Peroxide-controlled Degradation of Poly(propylene): Rheological Behaviour and Process Modelling

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SUMMARY: The control of the molecular weight distribution of poly(propylene) resins by peroxide degradation is widely used in polymer industry. It allows to adjust the viscosity of these resins to the level required for processing applications. The purpose of this work was to characterise the influence of peroxide degradation on the rheological behaviour of an homopolymer PP and a block copolymer PP/PE, and to use these results to obtain a predictive model of the degradation in a twin-screw extruder. By coupling a thermomechanical model of the twin-screw extrusion process, a kinetic model of the considered reactions and the rheological behaviour, it was possible to calculate the changes in molecular weight along the extruder, during the peroxide-controlled degradation.

Introduction

Polypropylene resins produced in most industrial polymerisation processes have a broad molecular weight distribution and a high molecular weight. In order to adjust the molecular weight distribution and improve the mechanical properties, polypropylene can be modified in reactive extrusion operations by means of peroxide initiated scission reactions. The process is initiated by free radicals formed from the thermal decomposition of organic peroxide which lead to significant polymer degradation by β-scissions, because of the low stability of tertiary hydrogen atoms of macroradicals1). In the present work, we present experimental studies of the free-radical initiated molecular weight degradation of two polypropylenes (an homopolymer and a block copolymer PP/PE) in a twin-screw extruder, and the modification of their rheological behaviours. We have prepared a series of differently degraded samples. The homopolymer exhibits a classical behaviour, whereas the rheological behaviour of the copolymer is influenced by the presence of the polyethylene phase, which greatly increases the viscosity when the polypropylene matrix is highly degraded.

Once the changes in viscosity with changes in molecular weight have been characterised, our second objective was to build a model which would be able to predict the evolution of the

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average molecular weight along the screws, in relation to the processing conditions and the geometry of the twin-screw extruder. Modelling the process involves resolving interactions occurring between the various flow conditions encountered in the extruder, the kinetics of the reaction and the changes in viscosity. We have studied the influence of operating parameters such as the initial peroxide concentration, the feed rate and the screw speed on the degradation reaction. Good agreement was found between theoretical results and experimental values.

Molecular weight distribution and rheological measurements

Two kinds of commercial polypropylenes have been studied: the first one was a standard homopolymer (PP 3050 BN 1, Appryl) and the second one was a block copolymer (PP 3060 MN 5, Appryl), which included an addition of a low percentage of polyethylene (less than 10 %). The homo- and copolymer had melt flow indices of 4.5 g/10 min and of 6 g/10 min (2.16 kg/230°C) and initial weight average molecular weights of 301600 g/mol and of 256100 g/mol, respectively. The peroxide used was the 2,5-dimethyl-2,5-di(*t*-butylperoxy) hexane (DHBP, Trigonox 101, Akzo Chemie). Reactive experiments were carried out in a co-rotating self-wiping twin-screw extruder (model 30/34, Leistritz). By using various amounts of peroxide (0.01 to 0.5 wt. %), we have obtained a series of polymers with different molecular weight distributions. Samples were collected at the die exit, after 15 minutes of steady state extrusion conditions (stable die pressure). Extrudates were quenched in water before being cut into pellets. The samples were dried under vacuum, at 80°C during a 24-hour period, in order to eliminate all residual peroxide.

The molecular weight distributions were analysed by size exclusion chromatography (SEC). The samples were dissolved at 145°C, at a polymer concentration of 0.8 g/L in the 1,2,4 Trichlorobenzene, which was used as a solvent, with the addition of an antioxidant to prevent any degradation. Irrespective of the material, we noted that increasing the peroxide concentration narrowed the molecular weight distribution and decreased the presence of high molecular weight species (Fig. 1a and b). Finally, we observed that the degradation of the homopolymer was more important than the copolymer's one. Indeed, the polydispersity is between 6.4 and 2.5 for the PP 3050 BN 1, and between 5.4 and 3.4 for the PP 3060 MN 5. Moreover, we noted the presence of high residual masses for the copolymer, even for the more degraded products (Fig. 2).

