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Thermal degradation of polypropylene reprocessed in a co-rotating twin-screw extruder: kinetic model and relationship between Melt Flow Index and Molecular weight

Degradación térmica del polipropileno reprocesado en una extrusora de doble husillo co-rotatorio: modelo cinético y relación entre el índice de flujo de fusión y el peso molecular

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Abstract

Thermo-mechanical degradation of polypropylene (PP) during reprocessing causes significant changes in its properties and often its reuse in various application fields presents a challenge. In this study, PP was reprocessed multiple times (1 to 5 cycles, at 240, 260, and 280 °C), and the physical and structural properties of the reprocessed material were evaluated. In comparison to virgin PP, the reprocessed polymer presented a higher carbonyl index, higher melt flow index, lower average molecular weight, and narrower polydispersity. Changes in these parameters became more pronounced as the processing time and temperature increased. Additionally, two different behavior regions were identified, the first one spanning between 240 - 260 °C, and the second one comprising higher temperatures (280 °C). Moreover, a kinetic model that calculates the M_w of PP reprocessed at different temperatures was evaluated. Finally, adjusted parameters for the relationship between MFI and M_w were obtained, and the MFI of reprocessed PP was also calculated.

Keywords:Polypropylene recycling, polypropylene degradation, kinetic model, melt flow index, molecular weight.

Resumen

La degradación termomecánica del polipropileno (PP) durante el reprocesamiento provoca cambios significativos en sus propiedades y, a menudo, su reutilización en varios campos de aplicación parece un desafío. En este estudio, el PP se reprocesó varias veces (de 1 a 5 ciclos, a 240, 260 o 280 ºC) y se evaluaron las propiedades físicas y estructurales del material reprocesado. En comparación con el PP virgen, el polímero reprocesado presentó un índice de carbonilo más alto, un índice de flujo de fusión más alto, un peso molecular promedio más bajo y una polidispersidad más estrecha. Los cambios en estos parámetros se hicieron más pronunciados a medida que aumentaba el tiempo de procesamiento y la temperatura. Además, se identificaron dos regiones de comportamiento diferentes, la primera entre 240 y 260 ºC y la segunda con temperaturas más altas (280 ºC). Además, se evaluó un modelo cinético que calcula el M_w de PP reprocesado a diferentes temperaturas. Finalmente, se obtuvieron parámetros ajustados para la relación entre MFI y M_w, y también se calculó el MFI de PP reprocesado.

Palabras clave: Reciclaje de polipropileno, degradación de polipropileno, modelo cinético, índice de fluidez, peso molecular.

1 Introduction

Polypropylene (PP) is one of the most versatile plastics in the market. Its remarkable thermal, mechanical, and physical properties, account for its widespread use in the production of fibers, films, sheets, containers, and other consumer goods for the packaging, automotive, household, and textile industries (Balow, 2003; Heggs, 2011; Kissel *et al.*, 2003). The production of PP, which

has constantly increased over the years, was estimated at 86 million tons in 2018 (Hutley *et al*., 2016).

With such large volumes of PP in the market, increasing attention has been placed on the fate of this polymer after use.

Recycling has been evaluated as an environmental friendly, sustainable option for the repurposing of polymers (Sanjuan-Raygoza *et al*., 2009; Rojas-León *et al*., 2019). Recycling is particularly suitable for post-industrial plastic waste and industrial scrap, since these are pre-consumer materials that normally have a well-defined, homogeneous composition, are not contaminated with other plastics, dirt or domestic waste, and can be obtained in large volumes from the same source (Al-Salem *et al*., 2009; Hubo *et al*., 2014). Twin screw extruder is used to combine polypropylene and tire waste material with the possibility of obtaining recycled material (Lee *et al*., 2007) by varying process parameters (Nunes *et al*., 2018), as in the manufacture of materials based on recycled polypropylene reinforced with cellulose (Zander *et al*., 2019). However, twin screw extruder is not strictly necessary, often when the recycled polypropylene is not mixed with reinforcing material, a single screw extruder might be sufficient (Fu *et al*., 2017). From an industrial perspective, re-extrusion and mechanical recycling are the preferred approaches for recycling of PP due to their low cost, simplicity, effectiveness, and reliability (Hamad *et al*., 2013; Singh *et al*., 2017). However, the heat and strain applied during this process can cause thermo-mechanical degradation of PP, resulting in changes in its physical, structural, thermal, rheological, and mechanical properties (Hamad *et al*., 2013; Ragaert *et al*., 2017). Amongst these, the weight average molecular weight (M_w) and the melt flow index (MFI) are strikingly affected by thermo-mechanical degradation. Changes in these parameters affect polymer viscosity and processability, and thus their end-use (Krassig *et al*., 1984). Therefore, it is crucial to study the effect of the reprocessing settings used in plastics recycling on the final properties of recycled PP.

