

Slurry 중합에서의 수소분압 및 촉매가 생성 폴리프로필렌의 고유점도 및 용융 특성에 미치는 영향

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(1989년 1월 19일 접수)

The Effects of Hydrogen Pressure and Catalyst on the Intrinsic Viscosity and the Melt Properties of Polypropylenes Prepared in a Slurry Process

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(Received January 19, 1989)

요약: 반회분형 슬러리 공정으로 부터 2종의 개량 Ziegler-Natta 촉매를 사용, 여러 수소 분압하에서 얻어진 폴리프로필렌의 고유점도, 평균분자량 및 분자량 분포, 용융지수, 복합점도 및 탄성율을 측정하였다. 또한 선형회귀 분석법을 이용, 이들 측정치간의 상관관계를 구했으며 이러한 상관관계는 대체로 촉매종에 무관하게 full log 혹은 semilog graph상에서 좋은 선형관계를 나타내었다. 또한 희박용액 성질인 고유점도나, 용융지수보다는 복합점도함수나 탄성율이 보다 분자량 분포에 민감함을 알 수 있었다.

Abstract: Intrinsic viscosity, average molecular weight and its distribution, melt index, melt viscosity and modulus of polypropylenes, prepared from a semibatch slurry process using two types of modified Ziegler-Natta catalyst under various hydrogen pressure, have been determined. Correlations among the measured properties have been made using a linear regressional analysis. Linear correlations independent of catalyst in semilog or full log plot were generally obtained. It was also found that complex viscosity and modulus were more sensitive to molecular weight distribution than the intrinsic viscosity, a dilute solution property, and melt index.

INTRODUCTION

Polypropylene(PP), with its reasonable cost and good combination of useful properties, has many industrial applications ranging from fiber to film.¹

PP is manufactured almost entirely in the low-pressure process using Ziegler-Natta(Z-N) catalyst. Therefore, process variables such as temperature and pressure in addition to the type of catalyst take important role in determining the molecular parameters such as molecular weight and molecular weight distribution(MWD) of products. On the other hand, these molecular parameters almost exclusively define the plausible method of processing leading to the desired end products.^{2,3}

This paper presents the flow properties of PP prepared in a semibatch slurry process. Two types of modified Z-N catalyst with respective overall activation energy of 10.4 (type I catalyst) and 12.4 kcal/moles (type II catalyst) were used to prepare PP at the total pressure of reactor 10kg/cm².^{4,5} The hydrogen pressures were varied from 0 to 2.56kg/cm².

Data are given in the form of figure. However, intensive correlations between the measured properties have been made using a linear regressional analysis. Domestic PP industry, which recently is growing rapidly, should take the the advantage of our results.

EXPERIMENTAL

Details in preparation of the polymer samples have been described in our earlier reports.^{4,5} Melt index (MI) (g/10min) was measured following ASTM-D 1238L, viz. at 230°C and a weight of 2.16kg. Intrinsic viscosity (IV) was measured in tetralin (1:1 by volume), 135°C using a autoviscometer (Mitsui Toatsu Chemical AVS-II). Prior to MI and IV measurements, a 0.1 wt% of 2,6-di-tert-butyl-4-methyl phenol was added to prevent the oxidation of PP samples.

Molecular parameters, i. e., \overline{M}_n (number average

molecular weight), \overline{M}_w (weight average molecular weight), \overline{M}_v (viscosity average molecular weight) and MWD(molecular weight distribution) were determined from a gel permition chromatograph (GPC). A 0.0005g of PP samples was first dissolved in 3.5ml of trichlorobenzene containing 2,6-di-tert-butyl-4-methyl phenol. GPC with Twin Shodex AT-80 M/S column(Waters 150C) was employed. Crosslinked polystyrene gels(Styragel) with pore sizes of 10⁷, 10⁶, 10⁵, 10⁴, and 10³μ in series were used as packing material. The solvent flow rate was 1.0ml/min, and the GPC column as well as the injector were kept at 140°C.

The linear viscoelastic properties of the melts were determined from a cone-and-plate type rheometer (Rheometrics Dynamic Spectrometer, 7700) with cone angle of 0.1 rad and radius of 1.25cm. In a separate experiment, it was determined that the viscoelastic response was linear up to 15% strain level, at which the frequency sweep experiments were performed throughout. Rheometer was operated isothermally at 230°C.

RESULTS AND DATA CORRELATIONS

The types of catalyst and hydrogen pressure were the major experimental parameters considered in the preparation of PP samples.

