Polymer(Korea) Vol. 19, No. 2, pp 207-212(1995)

폴리프로필렌 크랙킹에서의 압출특성

류 승 훈
경희대학교 화학공학과
(1994년 9월 5일 접수)

Extrusion Characteristics in Cracking of Polypropylene

Sung Hun Ryu
Department of Chemical Engineering, Kyung Hee University
Seocheon 1, Kiheung, Yongin
Kyunggi-Do, Korea
(Received September 5, 1994)

요약 : 본 실험은 peroxide를 혼합한 polypropylene의 일축압출기에서의 압출거동에 대하여 알아보았다. 압출량은 solid conveying zone의 barrel 온도가 감소할수록 증가하는 현상을 나타내었으며 이는 powder 상태의 고분자와 barrel간의 마찰계수의 증가로 인하여 solid conveying zone에서의 powder 상태의 고분자의 이송능력이 향상되었기 때문으로 추정되었다. 압출실험과 screw 냉각실험으로 부터 압출량을 증가시키기 위하여는 solid conveying이 속도결정인자임을 알 수 있었다. 서로 다른 혼합부의 형태 또한 압출량과 분자량 및 분자량분포에 영향을 나타내었다. 동일한 barrel 온도 조건하에서는 pin 형태의 혼합부에 비하여 blister ring 형태의 혼합부를 이용하는 것이 약간의 압출량 증가와 제품의 분자량이 상대적으로 낮고 분자량분포가 좁은 양상을 나타내었다.

Abstract : Effects of barrel temperature profile and type of mixing section on the extrusion characteristics of peroxide premixed polypropylene were studied using single screw extruder. Higher extrusion rate was observed with decreasing barrel temperature of solid conveying zone and it was attributed to the increase of coefficient of friction between polymer and barrel in solid conveying zone. From extrusion data and screw cooling experiments, it may be concluded that solid conveying is most likely to be the rate controlling factor to increase the extrusion output rate. Different type of mixing section also affected the extrusion output rate and the molecular weight and its distribution. Blister ring mixing section resulted in slightly higher extrusion rate and relatively low molecular weight and narrow molecular weight distribution of final product than that of pin mixing section.

Keywords : *polypropylene, controlled degradation, single screw extruder, mixing section, barrel temperature profile.*

INTRODUCTION

For many commercial end-uses, the melt flow characteristics of polypropylene (PP) produced with heterogeneous Ziegler-Natta catalysts are not suitable because of the resulting high melt viscosity and elasticity. Important end-uses where it has become well accepted that the melt flow characteristics of such polymers must be substantially improved in various extruded and injection molded products.

In view of this need, it has been shown that improved melt flow characteristics of PP can be achieved by chain scission since, in effect, this reduces longer and higher molecular weight chains. Controlled degradation of PP through the action of peroxides also known as "visbreaking" or "cracking"- is a reactive process that involves conversion of low melt flow index (MFI) commodity resins to polymers with higher MFI. A PP produced using this method is called controlled rheology PP (CR-PP). Reactive extrusion using a single or twin screw extruder is a common method to produce a CR-PP.

PP has been known as a difficult material to extrude than polyethylene due to its high crystallinity and low compressibility, etc.. In general, the output rate for PP from a given size of single screw extruder is lower than that of polyethylene. Screw configuration, processing conditions and type of material have been known as important factors in extrusion.[1-5] Cheng[3] reported that reversed barrel temperature profile, i.e. decreasing the barrel temperature from solid conveying zone to die, was more efficient to increase the output rate than ascending temperature profile.

Recently, many works were reported about the PP controlled degradation and those studies were emphasized on the changes of molecular weight and rheological properties and kinetic modeling.[6-8] Although understanding the extruder performance in the reactive extrusion of PP controlled degradation is important, it has only been marginally studied.[9] This study examines the effect of barrel temperature profile and configuration of mixing section on the output rate and molecular weight distribution of final product in peroxide-initiated PP controlled degradation using single screw extruder.

EXPERIMENTAL

Materials. PP resin premixed with peroxide (Lupersol 101, Atochem North America) in powder form was used to evaluate the extrusion characteristics. Nominal MFI of pure PP was 0.8 g/10min at 230℃ and 2.16 kg.

Characterization. The DuPont model 900 high temperature size exclusion chromatograph (HTSEC) was used to measure the molecular weight (MW) and molecular weight distribution (MWD) with 1,2,4-trichlorobenzene at 140℃ as a solvent at a flow rate of 0.75 mL/min in a bimodal column (DuPont zorbax PSM Bimodal-S 6.2 mm ID×25 mm). Infrared was used as a detector. Antioxidant was added to prevent the possible degradation during sample preparation and measurement. For universal calibration, six different polystyrenes of standard molecular weight (MW=900000, 300000, 100000, 50000, 10000, 2000; Pressure Chemical Co.) were used.

