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Polymer Testing 24 (2005) 86–93 Material Behaviour



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Rheological properties of polypropylene during multiple extrusion

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Received 26 May 2004; accepted 29 June 2004

Abstract

Polypropylene (PP) degradation during multiple extrusion at different temperatures was studied by following changes in rheological properties. Dynamic and transient experiments were carried out in a rheometer with parallel plate geometry. In addition, a statistical experimental design (2^2 , with replicates) was employed using die zone temperature (X_1) and number of extrusion cycles (X_2) varying at two levels. The system degradation was modeled using melt flow index (MFI) as a control variable. A rapid increase of chain scissions of the PP macromolecules and, consequently, a molecular weight reduction, was observed through abrupt increase of MFI and reduction of properties such as complex viscosity (η^*) and elasticity of the molten polymer.

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Keywords: Polypropylene; Rheological properties; Statistical experimental design; Degradation

1. Introduction

The wide range of properties that polypropylene (PP) has to offer makes it an extremely versatile material. The diverse properties of PP result from the variety of ways in which the polymer chains are built and the configuration of the monomer building blocks. In a general sense, there are three main PP types that even with similar rheologies (characterized by melt flow rate) can have widely different materials properties [1,2]:

- Homopolymers are the most common type of PP and they are built exclusively of propylene units;
- PP blocks copolymers. These are made by firstly polymerizing propylene, followed by the copolymerization of ethylene and propylene, to form a two-phase system consisting of particles of ethylene/propylene (EP) rubber in a continuous PP matrix. The EP-rubber is responsible for the material's good low-temperature

toughness. In addition, they show a milky, hazy appearance, and also have a high melting point;

 PP random copolymers. These consist of ethylene units (and sometimes butylene) that are randomly distributed along the polymer chain. Because the randomness does not favour the formation of stiff crystalline structures, these materials are characteristically soft, transparent and, above 0 °C, also very tough. Depending on the comonomer content, the melting point can range from 135 to 155 °C.

Recently, a fourth type of PP has emerged-the random block copolymers. Like block copolymers, they form twophase systems: particles of EP rubber in a random copolymer matrix. Because the continuous phase is somewhat softer than that of the block copolymers, the random block copolymers are less prone to stress whitening and able to match the stiffness/toughness properties of thermoplastic polyolefinic elastomers. Nowadays, there is also a growing market for atactic PP, an amorphous variety which was once an undersirable by-product in the production of istotactic PP and of little economic importance. For all these reasons, PP is used for a huge variety of applications: fibres, spunbonded

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non-wovens, tapes, film and sheet, board, tubes and blow moulding, and for all sorts of injection moulded parts. With new grades, the relative importance of PP is increasing and applications are being developed all the time [2–4].

However, when it comes to turning waste PP material directly back into new parts (so-called 'mechanical recycling'), this polymer's versatility and low price cause some problems. For maintenance of the properties of recycled PP, the PP must not only be separated from other polymers such as PE, PS, PVC and ABS, but also from itself (PP homopolymer from PP random copolymer, for example). Besides, it is necessary to have sufficient stabilization in order that direct recycling of PP presents no problems such as significant changes in molar mass, alterations to the polymer chains or morphology [1,3–5].

Polymer degradation is a problem that frequently occurs when a polymer is submitted to an extrusion process. Degradation usually manifests itself as discoloration, loss of volatile components (smoking) or loss of mechanical properties. According to mode of initiation, the following types of degradation can be distinguished: thermal, chemical, mechanical, and biological. Degradation processes are generally quite complex; often more than one type of degradation is operational, e.g. thermo-oxidative degradation, thermo-mechanical degradation, etc. [6].

So, the present work aims to study polypropylene degradation when it is subjected to multiple extrusion conditions. In order to achieve this goal, the PP rheological properties were determined after multiple extrusion cycles using various die temperatures.

2. Experimental

2.1. Materials and methods

Commercial polypropylene (HY-6100) was generously supplied by a Brazilian industry called Polibrasil and was used as received. The polymer physical characteristics from the manufacture are shown in Table 1. For extrusion, a single-screw extruder, Wortex model, with 30 mm diameter screw and length to diameter (L/D) ratio of 32, was used for multiple processing. The screw speed was fixed at 50 rpm for all experiments. This extruder has five temperature control zones and one melt pressure measuring device.