Crossplots between the measured properties are made in Figs. 1~5. What follows from now is the correlation between the measured properties given in the figures. Intrinsic viscosity is a property that can be easily measured in any laboratory,

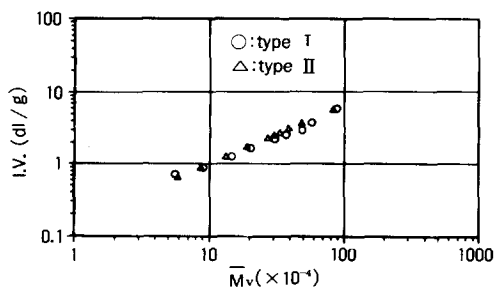


Fig. 1. Intrinsic viscosity vs. viscosity average molecular weight.

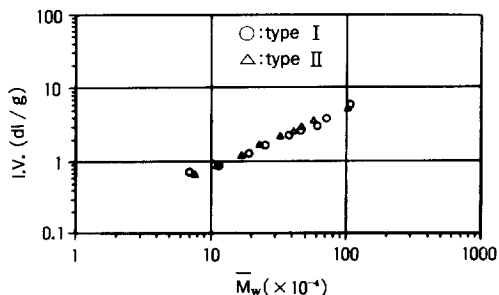


Fig. 2. Intrinsic viscosity vs. weight average molecular weight.

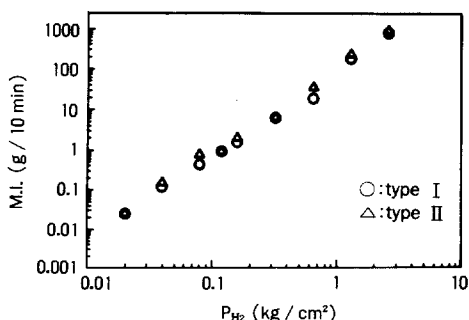


Fig. 3. Melt index vs. hydrogen pressure.

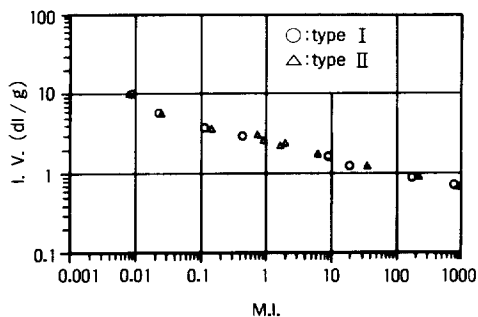


Fig. 4. Intrinsic viscosity vs. melt index.

and is related to the molecular weight via the Mark-Houwink equation :

$$IV = kM^a \quad (1)$$

where k and a are constants for a particular polymer-solvent pair at a given temperature. The constants, k and a are valid only within a limited range of molecular weight.⁶ The GPC data obtained in this experiment indicated that

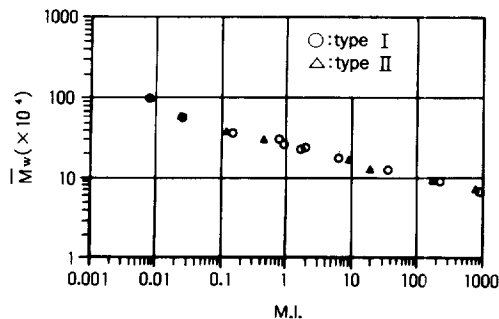


Fig. 5. Weight average molecular weight (\bar{M}_w) vs. melt index.

the molecular weights of the samples were in the range of 10^4 - 10^6 depending on the partial pressure of hydrogen. A reliable curve-fit technique, i.e., a linear regressional analysis using the experimental data provided correlations (eqs. (2)-(5)), correlation coefficient over 0.99 in most cases. The results are in good agreement with earlier data,⁶⁻⁸ and cover a broad range of molecular weight. In the equations, (I) and (II) respectively designate the type of catalyst employed in polymerization.

$$IV = 0.978 \times 10^{-4} \bar{M}_v^{0.795} \text{ (I)} \quad (2)$$

$$IV = 1.054 \times 10^{-4} \bar{M}_v^{0.795} \text{ (II)} \quad (3)$$

$$IV = 0.677 \times 10^{-4} \bar{M}_w^{0.811} \text{ (I)} \quad (4)$$

$$IV = 0.658 \times 10^{-4} \bar{M}_w^{0.820} \text{ (II)} \quad (5)$$

Practically, the processability of thermoplastic polymer melts is conveniently determined from the melt index (MI), an index inversely proportional to the viscosity which, on the other hand, is related to the average molecular weight of the polymer. For the general purpose polypropylenes, melt index ranges 1-10 at standard conditions. Presently prepared samples give melt index over approximately six orders of magnitude, 10^{-3} - 10^3 . A linear regressional analysis again gave a close fit to the experimental data as follows :

