Thermal Degradation Analysis of Polyamide 6 Processed at Different Cycles Using Sequential Pyrolysis

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ABSTRACT: The principal product from the degradation of polyamide 6 (PA6) is caprolactam, which is a consequence of the intramolecular exchange (cyclization) of PA6. The information obtained from certain thermal analysis techniques, such as differential scanning calorimetry (DSC), is not sufficiently detailed to study the degradation suffered by PA6 in function of these processes, whereas the study of this degradation using other more precise techniques (sequential pyrolysis) and the application of models (Guggenheim and Kezdy-Jaz-Bruylants methods) gives us more detailed information on the level of degradation in the many and diverse PA6 analyzed. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 713–719, 2009

Key words: polyamide; sequential pyrolysis; thermal degradation

INTRODUCTION

The recovery of polymers means using mechanical and thermal processes to obtain the new products.[1] There have been various studies on variations in behaviour, which take place in the polymers during their normal use (commodities). These studies have been based on the mechanical and thermal properties as well as those wich come about due to their processing.[2–4]

Until now, studies on recycled materials have mainly concentrated on commodities, but in recent years references to technical plastics have begun to appear in publications.[5–7]

There are diverse techniques available to carry out quality control on recycled material. The thermal techniques: differential scanning calorimetry (DSC), and thermogravimetry (TGA) have sometimes given good results in the study of commodities.[8,9] However, the results have often been unsatisfactory on technical polymers due perhaps to the low variations in the properties of the materials or even due to the limited sensitivity of the techniques used.

Other techniques with greater sensitivity are able to detect changes in the polymer however small, these techniques are infrared spectrophotometer (IR) and pyrolysis—gas chromotography/mass spectrometry (Py-GC/MS).[10–12]

Polyamide 6 (PA6) belongs to the group of technical plastics whose uses include bearings for windows, manufacture of safety ropes, reinforcement fibres, etc., which often means that they must have good mechanical properties but which are often aversely affected by the recovery processes.

The different thermal transitions that appear in the calorimetric curves do not indicate significant differences between the samples processed at different cycles. Pyrolysis analysis generally uses a simple pyrolysis of a polymer, but there are also studies where the authors are using successive pyrolysis to study the mechanisms of thermal degradation.[13] The objective of this work is to understand the evolution of caprolactam in PA6 when submitted to various cycles of processing using sequential pyrolysis for determining the degradation level of PA6.

EXPERIMENTAL

Preparation of samples

The PA used in the experiment is commercial products PA6 (Heramid® S 233 Black; Radici Plastics Iberica S.L., Jaen, Spain).

The injection moulding experiment was conducted on a conventional injection moulding machine, at 250°C injection moulding temperature.

In Figure 1 the different stages of the experimental method is represented.

Characterisation of samples

DSC curves were obtained using a Mettler-Toledo 821 DSC (Mettler-Toledo, Schwerzenbach, Switzerland) at 10°C min^{-1} heating rate in a nitrogen
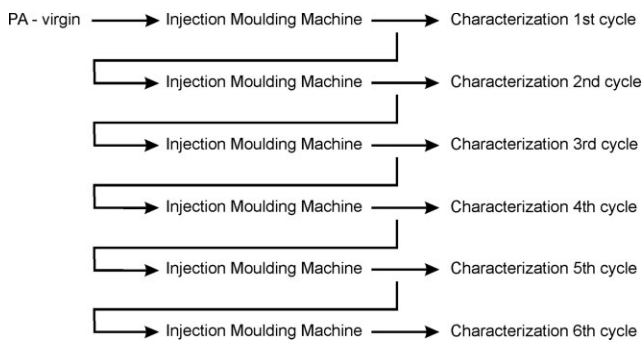
Figure 1 Investigation method.

atmosphere (60 mL min^{-1}). The weight of samples was $\sim$ 10 mg.

All samples were pyrolyzed with the use of a pyrolysator (Pyroprobe 1000, CDS Analytical, Oxford, Pennsylvania), which was interconnected to a gas chromatography/mass spectrometry apparatus (6890N, Agilent Technologies, España S.L., Madrid, Spain) equipped with a 5973N mass selective detector (Agilent Technologies). The sequential was programmed at 35°C for 2 min, followed by a stepped increase of 5°C min^{-1} to 200°C, where it was held for 15 min, and then the temperature was increased by 20°C min^{-1} to 300°C, where it was held for 5 min. The gas used was helium with a 50 : 1 split ratio. The mass selective detector was programmed to detect masses between 40 and 650 amu. Samples of PA6 (100 μg) were pyrolyzed at 400°C for 15 s. The samples were repeatedly subjected to sequential pyrolysis under the same conditions until the 10 cycles were completed.

