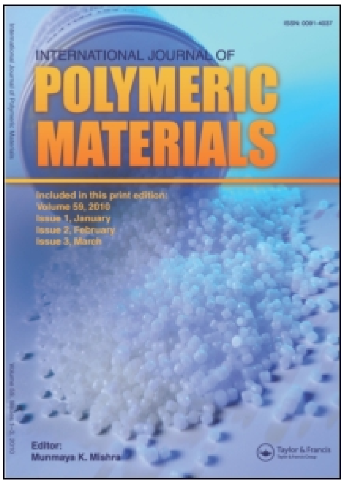

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Thermal degradation of polypropylene in a capillary rheometer

Jan-Chan Huang[a]; Junke Xu[a]
[a] Department of Plastics Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, USA

To cite this Article Huang, Jan-Chan and Xu, Junke(2003) 'Thermal degradation of polypropylene in a capillary rheometer', International Journal of Polymeric Materials, 52: 3, 203 — 209

To link to this Article: DOI: 10.1080/00914030304896

URL: http://dx.doi.org/10.1080/00914030304896

International Journal of Polymeric Materials, 52: 203–209, 2003
Copyright © 2003 Taylor & Francis
0091-4037/03 $12.00 +.00
DOI: 10.1080/00914030390119361

THERMAL DEGRADATION OF POLYPROPYLENE IN A CAPILLARY RHEOMETER

Jan-Chan Huang
Junke Xu
Department of Plastics Engineering, University of Massachusetts
Lowell, Lowell, Massachusetts, USA

Melt viscosity of a polypropylene (PP) resin was measured in a capillary rheometer between 220 and 260°C. The melt viscosity showed a power law behavior with strong shear rate dependence. The effects of temperature and shear rate on the degradation were studied in the rheometer by heating at 260 and 280°C, and extruding at shear rates up to 10000 sec^{-1}. Melt flow index (MFI) of samples after shearing and heating treatment was measured to characterize the molecular weight change. An increase in MFI was found for PP sheared at high temperature. Heating for longer time also increased MFI. Increase of shear rate had a small effect on increasing MFI at 260°C but produced a larger effect at 280°C. A constant increment in MFI was observed in PP subjected to high temperature processing and was attributed to degradation due to oxygenated products.

Keywords: polypropylene, melt viscosity, thermal degradation, melt flow index, extrusion

INTRODUCTION

Polypropylene (PP) is a thermoplastic material with a number of properties that make it a very versatile material among commodity plastics. Commercial isotactic PP is highly crystalline material and has a high melting point around 165°C [1]. This calls for a higher processing temperature than polyethylene and polystyrene. During

Received 13 November 2000; in final form 25 November 2000.

The authors would like to express their special thanks to Dr. R. D. Deanin of the Department of Plastics Engineering at the University of Massachusetts Lowell for his invaluable help and useful discussion.

Address correspondence to Jan-Chan Huang, Department of Plastics Engineering, University of Massachusetts Lowell, Lowell, MA 01854, USA. E-mail: jan_huang@uml.edu

processing, degradation occurs by thermo-mechanical degradation at high temperature and high shear rate, by the decomposition of hydroperoxide functional groups produced by auto-oxidation, or by reaction with oxygen [2, 3]. In the degradation process a chain scission occurs and the polymer molecule breaks into two smaller molecules. This process decreases the molecular weight and increases the melt flow index (MFI) [3, 4]. This reduction of molecular weight alters the mechanical properties of plastic parts. It also decreases properties of regrind or recycled resins as these materials experienced additional heat and shear in the subsequent processing step. The easiest way to follow PP degradation is to measure its melt viscosity. The zero-shear viscosity is proportional to the weight average molecular weight raised to the 3.4 power [5]. Measurement of melt viscosity in the low shear rate region can show the extent of molecular weight change. MFI is generally measured at a low shear rate. Small changes in molecular weight can easily be detected.