$$\log(MI) = 1.952 + 2.104 \log(P_{H_2}) \text{ (I)} \quad (6)$$

$$\log(MI) = 2.020 + 2.116 \log(P_{H_2}) \text{ (II)} \quad (7)$$

$$\log(IV)=0.409-0.202 \log(MI) \quad (I) \quad (8)$$

$$\log(IV)=0.422-0.202 \log(MI) \quad (II) \quad (9)$$

$$\log(\overline{Mw})=5.641-0.246 \log(MI) \quad (I) \quad (10)$$

$$\log(\overline{Mw})=5.617-0.246 \log(MI) \quad (II) \quad (11)$$

In eqs.(6) and (7), the unit of P_{H_2} (partial pressure of hydrogen) is kg/cm^2 . Regardless of catalyst type, the effect of hydrogen in terms of its partial pressure, gives a reasonably good linear relationship with the MI of PP when plotted in log-log scale. Basically same results were also obtained in a continuous process.⁹ Other correlations made above, i.e., correlations between \overline{Mw} and MI, IV and \overline{Mv} , and IV and \overline{Mw} essentially showed catalyst independence.

Though melt index is a readily measurable parameter of processability, it corresponds to a single value of shear rate. Therefore, depending on process condition and shear rate-viscosity relationship of the polymer melt, the melt index data alone do not give sufficient viscosity data for actual polymer processing. Consequently the non-Newtonian viscosity function should be measured in a wide range of shear rate.

Fig. 6 shows the complex viscosity of the samples measured at 230°C. Such viscosity function provides important informations concerning the average molecular weight and its distribution of the sample. The \overline{Mw} of the sample is related to the Newtonian

viscosity(η_0) through eq.(13) in which equation k and a are constants. The Newtonian viscosity can be directly read out from Fig. 6 when the viscosity function shows limiting behavior within the experimental range. A more reliable method to determine the Newtonian viscosity is in general from the Cole-Cole plot^{10,11} of the complex viscosity components, or Ferry's equation.¹² In this paper, it was determined from the Ferry's extrapolation

$$\frac{1}{\eta} = \frac{1}{\eta_0} + b\tau \quad (12)$$

where b is a constant and τ is the shear stress corresponding to η . A straightforward application of the linear regressional analysis, in the form of eq. (13), gave a relationship between the Newtonian viscosity and \overline{Mw} , (eqs. (14) and (15)).

$$\eta_0 = k\overline{Mw}^a \quad (13)$$

$$\eta_0 = 0.933 \times 10^{-14} \overline{Mw}^{3.465} \quad (I) \quad (14)$$

$$\eta_0 = 0.741 \times 10^{-14} \overline{Mw}^{3.503} \quad (II) \quad (15)$$

The storage modulus (G') and loss modulus (G'') are respectively given in Figs. 7 and 8. The storage and loss moduli respectively correspond to the energy stored and energy dissipated in a cyclic deformation.

Present experimental conditions i.e., 230°C, $10^{-2} < \omega < 10^3$, mainly cover the terminal zone and rubbery-terminal transition. None of the present

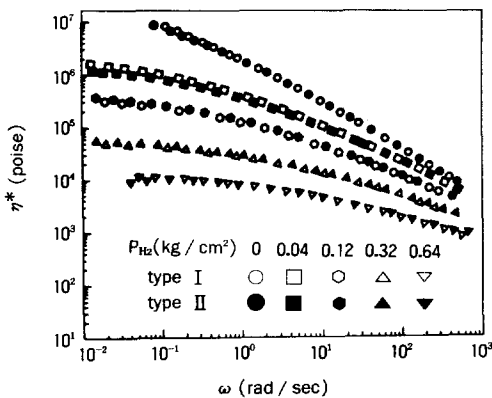


Fig. 6. Complex viscosity vs. frequency.

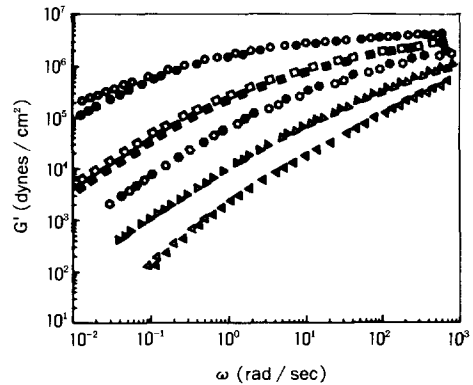


Fig. 7. Storage modulus vs. frequency. Same symbols with Fig. 6.

samples manifests the rubbery plateau, however, samples prepared at zero hydrogen pressure tend to define a plateau, reaching finally G' of 4.4×10^6 dyne/cm². The plateau modulus (G_N^0) is practically independent of molecular weight.¹³ Therefore G' curves in Fig. 7 should merge into same line in the glass transition zone (not seen in the figure). Samples prepared at zero and low hydrogen pressures should therefore assume broad rubbery plateau with smooth rubbery-flow transition, designating high molecular weight and broad MWD. On the contrary, those prepared at high hydrogen pressures should presume narrow rubbery plateau with sharp rubbery-flow transition, a low molecular weight and narrow MWD indicated. The limiting behavior of G' , viz. $G \propto \omega^2$ from Boltzman's superposition principle, was not observed at the lowest frequency tested.

