contributes strongly to the tensile properties. When the CR is taken as an explanatory variable in place of $CR^{1/2}$, the R-square is not changed significantly, indicating the CR is also a reasonable variable to describe the tensile properties in this experimental range of the CR. To obtain highly transparent iPP with high strength, forging at 50°C is recommended because the smectic phase is generated by the draw. For a highly transparent product with high modulus, on the other hand, forging at 140°C with a high CR is necessary. The desirable optical clarity and mechanical property of forged iPP can be designed by using eqs. (9)–(11). The multiple regression analysis is thus useful, not only understanding the property–structure–processing relationship but also controlling the properties of forged samples.

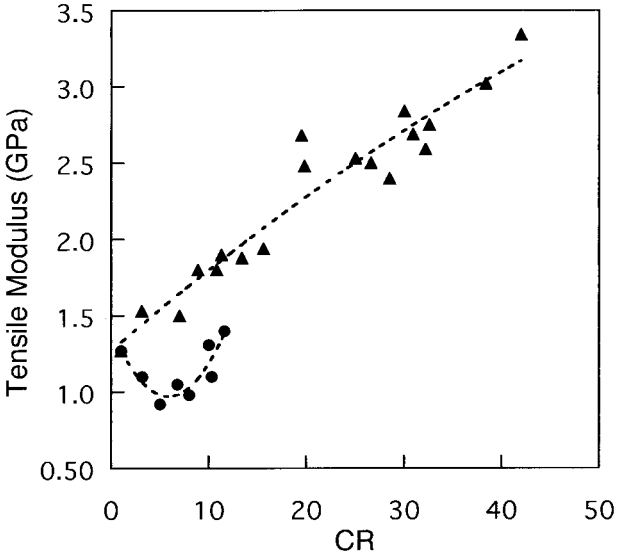

Figure 6 The tensile modulus versus CR for samples forged at 50 (●) and 140°C (▲).

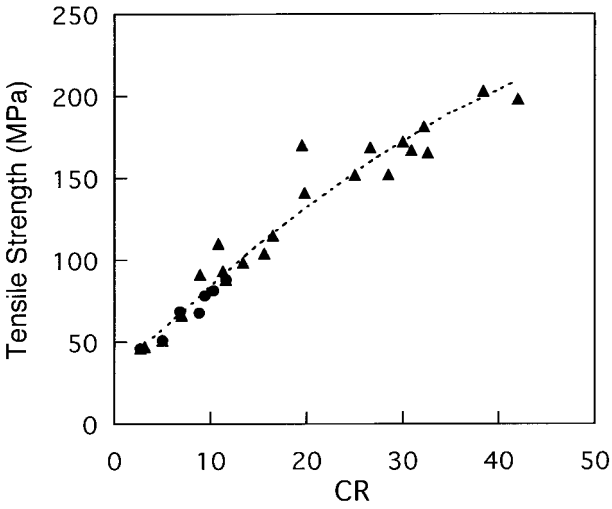

Figure 7 The tensile strength versus CR for samples forged at 50 (●) and 140°C (▲).

CONCLUSIONS

The multiple regression analysis is applied to understand the property–structure–processing relationship on forging of iPP. The analysis showed that the optical and mechanical properties of forged iPP can be well described quantitatively by phase fractions and the CR. For optical clarity, appropriate variables to explain the property are the smectic fraction (X_s), amorphous fraction (X_a) and CR^{-1}. The increase in the smectic fraction and the CR reduced the turbidity of the sample. The contribution of the smectic phase estimated by the analysis was about one-third of the compression draw, as revealed by CR^{-1}. For mechanical properties, X_s, X_a, and $CR^{1/2}$ were the appropriate variables. The existence of smectic reduced the tensile mechanical properties. The effect of X_s is much higher in modulus than that in strength.

This analysis is useful to design the desirable properties on forging of iPP.

REFERENCES

1. A. E. Zachatriades and R. S. Porter, Eds., *Strength and Stiffness of Polymers,* Vol. 4, Plastic Engineering Series, Marcel Dekker, New York, 1983.
2. N. Inoue and M. Ichihara, Eds., *Hydrostatic Extrusion: Theory and Applications,* Elsevier Applied Science, London, 1985.
3. J. R. Samuels, *Structured Polymer Properties,* John Wiley, New York, 1974.
4. A. A. Afifi, *Computer-aided Multivariate Analysis,* Lifetime Learning, Belmont, CA, 1984.
5. Y. Tanaka, T. Tarumi, and K. Wakimoto, *Personal Computer Statistical Analysis Hand Book II—Multivariate Analysis,* Kyouritu shuppan, Tokyo, Japan 1984, pp. 9–13.
6. T. Ogawa and T. Yamada, *J. Appl. Polym. Sci.,* **53,** 1663 (1994).
7. R. C. Weil, C. R. Mangararo, L. M. Parrinello, and R. Subramanian, *ANTEC,* **52,** 2770 (1994).
8. K. A. Borden, R. C. Weil, and C. R. Mangararo, *ANTEC,* **52,** 2761 (1994).
9. T. Wenniges and H. Potente, *ANTEC,* **53,** 659 (1995).
10. R. F. Saraf and R. S. Porter, *Polym. Eng. Sci.,* **28,** 842 (1988).
11. S. Osawa and R. S. Porter, *Polymer,* **35,** 540 (1994).
12. S. Osawa and R. S. Porter, *Polymer,* **35,** 545 (1994).
13. J. G. Fatou, *Eur. Polym. J.,* **7,** 1057 (1971).
14. S. K. Roy, T. Kyu, and R. St. J. Manley, *Macromolecules,* **21,** 499 (1988).
15. J. Brandrup and E. H. Immergut, Polymer Handbook, 3rd. ed, Wiley, New York, 1989.
16. S. Osawa, R. S. Porter, and M. Ito, *Polymer,* **35,** 551 (1994).
17. D. Takahashi, K. Katoh, M. Shibayama, and S. Nomura, *Rep. Prog. Polym. Phys. Jpn.,* **31,** 179 (1988).