# Effect of the Melt Flow Index and Melt Flow Rate on the Thermal Degradation Kinetics of Commercial Polyolefins

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**ABSTRACT:** In this study, several polyolefins, including different grades of polypropylene (PP), high-density polyethylene, linear low-density polyethylene, and low-density polyethylene, were tested by thermogravimetric analysis (TGA), and the relationships of their melt flow index (MFI) and melt flow ratio (MFR) values to the thermogravimetry (TG) curves, differential thermogravimetry (DTG) curves, and activation energy of thermal degradation were investigated. Kinetic evaluations were performed by Friedman and Kissinger analysis methods, and the apparent activation energy values for the overall degradation of different grades of polyethylenes (PEs) and PPs were determined. We found that for the samples with lower MFIs, the thermograms shifted to higher temperatures. Meanwhile, a higher activation energy was needed for their thermal degradation. Also, for samples with higher values of MFR, as a means of molecular weight distribution, a lower activation energy was needed for their thermal degradation, and their TGA thermograms shifted to lower temperatures. The breadth of the DTG curves depended on the MFR in the PEs, although MFR had little effect on the DTG curves in the studied PP grades. Among all of the samples studied, the injection-molding grades with medium MFIs and low MFRs degraded at higher temperatures and showed better thermal stability. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

**Key words:** activation energy; degradation; molecular weight distribution/molar; polyolefins; thermogravimetric analysis (TGA)

## INTRODUCTION

Polyethylene (PE) and polypropylene (PP) are the largest synthetic commodity polymers in terms of annual production and are widely used throughout the world because of their versatile physical and chemical properties.[1] Because this production generates huge municipal waste, the recovery of plastic waste has found growing importance.

The pyrolysis of polymers is a chemically complex process, where several reactions by different mechanisms, especially for PE, may occur simultaneously. A thorough study of the mechanisms of the thermal decomposition of polymers was presented by Cullis and Hirschler.[2] The four mechanisms proposed were

1. End-chain scission or unzipping.
2. Random-chain scission.
3. Chain stripping.
4. Crosslinking: Two adjacent stripped polymer chains can form a bond that results in a higher MW species.

Chain scission generally converts a low melt flow index (MFI) commodity resin into a high-MFI resin; however, chain stripping and crosslinking have the inverse effect on MFI.

The thermal pyrolysis of PP and PE is known to follow the random-chain scission route, resulting in mainly oligomers and dimers, although the chain-stripping and crosslinking mechanisms can affect the PE degradation. Thermogravimetric analysis (TGA) is a common method for studying the kinetics of polymer degradation. Kinetic analysis may effectively assist in the probing of degradation mechanisms and in the prediction of the thermal stability of polymers, especially in PP and PE.[3–7]

High-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and low-density polyethylene (LDPE), as famous types of commercial PEs, are divided by density, although the process type and process conditions of polymerization have a key role in this classification. In polyolefins, different grades are usually defined by MFI and melt flow rate (MFR) values. The MFI of a polyolefin resin depends on its molecular characteristics, primarily, the average molecular weight, molecular weight distribution (MWD), and branching characteristics, such as the degree of branching and its distribution frequency. The MFI reflects the average dimensions of the molecules in a resin and their entanglements with one another.[4] MFR is the preferred term for polyolefins.

### TABLE I
### Characteristics of the PEs Studied

| No. | Type | Grade | Manufacturer (Name, City, Country) | MFI (2.16, 230°C, as reported by the supplier) | MFI (2.16, 230°C, as determined by the laboratory) | MFI (21.6, 230°C, as determined by the laboratory) | MFR (21.6/2.16, as determined by the laboratory) | Apparent shape |
|---|---|---|---|---|---|---|---|---|
| 1 | HDPE | 0035 | Amirkabir, Mahshahr, Iran | 0.35 | 0.22 | 16.4 | 74.55 | Granule |
| 2 | HDPE | EX5 | Maroon, Mahshahr, Iran | 0.28 | 0.2 | 13.1 | 65.5 | Powder |
| 3 | HDPE | I2 | Amirkabir, Mahshahr, Iran | 10 | 11.4 | 396 | 34.73 | Granule |
| 4 | HDPE | 3840UA | Tabriz, Tabriz, Iran | 4 | 4.3 | 144.1 | 33.51 | Granule |
| 5 | HDPE | 6070 | Tabriz, Tabriz, Iran | 7.2 | 8.6 | 189 | 21.97 | Granule |
| 6 | LLDPE | 2230 | Borough, Abu Dhabi, UAE | 0.2 | 0.22 | 12.2 | 55.45 | Granule |
| 7 | LLDPE | 50035 | Sabic, Riyadh, Saudi Arabia | 5 | 5.66 | 185.2 | 32.72 | Granule |
| 8 | LDPE | 0075 | Bandar Imam, Mahshahr, Iran | 0.75 | 0.81 | 32.5 | 40.12 | Granule |
| 9 | LDPE | LF0200 | Bandar Imam, Mahshahr, Iran | 2 | 2.33 | 93.1 | 39.95 | Granule |