In addition to experimental analysis, mathematical modelling can assist in polymer characterization and in the study of polymer degradation as a result of recycling. For instance, polymer properties such as non-Newtonian shear viscosity and MWD can be predicted based on computer aided simulation (Seavey *et al*., 2003) or mathematical models (Luo *et al*., 2007). Parameter estimation encompassing key factors such as polymer concentration, screw temperature,

plasticizer concentration, and even extrusion rate, is also increasingly considered an important tool in polymer extrusion processing (Garcia-Cruz *et al*., 2020). Additionally, modeling has also been used to approximate the kinetic parameters of the thermal decomposition of polymers (Aranzazu Ríos *et al*., 2013), and to thoroughly study the reaction mechanisms involved in polymer degradation (Kruse *et al*., 2001; Kruse *et al*., 2002). In this regard, Kim and White proposed a detailed model of the thermal degradation of PP, which predicts the molecular weights of this polymer as a function of its processing conditions, e.g. temperature and residence time in the extruder (Kim *et al*., 1997). In its turn, the M_w predicted by this model can be used to predict MFI, since these parameters are correlated (Bremner *et al*., 1990; González-González *et al*., 1998). Detailed polymer characterization, through experimental analysis or mathematical modeling, is essential to ease the lingering concerns about polymer degradation during recycling and to address the lack of information on the quality and end-use applications of recycled polymers (Hopewell *et al*., 2009; Ragaert *et al*., 2017). In the present work we mimicked PP recycling by subjecting virgin polymer to multiple reprocessing cycles. The effect of reprocessing on polymer properties was evaluated using two approaches: (1) the characterization of reprocessed PP by IR spectroscopy, MFI and GPC; and (2) the description of a kinetic model for the calculation of M_w and MFI of PP processed at different temperatures and increasing extrusion time.

2 Materials and methods

2.1 Materials

PP homopolymer ValtecTM HS020 FM (150 ppm Irganox 1076 and 300 ppm Irgafos 168), with a typical MFI value of 4 g/10 min, was provided by Indelpro S.A. de C.V, Mexico. The polymer was used as received.

2.2 Polymer processing

PP extrusion was conducted in a co-rotating, twin-screw extruder (ZSK 26 MC[18], Coperion) at 400 rpm. The polymer was extruded 5 times (cycles 1 to 5) at either 240, 260, and 280 °C. The residence time was 3 minutes per cycle. This seemingly long extrusion

time allowed us to monitor the properties of PP after prolonged exposure to recycling conditions. Polymer samples were taken after each extrusion cycle and the properties of the reprocessed PP were compared to those of virgin PP (both were characterized as described in section 2.3).

2.3 Polymer characterization

2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

PP samples suitable for FTIR analysis (i.e. samples with flat and smooth surfaces) were prepared by compression of PP pellets in a melt flow index tester at 230 °C using a load of 2.16 kg. The FTIR measurements were performed with a Spectrum Two FT-IR spectrometer (PerkinElmer, USA). Spectra were recorded in a range of 450 to 4000 cm^{-1}, using 14 scans and a resolution of 4 cm^{-1} and processed with the PerkinElmer Spectrum software. The carbonyl index (CI) for the samples was calculated as the ratio of the absorbance of the carbonyl band at 1746 cm^{-1}, and the absorbance of the reference band at 2868 cm^{-1}, corresponding to the symmetric stretching of methylene groups (Barbeş *et al.*, 2014). Baseline corrections were applied to the spectra.

