NOTE

Effects of Molecular Weight on Mechanical Properties of Polypropylene

The relationship between molecular structure and mechanical properties is very complicated, compared with that of solution properties. Probably, the theoretical understanding of this relationship is very difficult. However, most polymers are used in the solid state. It is very important to control or to predict mechanical properties at the stage of polymerization. In practice, the most important factors are molecular weight and its distribution, which can control various mechanical properties of polypropylene homopolymers. Tacticity, which is one such factor, is nowadays not so important, because an excellent catalyst has been developed and high isotacticity is usually kept in commercial polymers. Furthermore, the influence of end groups is negligible in high molecular weight polymers.

Many investigators have been interested in the above relationship.[1] The following empirical equation was presented by Flory[2]:

$$P = A + B/M \qquad (1)$$

where P stands for mechanical properties, M molecular weight, and A and B are constants. Another equation was presented, for example, in the form of $M^2 + C$ instead of M in eq. (1).[3,4] More complicated equations will fit more precisely for experimental points. However, eq. (1) is very simple and more useful than any other equations for practical purpose. Equation (1) has been applied mainly for polystyrene so far.

In this article, we discuss tensile and flexural properties of crystalline polypropylene as a function of molecular weight, based on eq. (1).

EXPERIMENTAL

Materials

Commercial polypropylenes were used for this study, i.e., Mitsubishi polypropylene (Dia Polymer Co., Ltd., Japan), the molecular weight of which ranged from 160×10^3 to 235×10^3 in weight average. Molecular weights were determined by a Waters Model 150C gel permeation chromatograph equipped with a set of two columns of Shodex A-80M and a precolumn A-800P (Showadenko Co. Ltd.) at 135°C. The chromatograms were recorded with an RI detector. The calibration curve of polypropylene was prepared from that of polystyrene according to a relationship reported elsewhere.[5,6] Number and weight average molecular weights were determined, and geometrical mean values, i.e., $M = (\bar{M}_n\bar{M}_w)^{1/2}$, were adopted to discuss the relationship between molecular weight and mechanical properties.

## Mechanical Properties

Test pieces were prepared with an injection molding machine. The temperature in screw part was kept at 200°C and that of the mold at 40, 60, or 70°C. Type 3 test pieces were made for tensile test according to JIS K 7113. Test pieces for determining flexural properties were made in standard dimensions according to JIS K 7203. Tensile and flexural tests were carried out with a Shimadzu Autograph DSS-10T. Elastic modulus in tension was obtained in the crosshead moving rate of 1 mm/min, and strength and elongation at yield in the rate of 50 mm/min. Flexural properties were obtained by three-point method at the rate of 2 mm/min.

RESULTS AND DISCUSSION

Figure 1 reveals that the relationships between molecular weight and mechanical properties hold very well. The results are summarized in Tables I and II. Errors for curve fitting according to eq. (1) are small. There are two types on molecular weight dependence of mechanical properties, as shown in Figure 1. Similar curves are also observed in polystyrene[7] and polypropylene[8] on elongation and tensile strength. However, no quantitative evaluation was carried out. The B value of eq. (1) is positive in some properties, and that in the other one is negative. The properties of tensile strength and elongation at yield give a negative value, and the elastic modulus in tension and flexural properties gives a positive value. When B is positive, mechanical properties decrease with increase of molecular weight, while the tendency is reversed, when B is negative. Additionally, A and B values depend on properties that are taken out, and each property has a different meaning.

The effect of the temperature of the metallic mold was
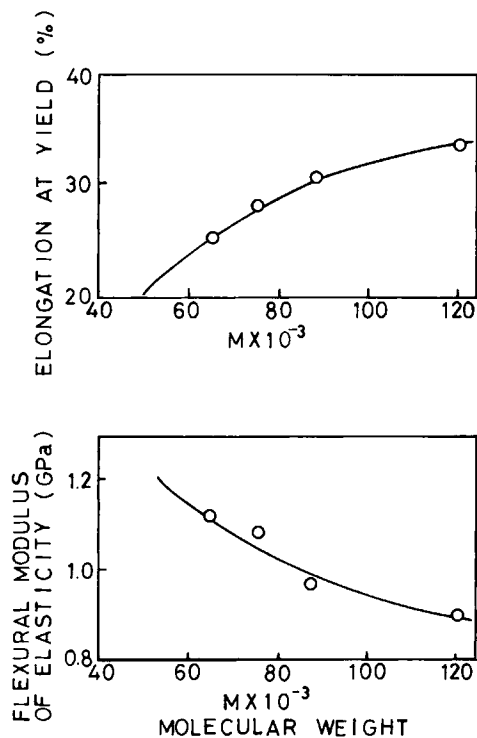
Figure 1 Molecular weight dependence of elongation at yield and elastic modulus in flexural test.