The purpose of this measurement is to provide a single value that reflects the ease of flow of a molten polymer. The MFR of a sample is primarily dependent on its average molecular weight, but this relationship can be strongly influenced by factors such as the MWD and degree of long-chain branching.[8] Usually, the extrusion grades, such as pipe, film, and blow-molding grades, have broad or bimodal MWDs or high MFRs. This causes good mechanical properties and better processability. On the other hand, injection-molding grades for lower shrinkage need to have a very narrow MWD.

There have been a number of studies reporting thermogravimetry (TG) curves indicating the degradation temperatures, activation energies, and other kinetic parameters during the thermal degradation of different PEs and PP.[9–21] The reported values have not always been consistent. It appears that except for the calculation method, virgin or waste polymer, heating rates, and sample mass and shape, the molecular specification, such as molecular weight, MWD, comonomer type and percentage, and catalyst type—Ziegler–Natta, Phillips, or metallocene—can affect the TGA results.

The purpose of this work was to study the degradation behaviors of different grades of the polyolefins with TGA by the Friedman and Kissinger methods to determine the kinetic parameters. The proposed methods were applied to consider the degradation of HDPE, LDPE, LLDPE, and PP. The weight loss of the sample as a function of temperature was determined by TG at three heating rates of 10, 20, and 30°C/min, and the effects of the MFI and MFR on the kinetic parameters of thermal degradation of the polyolefin resins were investigated.

## EXPERIMENTAL

### Materials

Tables I and II show the main characteristics (as provided by the supplier and tested by the laboratory of the Iran Polymer and Petrochemical Institute) of nine commercial grades of PE and five commercial grades of PP analyzed plus the notations used in this work. As shown, five HDPE, two LDPE, two LLDPE, and five PP samples were studied. The results show little difference between the reported and tested MFI values.

### Instruments

TGA was performed in a Netzsch TG 209 thermobalance instrument. The experiments for the determination of the thermal decomposition temperature were carried out with initial sample masses between 12 and 15 mg and at three heating rates (β) of 10, 20, and 30°C/min. The samples were weighed in a Mettler AJ150 balance with a precision of 0.01 mg. The

### TABLE II
### Characteristics of the PPs Studied

| No. | Grade | Manufacturer (Name, City, Country) | MFI (2.16, 190°C, as reported by the supplier) | MFI (2.16, 190°C, as determined by the laboratory) | MFI (21.6, 190°C, as determined by the laboratory) | MFR (21.6/2.16, as determined by the laboratory) | Apparent shape |
|---|---|---|---|---|---|---|---|
| 1 | EPD 60R | Arak, Arak, Iran | 0.35 | 0.4 | 26.2 | 65.5 | Granule |
| 2 | F040 | Tabriz, Tabriz, Iran | 4.2 | 4.7 | 212 | 45.11 | Granule |
| 3 | 575P | Sabic, Saudi Arabia | 10.5 | 11.6 | 423 | 36.47 | Granule |
| 4 | V305 HP8001 | Maroon, Mahshahr, Iran | 16 | 15 | 489 | 32.6 | Powder |
| 5 | PI080 | Bandar Imam, Mahshahr, Iran | 8 | 8.3 | 208.3 | 25.1 | Granule |
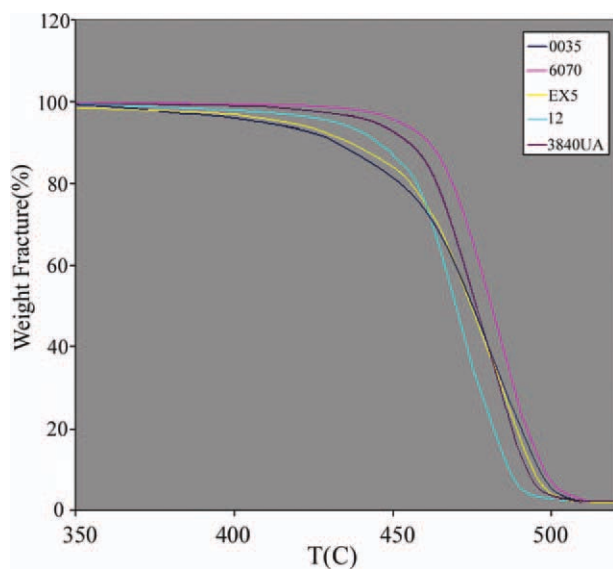
**Figure 1** TG curves of the HDPE grades at 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