2.3.2 Melt Flow Index (MFI)

The PP samples were processed in a melt flow index tester DW5450A (Fanyuan Instrument, China) according to the ASTM D1238 ("ASTM D1238-13, Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer", 2013) at a temperature of 230 °C using a load of 2.16 kg (procedure B, standard test conditions).

2.3.3 Gel permeation chromatography (GPC)

Samples for GPC were prepared by dissolving 25 mg of PP in 10 mL of 1,2,4 - trichlorobenzene for 1 h at 170 °C. The samples were filtered prior to injection (stainless steel filters pore size 0.5 μm). The PP samples were analyzed in a PL-GPC 220 system (Agilent), using three PL gel 10 μm Mixed-B LS columns and 1,2,4 - trichlorobenzene as mobile phase (1 mL/min) at 140 °C. Refractive index and viscometer detectors were used for analysis. Polystyrene standards in a range from 1950 to 3,250,000 g/mol were used for calibration.

2.4 Calculation of the M_w and MFI of reprocessed PP based on mathematical modeling Polymer characterization

2.4.1 Background: Calculation of the M_w of reprocessed PP

A thorough mathematical model of the thermal degradation of PP in a twin-screw extruder was proposed by Kim and White (Kim *et al.*, 1997). By correlating the moments of the molecular weight distribution, the model estimates the average molecular weights (M_n, M_w and M_z) of PP at a given temperature and time. According to these authors, the kinetic equations for thermal degradation can be solved as follows:

$$r = \frac{d(p_n)}{dt} = \frac{dQ_0}{dt} = -k_{th}(Q_1 - Q_0) \qquad (1)$$

$$\frac{dQ_1}{dt} = -k_{th}(Q_2 - Q_1) \qquad (2)$$

$$\frac{dQ_2}{dt} = -k_{th}(Q_3 - Q_2) \qquad (3)$$

$$k_{th} = Ae^{-b/T} \qquad (4)$$

The polymer number-average molecular weight is represented by $[P_h]$, k_{th} represents the rate constant for thermal degradation, and T is the extrusion temperature in Kelvin. In the present work, we determined specific parameters for the thermal degradation of PP based on experimental data obtained in a temperature range of 240 - 280 ºC.

The solution of the equations for distribution moments Q_0 to Q_3 is aided by the contributions of Hulburt and Katz (Hulburt *et al.*, 1964):

$$Q_3 = \frac{2Q_2}{Q_1Q_0}(2Q_2Q_0 - Q_1^2) \qquad (5)$$

Considering the molecular weight of the propylene monomer (m_0), the average molecular weights of PP can be calculated by the formulae:

$$\overline{M_n} = m_0\frac{Q_1}{Q_0} \qquad (6)$$

$$\overline{M_w} = m_0\frac{Q_2}{Q_1} \qquad (7)$$

$$\overline{M_z} = m_0\frac{Q_3}{Q_2} \qquad (8)$$

Table 1. Parameters for the relationship between MFI and M_w (Equation IX) as a function of temperature.

Temperature (ºC)	G	x
240	2.33×10^{-12}	2.00
260	2.93×10^{-13}	2.16
280	1.74×10^{-16}	2.75

2.4.2 Relationship between M_w and MFI

The relationship between the M_w and MFI for linear polymers, which has been studied by different authors (Bremner *et al.*, 1990; González-González *et al.*, 1998), is given by:

$$\frac{1}{MFI} = GM_w^x \qquad (9)$$

where G is a coefficient and x is the Mark-Houwink exponent.