Several studies have been made on the effect of processing conditions on degradation of PP. Steward and Bradley [6] studied the influence of extrusion parameters on the degradation of PP. The change of molecular weight was followed by measurement of MFI and complex viscosity at 0.1 rad/sec. In the study it was found that an increase of screw speed led to roughly linear increase in MFI. The amount of increase of MFI depended upon the die pressure levels and the barrel temperature profiles employed. A high die pressure led to a large increase of MFI. A reverse temperature profile, which had 225°C at zone 1 and 175°C at zone 5, led to a smaller increase of MFI than the result from a forward temperature profile. Linear relationships were found between complex viscosity and MFI for two PPs used in their study.

Billian and Fleischmann [7] studied the molecular weight distribution of injection molded PP after different injection rates and melt temperatures. Selected layers of molded parts were analyzed by gel permeation chromatography (GPC). Serious degradation was caused mainly by high melt temperature. The effect of high shear rates and high shear stress was found to be less important. The impact strength decreased with both increasing melt temperature and flow front velocity. The surface layer and the spherulitic core could not be differentiated with respect to molecular weight distribution and melting temperature. Therefore, it seemed likely that the degradation processes took place in the sprue and plasticating system. The results of thermal and mechanical measurements correlated with the changes in the weight average molecular weight.

More recently Canevarolo [8] studied the molecular weight distribution of PP by GPC after multiple extrusions. The molecular weight distribution was found to shift to the low molecular weight side. The chain scission function (CSFD) was calculated as a function of the initial molecular weight. PP subjected to multiple extrusion showed that the chain scission process during thermo-mechanical degradation displayed a CSDF curve with a constant positive value in the low molecular weight region but a rise in the higher molecular weight region. This indicated that the probability of chain breaking was dependent on the degradation agressiveness and the molecular weight of the chain. The behavior was measured during multiple extrusions and using different screw configurations. CSDF values were higher the greater the agressiveness of the degradation, i.e., number of extrusions and screw configuration.

EXPERIMENTAL

The purpose of this study is to investigate the effect of temperature, shear rate, and heating time on degradation of PP. MFI was used to characterize the molecular weight of PP. The PP used was Fina 3622. It is a medium molecular weight commercial grade polypropylene for general injection molding processes. A Goettfert model 2001 capillary rheometer was used to measure melt viscosity and for effecting thermo-mechanical degradation of PP. Its barrel diameter was 15 mm. The capillary die had 1 mm diameter and 2 cm length. Melt viscosity was measured at three temperatures: 220, 240, and 260°C.

Thermo-mechanical degradation was conducted by extruding PP through the capillary die at two temperatures, 260 and 280°C, and at three high shear rates, 2000, 5000, 10,000 sec^{-1}. Two preheat times, 6 and 12 minutes, were used to compare the effect of heating time. The extrudate was collected and cut for the measurement of MFI. MFI was measured in a Tinius Olsen Extrusion Plastometer melt indexer according to the procedure of ASTM D1238. Condition L of the standard was used. This condition uses 230°C and a weight of 2160 gm on the plunger.

RESULTS AND DISCUSSION

The relationship between melt viscosity and shear rate of PP is shown in Figure 1. Results at each temperature showed strong shear rate dependence. The slopes were similar for the three temperatures and were estimated to be 0.7. These data can be shifted to a single temperature by the following formula [5]:

$$\eta(\dot{\gamma}/a_T) = \eta(\dot{\gamma})T_o/T \qquad (1)$$

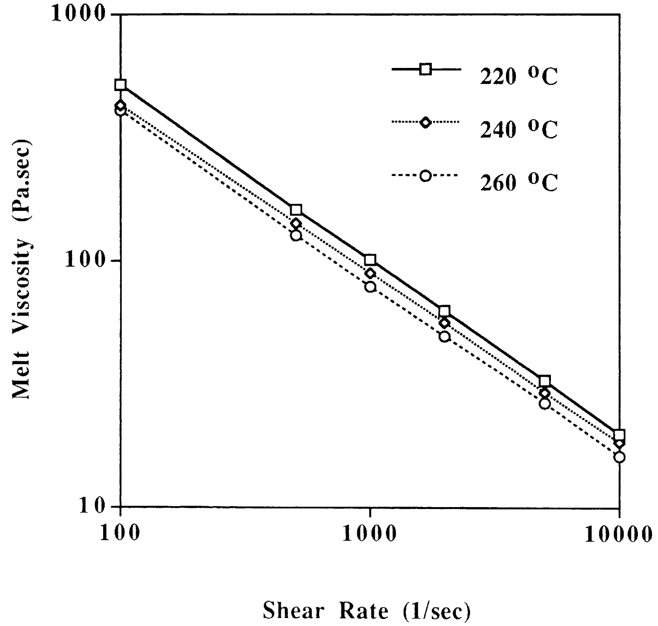

FIGURE 1 Melt viscosity of polypropylene.

Using 220°C as the reference temperature, T_o, the shift factors, a_T, were 1.6 and 2.5 for 240 and 260°C, respectively. From these shift factors the flow activation energy was calculated to be 11.9 kcal/mole based on the Arrhenius equation. This result is close to the value reported in the literature [9].

Table 1 shows the barrel pressure reading during extrusion of PP samples with heat treatment. A constant plunger speed was used for each shear rate and enough samples were collected for MFI measurement. Pressure readings indicated that heating for a longer time decreased the melt viscosity and reduced the pressure requirement in a constant shear rate extrusion. At 2000 $\sec^{-1}$ shear rate the melt took only 0.08 sec to pass a die with 1 mm diameter and 2 cm length. In such a short time the process can be considered as adiabatic. The adiabatic temperature increase was calculated based on the first law of thermodynamics:

$$\Delta T = \Delta P/\rho Cp \tag{2}$$

where ρ is the density and Cp is the specific heat of PP. In a steady state process all pressure energy is converted into thermal energy. The

TABLE 1 Barrel Pressure during Extrusion (Units = MPa)

	Barrel temperature			
	260°C		280°C	
Shear rate (1/sec)	6 min	12 min	6 min	12 min
2000	8.3	8.3	7.5	7.3
5000	11.0	10.7	10.0	9.5
10,000	13.4	13.3	12.1	11.7

largest temperature increase occurred at the lowest barrel temperature and highest shear rate. This is because the melt viscosity and barrel pressure were the highest at this condition. Using the density value of 850 kg/m^3 and specific heat of 2700 KJ/Kg°C for PP the maximum temperature increase was estimated to be 5.8°C. Note that this number may be reduced by heat conduction through the die surface. Therefore, the adiabatic temperature rise in the die was small compared to the difference in the barrel temperature settings.

Table 2 shows the effects of temperature, shear rate and heating time on the MFI. It can be seen that variation of shear rate had a small effect at 260°C, but a larger effect was seen at 280°C. The effect of temperature was more noticeable. When barrel temperature increased the MFI also increased. Longer heating time also increased MFI. The MFI of virgin PP was determined to be 10.2. It was noted that, when heating time increased twice, MFI increased more than twice. The relationship between increase in MFI and heating time was a linear but not proportional one. This can be explained as the result of two degradation mechanisms. The first mechanism includes oxygen. After PP is produced auto-oxidation takes place during storage [3].

TABLE 2 Melt Flow Index of Polypropylene after Different Shear Rates and Heating Times (Units = g/10 min)

	Barrel temperature			
	260°C		280°C	
Shear rate (1/sec)	6 min	12 min	6 min	12 min
2000	11.3	11.6	12.6	13.7
5000	11.7	12.1	13.5	15.7
10,000	12.1	12.6	14.6	17.5

Auto-oxidation generated hydroperoxide groups on carbon-carbon chain. During heating these hydroperoxide groups decomposed and broke the polymer chains. Another source of the breakage was the oxygen in air, which exists during normal processing. The amount of oxygen remaining in the barrel of the rheometer was constant for different temperatures and shear rates. Heating for a longer time would not increase the degradation due to oxygen. Therefore, it produced a constant effect in degradation. The second degradation mechanism was the pure thermo-mechanical process without participation of oxygen, which was dependent on temperature and shear rate, and would be expected to produce an effect proportional to the heating time. The combination of both mechanisms gave a linear increase of MFI with respect to time.