carrier gas was $N_2$ (99.99% minimum purity) at a flow rate of around 30 mL/min.

''$x$'' the degree of advance in thermogravimetry defined by $x = (W_0 - W)/(W_0 - W_f)$

Where $W$ is the weight of the sample at a given time $t$, $W_0$ and $W_f$, refer to values at the beginning and the end of the weight loss event of interest respectively.

As specified in ASTM D 1238, the MFI values of polyolefin were measured with weight of 2.16 kg ($MFI_2$) and 21.6 kg ($MFI_{21}$) at 190°C for PE and 230°C for PP; the results are expressed in grams per 10 min. The $MFI_{21}/MFI_2$ ratio is referred to as the MFR.
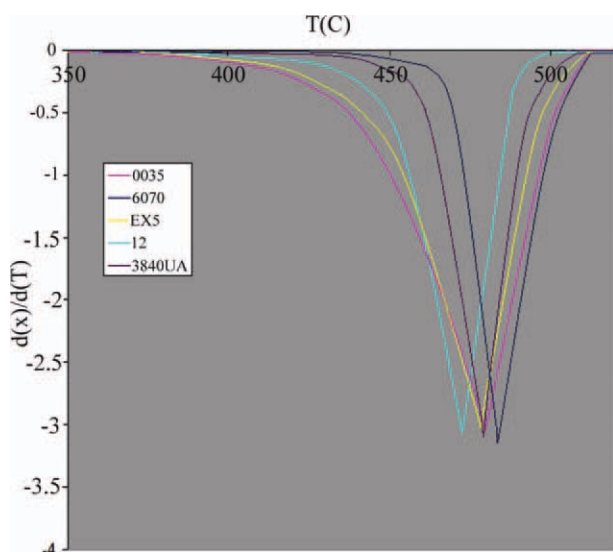


**Figure 2** DTG curves of the HDPE grades at 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**TABLE III**
**Values of $T_5$ and $T_{95}$ and Their Difference for the HDPE Grades at a Heating Rate of 10°C/min**

| Grade name | MFI (2.16, 230°C, as determined by the laboratory) | MFR | $T_5$ | $T_{95}$ | $\Delta T$ |
|---|---|---|---|---|---|
| 6070 | 7.2 | 21.97 | 451.5 | 503.9 | 52.4 |
| 3840UA | 4.3 | 33.51 | 442 | 496.3 | 54.3 |
| I2 | 11.4 | 34.73 | 428.5 | 491.2 | 62.7 |
| EX5 | 0.2 | 65.5 | 419.5 | 497.1 | 77.6 |
| 0035 | 0.22 | 74.55 | 409.1 | 501.4 | 92.3 |

## RESULTS

### HDPE

As shown in Table I, the commercial HDPE grades had different MFIs, from 0.2 to 11.4 g/10 min, and MFRs from 21.97 to 74.5. These HDPE grades were analyzed by TG at rates of 10, 20, and 30°C/min. Figure 1 shows the TG curves of the HDPE grades at a heating rate of 10°C/min. Figure 2 shows the differential thermogravimetry (DTG) curves for the same samples.