In their work, Bremner and Rudin analyzed several linear polymers with different MFI values by size exclusion chromatography and established that for PP $x = 3.7$ and $G =\sim 1 \times 10^{-21}$ (Bremner *et al.*, 1990). Years later, González-González *et al.* studied PP degradation during multiple extrusion steps at different temperatures and reported that $x = 3.5$ (González-González *et al.*, 1998). Furthermore, these authors studied the relationship between MFI and Mwn (the geometrical mean between M_w and M_n), instead of M_w alone, and therefore did not establish a value for G. We propose adjusted values for G and x at different temperatures, based on the M_w and on the MFI measured for reprocessed PP. The parameters obtained for Equation IX for the different temperatures are shown in Table 1.

2.4.3 Calculation of the M_w and MFI of reprocessed PP

In the present work, the M_w and MFI of PP processed under different conditions were calculated based on the equations I - IX, as follows:

1) The experimental MFI value of virgin PP was used to calculate the M_w of virgin PP (Equation IX).

2) The M_w value of virgin PP was used to solve the differential equations presented in section 2.4.1 (Equations I - V) using the Runge-Kutta fourth-order method in GNU Octave version 5.1.0 (Eaton *et al.*, 2019).

3) The equations solved in the second step were used to calculate the M_w of PP processed at different temperatures and extrusion times (Equation VII).

4) Finally, the MFI of PP processed at different temperatures and extrusion times was obtained by introducing the M_w of reprocessed PP in the equations that describe the relationship between M_w and MFI (Equation IX).

3 Results and discussion

3.1 Polymer characterization

3.1.1 FTIR analysis

Structural changes are often observed in degraded PP. These changes include the appearance of functional groups such as unsaturated, carbonyl and hydroxyl groups, which can be identified by FTIR spectroscopy (Andreassen, 1999). In the present work we focused on the FTIR analysis of carbonyl groups, which are present in several compounds, such as esters, aldehydes, and ketones. The carbonyl band is easily recognizable in IR spectra due to its relatively constant position (region 1870 - 1540 cm^{-1}), high intensity, and absence of interference with other bands (Silverstein *et al.*, 2005). For this reason, it has been studied for several decades to characterize polymer degradation (Hinsken *et al.*, 1991; Mellor *et al.*, 1973; Mylläri *et al.*, 2015; Xiang *et al.*, 2002).

A comparison of the FTIR spectra of PP processed multiple times (1 - 5 cycles, 240 - 280 °C) shows the progressive appearance of peaks in a range of 1760 - 1700 cm^{-1} (Figure 1). Within this range, the most prominent peak has its maxima at ~1746 cm^{-1}, and is in the region commonly attributed to esters (1750 - 1735 cm^{-1}). The shoulder at ~1710 cm^{-1} probably corresponds to carboxylic acids (region 1720 - 1706 cm^{-1}, carboxylic dimer) (Hinsken *et al.*, 1991; Silverstein *et al.*, 2005). The presence of carbonyl groups in the PP samples likely result from a mixture of mechanical, thermal, and oxidative degradation mechanisms (Wang *et al.*, 2011), since the samples were subjected to shear stress at relatively high temperatures (> 200 ºC) and in the presence of oxygen.
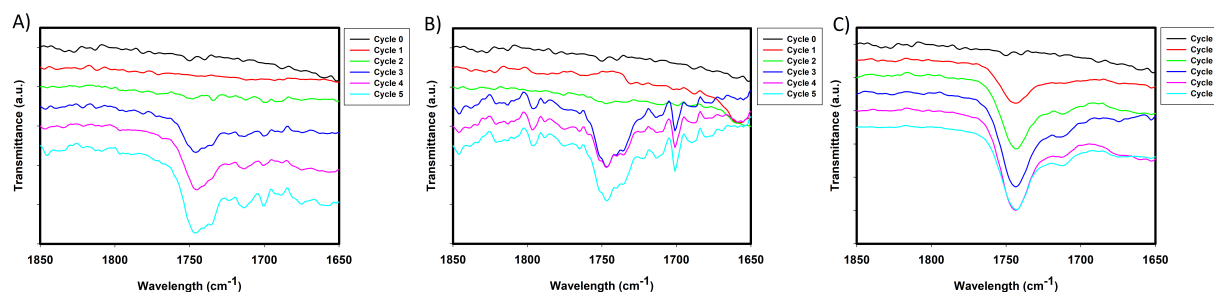
Fig. 1. FTIR spectra showing characteristic carbonyl bands in reprocessed PP. The polymer was processed multiple times at A) 240 °C, B) 260 °C, and C) 280 °C. Peak at 1746 cm^{-1} is in the carbonyl region. Spectra were normalized to 0.5.