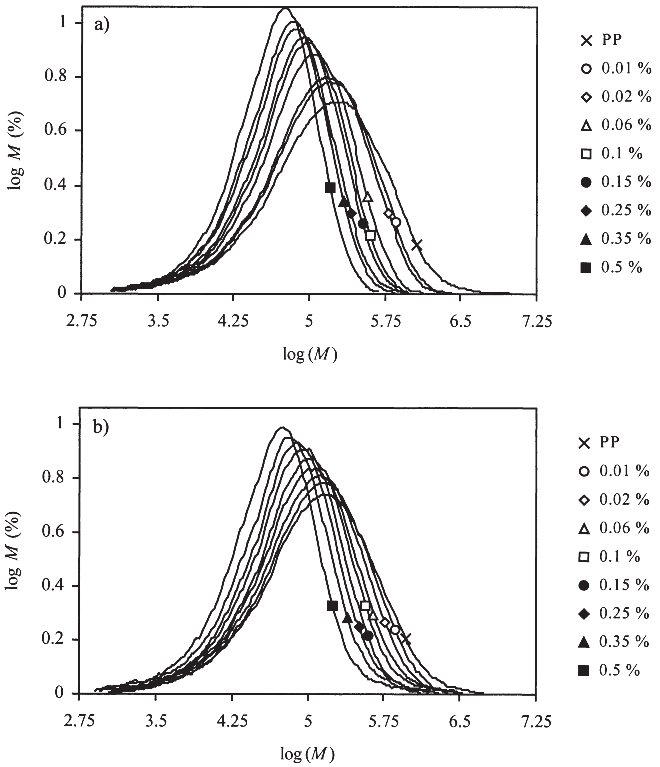

Fig. 1: Distribution of molecular weights in function of DHBP concentration for the homopolymer a) and copolymer b)

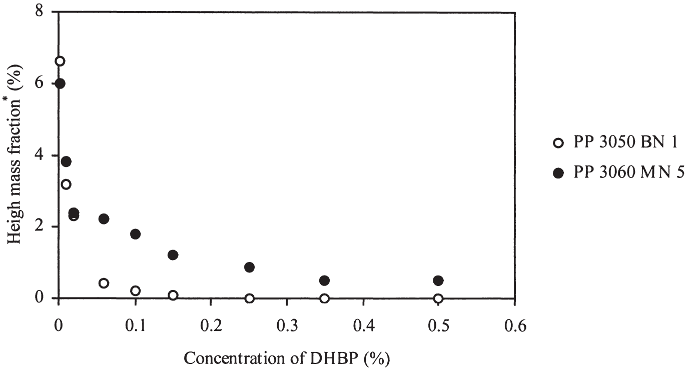

Fig. 2: Comparison of high mass fraction (*superior to 800000 g/mol) in function of the peroxide concentration between the homo- and the copolymer

The viscosity of these different molecular weight polypropylenes (301600 to 62970 g/mol for the homopolymer and 256100 to 74430 g/mol for the copolymer) were measured in a Rheometrics RMS 800 spectrometer, using parallel-plate geometry, in oscillatory mode. The dynamic measurements were carried out for frequencies ranging from 0.1 to 100 rad/s and at five temperatures (185°C to 245°C). Time sweep tests, made at these temperatures and at a frequency of 1 rad/s, showed that the complex viscosity and the storage and loss moduli were constant with time (30 min), whatever the homo- or copolymer. Fig. 3 shows the result of the time-temperature superposition, for the complex viscosity (reference temperature of 215°C). For the homopolymer, we observe the usual decrease in viscosity with decreasing molecular weight (Fig. 3a) and a pronounced shift towards more Newtonian behaviour$^{2)}$. For the copolymer (Fig. 3b), these tendencies are verified only for low amounts of peroxide (below

