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Investigation of Molecular Weight Distributions during Extrusion Process of Polypropylene by Rheometry Experiment

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Abstract. Edge waste is an inevitable consequence of the cast film extrusion process, since the edges of the film are trimmed due to dimensional distortion and unpleasant layer distribution. On the other hand, most of the materials which are used in film production are not biodegradable. Therefore, for protecting the environment, the waste output should be reduced. For this reason, nowadays film production lines are equipped with inline recycling units which are also acceptable from the economic aspect, although, it caused degradation in polymer materials. Upon degradation, the film quality decreases which is associated with the molecular weight and molecular weight distribution (MWD) alterations. Despite this, film quality should be kept at a high rate as much as possible to be acceptable in the market. Hence, chasing MWD which is changed during the recycling process, is one of the hints for controlling the film quality. In this study, the degradation of the film grade polypropylene through recycling by twin screw extruder at 170°C and 220°C was investigated. It was assumed the material in the extruder was degraded by extremely high temperature and shear rate. The degradation of polypropylene subjected to multiple extrusions was evaluated by following the changes in the MWD curves in each run, which were indirectly obtained by rheometry based on the generalizing mixing rule. In this equation, Kernel function describes the relaxation behavior of a monodisperse component of molecular weight, and time is related to molecular weight, and the exponent β characterizes the mixing behavior of the chains. As its calibration, gel permeation chromatography (GPC) was also used. In this regard, two values of β ($\beta=2.5$ and $\beta=3$) and different kernel functions such as Tumulino, single exponential and Doi-Edward were used. According to the MWDs obtained from rheometry and GPC data, chain scission during the recycling processes was evaluated.

Keywords: molecular weight distribution, degradation, rheology, GPC
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INTRODUCTION

Recycling of polymer materials by extruding them is serious for economy and the environment, on the other hand degradation during extrusion is very common which could not be ignored. Degradation can be in various types such as chain scission and chain branching. The level of degradation is directly affected by the processing conditions and the intrinsic properties of the material [1, 2]. Expressions for the rate of chain rupture are obtained in terms of the melt viscosity, shear rate, and molecular weight. The variation of molecular weight distribution with shear degradation is considered, Moss and Zweifel studied the degradation of HDPE under multiple extrusions in a single screw extruder and observed that the Phillips HDPE type showed an increase in molecular weight, whereas a reduction was observed for the Ziegler-Natta type [3, 4]. The primary method for obtaining molecular weight distribution (MWD) parameters of a polymer, sufficient to describe the molecular structure, is size exclusion chromatography (SEC) also known as GPC. However, many polymers of commercial importance hardly dissolve in solvents, so that the chromatography column must be operated at high temperature or is not an option at all [5], which it is expensive and it's no economical. The rheological or viscoelastic properties of a polymer melt is strongly affected by its molecular architecture. Many attempts have been made to determine the MWD of entangled polymers from rheological data, mainly from linear viscoelastic response, by rheological models based on molecular dynamics [6, 7]. A generalized relation between MWD and relaxation time spectrum has been proposed to properly account for sharp MWDs of nearly monodisperse or blends of nearly monodisperse polymer samples [8]. On the other hand, it has been shown that the rheology method is of relevance in determining very high molar masses [9]. In the current study, molecular weight distribution (MWD) of bimodal polypropylene grade during extrusion process is investigated by GPC and rheometry,

and the changes in their MWD regarding either thermomechanical degradation or macro-radical reactions are discussed [10].

EXPERIMENTAL

Material

iPP1 as a bimodal polypropylene grade was provided by LyondellBasell, having a MFI of 8.0 g/10min (230 °C, 2.16 kg, ISO 1133), and density of 0.90 g/cm³. The resin initially were in a granule form in which no additive or stabilizer was added.

Sample preparation

The samples were prepared and degraded by a Werner-Pfleiderer modular intermeshing co-rotating twin-screw extruder. The diameter is 25mm and L/D is 40. The degradation conditions are written in Table 1.

TABLE 1. Degradation Conditions.

Material	Rotation Speed (rpm)	Runs	Output	Melt Temperature
Polypropylene	250	2	15 Kg/h	170 °C
Material	250	2	15 Kg/h	220 °C

The first time the polymers were processed as granules, and in the subsequent extrusions as pellets. After each extrusion enough sample was collected in order to carry out the characterization measurements in GPC and rheometer. All extrusions were done in air.