For PP processed at 240 °C and 260 °C, carbonyl-containing groups are first clearly visible in samples subjected to 3 reprocessing cycles. In contrast, for PP processed at 280 °C, carbonyl-containing groups are already visibly in samples subjected to 1 cycle. It is therefore possible that the antioxidant(s) present in the commercial-grade PP samples under study can limit polymer degradation at temperatures ≤ 260 ºC, and at extrusion times < 15 minutes. In line with our findings, other authors have reported that antioxidants protect PP from thermal-oxidation under certain processing conditions. This protective effect was demonstrated by IR analysis, where the carbonyl bands were either non detectable or weak (Hoff *et al*., 1984; Wang *et al*., 2007). Interestingly, it was reported that Irganox B561 (1% w/w) prevented the degradation of PP after 2 minutes of oxidative treatment at 280 ºC, but that it could not protect the polymer at longer times. In fact, after 3 minutes, considerable oxidation (represented by strong carbonyl absorption) was observed (Hoff *et al*., 1984).
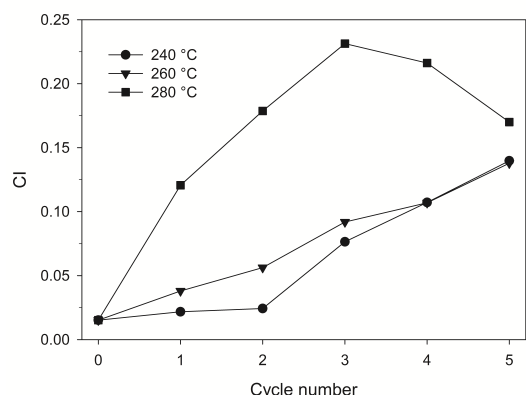
The structural changes in reprocessed PP can also be presented in terms of CI, which allows for a more direct comparison of the effects of processing conditions on the degradation of PP. CI of processed PP increased in a time and temperature dependent manner (Figure 2). Notably, for any given cycle, the increase in CI was more pronounced at 280 °C compared to 260 °C and 240 °C. Other authors have also used CI to study the photodegradation (Mylläri *et al*., 2015), thermal degradation (Qian *et al*., 2011), and thermomechanical degradation of PP (Canevarolo *et al*., 2002; Wang *et al*., 2011). In all these cases, the authors also observed an increase in CI with increasing treatment time. Nevertheless, unlike in our study, these authors did not evaluate the effect of temperature changes on carbonyl buildup.

3.1.2 MFI analysis

The MFI correlates with polymer molecular weight, viscosity and flow, and provides crucial information on polymer processability and end use. Therefore, we studied the impact of different processing conditions on the MFI of PP. At a fixed temperature, the MFI of the polymer increased directly with the number of processing cycles, thus a time dependent increase was observed (Figure 3). For PP processed at 240 °C, the MFI increased by ~90% from cycle 1 to cycle 5 (3.08 vs 5.93 g/10 min), and a similar trend was observed for PP processed at 260 °C (3.52 vs 6.88 g/10 min). More pronounced changes were observed for PP processed at 280 °C, for which the MFI increased more than 600% from cycle 1 to cycle 5 (4.58 vs 28.82 g/10 min).