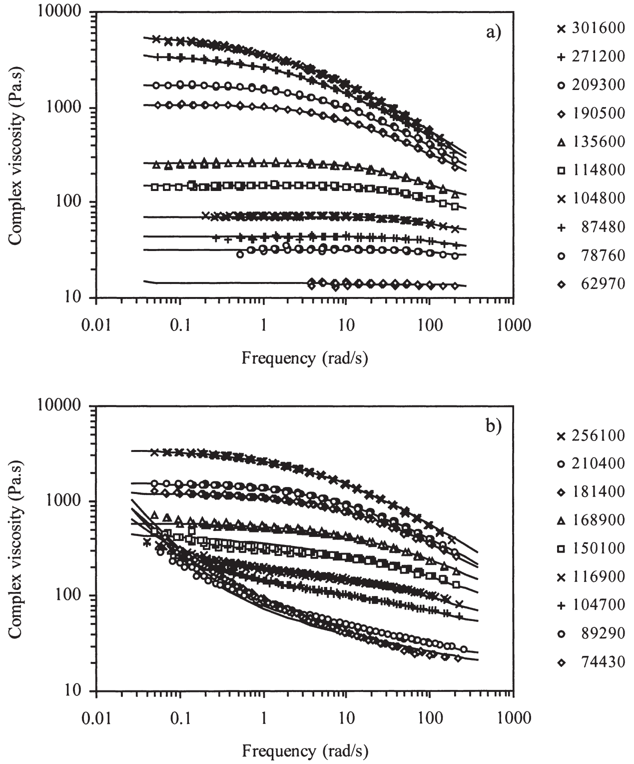

Fig. 3: Complex viscosity master curves at 215°C for the homopolymer a) and copolymer b) Symbols are experimental points corresponding to the different weight average molecular weight values (full lines are the theoretical fits using a model)

0.1 wt. %). When increasing this amount, and thus decreasing the molecular weight, we observe an increase in the complex viscosity first at low frequencies, and then even for high frequencies. For the more reacted samples, the copolymer has the comportment of a yield stress fluid: the complex viscosity tends to infinite at low frequencies. This behaviour is due to the presence of the polyethylene phase in the polypropylene matrix[3)]. The polypropylene is highly degraded and has nearly a Newtonian behaviour (Fig. 3a), whereas the polyethylene is much more viscous, eventually partially crosslinked, and behaves as a "solid" filler. The representation of the imaginary part η'', as a function of the real part η' of the complex viscosity (Cole-Cole plot) shows clearly the influence of the polyethylene phase for low molecular mass samples. Fig. 4 shows the difference in behaviour between the homo- and copolymer, at a same peroxide concentration equal to 0.08 wt. %. The weight

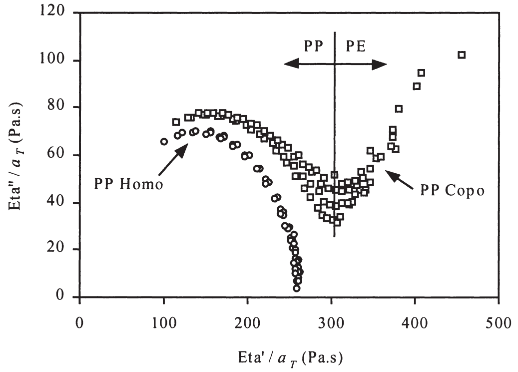

Fig. 4: Cole-Cole plot (reference temperature of master curves: 215°C)

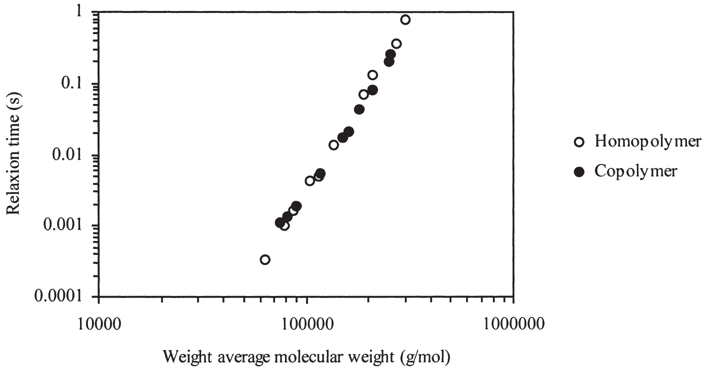

Fig. 5: Evolution of the average relaxation time

average molecular weight is 135600 g/mol and 150100 g/mol for the homo- and copolymer, respectively. For the copolymer, we observe a second relaxation mechanism, due to the PE phase, with much higher relaxation times. From the Cole-Cole plots, we can deduce the average relaxation times of the polypropylene phase, which are equal to the inverse of the maximal frequencies corresponding to the horizontal tangents at the top of circles. It can be observed that decreasing the molecular weight decreases the relaxation time4), whatever the homo- or copolymer (Fig. 5).