The weight loss behavior of these five types of HDPE appeared to be closely related to their general molecular specifications, including MFI and MFR values. The results show that the breadth of the DTG curves depended on the MFR values so that high MFR samples broadened the curves obviously. It was apparent that subtle changes in MFR due to factors such as branching and the presence of high- and or low-molecular-weight tails in the MWD were readily detected in the weight loss graph of a PE. The low-molecular-weight chains helped to start the weight loss by low-molecular-weight evaporation or pyrolysis or at lower temperatures by evaporation and eased moving and increased of vibration. On the other hand, the higher molecular weight chains, by high viscosity and a crosslinking mechanism, increased the thermal stability, and the polymer residue degraded at higher temperatures. Table III indicates the temperature interval for the decomposition of the HDPE grades defined between the temperature at 5% conversion ($T_5$), the temperature at 95% conversion ($T_{95}$), and their difference. These two temperatures were defined, respectively, as the temperature at which the conversion started ($T_5$) and the temperature close to the end of conversion ($T_{95}$). It was obvious that the difference between $T_5$ and $T_{95}$ as a function of DTG breadth increased with increasing MFR.

When we compared MFRs, we observed that MFI had less of an effect on the weight loss, but it seemed that at the same MFR, a lower MFI shifted the weight loss curve toward higher temperatures.

**Activation Energy Values Determined by the Friedman and Kissinger Methods for the HDPE Grades Studied**

| No. | Grade | MFI (2.16, 230°C, as determined by the laboratory) | MFR | Activation energy (kJ/mol, FR method) | Average of regressions (FR) | Activation energy (kJ/mol, KG method) | Regression (KG) |
|---|---|---|---|---|---|---|---|
| 1 | 6070 | 7.2 | 21.97 | 276.81 | 0.98 | 244.67 | 0.99 |
| 2 | 3840UA | 4.3 | 33.51 | 269.55 | 0.99 | 234.91 | 0.97 |
| 3 | I2 | 11.4 | 34.73 | 252.64 | 0.98 | 217.67 | 0.98 |
| 4 | EX5 | 0.2 | 65.5 | 259.36 | 0.99 | 228.58 | 0.98 |
| 5 | 0035 | 0.22 | 74.55 | 266.55 | 0.99 | 229.69 | 0.98 |

The calculation of the kinetic parameters for degradation was carried out with the Friedman (FR) and Kissinger (KG) methods. To estimate the decomposition activation energy through the Kissinger method, the peak melting temperature ($T_m$) values [$T_m$ is the most rapidly decomposing temperature (K)] were measured from the DTG curves. In the Kissinger method, the thermal decomposition activation energies were obtained from the slopes of the corresponding plot of $\ln(\beta/T_m^2)$ against $1/T_m$.

The average values of the activation energies for all of the HDPE grades used in this work were calculated by the Friedman and Kissinger methods, and the results obtained are presented in Table IV. The results show that the trend of the Friedman and Kissinger methods for the calculation of activation energy were almost like each other, but the calculated activation energy by the Friedman method was higher than that by the Kissinger method.

These results also demonstrate that sample 6070 (injection grade with medium MFI and low MFR) needed more degradation activation energy in comparison with the others.
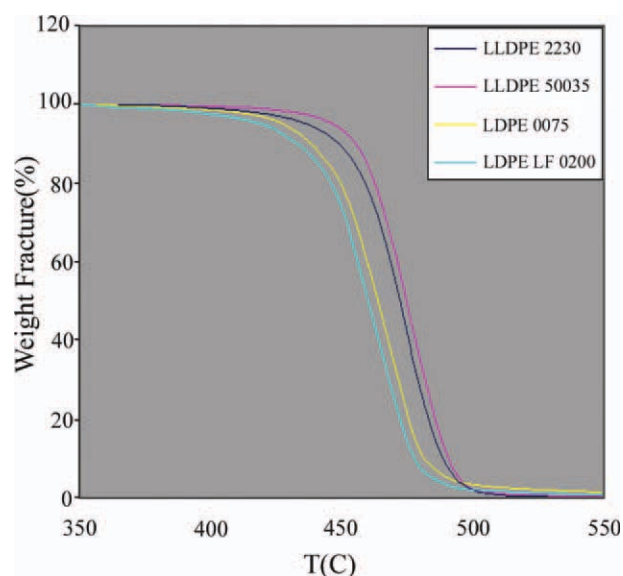
**LLDPE and LDPE**

In comparison with the HDPE grades, four grades of LDPE and LLDPE were tested. Figure 3 shows the plots of the weight fracture against temperature ($T$; °C) for all LLDPE and LDPE samples at heating rate of 10°C/min. Figure 4 shows the DTG curves for these polymers under the same conditions.