A temperature dependent increase in MFI was also observed for PP samples. For instance, at equal processing times (cycles), the MFI of PP processed at 260 °C was between 12 and 35% higher than PP processed at 240 °C.
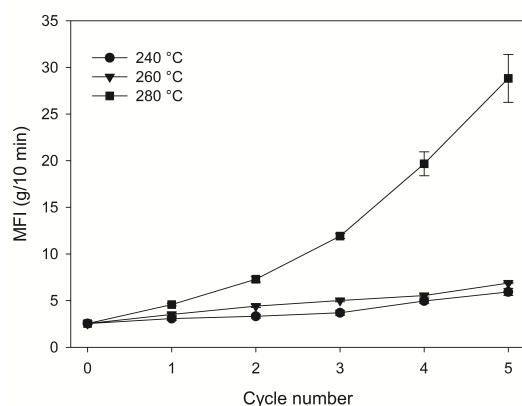

Fig. 2. Carbonyl index of reprocessed PP. The polymer was processed multiple times at 240 °C, 260 °C, and 280 °C.

Fig. 3. MFI of reprocessed PP. The polymer was processed multiple times at 240 °C, 260 °C, and 280 °C. MFI was measured at 230 °C / 2.16 kg, n = 3. MFI of virgin PP = 2.54 g / 10 min.

A striking difference was observed for PP processed at 280 °C, which presented MFI values between 49 and 386% higher than PP processed at 240 °C. The difference in changes in MFI observed at 280 °C in comparison to 240 °C and 260 °C could be explained by the increase in thermal degradation reported for PP at temperatures above 275 °C (Chrissafis *et al.*, 2007; González-González *et al.*, 1998; Waldman *et al.*, 1998).

Similar to our findings, other authors have reported that MFI increases directly with processing temperature and/or time (González-González *et al.*, 1998; Guerrica-Echevarría *et al.*, 1996; Huang *et al.*, 2003; Tochacek *et al.*, 2012; Wang *et al.*, 2012), but few of these authors evaluated temperatures > 270 °C in their work. Tochacek and Jancar compared the MFI of PP after multiple extrusion cycles at 220 °C - 280 °C and, in line with our results, they found that the samples processed at 280 ºC had the highest

MFI values (Tochacek *et al.*, 2012). Nevertheless, these MFI values were much lower than the ones we found, which could be explained by differences in polymer additive and/or differences in polymer processing conditions, for instance, residence time in the extruder.

3.1.3 GPC analysis

Degradation of PP proceeds preferentially by chain scission and can therefore be followed by monitoring the changes in molecular weight (the polypropylene chromatograms are presented as supplementary material for the reader's assistance).

A progressive decrease in polymer molecular weight was observed with increasing number of processing cycles, and with increasing temperatures (Table 2), which has also been reported by other authors (Billiani *et al.*, 1990; Canevarolo, 2000; González-González *et al.*, 1998; Spicker *et al.*, 2019). This decrease was more evident for M_w than for M_n, in agreement with reports that chain scission occurs preferentially at the center of long chains (Bueche, 1960; Canevarolo, 2000), and therefore has a larger effect on M_w. Chain scission also results in narrower molecular weight distributions for reprocessed polymers (Canevarolo, 2000), which was observed in the present study as well.

Polymer degradation, reflected as a decrease in M_w, proceeded much faster at 280 °C than at the other temperatures under study. In fact, the M_w of PP after 1 cycle at 280 °C decreased to a similar extent as the M_w after 3 cycles at 240 °C and 260 °C, i.e. 25%, 24%, and 29% decrease respectively. In addition, after 5 cycles of processing, polymer degradation was also more intense for PP processed at 280 °C. The M_w of this PP sample decreased by 57% compared to the virgin polymer, while PP processed at 240 °C and at 260 °C decreased by 33% and 36%.

Table 2. Molecular weight analysis of virgin and reprocessed PP (GPC).