Table II *A* and *B* Values in Eq. (1) on Flexural Properties

Temperature of Metallic Mold (°C)	Flexural Strength (MPa)	Flexural Modulus of Elasticity (MPa)
45		
A	19.4	606
B	8.92×10^5	3.28×10^7
Error (%)	3.93	3.20
60		
A	28.1	861
B	1.42×10^4	4.46×10^6
Error (%)	1.74	2.63
75		
A	26.2	809
B	3.03×10^5	1.24×10^7
Error (%)	0.84	0.52

not observed so clearly. It is interesting that *B* is negative in tensile strength at yield, while *B* is positive in flexural strength. This fact suggests that tensile properties increase with molecular weight, while compressive properties de-

crease with it. Furthermore, strength and elongation at yield increase with molecular weight, while elastic modulus in tension decreases with it. Additionally, any clear difference was not observed among samples in the degree of crystallinity, which was obtained by differential scanning calorimetry. Therefore, various changes in mechanical properties can be attributed to the effect of molecular weight.

The extent of molecular weight dependence on mechanical properties can be expressed by

$$dP/dM = -B/M^2 \tag{2}$$

Table I *A* and *B* Values in Eq. (1) on Tensile Properties

Temperature of Metallic Mold (°C)	Tensile Strength at Yield (MPa)	Elongation at Yield (%)	Elastic Modulus in Tension (MPa)
45			
A	38.5	42.1	363
B	-3.58×10^5	-1.08×10^5	4.61×10^7
Error (%)[a]	1.26	3.90	8.70
60			
A	40.2	36.7	393
B	-3.97×10^5	-4.58×10^5	7.92×10^5
Error (%)[a]	1.23	4.95	6.90
75			
A	37.1	43.8	263
B	-1.26×10^5	-1.18×10^6	3.55×10^7
Error (%)[a]	0.77	1.96	11.6

[a] Error: $\sigma = \{1/(n-1) \times [(y_i - y_j)/y_j]^2\}^{1/2} \times 100$, where y_i is experimental value, y_j the value obtained from fitted curve on mechanical properties, and n the number of experimental points.

Accordingly, it is possible by using the B value to compare the difference of molecular weight dependence among polymer species. However, this comparison should be conducted by taking into account the difference of molecular weight for equal degree of polymerization. The B value for polystyrene was calculated from the data presented by McCormick et al.[7] in order to compare it with those in Table I and II. On strength, the B value is $-8.5 \times 10^4 \sim -7.1 \times 10^4$, which is already converted so as to compare with the values of Table I in identical meaning, and is almost equal to that of polypropylene. In spite of the fact that polystyrene is amorphous, and polypropylene is crystalline, both polymers have almost the same value in B. This fact suggests that the amorphous part contributes predominantly to mechanical properties rather than the crystalline one in crystalline polymers. Concerning elongation, the B value in polystyrene is $-4.70 \times 10^4 \sim -1.08 \times 10^5$. Polypropylene is higher in the B value than polystyrene. Probably, this difference is due to the low glass transition temperature of polypropylene.

We tried to apply eq. (1) for tensile strength and elongation at break. However, no satisfactory result was obtained. Factors such as thermal history in preparing test species may be more predominant than molecular weight.

In the case of copolymers, it goes without saying that the content and sequence length of the comonomer in a polymer chain govern more strongly mechanical properties. Therefore, it is certain that a simple equation such as eq. (1) does not hold in copolymers.

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Toshio Ogawa

Program of Material Design Engineering,
Graduate School of Engineering,
Kanazawa Institute of Technology,
7-1, Ohgigaoka Nonoichi Ishikawa 921, Japan