Methods of evaluating the rate constant (k)

There are five methods to evaluating the rate constant (k), all these methods use the same basic equation to obtain the value of k, eq. (1):

$$- \mathrm{Ln}\left[1 - \left(\frac{m}{m_\infty}\right)\right] = k.t \qquad (1)$$

Where m is the mass of volatile from pyrolysis time t, k is the rate constant and m_∞ is the original mass of polymer.

The value of m is obtained from the peak area of the chromatogram of the polymer studied, which is representative of this. In this case, we use peaks from peak areas at retention time (RT) 17 min in Py -GC/MS.

Method 1 – normal log plot method

Although this is the most direct method, it is more laborious than some of the others methods, because each point on the plot requires the pyrolysis of a new sample twice (primary pyrolysis of a sample for a selected time and temperature to obtain a peak area of the compound, A; and a second pyrolysis to obtain a peak area of the remaining compound, B).

Fractional conversion is equal to eq. (2):

$$\frac{m}{m_\infty} = \frac{A}{A + B} \qquad (2)$$

Finally, plot of $-\mathrm{Ln}\,[1 - (m/m_\infty)]$ versus t where the gradient of the line is the rate constant k.

Method 2 – product yield dependence on sample size method

This method involves plotting the measured yield versus sample size. This method, just as in normal log plot method, requires pyrolysis of a new sample for each point on the plot, but in this case, pyrolysis time and pyrolysis temperature is the same in all experiments. Then the peak area of the compound versus size of the sample is plotted, and rate constant can be calculated from the gradient. The background to this approach is shown in Scheme 1.

Sequential pyrolysis[14]

The disadvantage of the above methods is that they require the preparation of a new sample for each

$$- Ln\left[1 - \left(\frac{m}{m_\infty}\right)\right] = k \cdot t \rightarrow \text{rearranges to} \rightarrow \frac{m}{m_\infty} = 1 - e^{-k \cdot t}$$

Hence for pyrolysis performed at the same temperature (k = constant)

and the same pyrolysis time (t = constant)

$$1 - e^{-k \cdot t} = \text{constant } \Omega$$

$$\frac{m}{m_\infty} = \Omega \rightarrow m = \Omega \cdot m_\infty$$

Plot m versus m$_\infty$, the slope of this line is equal to Ω from which k can be evaluated.

Scheme 1 Theory of Method 2.

$$-Ln\left[1-\left(\frac{m}{m_\infty}\right)\right] = k \cdot t \rightarrow \text{rearranges to} \rightarrow \frac{m}{m_\infty} = 1 - e^{-k \cdot t}$$

$$\frac{m}{m_\infty} = 1 - e^{-k \cdot t} \rightarrow m = m_\infty - m_\infty \cdot e^{-k \cdot t} \rightarrow m_\infty - m = m_\infty \cdot e^{-k \cdot t}$$

if m is peak area compound at pyrolysis time t

and m' is the peak area compound at pyrolysis time t'

$$\text{at time } t \rightarrow m_\infty - m = m_\infty \cdot e^{-k \cdot t} \; [1]$$

$$\text{at time } t + t' \rightarrow m_\infty - m^* = m_\infty \cdot e^{-k \cdot (t+t')} \; [2]$$

Where m * is the cumulative peak area (m + m')compound at time t + t'

Substracting [2] from [1]

$$m^* - m = m_\infty \cdot \left(e^{-k \cdot (t+t')} - e^{-k \cdot t}\right) \rightarrow m^* - m = m_\infty e^{-k \cdot t} \cdot \left(1 - e^{-k \cdot (t')}\right)$$

$$\ln(m^* - m) = -kt + \underbrace{\left\{n(m_\infty) + \ln\left(1 - e^{-k \cdot (t')}\right)\right\}}_{Cons\tan t}$$

Hence plot $\ln(m^* - m)$ versus t, the slope of this line is equal to rate constant k.