Physical characteristics of polypropylene

Properties	Values
Density (g/cm ³) (ASTM D792)	0.905
Tensile strength (MPa) (ASTM D638, 50 mm/min)	34
Hardness (Shore D) (ASTM D2240, 1 s)	70
Melt flow index (g/10 min) (ASTM D1238, 230 °C/2.16 kg)	1.8

Table 2	
Extruder temperature profile	

Barrel zone 1 (°C)	Barrel zone 2 (°C)	Barrel zone 3 (°C)	Barrel zone 4 (°C)	Die zone (°C)
195	215	225	225	240
195	215	225	225	270

The control zones correspond to the screw feed, transition and metering sections, and the last zone to the die.

2.2. Statistical experimental design

The experiments were arranged in a two level factorial design (2^2 with replicates) in order to evaluate the effect of die temperature (X_1) and number of extrusion cycles (X_2) on the PP degradation. Table 2 summarizes the extruder temperature profile used for multiple extrusion experiments. Four treatment combinations were carried out (Table 3) and two samples were taken at each particular treatment combination for melt flow index (MFI) evaluation. Virgin polypropylene was passed through the extruder, at conditions given in Table 3. The extrudate was quenched in a cold water bath (5–10 °C), air dried, and pelletized. This material, in a subsequent step, was then used for a new extrusion cycle.

2.3. Melt flow index (MFI)

MFI values were measured at 230 °C following ASTM D1238 using a Tinius–Olsen extrusion plastometer. The melt index tester is essentially a simple capillary rheometer. So, from the dimensions of the MFI apparatus, the weight on the plunger and MFI value, one can determine the approximate shear stress, shear rate and viscosity. The apparent viscosity can be determined from [6]:

$$\eta_{a} \cong \frac{4.86 * \rho F_{p}}{MFI} \tag{1}$$

where η_a is apparent viscosity (Pa s), ρ is polymer density (g/cm³), F_P is the weight on the plunger (2160 grams in 'L'

Table 3								
Algebric	signs	for	different	experiments	in	the	2^{2}	design

	-		-	
Variable	E1 ^a	E2	E3	E4 ^b
Die temperature (X_1)	_	—	+	+
Number of extrusion cycles (X_2)	-	+	_	+

^a –, Low level for extrusion conditions: $X_1 = 240$ °C and $X_2 = 5$ cycles.

^b +, High level for extrusion conditions: $X_1 = 270$ °C and $X_2 = 19$ cycles.

condition for polypropylene), and MFI is the melt flow index value in grams per 10 min.

2.4. Rheological analysis

The rheological properties of PP were determined using a Universal Stress Rheometer, Rheometric Scientific, SR5 All experiments were performed in parallel plate geometry, 25 mm diameter, at a temperature of 200 °C.

2.4.1. Dynamic mode operation

The dynamic mode was used to measure the complex viscosity (η^*), the storage (G') and the loss (G'') moduli as a function of frequency. A range of 10^{-1} to 10^2 rad/s frequency, with 5% strain and 2.00 mm gap, was chosen. In these experiments, a sinusoidal strain deformation, γ , is applied to a sample at a frequency, ω , and a strain amplitude, γ_0 [7]:

$$\gamma_{xy}(t) = \gamma_o \sin(\omega t) \tag{2}$$

The resulting stress, τ_{xy} , has two components, one in phase with the strain and related to the elastic modulus (G') and one 90° out of phase with the strain related to the viscous modulus (G'') [7]:

$$\tau_{xy}(t) = G' \gamma_o \sin(\omega t) + G'' \gamma_o \cos(\omega t)$$
(3)

The complex viscosity, η^* , is related to G' and G'' through the following equation and is often used to depict material properties [7]:

$$\eta * = (G' + G'')^{1/2} / \omega \tag{4}$$

2.4.2. Transient mode operation

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The transient mode was used to obtain more information about PP degradation. Transient or time-dependent shear flows are associated, for example, with start-up of processes involving the displacement of viscoelastic materials. Under such initial flow conditions, stresses can reach magnitudes which are substantially higher than their steady-state values achieved for the applied shear rate [7,8].