Modelling of the rheological behaviour

For modelling purpose, we need to define rheological relationships describing the behaviour of the polymers as function of molecular weight. We assumed the validity of the Cox-Merz rule and, for the homopolymer, we fitted a Carreau law model to the master curves to characterise the influence of the modifications induced by the peroxide. For the copolymer, we chose a yield stress Carreau law, to account for the viscosity increase at low shear rate :

$$\eta = \frac{\sigma_0}{\dot{\gamma}} + \eta_0 . a_T \left[1 + (\lambda \dot{\gamma} . a_T)^a\right]^{\frac{m-1}{a}} \quad \text{with} \quad a_T = e^{\frac{E_a}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]}$$

where a_T is the temperature shift factor, E_a the activation energy and R the gas constant. T_0 is the reference temperature (215°C) at which are determined the viscosity η_0, the stress σ_0, (for the homopolymer, $\sigma_0 = 0$), the characteristic time λ and the indices m and a. The result of the superposition of the experimental and calculated curves is shown on Fig. 3. These laws were later introduced into the twin-screw extruder global model. The determination of the parameters η_0, λ, m, a and σ_0 was done using identification software which minimised the differences between the measured and calculated viscosities.

Fig. 6 shows the evolution of each factor in function of the weight average molecular weight. We noted that the viscosity, η_0, which is characteristic of the Newtonian plateau, varied linearly with the logarithm of $\overline{M}_w$ (with a slope of 3.9 for the homopolymer and of 3.5 for the copolymer). For the homopolymer, we have observed that λ increased while m and a decreased continuously when increasing the molecular weight. For the copolymer, the tendencies are the same only for the power-law index m. The evolution of the indices a and λ is less regular. Their identification is more difficult to realise because there is no longer a Newtonian plateau for low frequencies and low molecular weights. We have noted that the characteristic time λ (average relaxation time) increased for the more degraded products, this increase is linked to the second relaxation mechanism, which is evidenced on the Cole-Cole plots. The values obtained for the stress, σ_0, reached about 20-25 Pa for the lowest molecular weights. Finally, we have observed that the activation energies, which were calculated by the horizontal and vertical shift of viscosity curves, decreased when increasing the molecular weight. This phenomenon is more pronounced for the copolymer (65 to 42 kJ/mol) than for the homopolymer (45 to 39 kJ/mol).