Scheme 2   Guggenheim theory.

pyrolysis, and this requires a high degree of control in the preparation of each sample. On the other hand, sequential pyrolysis methods decrease considerably experimental time because this method only requires one sample to obtain kinetic degradation data. All these methods were developed from eq. (1), where m is the cumulative yield at cumulative time (t), and they show the differences used to obtain m_∞ value.

In the Ericsson method, we use sequential pyrolysis on the same sample until no further product is obtained [peak area 1(a_1) to pyrolysis time 1 (t_1), peak area 2 (a_2) to pyrolysis time 2 (t_2), peak area 3 (a_3) to pyrolysis time 3 (t_3),... peak area n (a_n) to

pyrolysis time (t_n)]; then m_∞ is found by estimating the asymptote when the cumulative peak area (a_1, $a_1 + a_2$, $a_1 + a_2 + a_3$, ... , $a_1 + a_2 + a_3 + ... a_n$) is plotted against the cumulative pyrolisis time (t_1, $t_1 + t_2$, $t_1 + t_2 + t_3$, ... , $t_1 + t_2 + t_3 + ... t_n$). Finally, the data are plotted as in method 1.

In the Guggenheim method, m_∞ values are not necessary if all pyrolysis have the same duration and is expressed as follows (Scheme 2).

Finally, the Kezdy-Jaz-Bruylants (KJB) method is a variant of the Guggenheim method, but this method allows more convenient and reliable estimates of asymptotic limit. It is expressed as follows (Scheme 3).

$$-Ln\left[1-\left(\frac{m}{m_\infty}\right)\right] = k \cdot t \rightarrow \text{rearranges to} \rightarrow \frac{m}{m_\infty} = 1 - e^{-k \cdot t}$$

$$\frac{m}{m_\infty} = 1 - e^{-k \cdot t} \rightarrow m = m_\infty - m_\infty \cdot e^{-k \cdot t} \rightarrow m_\infty - m = m_\infty \cdot e^{-k \cdot t}$$

if m is peak area compound at pyrolysis time t

and m' is the peak area compound at pyrolysis time t'

$$\text{at time } t \rightarrow m_\infty - m = m_\infty \cdot e^{-k \cdot t} \; [1]$$

$$\text{at time } t + t' \rightarrow m_\infty - m^* = m_\infty \cdot e^{-k \cdot (t+t')} \rightarrow m_\infty - m^* = m_\infty \cdot e^{-k \cdot t} \cdot e^{-k \cdot t'} \; [2]$$

Where m * is the cumulative peak area (m + m')compound at time t + t'

Dividing [1] by [2]

$$(m_\infty - m)/(m_\infty - m^*) = m_\infty \cdot e^{k \cdot t'}$$

$$m = m^* \cdot e^{k \cdot t'} + m_\infty \cdot \left[1 - \cdot e^{k \cdot t'}\right]$$

Hence, if m is plotted against m*, k value can be calculated the measured slope.
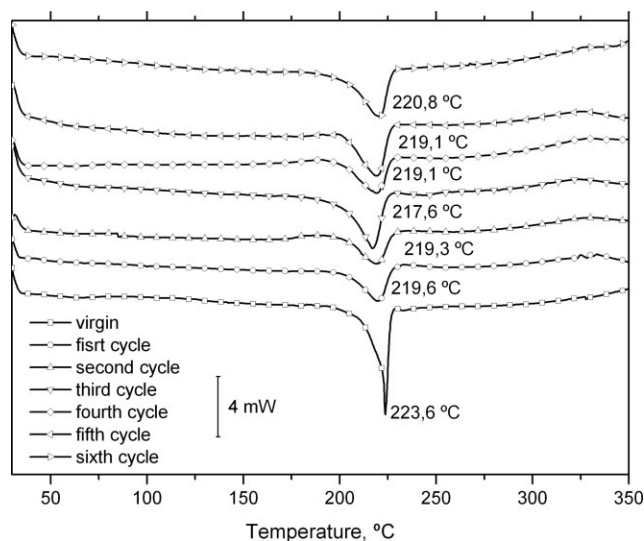
Scheme 3   Kezdy-Jaz-Bruylants theory.

Figure 2 Calorimetric curves of polyamide 6 reprocessed.