Stress growth experiments were carried out using straincontrolled mode with 1 rad/s shear rate and 1.5 min gap. For stress growth after onset of steady simple shear, the shear rate is given by the following expression [7,8]:

$$\dot{\gamma}(t) = \dot{\gamma}_{\infty} * h(t) \tag{5}$$

where $\dot{\gamma}_{\infty}$ is the constant velocity gradient for t > 0, and h(t) is the unit step function—h(t)=0 for t < 0 and h(t)=1 for t > 0. One defines the time-dependent viscosity (η^+) and primary normal stress difference (N_1^+) as [7,8]:

$$\eta^{+}(t, \dot{\gamma}_{\infty}) = -\frac{\sigma_{yx}(t)}{\dot{\gamma}_{\infty}} \tag{6}$$

$$N_{1}^{+}(t, \dot{\gamma}_{\infty}) = -[\sigma_{xx}(t) - \sigma_{yy}(t)]$$
(7)

Creep analysis was done imposing a constant stress of 100 Pa on the PP for five minutes. After this time, the stress was removed and the material was allowed to recover for 10 min. A 1.5 mm gap was employed and the creep compliance data, J(t), were estimated by [8]:

$$J(t) = J_{\rm e}(t) + t/\eta_o \tag{8}$$

where $J_e(t)$ is the elastic component of the creep compliance, i.e. after the flow term has been subtracted. The calculation of $J_e(t)$ obviously requires knowledge of the zero shear viscosity η_0 . In the conditions used in dynamic mode for the rheological experiments, η_0 was not determined. In this case, when η_0 is not known, the zero shear viscosity can be calculated from the reciprocal of the slope of J(t) at steady state, which is automatically determined by comparing slopes using rheometer software. The recoverable shear compliance, J_e^o , was obtained by extrapolation to the y-axis, where t=0, of the line resulting from the least squares fit [8].

3. Results and discussion

3.1. Statistical experimental design

The analysis of variance for an experimental design is useful to estimate the average effects and the more significant variables in a process. In the particular case, PP degradation was studied using a 2^2 factorial design and the MFI as the control variable. The calculation methodology is described in the literature [9] and the analysis of variance is summarized in Table 4.

If a level of significance $(\alpha) = 0.01$ is used, since the F_0 values found were greater than $f_{0.01,1,4} = 21.20$, it is possible conclude that the effects of die zone temperature (X_1) and number of extrusion cycles (X_2) greatly affect PP degradation. Furthermore, there is indication that the interaction effect between the die zone temperature (X_1) and the number of extrusion cycles (X_2) is more important than the number of extrusion cycles (X_2) alone.

Table 4							
Analysis	of	variance	table	for	PP	degradati	ion

Source variation	Sum of squares	Degree of freedom	Mean square	F_0
X_1 (die zone temperature)	983.24	1	983.24	2234.6
X_2 (number of extrusion cycles)	64.14	1	64.14	145.8
Interaction (X_1X_2)	495.65	1	495.65	1126.5
Error Total	1.77 1544.80	4 7	0.44	

A simple regression model can be used for a correlation between the results and the variables investigated:

$$\Psi = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 \tag{10}$$

where X_1 , X_2 and X_1X_2 represent die zone temperature, number of extrusion cycles and the interaction effect, respectively; β_1 , β_2 and β_{12} are estimated by one-half of the corresponding effect estimates, and β_0 is the global average; Ψ is the MFI. Thus, the equation for PP degradation was found to be:

$$\Psi = 17.5163 + 11.0863 * X_1 + 11.3263 * X_2 + 7.8713 * X_1 X_2$$
(11)

In Fig. 1, a three-dimensional surface plot resulting from the model used is shown. According to González et al. [10], three zones for the effect of temperature on PP degradation are observed: first, below 230 °C no degradation takes place; second, between 230 and 250 °C, the temperature is the defining degradation parameter; third, above 250 °C but below the initial degradation temperature, defined by thermogravimetric analysis, the increase of temperature had no effect on the degradation. Thus, Fig. 1 can be used as a model for defining the best extrusion conditions for PP waste recovery processes.

3.2. Rheological properties-dynamic mode

40

MH 30

20

10

The viscosity at very low shear rates is essentially independent of shear rate and, then, the fluid behaves as a Newtonian fluid. However, in the range of shear rates of 1-10,000 rad/s, frequently found in processing operations, most polymers develop a straight line relationship between viscosity and shear rate represented by the power law:

$$\eta(\dot{\gamma}) = m * \dot{\gamma}^{n-1} \tag{12}$$

where m is the consistency index and n the power law index. For pseudoplastic fluids, as most polymers, n indicates



0.5

Ó

X1

0.5

0 X2

-0.5



Fig. 2. Complex viscosity versus frequency for PP extruded. (A) Die zone temperature at 240 $^{\circ}$ C (B) Die zone temperature at 270 $^{\circ}$ C.

the degree of non-Newtonian behaviour. For PP, a typical n value is, approximately, 0.35 [11–13].