Temperature (ºC)	Cycle number	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_w/M_n
Not applicable	0	64,079	400,644	1,495,247	6.25
240	3	69,782	305,739	759,792	4.38
240	5	70,081	268,425	612,489	3.83
260	3	63,922	285,730	733,433	4.47
260	5	94,574	255,253	495,746	2.7
280	1	60,659	298,632	834,075	4.92
280	3	58,768	206,240	419,811	3.51
280	4	56,945	180,630	363,553	3.17
280	5	51,031	171,109	346,136	3.35

The characterization data obtained in our study for CI, MFI, and M_w, suggest that two temperature regions can be identified for the degradation of PP. One region, with similar behavior in terms of rate and extent of degradation, is located below 280 °C, more precisely between 240 °C and 260 °C. The other region, in which faster and more extensive degradation is observed, is located at 280 °C or above. A more comprehensive study would be necessary to exactly define the cutoff of these regions. Abrupt changes in polymer properties at degradation temperatures ~ 280 °C have also been reported by other authors. For instance, Závadský *et al.* studied the effective viscosity of PP extruded between 190 °C and 310 °C, and found that only the data for PP extruded below 280 °C could be fit into a single curve (Závadský *et al.*, 1982). In addition, da Costa *et al.* reported a sharp decrease in the apparent viscosity of PP extruded at 270 °C, in comparison 240 °C (da Costa *et al.*, 2005), and a sharp decrease in the break properties of PP processed multiple times at 260 °C or 270 °C, compared to 240 °C or 250 °C (da Costa *et al.*, 2007).

3.2 Mathematical modeling of polymer properties

3.2.1 Model of the rate constant for thermal degradation of PP

In this work, a model for the thermal degradation of PP was described (Equations I - V) based on the experimental M_w and MFI data obtained for PP reprocessed at 240, 260 and 280 °C. The behavior of the rate constant for thermal degradation (k_{th}) is shown in Figure 4.
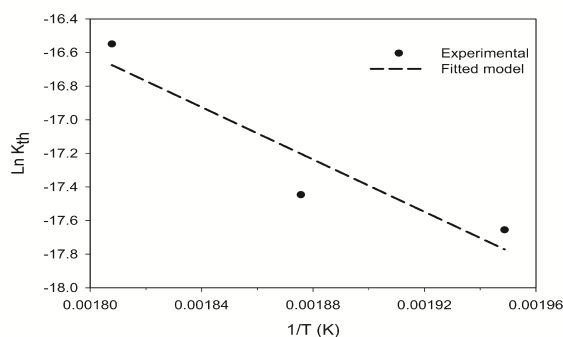

Fig. 4. Model of thermal degradation for polypropylene as a function of temperature. $R^2 = 0.8716$.

According to Equation IV, shown in Figure 4, the following parameters were obtained by linear adjustment for the temperature range of 240 - 280 °C:

$$k_{th} = 1.43 \times 10^{-2} e^{-\frac{7786.1}{T}} \qquad (10)$$

The value for b obtained in our work (7786) is larger than the value for b reported by Kim and White (1686) (Kim *et al.*, 1997), which indicates that in our model PP degradation is more sensitive to temperature. The difference in these parameters could be related to differences in additives of the PP used in both studies, and/or differences in the processing conditions of the PP. For instance, Kim and White used data from experiments in an internal mixer to define the value of k_{th}, while we used data from experiments in a twin-screw extruder. In addition, we used long extrusion times (i.e. between 3 and 15 min), which could have contributed to an increased degradation of PP.

3.2.2 Calculation of the M_w of reprocessed PP

The M_w of PP can be measured by GPC, but this technique is often deemed too costly and time-consuming for routine use in industrial settings. Therefore, it is of interest to use mathematical methods to calculate the M_w of reprocessed PP, and to predict the impact of different processing conditions on the M_w of the polymer. As observed in Figure 5, the degradation model proposed in this paper (Equation X) accurately models the experimental observations reported in section 3.1.3, namely a decrease in M_w with increasing processing temperature and time. The absolute % error for the calculated values of M_w was low and ranged between 2 and 11%.