RESULTS AND DISCUSSION

Thermal analysis

DSC provides information on the transitions that take place in the material due to heating. The variations in these transitions allow us to identify the structural changes that have occurred in the material.[15] da Costa et al. analyzed the effects of extrusion cycles on thermal properties of PP. They observed that the degree of crystallinity increases with an increase in the number of extrusion cycles,[16] but other authors, have not observed the same trend with the thermal properties of PA. DSC did not show any significant differences in the crystallinity of the recycled PA; however, the melt peak temperature of PA decreased due to the oxidation reaction.[17] DSC analysis of PA6 shows two thermal processes, glass transition temperature (T_g) at around 50°C, and enthalpy of fusion of the PA6 at around 215°C, which allows us to obtain the level of crystallinity. The degree of crystallinity was calculated based on

TABLE I
Evolution of Glass Transition Temperature, Melting Enthalpy and Crystallinity in Function of the Processing Cycles of Polyamide 6

Processing cycle	Glass transition temperature, °C	Melting enthalpy, $J\,g^{-1}$	Crystallinity, %
Virgin	51.15	−55.99	29.5
1° cycle	50.48	−49.80	26.2
2° cycle	48.20	−45.02	23.7
3° cycle	50.29	−47.60	25.1
4° cycle	51.50	−46.42	24.4
5° cycle	49.89	−45.12	23.7
6° cycle	47.05	−46.35	24.4

the melting temperature for 100% crystalline PA6 ($\Delta H_m = 190\,J\,g^{-1}$).[18]

DSC curves in Figure 2 show calorimetric curves of reprocessed PA, where we can observe that the melting temperature decreases slightly with each reprocessing cycle.

In the present work, the DSC method does not show significant differences in glass transition temperature and crystallinity (Table I). Therefore, a much more sensitive technique is needed, which allows the observation of structural differences as a function of reprocessing PA6.

Sequential pyrolysis of PA6

The scarcity of information provided by thermal analysis techniques has led to the study of PA6 using pyrolysis—gas chromatography/mass spectrometry. This technique has greater sensitivity and allows us to analyse the evolution of the products obtained from pyrolysis.

Figure 3 shows the chromatograph obtained from pyrolysis of PA6 reprocessed once and pyrolyzed once. In this we can see the presence of a peak which appears at a retention time of 17'90 min. This peak corresponds with the formation of caprolactam during the degradation process.

The degradation kinetics can be studied using Py–GC/MS and the later application of other diverse methods, in which the constant rate is evaluated.[19] Each of these methods proposes a different evaluation system. In the case of Method 1 (normal log plot method) and Method 2 (from dependence of product yield on sample size), we need to prepare a new sample of the material for each pyrolysis, which requires on the part of the researcher an exhaustive set of controls during preparation of the samples.
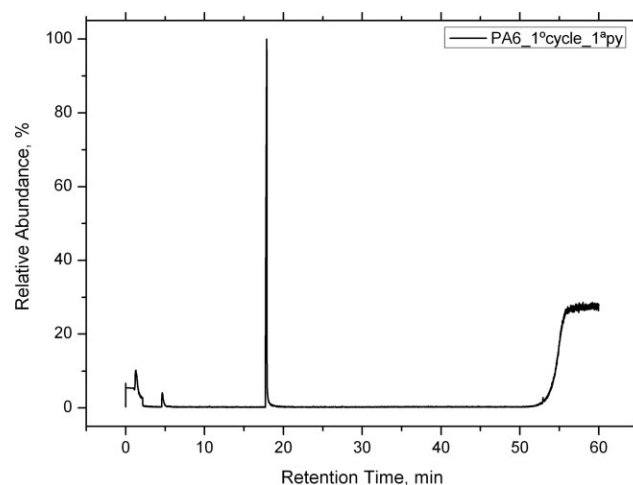

