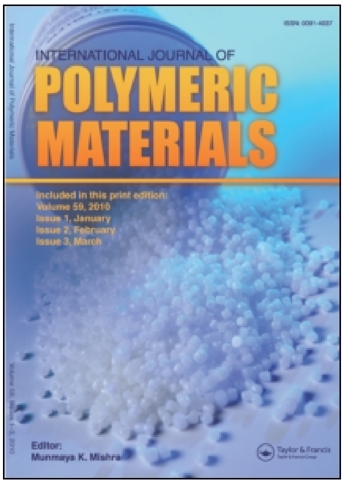

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Huang, Jan-Chan and Sirani, Venkateswarlu(2000) 'Controlled Degradation of Polypropylene by Reactive Extrusion', International Journal of Polymeric Materials, 46: 1, 151 — 155

To link to this Article: DOI: 10.1080/00914030008054849

URL: http://dx.doi.org/10.1080/00914030008054849

Intern. J. Polymeric Mater., 2000, Vol. 46, pp. 151-155
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Controlled Degradation of Polypropylene by Reactive Extrusion

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(Received 30 October 1998)

Controlled degradation of polypropylene is conducted in a single screw extruder using a peroxide initiator. Melt flow index was measured to study the effect of peroxide concentration and extrusion temperature on molecular weight. The increase in the melt flow index has been found to be mainly influenced by the peroxide concentration, not by the barrel temperature. Little change in melt flow index was seen after second extrusion. This is a clear evidence that total decomposition of peroxide was carried out in the extruder.

Keywords: Polypropylene; degradation; peroxide; reactive extrusion

INTRODUCTION

Polypropylene is a thermoplastic material with a number of properties that makes it a very versatile material among commodity plastics. When propylene is polymerized using heterogeneous Ziegler-Natta catalysts the polypropylene produced has weight-average molecular weight in the range of 3×10^5 to 5×10^5 and polydispersity between 5 and 20 [1]. The level of elasticity of high molecular weight polypropylene is very high and could cause some elastic strain be frozen into the product in high speed processing.

The influence of molecular weight on the bulk properties of polypropylene is different from other polymers. Increase in molecular

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weight of polypropylene leads to an increase in melt viscosity and impact strength, but a decrease in hardness, stiffness and softening point. This is believed due to the fact that high molecular weight polymer does not crystallize so easily as low molecular weight and leads to a reduction in stiffness [2]. Since the molecular weight distribution (MWD) largely determines the properties and the performance in processing, this parameter must be controlled in order to produce various grades suitable for different end use applications. In industry a single most important measurement on molecular weight is the melt flow index (MFI). A list of MFI of polypropylene for different end-use is giving in Table I [1].

In the case of polypropylene the MWD can be modified easily and economically in a simple post reactor process by employing controlled degradation in an extruder that removes the high molecular weight tails and leads to the production of speciality polypropylene having narrowing tailor made MWD's. Peroxide-initiated degradation requires less energy input and can be processed at a lower temperature than thermal degradation. Since the first report on controlled degradation through initiators [3] it has been a popular research subject [4–9]. The polypropylenes produced in this way exhibit reduced viscosity and elasticity compared to the parent commodity polymer while some of their mechanical properties like tensile strength, flexural modulus, and their crystallinity remains unchanged [1, 3, 4]. When a diversity of small batches of polypropylene is needed for the market place, controlled degradation using mass produced raw materials appears to be an economically feasible route. In this study the controlled degradation is studied in a single screw extruder smaller than those in other studies [3–9].

TABLE I End-use applications of polypropylene

MFI	*End-use applications*
2	Compression Moldings
1–5	Extrusion Blow Moldings
5–15	Film Tapes, Monofilaments
5–15	Biaxially Oriented Moldings
5–20	Injection Moldings
30	High Speed Injection Moldings
30–40	Flat Films
40–80	Staple Films
60	Spun-bounded Fabrics

EXPERIMENTAL

The peroxide used in this study is 2,5-Dimethyl-2,5-Bis(*t*-butyl peroxy) Hexane. It was obtained from AKZO chemie as Trigonox® 101. It is an odorless liquid with a boiling point of 249°C. Its one-hour half-life is 140.3°C [5]. The polymer used is Himont Pro-fax® 6801. It is a high molecular weight commercial grade of polypropylene homopolymer with melt flow index 0.3 gm/10 minutes. This material is designed for general extrusion processes.