3.2.3 Calculation of the MFI of reprocessed PP

Even though MFI can be easily and systematically measured in industrial settings, it is of interest to predict changes in this parameter, particularly when considering modifications to PP processing conditions. In this study, adjusted parameters were calculated for the relationship between MFI and M_w (Equation IX). It was found that the parameter G decreases in order of magnitude as the temperature increases, while the parameter x increases (Table 1). In addition, an abrupt change in the temperature range of 280 °C is shown, which may be related to changes in the mechanism of degradation.
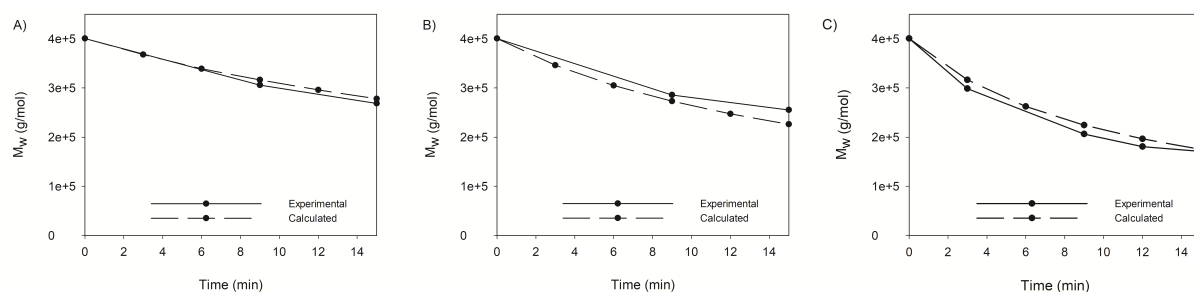
Fig. 5. Experimental and calculated M_w of PP processed at a) 240 °C, b) 260 °C, or c) 280 °C.

In fact, it has been reported that above 260 °C degradation of PP occurs mainly by chain scission (He *et al*., 2005), which would explain the sharp experimental and theoretical changes in MFI and M_w discussed in our work.

Chan and Balke have also described the existence of two regions in the degradation mechanism of PP: the first, observed at low degradation temperatures, corresponds to the scission of weak links (i.e. oxidized functionalities on the polymer chain), while the second, observed at high degradation temperatures, and corresponds to random scission of the polymer chain (Chan *et al*., 1997). Recently, studies of recycled polypropylene have been published and have shown that the melt flow rate (MFR) for polypropylene increases as a function of the number of cycles. In addition, they showed that the MFR has an exponential behavior at high temperatures while if moderate temperatures are maintained, the MFR is more uniform. This behavior is comparable to what we have obtained (Esmizadeh *et al*., 2020).

The model described in the present study (Equation X), combined with the parameters in Table 1, and accurately portrays the experimental observations reported in section 3.1.2, namely an increase in MFI with increasing temperatures and processing times (Figure 6). The % error for the calculated values of MFI was low (-6 to 15%) for all processing temperatures at processing times ≤ 9 min. At longer times, the absolute % error ranged between 2 and 29%.

as a decrease in M_w. Our findings indicate that two temperature regions exist for PP degradation, one between 240 °C and 260 °C, and the other at 280 °C, where faster and more extensive polymer degradation is observed. A kinetic model that calculates the M_w of PP reprocessed at different temperatures was studied, and adjusted parameters for the relationship between MFI and M_w were calculated based on the experimental data from this work. The adjusted values for the kth show that the degradation of PP is more sensitive to temperature than previously reported, possibly due to differences in additives and/or processing conditions of PP between studies. The M_w and MFI values of reprocessed PP that were calculated based on the kinetic model accurately reflected the M_w and MFI values that were obtained experimentally. These findings indicate that mathematical modeling can be a valuable tool to calculate polymer properties, namely M_w and MFI. In industrial settings, this information can be used to anticipate the impact of processing conditions, such as temperature and residence time, on the characteristics of recycled PP.

Conclusions

The results presented in this work show that PP degradation increases directly with processing temperature and time. This degradation is characterized by an increase in CI and MFI, as well

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