Figure 3 Chromatogram of the products of PA6 (first reprocessing cycle and first pyrolysis).
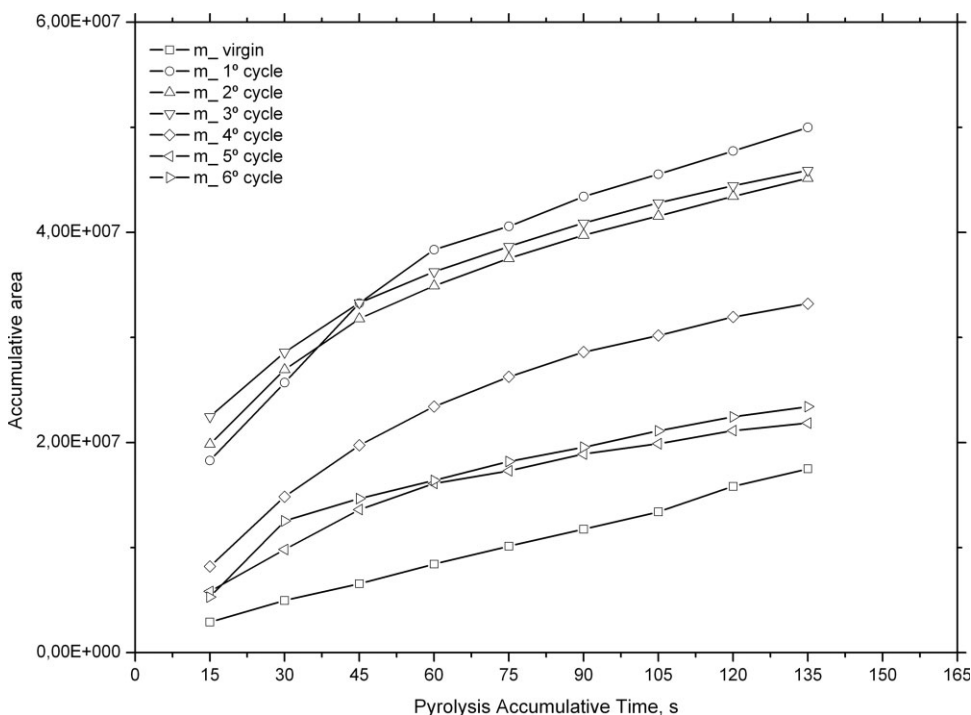
Figure 4 Cumulative plot from sequential pyrolysis of polyamide 6 processed at different cycles.

On the other hand, Method 3 (Ericsson method), Method 4 (Guggenheim method), and Method 5 (KJB method), base their model on sequential pyrolysis, which allows the study to be carried out with a single sample.

Although these last three methods (Ericsson, Guggenheim, and KJB) clearly have advantages over other methods, there are significant differences between them, given that the Ericsson method requires sequential pyrolysis to be carried out until the product under analysis disappears completely, thus obtaining m_∞ (accumulated area of the product analysed from all the pyrolysis carried out). The Guggenheim and KJB methods, however, can be
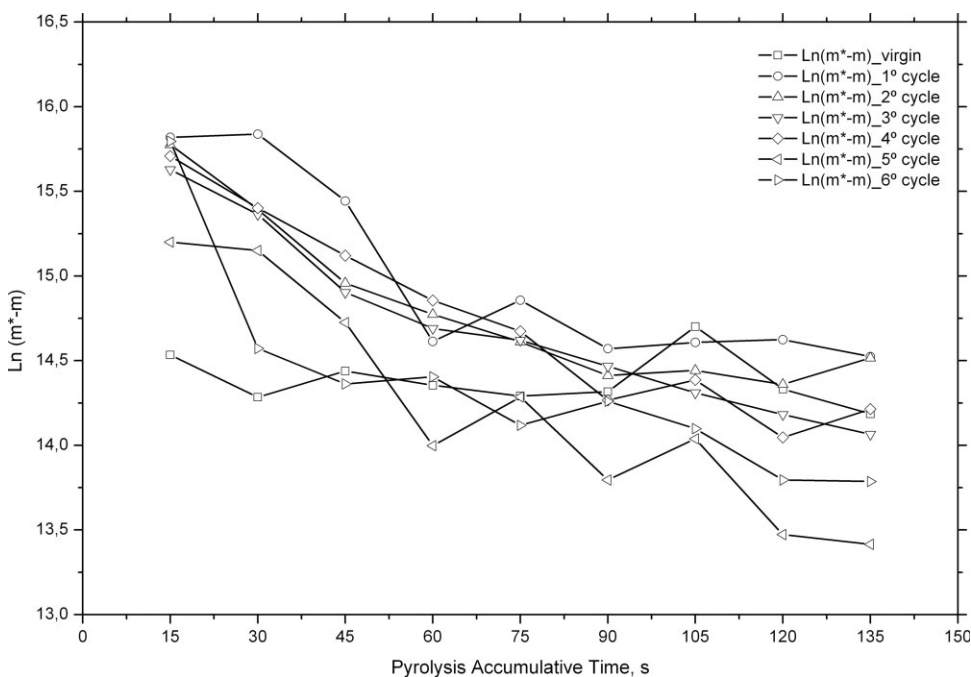