Table V shows $T_5$, $T_{95}$, and their difference at a rate of 10°C/min for the LDPE and LLDPE grades. The concluding results indicate that MFR increased the breadth of the DTG curves of these PEs.

The average activation energies calculated from the Friedman and Kissinger methods for these PEs are summarized in Table VI.

The results show that in comparison with the HDPE samples, the LDPE samples needed lower activation energies. However, the activation energies for the LLDPE samples were in the range of those for the HDPE samples and were acceptable by similar processes and close molecular structures.

Table VI shows that although sample 0035 had a similar MFI to sample 2230 from the LLDPE grades,
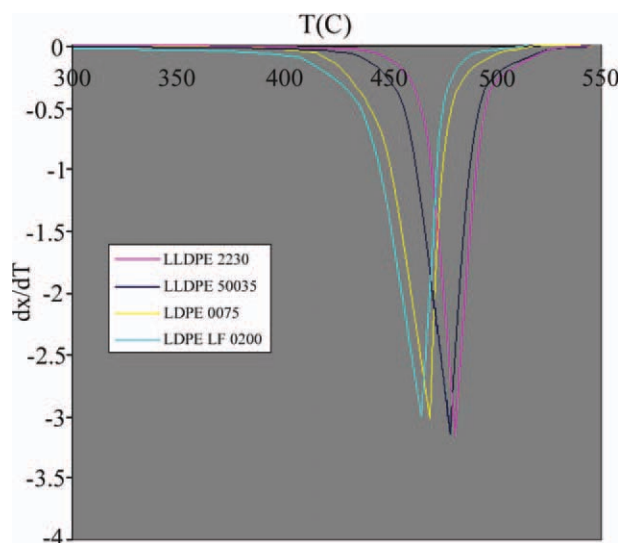


**Figure 3** TG curves of the LDPE and LLDPE grades at 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 4** DTG curves of the LLDPE and LDPE grades at 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**TABLE V**
**Values of $T_5$ and $T_{95}$ and Their Difference for the LDPE and LLDPE Grades at a Heating Rate of 10°C/min**

| No. | PE | Grade | MFI (2.16, 230°C, as determined by the laboratory) | MFR | $T_5$ | $T_{95}$ | $\Delta T$ |
|---|---|---|---|---|---|---|---|
| 1 | LLDPE | 2230 | 0.22 | 55.45 | 436.3 | 493.2 | 56.9 |
| 2 | LLDPE | 50035 | 5.66 | 32.72 | 447.6 | 495.9 | 48.3 |
| 3 | LDPE | 0075 | 0.81 | 40.12 | 427.6 | 488.6 | 61 |
| 4 | LDPE | LF0200 | 2.33 | 39.95 | 421.1 | 483.5 | 62.4 |

the former needed a higher activation energy, probably due to its lower MFR.

The results show that the LDPE samples, by having a long branched structure, tended to lose weight at lower temperatures. The branched structure helped to ease the movement of the polymer chains and decreased the activation energy. The acceleration caused by the increasing temperature of chain movement in the branched polymer was greater than that of the same linear polymer, and the vibration of these chains helped the chain scissions and decreased the activation energy.

## PP

As shown in Table II, the commercial PP grades had different MFIs from 0.4 to 15 g/10 min and MFRs from 25.1 to 65.5. Figure 5 shows the TGA curves of the five PP grades. Table VI indicates the temperature intervals for weight loss of the PP defined between $T_5$ and $T_{95}$.

As shown in Figure 6 and Table VII, the PP grades did not have very obvious trends in the DTG curve by MFR, although sample EPD 60R, with a very high MFR, showed a broader DTG curve in comparison with the others.