To verify the above argument, Figure 2 compared the MFI at different heating times. It can be seen that lines converge to a range of MFI from 11.1 to 11.7 at zero heating time. The intercept value of MFI at zero heating time was higher than MFI of the virgin material, which was measured to be 10.2. This indicated that the oxygen or

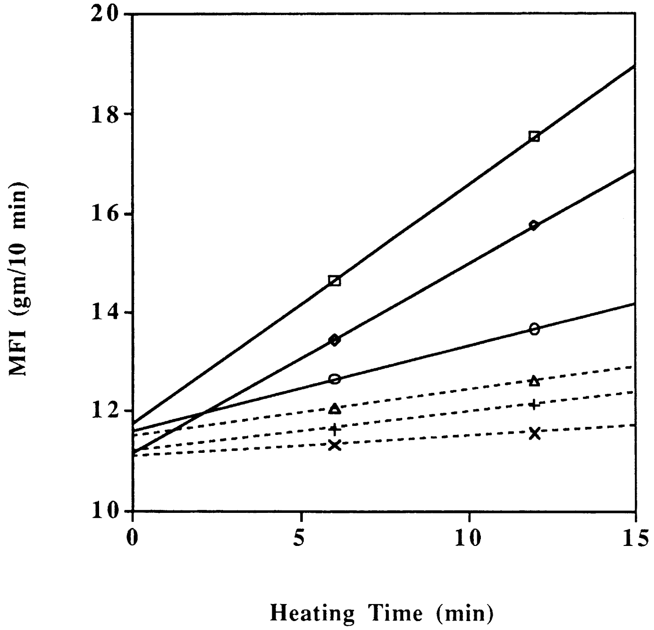

FIGURE 2 Effect of heating time on MFI of PP. Solid lines are 280°C and dashed lines are 260°C. For each temperature, from top to bottom, $\dot{\gamma} = 10000\,s^{-1}$, $5000\,s^{-1}$, and $2000\,s^{-1}$.

oxygenated products that existed in virgin PP were not completely reacted during the MFI measurement at 230°C but they were reacted during the capillary heating process. The effect of these reactions formed a constant increase in MFI for samples heated above 260°C and over six minutes. The difference in slope at different temperatures indicated that heating at higher temperature produced a higher degradation rate.

CONCLUSIONS

Thermo-mechanical degradation of PP was examined by the increase in MFI. High barrel temperature and long heating time increased MFI. Shear rate had a small effect at 260°C but a larger effect at 280°C. When compared with virgin PP, an additional increase of MFI was observed for PP heated at 260°C and 280°C. This was explained as the decomposition of oxygenated products.

REFERENCES

[1] Brydson, J. A. (1989). "Plastics Materials", 5th edn. Butterworths, Boston.

[2] Hinsken, H., Moss, S., Pauquer, J. R. and Zweifel, H. (1991). *Polym. Degrad. Stab.*, **34**, 279.

[3] Schnabel, W. (1991). "*Polymer Degradation. Principles and Practical Applications*", Hanser, New York.

[4] Huang, J. C. and Sirani, V. (2000). *Int. J. Polym. Mater.*, **46**, 151.

[5] Ferry, J. D. (1980). "*Viscoelastic Properties of Polymers*", 3rd edn., Wiley, New York.

[6] Steward, E. L. and Bradley, M. (1991). *J. Plast. Film Sheet*, **7**, 355.

[7] Billiani, J. and Fleischmann, E. (1990). *Poly. Degrad. Stab.*, **28**, 67.

[8] Canevarolo, S. V. (2000). *Polym. Degrad. Stab.*, **70**, 71.

[9] Van Krevelen, D. W. (1976). "*Properties of Polymers*", Elsevier, New York.