The effects of molecular weight and its distribution on the viscoelastic properties of the samples are clearer in G'' than in η^* or G' . The terminal loss peak, a relaxation mechanism due to the entanglement slippage,^{14,15} is shown for the highest molecular weight samples, prepared at zero hydrogen pressure. The shift of the loss peak toward the lower frequency with increasing molecular weight is of no doubt, and such tendency is expected in Fig. 8. The peak in Fig. 8 is just a shoulder due to the broad MWD of the sample. A tendency to define a sharper one with increasing hydrogen

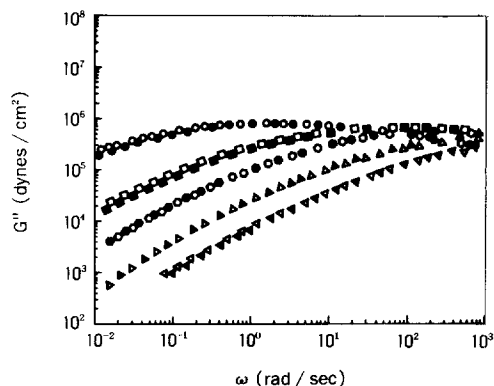


Fig. 8. Loss modulus vs. frequency. Same symbols with Fig. 6.

pressure should be noted in the figure. The limiting behavior of G'' at low frequency, i. e., $G'' \propto \omega$ is also clear for the samples prepared at $P_{H_2} \geq 0.12$ kg/cm². This is mainly due to the narrow MWD of those samples, and should be consistent with the existence of Newtonian viscosity in Fig. 6.

The relaxation spectrum of the sample calculated from the Ninomiya-Ferry's first order approximation (eq. 16)¹² using the loss modulus data is shown in Fig. 9.

$$H(\tau) = (2/\pi)G''(\omega) - a/(a-1)^2 [G''(a\omega) + G''(\omega/a) - 2G''(\omega)] \quad (16)$$

In the above equation $\tau = 1/\omega$, and a was set to be 1.259. The relaxation spectrum is useful qualitatively in gauging the relaxation time distribution which should be related to the average molecular weight and MWD of the sample. Relaxation spectra for PP's prepared at zero and low hydrogen pressure show an extended rubbery plateau, sign of intensive physical crosslinking. On the contrary, those prepared at relatively high hydrogen pressure, say $P_{H_2} > 0.12$ kg/cm², show typical of terminal zone relaxation.

In most cases melt properties again do not give any significant difference between the two PP's prepared from different types of catalyst at same hydrogen pressure. This is especially true for polymers obtained at relatively high hydrogen pressure. However a difference is also

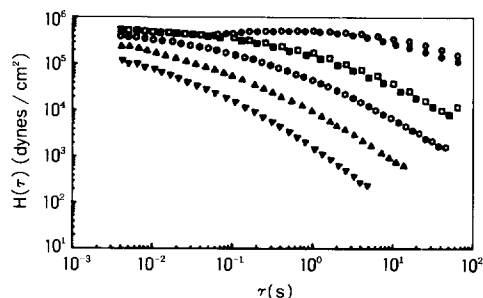


Fig. 9. Relaxation spectra from loss modulus data. Same symbols with Fig. 6.

true for samples prepared at low hydrogen pressure and shear rate. Samples prepared from type I catalyst show higher values of complex viscosities and moduli at zero and low P_{H_2} , at low rate of shear, an indication of higher molecular weight and broad MWD compared to those prepared from type II catalyst. Such difference was not recognized in MI and IV measurements. This is not surprising at all. As mentioned earlier, the MI measurement corresponds to a single and relatively high value of shear rate, at such level of shear rate the catalyst effect should certainly be ignored in Fig. 6~8 also. The reason why the viscoelastic property is more sensitive, over the dilute solution property, to the molecular weight and MWD of the sample should be as follows: Fully viscoelastic state of polymer corresponds to its melt state, a state where the terminal zone relaxation occurs. The terminal zone relaxation is a long time response of the polymer mainly governed by the MWD in the high molecular weight tail of the GPC trace. Therefore even a small difference in molecular parameters near the high molecular weight tail should be clearly showed up in viscoelasticity measurement. However such difference may be ignored when the elastic deformation dominates over the viscous deformation at high rate of shear.

CONCLUSIONS

The data base reported in this paper was obtained from a semibatch slurry process using modified Ziegler-Natta catalysts. Correlations among the measured properties generally indicated catalyst independence. It was also found that the melt properties were more sensitive to the molecular weight distributions of the samples than the intrinsic

viscosities. These data and correlations should practically be valid regardless of catalyst type and process as well.

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