Figure 5 Fist-order plots according to Guggenheim method of the cumulative data from the Figure 4.
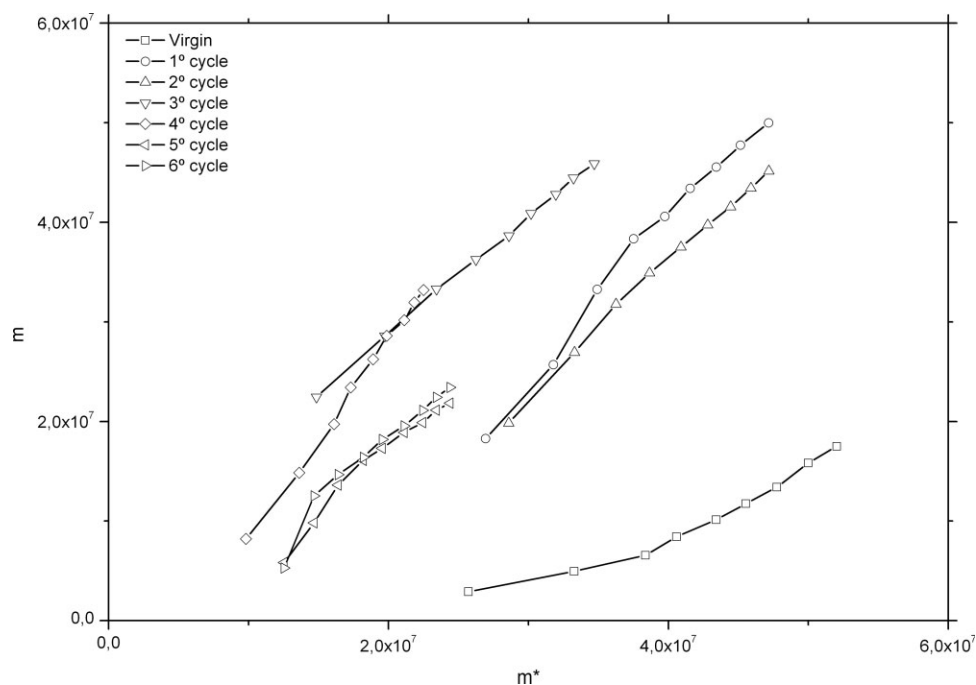
Figure 6 Fist-order plots according to Kezdy-Jaz-Bruylants method of the cumulative data from the Figure 4.

applied out without having to carry out numerous pyrolysis cycles. The general experience of other authors also recommends not completing the pyrolysis sequences as the results can sometimes be anomalous because of successive heating and cooling of the sample under analysis.[19] For this reason, the following study was based on sequential pyrolysis followed by the application of the Guggenheim and KJB methods.

Figure 4 shows the results obtained from the application of sequential pyrolysis to PA6 submitted to different processing cycles in which we can see the accumulated area of caprolactam in function of the accumulated pyrolysis time.

Sequential pyrolysis carried out on various samples of PA6 over different processing cycles indicates a trend toward lower values in the accumulated area (m_∞) as the number of processing cycles increases. On the other hand, accumulative area values of virgin PA show the lowest values among samples (reprocessed PA); which is due to less sensitivity to pyrolysis temperature of the virgin PA. By the other hand, reprocessed PA suffers shear stress and reprocessing temperature and it leads to more susceptibility front pyrolysis temperature.

The evaluation of the overall and specific rate constants for the degradation of the PA6 was determined by use of the Guggenheim and KJB methods,[14,19] and the results obtained are shown in Figures 5 and 6, respectively, and Table II.

The values of the rate constant (k) obtained using the Guggenheim method and KJB method show the same trend toward increasing values as the number of reprocessing cycles increases, although it is important to note the greater reliability of the values obtained via the KJB method given that the line adjustment is much greater than that of the Guggenheim method (Table III).