Fig. 2 shows the change of the complex viscosity, η^* , with frequency for multiple extrusion cycles of PP at different die zone temperatures (240 and 270 °C). It can be observed that at 240 °C (Fig. 2A), a Newtonian plateau is not clear even at low shear rate (0.1 rad/s) and as frequency is increased a relationship seemingly equal to the power law is obtained. In addition, η^* decreases gradually with the number of extrusion cycles. On the other hand, Fig. 2B (extrusions at 270 °C) shows not only η^* with lower values than η^* measured at 240 °C but, after 12 extrusion cycles, the formation of a Newtonian plateau which is extended until frequencies around 10 rad/s.

Viscous flow, the irreversible bulk deformation of polymeric material, is associated with irreversible slippage of molecular chains past one another. The most important structural variable determining the flow properties of polymers is molecular weight or, alternatively, chain length (the number of atoms in the chain). While the Newtonian melt viscosity is determined by weight-average molecular weight (M_w) [11,12], the dependence of viscosity on shear rate also depends on the molecular weight distribution

(MWD). The drop in melt viscosity below its Newtonian value begins at a lower shear rate and continues over a broader range of shear rates for polymers with broader distributions of molecular weight. At sufficiently high shear rates, the melt viscosity appears to depend primarily on number-average molecular weight (M_n) rather than weight-average molecular weight (M_w) [13].

Thus, in PP extrusion at 270 °C, η^* decreases not only by a temperature effect that increases the mobility of the polymer molecules, but also by a continuous thermomechanical degradation process caused by chain scissions. The highest molecular weight chains are preferentially broken during the degradation and the scissions may be located close to the macromolecule center. According to González et al. [10], when the macromolecules are extended in a shear field, in the direction of motion, the strain is primarily concentrated at the middle of the chain.

The crossover modulus, G_c , defined as the point where G' = G'', and the correspondent frequency, ω_c , can be used for an investigation of the structural modifications in the PP. The results for multiple extrusions at 240 and 270 °C are summarized in Table 5. The apparent viscosity, η_a , was also calculated from Eq. (1).

According to the literature [14], all viscoelastic materials behave more or less as a solid-like material (elastic) or liquid-like material (viscous) in response to a deformation rate at which they are deformed. This behaviour is related to the fact that strained macro-molecules tend to pull back to their original shape. The dynamic storage modulus (G') translates the elastic behaviour of the material and may be considered as the amount of the stored energy. The dynamic loss modulus (G'') represents the amount of dissipated energy. The change of G' and G'' with frequency is a measure of the relative motion of all molecules in the bulk.

Thus, from Table 5, it can be concluded that at lower temperatures, such as at 240 °C, PP still has several

Table 5

Crossover modulus, G_c , frequency associated to G_c and apparent viscosity for PP multiples extrusion

Condition ^a (die zone temperature (°C)/number of extrusions)	G _c (kPa)	$\omega_{\rm c}$ (rad/s)	η _a (Pa s)
240/5	15.1	24	3220.4
240/8	16.4	39.9	2357.4
240/12	16.5	41.3	1411.6
240/16	19.7	48.3	909.1
240/19	26.1	54.3	760.0
270/5	25.4	50.9	968.4
270/8	27.0	67.6	858.2
270/12			459.0
270/16			273.0
270/19			195.5

^a Above 12 extrusions cycles at 270 °C, G_c values were not detectable in the measuring range.

entanglement points and the mechanical chain breaking does not reach a level where extensive degradation occurs, especially, for a low number of extrusion cycles. In addition, $G_{\rm c}$ is measured at low frequencies (G' reaches G" in a short time) or, in other words, the number of high molecular weight chains is still significant so that the strained macromolecules show a pronounced elastic behaviour when they are exposed to low shear rates. On the other hand, when PP is extruded at 270 °C there is an abrupt degradation process and low values of apparent viscosity (η_a) and increase of the crossover modulus (G_c) are observed. The chain entanglements prevent irreversible flow by causing the formation of temporary networks (physical crosslinking), thus, a reduction in the high molecular weight chains will reduce the elastic contribution in the viscoelastic material or, in the other words, the dynamic storage modulus (G') of the polypropylene will be greater than the dynamic loss modulus (G'') only at higher frequencies.

3.3. Rheological properties-transient mode

Fig. 3 shows the curves of $\eta^+(t,\dot{\gamma}_{\infty})$ and $N_1^+(t,\dot{\gamma}_{\infty})$ versus time for PP samples extruded at 240 and 270 °C.