Characterization

Gel permeation chromatography (GPC)

The molecular weight distribution MWD curves were obtained from the GPC traces. The samples were accurately weighed and 9 ml of 1,2,4-trichlorobenzene (TCB) was added. After a Solubilization of 2 hours at 160 °C, the samples were injected in a flow of 1 ml/min. with 200 µl for measurement, at the end the Molecular weight MW curves were calculated by it results.

Rheology test

Dynamic melt rheological measurements were conducted by using Physica Anton Paar, MCR-501, Germany, with plate-plate geometry and gap of 1 mm. Their granule were used as a sample in this test. The tests were carried out in the frequency range of 0.01-100 Hz and at strain of 5. All measurements were performed at 230 °C. Material functions of complex viscosity, elastic and loss moduli, and weighted relaxation spectrum were determined. Afterwards, using the principles of double reptation theory, the average molecular weights as well as MWD were also determined.

RESULTS AND DISCUSSIONS

The MWD behavior of the samples has been measured by GPC, and their MWD are compared with one another. In figure 1 the MWD of the polypropylene grade is shown.

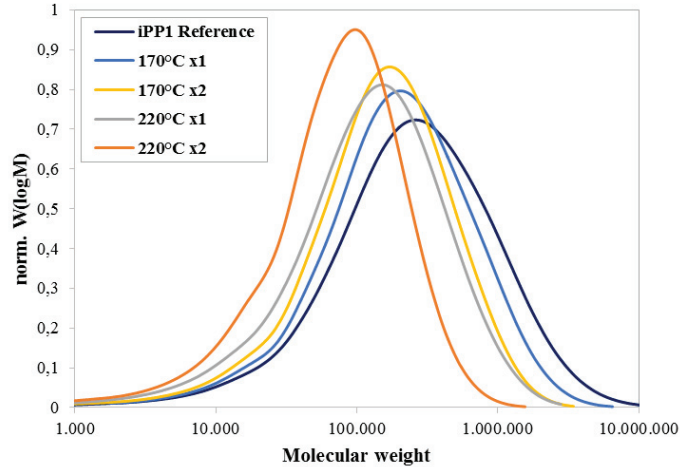


FIGURE 1. Molecular Weight Distribution of iPP1 by GPC

In figure 1, the thermo-mechanical degradation shifts the MWD curves to the low molecular weight (MW) side after each recycling turn, it means that chain scission is happened. i.e. some left shifts to low molecular weight in MWD of polypropylene grade appears due to its degradation and chain scission. Furthermore, the polydispersity index (PDI) of polypropylene, after being extruded, decreases and the height of curves, after decreasing the PDI, will increase. There is a stronger shift to the left for the sample which is degraded at 220°C x1 than 170°C x2, since temperature has more influence on degradation. In critical situation with continuing this recycling and chain scission phenomenon, the polymer changed to liquid like material.

Also MWD of these samples are estimated from rheology data as well. In this method, dynamic or oscillatory shear measurements were conducted first to determine the relaxation time spectrum, $h(\tau)$, from the measured dynamic shear moduli, $G'(\omega)$ and $G''(\omega)$. Second, the MWD was estimated from $h(\tau)$ using the double reptation theories proposed by Des Cloizeaux and Tsenoglou [11, 12] based on entanglement concepts, combined with a generalized mixing rule applying Thimm kernel function [13]. In this regard the generalized mixing exponent had to be adjusted and fixed. The computational method, on which their algorithms are based, is named Rheoplus software. The mixing parameter, β , is equal to 1 in simple reptation or tube model which corresponds to the theory of Doi-Edwards, equal to 2 in double reptation model [14]. Results are shown in figure 2.