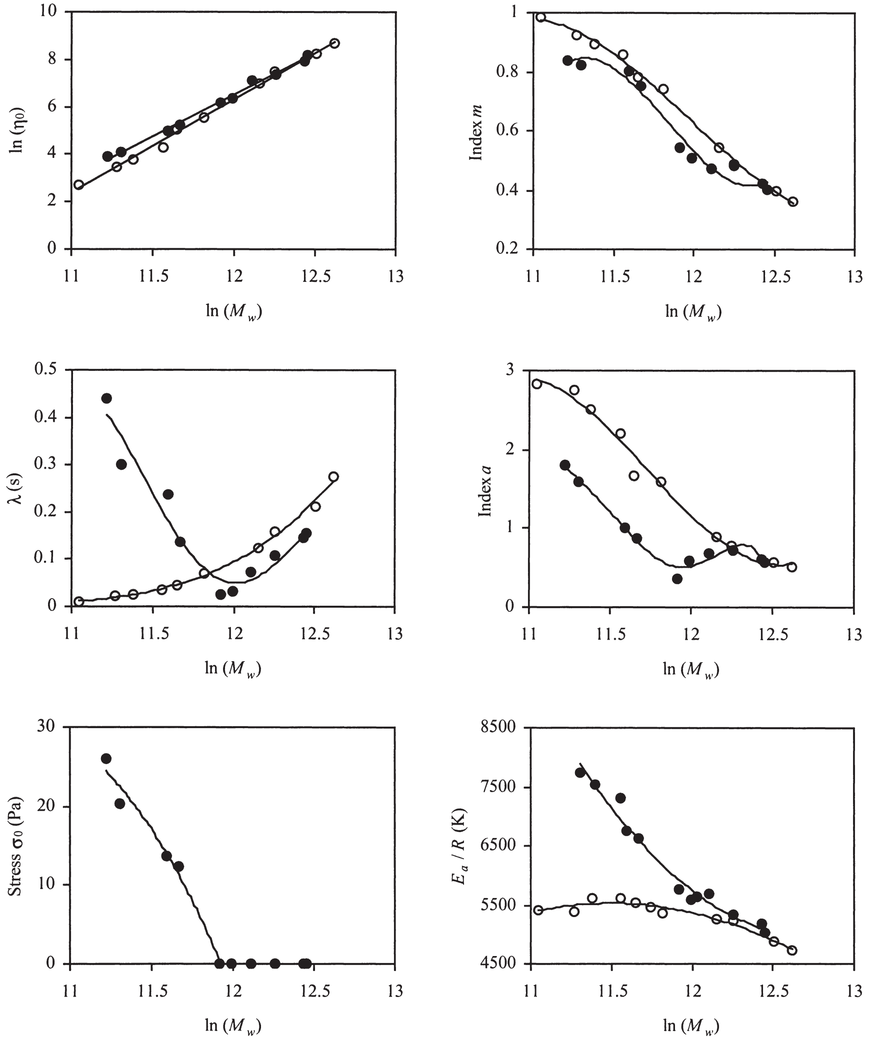

Fig. 6: Evolution of η_0, m, λ, a, σ_0 and E_a with the weight average molecular weight; empty symbols are used for the homopolymer and full symbols for the copolymer

Reactive twin-screw extrusion experiments and theoretical modelling

Our objective was to build a model which would be able to predict the evolution of the average molecular weight along the screws, in relation to the processing conditions and the geometry of the twin-screw extruder. In order to check the influence of operating conditions on the peroxide promoted degradation of polypropylene, we studied the effect of initiator concentration, throughput, screw speed and barrel temperature profile. The modelling of the process requires the resolution of the interactions between the various flow conditions encountered in the extruder, computed using the Ludovic® software package5), the kinetics of the reaction6) and the changes in viscosity with changes in molecular weight.

• Experiments

Reactive experiments were made in a co-rotating self-wiping twin-screw extruder (model ZSK 30, Werner & Pfleiderer), which included twelve barrel sections. The centreline distance was 26 mm, the screw diameter, *D*, 30.85 mm and the *L*/*D* ratio was 36, where *L* is the total length of the screws. The polypropylene pellets were fed via a weighted feeding system. The peroxide diluted in trichlorobenzene was injected into the extruder by a piston pump. The screw configuration used is shown in Fig. 7. The melting of the polypropylene was assured by kneading disc blocks and left-handed screw elements. The injection system for the peroxide was housed just after the melting zone, in an unfilled area. The reaction area included a first block of kneading discs, designed to improve the mixing between free-radicals and polypropylene, which was followed by conveying right-handed screw elements with decreasing pitches and a left-handed screw element just before the venting zone. At this level, the degradation reaction of polypropylene was stopped by the elimination by a vacuum pump of all volatile reactants which did not react. During the tests, the following parameters were varied : quantity of peroxide I_0 (0.0 to 0.4 wt. %), feed rate *Q* (2.5 to 20 kg/h), screw speed *N* (150 to 300 rpm). The barrel regulation temperature was fixed at 170°C. We chose a relatively low barrel temperature such that the degradation reaction was still unfinished upon reaching the devolatilization zone. This choice allowed us to examine the influence of the feed rate and screw speed (i.e. the influence of the residence time and temperature along the screws) on the molecular weight measured at the die exit. Indeed, tests conducted at higher barrel regulation temperatures (greater than 220°C) did not permit us to characterise the influence of processing conditions, as the reaction was finished before the vent zone, due to the very short half-life time of peroxide at these temperatures. At the die exit, extrudates were quenched in water before being dried and cut into pellets. Samples were collected after about 20 minutes of steady state extrusion conditions (stable die pressure and motor torque).