Extrusion. A 2", 32:1 L/D two stage single screw extruder was used with pin or blister mixing section in the first metering section. Melt temperature was measured with a thermocouple at die. Five heaters were used to control the barrel and die temperature. A schematic diagram of extruder is shown in Fig. 1. To determine the effect of barrel temperature on extrusion rate, experiments were carried out as follow;

	Temperature			
	Zone 1A	Zone 1B	Zone 2-4	Die
CASE I	227℃	227℃	227℃	227℃
CASE II	182℃	182℃	227℃	227℃
CASE III	127℃	182℃	227℃	227℃

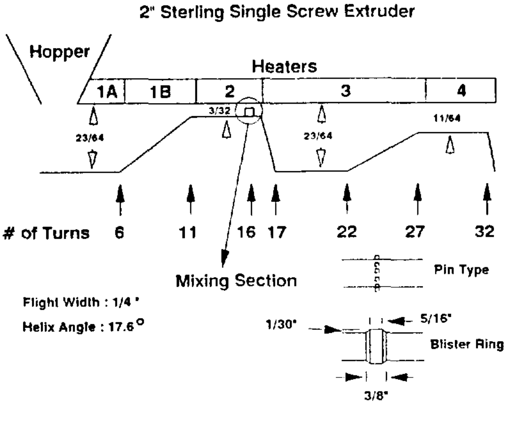

Fig. 1. Schematic diagram for single screw extruder.

Zone 1A and zone 1B represent the solid conveying and compression zone of first stage, respectively. Extrusion rate was measured more than 30min elapsed to ensure the steady state condition. The reported data are the average of three determinations. The data were quite reproducible within 10% error.

RESULTS AND DISCUSSION

Effect of Barrel Temperature. Fig. 2 shows the effect of barrel temperature of zone 1A and 1B, i.e. solid conveying and compression zone, on extrusion rate with different rpms. It is interesting that the output rate for CASE II shows 30-100% higher than that of CASE I. The specific output rates, defined as output rate/rpm, are also plotted in Fig. 3. The specific output rate appears to increase moderately with increasing rpm for CASE II, while CASE I shows more or less constant value.

Screw cooling experiments were carried out to find out the effect of each zone on the extrusion rate. Screw cooling experiment is known as a simple and ingenious experimental technique that permits a visual analysis of the extrusion process. From a screw cooling experiment, starved melt conveying behavior in the first metering section is observed(Fig. 4). It indicates that the melt conveying capacity of the metering section is higher than melting rate of the compression zone. Same phenomena were observed for all experiments (CASE I to CASE III) with a little variation of degree of fill of the metering zone. Fulfillment of metering zone was not observed within experimental range. Partial fill of the metering zone means that metering zone can convey more melt provided the increase of solid conveying rate or melting rate can be occurred. Thus, it can be concluded that solid conveying or melting process is a bottleneck for the increase of the extrusion rate.

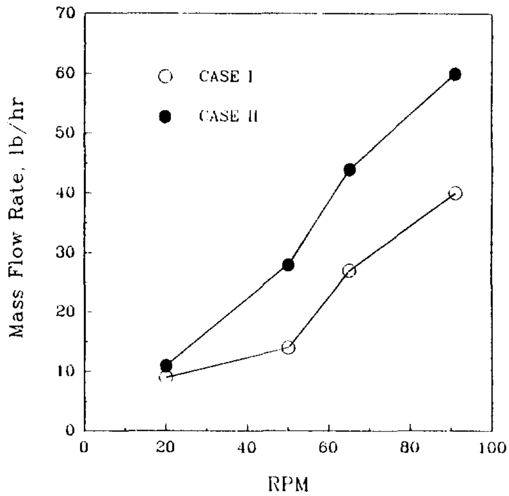

Fig. 2. Comparison of output rate between case I and II.

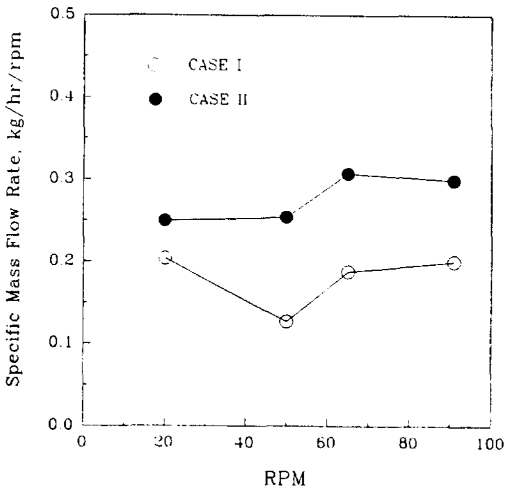

Fig. 3. Specific output rates for case I and II.