The mean values of the activation energies obtained for different $x$ values by the Friedman method and the results calculated by the Kissinger method are included in Table VIII for all of the PP
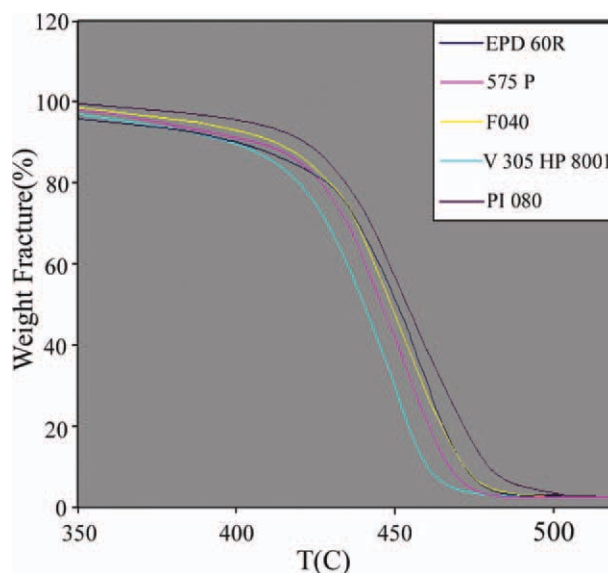


**Figure 5** TG curves of the PP grades at 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

grades. The results show that like all if the PEs, the trend of activation energy did not change with changing calculation method, although the calculated activation energy by the Friedman method was higher than that by the Kissinger method.

These results allowed us to conclude that like HDPE, injection grades with lower MFR and medium MFI had the highest activation energies.

## Mechanism

The results show that the activation energy increased with decreasing MFI at the same MFR; MFR affected the weight loss and played an important role in the weight loss, especially in the PEs. At higher MFRs, the commercial polymer had more low molecular weights, and these chains needed less energy for scission or evaporation. This part had more thermal stability in comparison with the longer chains, although it evaporated without degradation or, by several chain scissions, reached the evaporation temperature. The evaporation and ease of

**TABLE VI**
**Activation Energy Values Determined by the Friedman and Kissinger Methods for the LLDPE and LDPE Grades Studied**

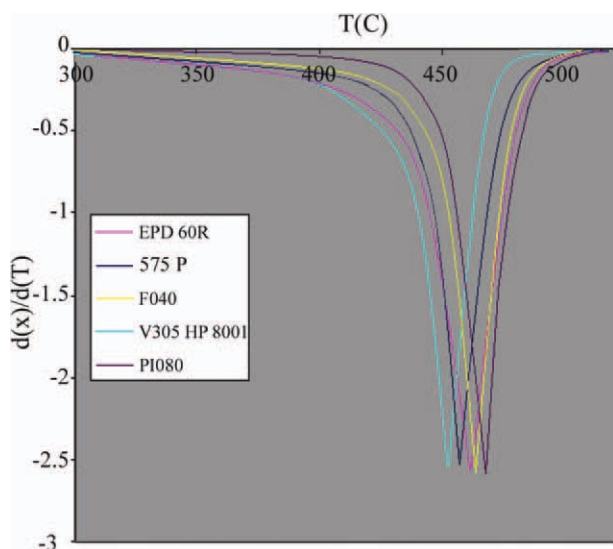| No. | PE | Grade | MFI (2.16, 230°C, as determined by the laboratory) | MFR | Activation energy (kJ/mol, FR method) | Average of regressions (FR) | Activation energy (kJ/mol, KG method) | Regression (KG) |
|---|---|---|---|---|---|---|---|---|
| 1 | LLDPE | 2230 | 0.22 | 55.45 | 265.27 | 0.97 | 226.4 | 0.99 |
| 2 | LLDPE | 50035 | 5.66 | 32.72 | 267.91 | 0.98 | 231.2 | 0.98 |
| 3 | LDPE | 0075 | 0.81 | 40.12 | 245.7 | 0.99 | 206.68 | 0.98 |
| 4 | LDPE | LF0200 | 2.33 | 39.95 | 241.48 | 0.99 | 197.21 | 0.99 |

**Figure 6** DTG curves of the PP grades at 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

moving could act as process aids and decrease the viscosity of the molten polymer, and they could increase the vibration of the long chains in the polymer bulk. The movement of this part of the polymer increased the contacts in the bulk of the polymer and helped to crack the high-molecular-weight chains and decrease the activation energy for the cracking of the long polymer chains, and the polymer degraded at lower temperatures.