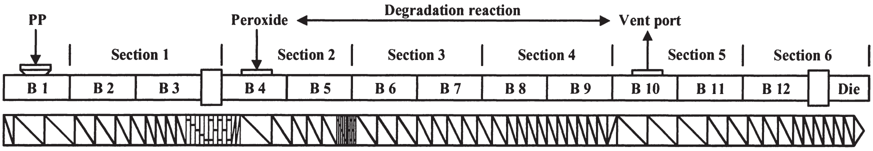

Fig. 7: Screw profile used for the experimental degradation of the homo- and copolymer

• Theoretical modelling

Kinetic Scheme: The following mechanism has been proposed by numerous authors$^{6\text{-}8)}$.

- Free-radical initiation:

$$I \xrightarrow{k_d} 2\,R^{\bullet} \tag{i}$$

- Hydrogen abstraction and chain β-scission:

$$P_n + R^{\bullet} \xrightarrow{k_1} P_r + P_{n-r}^{\bullet} + R \tag{ii}$$

- Inter-molecular chain transfer:

$$P_n + P_r^{\bullet} \xrightarrow{k_2} P_r + P_s^{\bullet} + P_{n-s} \tag{iii}$$

- Thermal degradation:

$$P_n \xrightarrow{k_3} P_r^{\bullet} + P_{n-r}^{\bullet} \tag{iv}$$

- Termination by disproportionation:

$$P_n^{\bullet} + P_r^{\bullet} \xrightarrow{k_4} P_n + P_r \tag{v}$$

I represents the free-radical initiator, $R^{\bullet}$, the peroxide free-radicals, P_n, the polymer, $P_n^{\bullet}$, the polymer macroradical and k_i, the rate constants.

By writing the change of concentration of the different species with time (peroxide, radical, polymer and polymer macroradical balance), we obtain an infinite set of differential equations. In order to reduce the dimensions of the infinite set of the obtained coupled differential equations, the i^{th} moment equations of the chain length distribution for the polymer (Q_i) and polymer radicals (Y_i) are introduced. Introducing these quantities into the infinite set of differential equations leads to a system of only eight equations[6-8]. To solve the problem, the majority of authors takes only into account the free-radical initiation (i) and chain scission reactions (ii), and neglect the contributions from transfer (iii), thermal degradation (iv) and termination reactions (v). In this work, we decided to solve the equations without neglecting any reaction, using the kinetic data provided by Krell et al.[6]. A Runge-Kutta method with adaptive stepwise control was used to solve the system of equations[9]. This kinetic model, which can accurately predict the reduction of the molecular weight, has a single variable parameter, f, the efficiency of peroxide.

Reactive Twin-Screw Extrusion Model: Degradation reaction was simulated using a one-dimensional global model developed for calculating the polymer flows in co-rotating self-wiping twin-screw extruders. The model used is described into details in previous papers[5, 10]. It allows to calculate the profile along the screws of the main flow parameters such as the pressure, mean temperature, residence time, shear rate, viscosity and filling ratio, by using a local one-dimensional approach. Elementary models of the flow in screw elements and blocs of kneading discs are linked together to obtain a global description of the flow field along the extruder. It is assumed that the melting is instantaneous and takes place before the first restrictive element of the screw profile. As the screws are starve fed, the filling ratio of the system is not known. So, the computation has to start from the die and to proceed backwards. But, as the final product temperature is unknown, an iterative procedure is used. Starting from an arbitrary value of exit temperature, the software computes the successive pressures and temperatures in each element, until the first restrictive element is encountered, in which the melting is assumed to take place. Convergence is achieved when, at this location, the temperature equals the melting temperature of the product. Otherwise, the exit temperature is modified and the computation restarted. The modelling of the reaction requires knowledge of the residence time spent inside each screw element and of the local temperature. We assume that the restrictive elements (left-handed kneading discs and screw elements) and the right-handed screw elements under pressure are completely full. For a sub-element, the mean residence time is assessed on the basis of the ratio of the free volume occupied by the molten polymer over the total flow rate. The calculation of average temperature is based on a local thermal balance, including the dissipated power, the heat transfer towards barrel and screws, and eventually the heat of reaction.