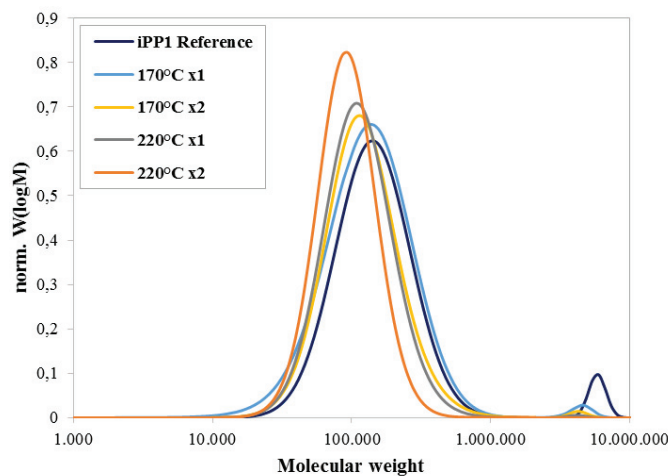


FIGURE 2. Molecular Weight Distribution of iPP1 by rheometer

After obtaining the rheology results, they were calibrated with GPC results. For better coincidence of GPC and rheology curves, after numerous attempts and tests, a value of $\beta=3$ was reached and Tumilino kernel function was chosen for calculation. It has been proposed that considering values slightly higher than 2 for β can describe contributions of higher-order entanglements in high molecular weight chains [15, 16]. As a result, curves are bimodal but unfortunately, due to the disablement of GPC, the second peak of the iPP1 is not clearly seen in figure 1. Rheology result also show chain scission by recycling as same as GPC result which is mostly happen for higher molecular weight. After recycling, the bimodal distribution was getting faded with higher degradation. Results in figure 2 shows that rheological material functions were much more sensitive to high molecular weight fraction than GPC elution curves, although they generated slightly narrower MWD curves with smaller polydispersity index (PDI).

The complex viscosity of the samples are shown in figure 3. Viscosity decreases obviously after recycling, especially at higher extrusion temperatures.

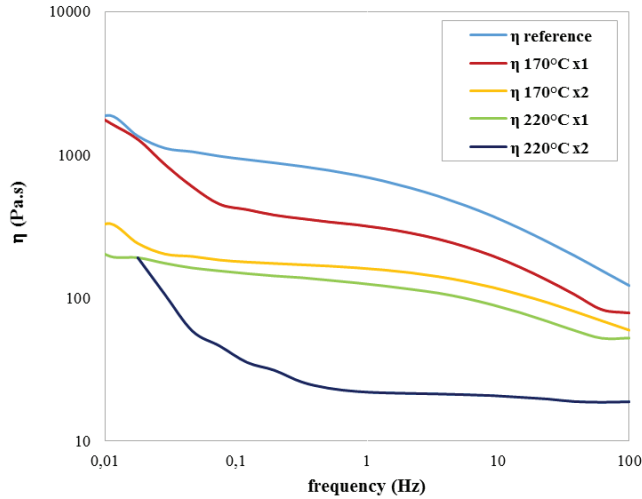


FIGURE 3. Complex viscosity was obtained by rheometer

Results of storage and loss moduli are displayed in figure 4. The characteristic relaxation time can be obtained from the inverse of the frequency where G' and G'' cross over in the flow transition regime (Eq. 1).

$$\text{Relaxation time} = \lambda = \frac{G'}{G''\omega} \quad (1)$$

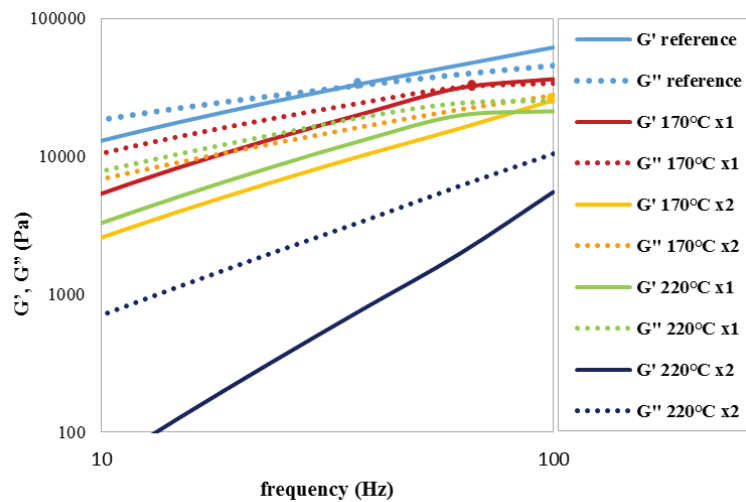


FIGURE 4. Storage and loss moduli and their cross over point (•) were obtained from rheometer

In figure 4, the crossover frequency increases upon decreasing molecular weight. Thereupon, with recycling, the relaxation time will become shorter and chain scission will occur.