Fundamentals of solid conveying in single screw extruder is a drag induced mechanism which is largely dependent on the friction between barrel and polymer.[1,2,10] In general, the coefficient of friction is known as a function of temperature, pressure and the relative velocity of polymer with respect to the metal surface. Small changes in coefficient of friction can cause dramatic changes in extrusion rate. An external means of altering the coef-

Fig. 4. Starved flow visualization in the 1st metering section. It represents the flow behavior from 6 to 16 turns at 90 rpm for case II.

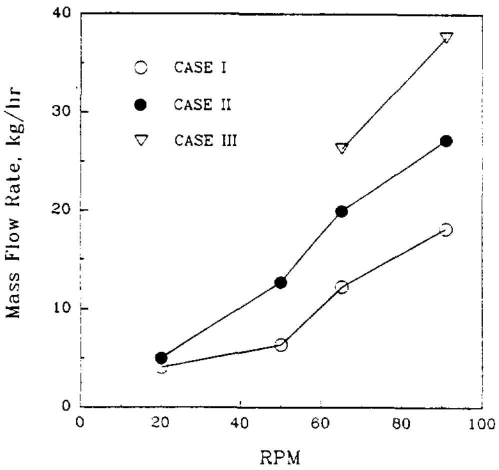

Fig. 5. Comparison of output rate of case I, II, and III.

ficient of friction is the barrel temperature setting. By choosing the optimum barrel temperature, the maximum coefficient of friction of polymer on the barrel can be obtained. To elucidate the effect of barrel temperature on the solid conveying rate further, zone 1A and 1B were controlled at 127℃ and 182℃, respectively.(CASE III) Comparison of extrusion output rate of CASE I, II and III is shown in Fig. 5. Extrusion output rate of CASE III is 40-50% higher than that of CASE II. The only difference between CASE II and CASE III is the barrel temperature of zone 1A. It demonstrates that lower the temperature of solid conveying zone results in higher extrusion output rate and it is probably related to the increase of coefficient of friction between barrel and polymer. The existence of maximum coefficient of friction of PP was reported between the glass transition temperature and melting temperature.[11,12] Huxtable[11] reported the presence of maximum coefficient of friction at ca. 100℃, while Kirkpatrick[12] observed it at 70℃ and 130℃. Difference can be attributed to different experimental conditions, such as sliding speed, normal load and surface condition. Surging, which occurs when overfeeding prevents a steady solid bed profile in the compression zone, was not reported during extrusion within experimental range. From the result of screw cooling experiment and the increase of extrusion output rate with decreasing barrel temperature of solid conveying zone without surging, it can be concluded that the solid conveying process affects the extrusion rate in cracking of PP more significantly than melting and metering processes. However, it has to be cautious that too much lowering temperature for zone 1A can cause a rapid increase of pressure in solid conveying and plasticating zone and can cause a failure of extruder.

Effect of Mixing Section. The quality of the extrudate is important in industrial process. The MW and MWD of the extrudates using blister ring or pin type mixing section as determined by high temperature size exclusion chromatography, Du Pont 900, are shown in Fig. 6 and Table 1. From the comparison of curves in Fig. 6, it is obvious that pin type shows larger amount of high and low molecular weight region than that of blister ring. It indicates that more uniform degradation reaction was obtained by blister ring mixing section. To find out the effect of mixing section on the extrusion characteristics, blister ring type was compared to pin mixing type. As shown in Fig. 7, slightly higher extrusion rate is observed with blister ring at 60 and 106 rpm. Specific energy is calculated from the gross energy input from the extruder drive divided by the output rate. Blister ring shows slightly lower specific energy than that of pin type (Fig. 8). One of reasons for the above results (Figs. 7 and 8) can be attributed to the lower MW (i.e. lower viscosity) of the extrudate with blister ring mixing section as shown in Fig. 6. More detailed investigation, such as pressure distribution in mixing section, will be carried out to find out the effect of mixing section on the extrusion rate.

CONCLUSIONS

It may be concluded that solid conveying rate is most likely to be the rate controlling factor in reactive single screw extrusion of peroxide premixed PP. Barrel temperature profile affect the extrusion rate significantly. High extrusion rate can be obtained by lowering the barrel temperature of solid conveying zone and it is attributed to the increase of coefficient of friction between polymer and barrel.