As seen before, the modelling of the flow parameters proceeds from the die towards the hopper, because, the screws being starved, the points at which the pressurisation of the material begins are not known. However, the calculation of the reaction progress of a chemical reaction must proceed in the opposite direction, because neither the final reaction rate, nor the residence time within the extruder is known. The calculation of the reaction begins at the place specified by the user, in the present case at the peroxide injection point. It is assumed that the peroxide is immediately homogenised. The coupling between the chemical reaction and thermo-mechanical parameters has been implemented as follows, assuming that the evolution in viscosity due to the chemical reaction progress does not modify in a significant way the filling ratio along the screws 9, 11):

- a first calculation without any coupling is started, with the rheological and physical properties of the virgin material (i.e. the polypropylene alone). During this backward calculation, points where the pressurisation of the polymer begins are identified.
- Then, a second calculation, in downstream direction, is started, which takes into account the interactions between the reaction conversion rate, the rheological changes and the flow parameters.

Results and discussion

General considerations: Fig. 8 represents the evolution along the screw axis of the temperature, the pressure, the cumulated residence time as well as the weight average

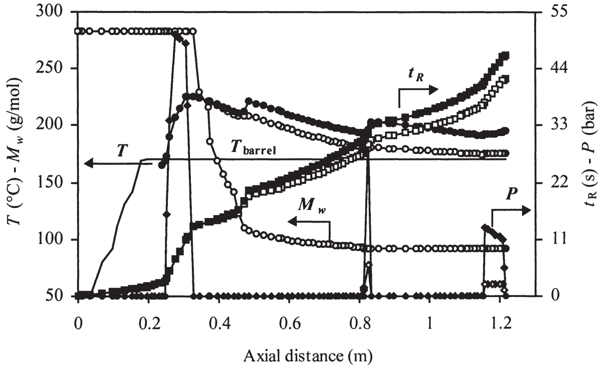

Fig. 8: Theoretical values of temperature, *T*, pressure, *P*, cumulated residence time, t_R, and weight average molecular weight $\overline{M}_w$; filled symbols: virgin PP; open symbols: degraded PP (10 kg/h, 225 rpm, 170°C, 0.4 wt. %, $f = 0.44$)

molecular weight. The calculation of reaction starts at the place where the reactants have been injected and stops at the level of the vent zone. It is worthwhile to mention that the calculations have been made with adiabatic conditions for the screw and a heat transfer coefficient towards the barrel, identical for virgin and degraded polypropylene, and regardless of the experimentally observed conditions.

Influence of peroxide concentration: As explained previously, the peroxide efficiency f is an unknown parameter of the model. In the literature, values between 0.6 and 1 are often used for peroxide concentration lower than 0.1 wt. %. In the present work, we decided to define f as a function of peroxide concentration. Efficiency values were obtained by fitting the model to the experimental weight average molecular weight measured by SEC. We chose $\overline{M}_w$ instead of $\overline{M}_n$ because the SEC's results are more reliable and accurate for the weight average than for the number average molecular weight. We observe that f decreases when the peroxide concentration increases (from $f = 0.96$ at 0.025 wt. % to $f = 0.44$ at 0.04 wt. % for the homopolymer and from $f = 0.92$ at 0.025 wt. % to $f = 0.38$ at 0.04 wt. % for the copolymer). In the next sections, when we will study the influence of processing conditions, f will be kept constant and just defined according to the amount of peroxide.

Influence of throughput and of screw speed: The change in mass average molecular weight along the screws for three different throughputs (at constant screw speed, $N = 225$ rpm) has been studied. We observe that the degradation is more rapid and more severe when the feed rate is low. This is principally due to a higher residence time, which increases from 40 s at 20 kg/h to 120 s at 2.5 kg/h. The experimental measurements made at the die exit show a very good agreement with the predictions of the model, for the two studied peroxide concentrations (0.1 and 0.2 wt. %). The influence of screw speed at constant feed rate is more difficult to foresee, because screw speed has an opposite effect on the two parameters which control the reaction: an increase in rotation speed decreases the residence time but increases the product temperature, due to a higher viscous dissipation. Despite a reduction of residence time from 65 to 40 s (when the screw speed is increased from 150 to 300 rpm), the polypropylene samples are more degraded at high rotation speed. This, is due to the fact that, all along the screws, the temperatures are higher at higher screw speed. Once again, the predictions of the model are confirmed by the SEC's measurements made at the die exit.