CONCLUSIONS

In conclusion, chain scission followed by degradation for iPP1 with these conditions. If the degradation is preferentially carried out by chain scission the curve shifts towards the lower molecular weight side. Polypropylene will get liquid like material with continuing degradation.

To follow the degradation, molecular weight distribution (MWD) of the samples were investigated by using GPC and rheology analyses. Results showed that rheological material functions were much more sensitive to high molecular weight fraction than GPC elution curves, although they generated slightly narrower MWD curves. So that GPC was not able to show low amount of high molecular weight fraction while rheology clearly predicted a shoulder of high molecular weight fraction. The bimodal grade presented contributions of higher-order entanglements as existed in high molecular weight resins which led to more relaxation with longer times, higher elasticity and melt strength. With recycling the bimodal polypropylene MW will raise down and chain scission will be occur. In the stronger degradation situation the bimodal distribution will change to monomodal one.

REFERENCES

1. L.A. Pinheiro, M. A. Chinelatto and S. V. Canevarolo, "The role of chain scission and chain branching in high density polyethylene during thermo-mechanical degradation". *Polymer Degradation and Stability*, 86(3), 2004, pp. 445-453.
2. C. Capone, L. Di Landro, F. Inzoli, M. Penco, and L. Sartore, "Thermal and mechanical degradation during polymer extrusion processing". *Polymer Engineering & Science*, 47(11), 2007, pp. 1813-1819.
3. M. K. Loutcheva, M. Proietto, N. Jilov and F. P. La Mantia, "Recycling of high density polyethylene containers". *Polymer degradation and stability*, 57(1), 1997, pp. 77-81.
4. R. Gensler, C. J. G. Plummer, H. H. Kausch, E. Kramer, J. R. Pauquet and H. Zweifel, "Thermo-oxidative degradation of isotactic polypropylene at high temperatures": phenolic antioxidants versus HAS. *Polymer Degradation and Stability*, 67(2), 2000, pp. 195-208.
5. Dealy, J. M. and Larson, R. G., "Structure and rheology of molten polymers", Munich: Hanser, 2006
6. Borg, T. and Pääkkönen, E. J., "Linear viscoelastic models: Part II. Recovery of the molecular weight distribution using viscosity data", *Journal of Non-Newtonian Fluid Mechanics* **156**, 129-138 (2009)
7. Friedrich, C., Loy, R. J., and Anderssen, R. S., "Relaxation time spectrum molecular weight distribution relationships", *Rheologica Acta* **48**, 151-162 (2009)
8. Nobile, M. R. and Cocchini, F., "A generalized relation between MWD and relaxation time spectrum", *Rheologica Acta* **47**, 509-519 (2008)
9. Talebi, S., Duchateau, R., Rastogi, S., Kaschta, J., Peters, G. W., and Lemstra, P. J., "Molar mass and molecular weight distribution determination of UHMWPE synthesized using a living homogeneous catalyst", *Macromolecules* **43**, 2780-2788 (2010)
10. C. A. Caceres and S. V. Canevarolo, Calculating the chain scission distribution function (CSDF) using the concentration method. *Polymer degradation and stability*, 86(3), 2004, pp. 437-444.
11. C. Tsenoglou, "Molecular weight polydispersity effects on the viscoelasticity of entangled linear polymers", in *Macromolecules* **24**, 1762-1767 (1991)
12. J. Des Cloizeaux, "Double reptation vs. simple reptation in polymer melts", *EPL (Europhysics Letters)* **5**, 437 (1988)
13. W. Thimm, Friedrich, C., Marth, M., and Honerkamp, J., "An analytical relation between relaxation time spectrum and molecular weight distribution", *Journal of Rheology* **43**, 1663-1672 (1999)
14. S. J. Park, and R. G. Larson, "Tube dilation and reptation in binary blends of monodisperse linear polymers", *Macromolecules*, **37**, 597-604 (2004)
15. E. Van Ruymbeke, R. Keunings and C. Bailly, "Determination of the molecular weight distribution of entangled linear polymers from linear viscoelasticity data", *Journal of Non-Newtonian Fluid Mechanics* **105**, 153-175 (2002a)
16. Van Ruymbeke, E., Keunings, R., Stéphenne, V., Hagenaars, A., and Bailly, C., "Evaluation of reptation models for predicting the linear viscoelastic properties of entangled linear polymers", *Macromolecules* **35**, 2689-2699 (2002b)