The first step towards experimentation was to make a master batch of polypropylene and the peroxide. The masterbatch prepared was of 1% concentration of peroxide. First 300 grams of virgin powder polypropylene is weighed, then 3 grams of peroxide is weighted and mixed with ten times volume of acetone. The solution and polypropylene are mixed in a capped container, then hand shaken and also ball milled for approximately 20 minutes till a uniform mixture is made. Then the powder is placed in a stainless steel tray and left to evaporate acetone at room temperature till dry powder is obtained. The dry mixture is further diluted with polypropylene powder to make 750 grams mixture with the overall peroxide concentration range from 0.01% to 0.04% by weight.

The extrusion was conducted in a Brabender single screw extruder. The extruder has a constant square pitch screw with diameter of 19 mm, an L/D of 22, and a compression ratio of 2.95. The screw rpm was set at 20. To compare the effect of temperature and residence time two temperatures, 200°C and 220°C, were used and some samples were extruded twice After extrusion the samples were tested for the melt flow index according to the procedure of ASTM D1238.

RESULTS AND DISCUSSION

Results of melt flow index measurement are shown in Table II. The MFI of polypropylene before degradation is 0.3. Results clearly show that addition of the peroxide decreases the molecular weight of polypropylene leading to an increase in melt flow index. When processed at 220°C extrusion temperature, the result is close to the values obtained under 200°C. An increase in the processing temperature does not

TABLE II Melt flow index on polypropylene after extrusion

Peroxide concentration	*Extrusion conditions*		
	200°*C*	220°*C*	200°*C Twice*
0.01	1.75	1.50	NA
0.02	3.30	2.65	NA
0.03	4.75	4.69	5.44
0.04	6.05	7.13	6.19

give different results. It is clear that the reaction mechanism was not affected by a change in the temperature. Evaporation of the initiator in the extruder is not a problem neither even though 220°C is close to the boiling point of 249°C.

When extruded material was palletized and extruded again, the results show that there was no considerable effect of second extrusion on the melt flow index. This implies that the peroxide was totally decomposed in the first run, producing a peroxide free polypropylene. For a first-order decomposition kinetics, a residence time of six or seven half-lives in the extruder will give 98–99% decomposition of the initiator. The half-life of the initiator at 200°C has been reported to be ranging from 5.9 seconds [10] to 12 seconds [7]. Half-lives are known to depend on type and viscosity of the medium, the distribution of the peroxide in the melt and the presence of interfering species. The retention time of the extruder at low speed of 20 rpm appears to be sufficient to ensure total decomposition of the initiator.

The melt flow index appears to be linear with respect to the concentration of the initiator. A linear increment of MFI with peroxide concentration was reported by several investigators [4, 7, 9] in a relatively low concentration range up to 0.1 wt%. A linear least square fit of our data gives the following relationship between MFI and the initiator concentration [I] in wt%:

$$\mathrm{MFI} = 157[\mathrm{I}] + 0.107 \tag{1}$$

A similar relationship was obtained by Fritz [9] and by Suwanda *et al.* [5]. The former has a slop of 466 and the later group obtained a slope 126. Our slope compares closely to the result of Suwanda *et al.* In the study of Ryu *et al.* [7] a comparison was made between MFI of unstabilized polypropylene and the same polypropylene stabilized with 0.1 wt% of antioxidant Irganox® 1010 (Ciba-Geigy Co.). The results are both linear with different slopes. The stabilized samples have a slope of about 300 while the slope of unstabilized sample is about 600. It can be concluded that stabilizes have an effect in decreasing the slope. Both Fritz [9] and Suwanda *et al.* [5] reported their samples contained stabilizers. It is likely that the difference of stabilizers in samples causes the difference in slope.

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