Other experiments have been carried out to check the validity of the theoretical model, using another machine (Werner & Pfleiderer ZSK 58). The computed ant measured results obtained for the copolymer are in good agreement, even if we did not take into account the presence of the polyethylene phase into the kinetic scheme. A general comparison is proposed in Fig. 9. The agreement concerning the weight average molecular weight is pretty good. For the number average molecular weight, the model leads to an overestimation, mainly at high peroxide concentration. Nevertheless, the order of magnitude is correct.

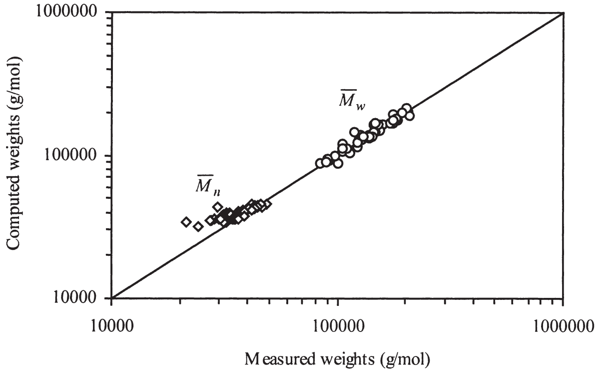

Fig. 9: General comparison between computed and measured average molecular weights

Conclusion

By reactive extrusion process, we have prepared series of differently degraded samples for both a PP polymer and a block copolymer PP/PE. We put in evidence the difference of rheological behaviour particularly at high level of peroxide between the two materials and the importance played by the presence of PE in the copolymer. The homopolymer exhibits a classical behaviour, whereas the rheological behaviour of the copolymer is influenced by the presence of the polyethylene phase which greatly increases the viscosity when the polypropylene matrix is highly degraded. Then we have proposed a modelling of the peroxide induced degradation of polypropylene in a co-rotating twin-screw extruder. Using a kinetic scheme taken from the literature and a rheological model accounting for the changes in viscosity with the weight average molecular weights, we have developed a specific method to couple the computation of the thermo-mechanical parameters of the flow along the screws with the reaction's progress. Once the efficiency of the peroxide is assumed, we are able to predict the changes in average molecular weights along the screw profile, accounting for the processing conditions (feed rate, rotation speed, barrel temperature). Experiments carried out with different machines provided results in good agreement with the predictions of the model.

References

1. H.-G. Fritz, B. Stöhrer, *Intern. Polym. Proc.* **1**, 31 (1986)
2. C. Tzoganakis, J. Vlachopoulos, A. E. Hamielec, *Polym Eng Sci* **29**, 390 (1989)
3. D.W. Yu, M. Xanthos, C.G. Gogos, *Adv. Polym. Tech.* **10**, 163 (1991)
4. C. Tzoganakis, *Can. J. Chem. Eng.* **72**, 749 (1994)
5. B. Vergnes, G. Della Valle, L. Delamare, *Polym. Eng. Sci.* **38**, 1781 (1998)
6. M. J. Krell, A. Brandolin, E. M. Vallés, *Polym. React. Eng.* **2**, 398 (1994)
7. C. Tzoganakis, J. Vlachopoulos, A. E. Hamielec, *Polym. Eng. Sci.* **28**, 170 (1988)
8. R. H. Ryu, Fundamental Studies on the Peroxide Controlled Degradation of Polypropylene, Ph. D. Thesis, Stevens Institute of Technology (1991)
9. F. Berzin, Etude expérimentale et modélisation d'une opération d'extrusion réactive, Ph. D. Thesis, Ecole des Mines de Paris (1998)
10. F. Berzin, B. Vergnes, *Int. Polym. Proc.*, **13**, 13 (1998)
11. F. Berzin, B. Vergnes, L. Delamare, P. Dufossé, *Polym. Eng. Sci.* (in press)

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