Fig. 3. Stress overshoot for PP samples (A) at 240 $^{\circ}\mathrm{C}$ and (B) 270 $^{\circ}\mathrm{C}.$

Table 6 Recoverable shear compliance (J_e^o) and zero shear viscosity (η_0) from creep and recovery analysis of PP samples

Condition ^a (die zone temperature (°C)/number of extrusions)	J_e^o (MPa ⁻¹)	η ₀ (Pa s)
240/5	453.9	42700
240/8	427.1	11260
240/12	411.5	8881
240/16	304.3	8729
240/19	288.3	7019
270/5	433.8	5457
270/8	311.8	4059
270/12	221.5	2265
270/16	135.5	1104
270/19		691

 $^{\rm a}$ At 270 °C, 19 extrusion cycles, it was not possible the determination of $J_{\rm e}^o.$

It is possible to observe that $\eta^+(t,\dot{\gamma}_{\infty})$ increases up to a maximum level. This maximum, stress overshoot, is related to the fact that macromolecules, although continuously strained, do not get to relax and to give an instantaneous response to imposed strain, because their relaxation times are much greater than the time scale of the experiment. Thus, a stress accumulation occurs since macromolecular conformation changes need a time greater than the time associated with viscoelastic response. For PP samples at 270 °C, the increase of $\eta^+(t,\dot{\gamma}_{\infty})$ is small when compared to the PP samples at 240 °C due to thermomechanical degradation. The number of long chains and entanglements was reduced and, consequently, there was a reduction of the melt elasticity and more stress dissipation.

This fact can be better analysed by $N_1^+(t, \dot{\gamma}_{\infty})$, which is a useful parameter for evaluation of die swell (a measure of the elastic recovery of the deformation that the polymer



Fig. 4. Creep and recovery for PP samples.

suffers when extruded). The elastic recovery process is time-dependent and the polymer has what is often called 'fading memory'. A deformation can be recovered to a large extent shortly after occurrence of the deformation; however, after large times the recoverable deformation reduces [7,14]. The reduction of $N_1^+(t, \dot{\gamma}_{\infty})$ in high temperatures conditions and with increasing number of reprocessing steps, is more evident in the PP sample at 270 °C and 19 extrusion cycles. Again, these results are derived from PP degradation.

In order to get more information about PP degradation and, consequently, about the elasticity reduction, polymer samples were also submitted to creep and recovery analysis. Parameters J_e^o and η_0 were estimated as previously described in Section 2. The results are presented in Table 6 and Figs. 4 and 5.

When a mechanical stress is applied to a polymer, introducing deformations of the chains, the entropy of the system decreases as less probable conformations are taken up. The free energy correspondingly increases. Using a simple mechanical model which combines a Maxwell and a Voigt element in series, a polymer sample in creep will show an elastic deformation at time t_1 as response to an applied, a viscoelastic response and a viscous flow. On the removal of the stress at time t_2 , the elastic element relaxes immediately and the viscoelastic one relaxes slowly. However, the viscous flow is never recovered [15–18].

Thus, considering the J_e^o and η_0 values and creep and recovery curves, it is clearly observed that the scission of the macromolecules decreases the elastic portion of the PP. For samples processed at high temperatures or extruded many times, η_0 decreases rapidly and the sample flows more easily and it presents more permanent deformation.

Polypropylene degradation at 270 °C, after 19 extrusion cycles, is pronounced so that the sample presents a high deformation during creep (above 3000%). Also, it can be observed that a steady-state was reached. On the other hand, for other samples this characteristic was not found. This fact is an indication of the reduction in viscoelastic nature. With the increase of the number of short chains and reduction of molecular weight, the polymer sample behaves more as a liquid-like material of low viscosity [13].



Fig. 5. Strain and recovery strain in creep for PP samples.

4. Conclusions

Polypropylene is a versatile thermoplastic with many applications but, although the recycling of PP wastes is important, a great loss in mechanical properties can occur by degradation during multiple extrusion processes by a combination of thermal, mechanical, and chemical degradation.

It was verified that high temperatures and multiple processing cycles conditions change rheological properties dramatically; not only does viscosity decrease but also the elasticity of the polymer is lost, as verified in creep and recovery analysis. In this manner, factors that are important in determining the rate of degradation are: residence time and residence time distribution, which is determined by the velocity profiles in the machine; stock temperature and distribution of stock temperatures; deformation rate and deformation rate distribution and the presence of degradation agents.

Hence, control of the extrusion process is an important step in thermoplastics recycling such as polypropylene.

Acknowledgements

The authors gratefully acknowledge the financial support for this project by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

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