In the PEs, high-molecular-weight chains, which increased with MFR ratio, intensified the chain-stripping and crosslinking mechanisms, and these crosslinked chains degraded at higher temperatures. These chains, in addition to their low molecular weights, affected the breadth of the DTG curves and broadened the DTG curve. For example, the quantities of low- and high-molecular-weight chains in grade I2, with low MFR and medium MFI, were low in comparison with those of the 0035 grade, with high MFR and low MFI. They increased the low-temperature thermal stability and $T_5$ of I2, although high molecular weights and the crosslinking mechanism increased the high-temperature thermal stabil-

**TABLE VII**
**Values of $T_5$ and $T_{95}$ and Their Differences for the PP Grades at a Heating Rate of 10°C/min**

| Grade name | MFI (2.16, 230°C, as determined by the laboratory) | MFR | $T_5$ | $T_{95}$ | $\Delta T$ |
|---|---|---|---|---|---|
| EPD 60R | 0.4 | 65.5 | 353.6 | 473.7 | 120.1 |
| F040 | 4.7 | 45.11 | 386.5 | 482.4 | 95.9 |
| 575P | 11.6 | 36.47 | 374.9 | 476.3 | 101.4 |
| V305 HP8001 | 15 | 32.6 | 367.2 | 468.2 | 101 |
| PI080 | 8.3 | 25.1 | 404 | 493.1 | 89.1 |

ity and $T_{95}$ of the 0035 grade. In low-MFI grades, the high molecular weights shifted the end tail of the weight loss graph toward higher temperatures.

LLDPE and HDPE with different morphologies and comonomers almost showed the same behavior, especially in activation energy, although LLDPE showed a narrower breadth of DTG. This showed that the morphology and comonomer type and distribution in a special PE, such as HDPE or LLDPE, with little difference could not affect the thermal degradation. Because the comonomer was 1-butene or 1-hexene and they could affect the low-temperature properties at ambient temperature, and at higher temperatures, they could not play an important role in the thermal degradation. Although in polar polymers, the morphology and comonomer content by hydrogen banding and polar banding can very much affect the degradation.

In PP grades, MFI and MFR did not have a remarkable effect on the breadth of the DTG curve and may have been affected by the chain-scission mechanism that only happened in PP thermal degradation.

## CONCLUSIONS

The main goal of this work was to investigate the effects of MFI and MFR on the thermal degradation behavior of polyolefins. As shown, the activation energies for the thermal degradation of polyolefins

**TABLE VIII**
**Activation Energy Values Determined by the Friedman and Kissinger Methods for the PP Grades Studied**

| No. | Grade | MFI (2.16, 230°C, as determined by the laboratory) | MFR | Activation energy (kJ/mol, FR method) | Average of regressions (FR) | Activation energy (kJ/mol, KG method) | Regression (KG) |
|---|---|---|---|---|---|---|---|
| 1 | EPD 60R | 0.4 | 65.5 | 187.01 | 0.98 | 154.65 | 0.99 |
| 2 | F040 | 4.7 | 45.11 | 187.13 | 0.99 | 155.64 | 0.99 |
| 3 | 575 | 11.6 | 36.47 | 184.06 | 0.99 | 152.76 | 0.98 |
| 4 | V305 HP8001 | 15 | 32.6 | 178.43 | 0.97 | 145.11 | 0.99 |
| 5 | PI080 | 8.3 | 25.1 | 195.4 | 0.98 | 166.59 | 0.98 |

were affected by the molecular specifications, although these effects were not very great. The Friedman method used in this work gave apparent activation energies of 252–277, 265–268, 241–246, and 178–195 kJ/mol and the Kissinger method gave values of 218–244, 226–231, 197–206, and 145–167 kJ/mol for HDPE, LLDPE, LLDPE, and PP, respectively.

On the basis of the results of this study, we drew the following main conclusions:

1. The polyolefin grades with medium or low MFI and lower MFR had greater thermal stabilities and needed more activation energy in the thermal degradation process.
2. Samples with low MFI and MFR values shifted the weight loss curve toward higher temperatures.
3. The activation energy increased in the following order: HDPE and LLDPE > LDPE > PP.
4. MFR affected the breadth of the DTG curve of the PEs by chain-stripping and crosslinking mechanisms and low molecular weights but did not have a very obvious effect on the breadth of the DTG curve of the PP grades.
5. A comparison of the HDPE and LLDPE results showed that the morphology and comonomer did not play important roles in the weight loss and these parameters almost could not affect the degradation mechanism, although LDPE with a branched structure showed different weight loss behavior.

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