TABLE II
Overall Rate Constants (s^{-1}) for Pyrolysis of Polyamide 6 at Different Processing Cycles

Processing cycle	Guggenheim, (s^{-1})	Kezdy-Jaz-Bruylants (s^{-1})
Virgin	0.0008	0.0006
1° cycle	0.0083	0.0117
2° cycle	0.0104	0.0148
3° cycle	0.0106	0.0136
4° cycle	0.0134	0.0160
5° cycle	0.0153	0.0169
6° cycle	0.0123	0.0204

TABLE III
R^2 of the Adjustments Obtained from the Guggenheim and Kezdy-Jaz-Bruylants Methods

Processing cycle	Guggenheim method, R^2	Kezdy-Jaz-Bruylants method, R^2
Virgin	0.0505	0.9965
1° cycle	0.6877	0.9890
2° cycle	0.7682	0.9915
3° cycle	0.8688	0.9951
4° cycle	0.9226	0.9982
5° cycle	0.8866	0.9937
6° cycle	0.7021	0.9469

CONCLUSIONS

The DSC technique has often been used as a control tool in the field of commodity recovery; however, its use has not always given satisfactory results when applied to technical plastics. In the case of the PA6 analyzed, we only observed a slight decrease in crystallinity and glass transition temperature values show little difference. It is difficult to be certain that these changes are a consequence of PA degradation as there many other factors which influence the degree of crystallinity in a polymer.

The results obtained using Py–GC/MS show significant differences between reprocessed PAs (not reprocessed, reprocessed once, twice, three,... six times). This technique is more sensitive than other techniques and it allows us to observe variations in the pyrolysis products of reprocessed PA however small they may be. The results from a simple pyrolysis, as well as sequential pyrolysis, are valid for determinating polymer degradation level, whenever there is virgin polymer to be used as a control reference.

Sequential pyrolysis provides more information on the degradation process with the use of different evaluation methods, which in turn allows us to obtain the rate constant (k) of different PAs. In this case, we can see in both methods (Guggenheim and KJB methods) the rate constant increase with reprocessing cycle increase, but the KJB method shows better adjustment than the Guggenheim method. The increase of the rate constant indicates a higher level of degradation in PA6.

References

1. Bernasconi, A.; Rossin, D.; Armanni, C. Eng Fract Mech 2007, 74, 627.
2. Cui, J. R.; Forssberg, E. J Hazard Mater 2003, 99, 243.
3. Javierre, C.; Claveria, I.; Ponz, L.; Aisa, J.; Fernandez, A. Waste Manag 2007, 27, 656.
4. Yamakita, R.; Miura, K.; Ishino, Y.; Ohiwa, N. JSME Int J Ser B: Fluids Therm Eng 2005, 48, 83.
5. Achilias, D. S.; Roupakias, C.; Megalokonomos, P.; Lappas, A. A.; Antonakou, E. V. J Hazard Mater 2007, 149, 536.
6. Ito, M.; Nagai, K. Polym Degrad Stab 2007, 92, 1692.
7. Lin, C. H.; Lin, H. Y.; Liao, W. Z.; Dai, S. H. A. Green Chem 2007, 9, 38.
8. Contat-Rodrigo, L.; Ribes-Greus, A.; Imrie, C. T. J Appl Polym Sci 2002, 86, 764.
9. Contat-Rodrigo, L.; Ribes-Greus, A.; Imrie, C. T. J Appl Polym Sci 2002, 86, 174.
10. Parres, F.; Balart, R.; Crespo, J. E.; Lopez, J. J Appl Polym Sci 2007, 106, 1903.
11. Schade, C.; Heckmann, W.; Borchert, S.; Siesier, H. W. Polym Eng Sci 2006, 46, 381.
12. Sojak, L.; Kubinec, R.; Jurdakova, H.; Hajekova, E.; Bajus, M. J Anal Appl Pyrolysis 2007, 78, 387.
13. Parres, F.; Sanchez, L.; Balart, R.; Lopez, J. J Anal Appl Pyrolysis 2007, 78, 250.
14. Soto-Oviedo, M. A.; Lehrle, R. S.; Parsons, I. W.; De Paoli, M. A. Polym Degrad Stab 2003, 81, 463.
15. Kong, Y.; Hay, J. N. Eur Polym J 2003, 39, 1721.
16. Da Costa, H. M.; Ramos, V. D.; De Oliveira, M. G. Polym Test 2007, 26, 676.
17. Groning, M.; Hakkarainen, M. J Appl Polym Sci 2002, 86, 3396.
18. Kaisersberger, E.; Knappe, S.; Rahner, S.; Moehler, H. TA for Polymer Engineering: DSC, TG, DMA, TMA; Selb-Würzburg, Burlington EEUU, 1994.
19. Bate, D. M.; Lehrle, R. S.; Pattenden, C. S.; Place, E. J. Polym Degrad Stab 1998, 62, 73.