From a given screw configuration, blister ring

Table 1. Molecular Weight and Molecular Weight Distribution of Raw PP and Reacted Extrudates Using Different Type of Mixing Section

Description	M_n	M_w	M_w/M_n
Paw PP	6.4×10^4	3.86×10^5	6.0
Pin	3.8×10^4	1.81×10^5	4.72
Blister	4.4×10^4	1.73×10^5	3.89

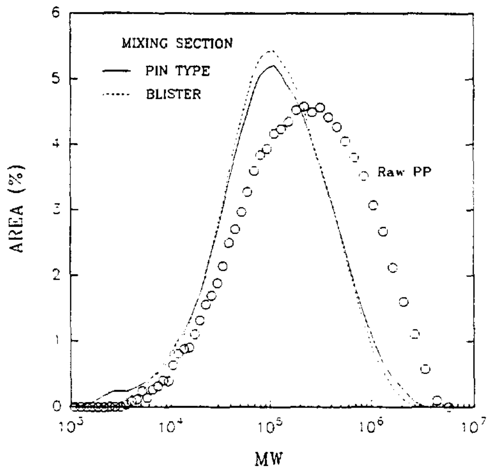

Fig. 6. HTSEC diagram of CR-PP and raw PP. Lines represent the CR-PP and circle represents a raw PP.

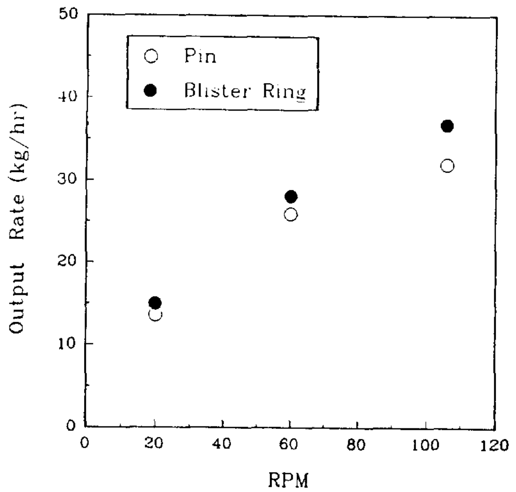

Fig. 7. Effect of type of mixing section on the output rate.

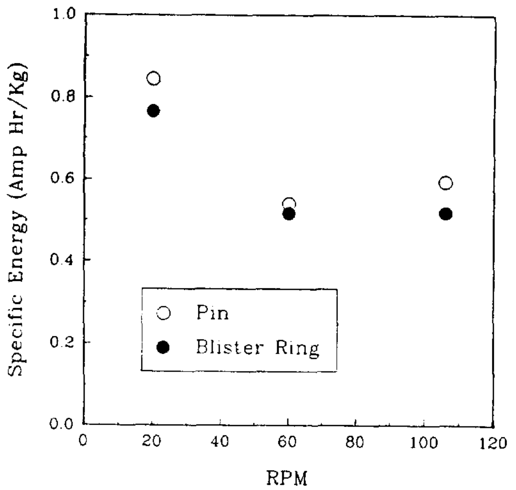

Fig. 8. Effect of type of mixing section on the specific energy.

mixing section resulted in slightly higher extrusion rate and relatively low molecular weight and narrow molecular weight distribution of final product than that of pin mixing section. However, it can be reversed by changing the dimension of the mixing section such as clearance and width of the blister ring.

ACKNOWLEDGEMENT. Author acknowledges the thanks to Professor C. G. Gogos and Dr. M. Xanthos of Polymer Processing Institute at Stevens Institute of Technology for their helpful discussion.

REFERENCES

1. Z. Tadmor and C. Gogos, "Principles of Polymer Processing", John Wiley, New York, 1979.
2. C. Rauwendal, "Polymer Extrusion", Hanser, New York, 1986.
3. C. Cheng, *46th SPE ANTEC,* 34 (1988).
4. R.E. Christensen and C.Y. Cheng, *49th SPE ANTEC,* 74 (1991).
5. C.Y. Cheng and R.E. Christensen, *50th SPE ANTEC,* 2165 (1992).
6. C. Tzoganakis, Y. Tang, J. Vlachopoulos, and A. E. Hamielec, *Polym. Plast. Technol. Eng.,* **28,** 319 (1989).
7. R. Lew, D. Suwanda, and S.T. Balke, *J. Appl. Polym. Sci.,* **35,** 1049 (1988).
8. S.H. Ryu, C.G. Gogos, and M. Xanthos, *Adv. Polym. Tech.,* **11,** 121 (1992).
9. C. Tzoganakis, Y. Tang, J. Vlachopoulos, and A. E. Hamielec, *J. Appl. Polym. Sci.,* **37,** 681 (1989).
10. M.A. Spalding, D.E. Kirkpatrick, and K.S. Hyun, *Polym. Eng. and Sci., Mid-April,* **33,** 423 (1993).
11. J. Huxtable, F. N. Cogswell, and J. D. Wriggles, *Plastics and Rubber Processing and Applications,* **1,** 87 (1981).
12. D. E. Kirkpatrick, K. S. Hyun, and C. I. Chung, *Polym. Eng. and Sci., Mid-October,* **33,** 1261 (1993).