

Improvement to the Flynn–Wall Method of Determining Apparent Activation Energies of the Thermal Degradation of Polymers[†]

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An improvement to the Flynn–Wall method of determining apparent activation energies of the thermal degradation of polymers is presented. The method involves the deconvolution of differential thermogravimetric (TG) curves and the reconstruction of the corresponding TG curves of the individual thermal degradation processes, to which the Flynn–Wall method is then applied separately. The method is illustrated using poly(diisobutyl itaconate) as an example.

Introduction

There are many semiempirical methods^{1–3} of determining the apparent activation energy of thermal degradation, E_a , from nonisothermal thermogravimetric (TG) curves. Among them, the Flynn–Wall method⁴ is frequently used to determine the E_a of polymers. It enables the determination of E_a from nonisothermal TG curves recorded at different heating rates. The E_a of the material at a defined mass loss is proportional to the slope, $d\beta/d(1/T)$, of the linear dependence of the reciprocal absolute temperature at which the mass loss occurs, $1/T$, on the logarithm of the applied heating rate, β . The final value of E_a is the product of the above slope and a coefficient. One of the drawbacks of the method is that this coefficient and therefore E_a are dependent on the slowest applied heating rate. The goal of the present study, however, was to analyze another aspect of the determination of E_a by the Flynn–Wall method involving the complexity of the degradation mechanism.

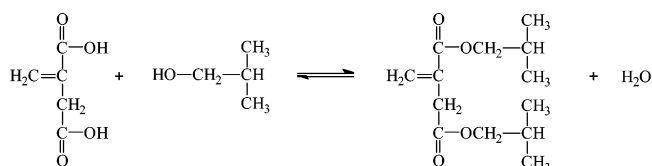
The thermal degradation of polymers is generally complex, with more than one mechanism being operative depending on the degradation temperature. This manifests itself in changes in the slope of the TG curves; consequently, the corresponding differential TG (DTG) curves exhibit multiple peaks or asymmetrical peaks with more or less pronounced shoulders. Except when the mass losses corresponding to each mechanism occur in different temperature ranges, for example, those for PVC⁵ and poly(*sec*-butyl methacrylate),^{6,7} the relative magnitudes of the mass of polymer lost by each mechanism change with the heating rate. The Flynn–Wall method may be applied to polymers with complex degradation mechanisms, and the values of E_a may vary with mass loss.⁸

When the extent of the degradation reactions depends on the heating rate and when successive reactions overlap, the determination of E_a becomes ambiguous. The method introduced in this paper overcomes the denoted difficulty by the deconvolution of the recorded DTG curves and the reconstruction of individual sets of TG curves for the different processes. The Flynn–Wall method is then applied to these individual sets of reconstructed TG curves, whereby the apparent activation energies of the individual processes are obtained.

The method is illustrated using poly(diisobutyl itaconate) as an example.

Experimental Section

Diisobutyl itaconate (DiBI) was prepared by the acid-catalyzed esterification of itaconic acid (methylene succinic acid) (Fluka) with isobutanol (3-methyl propan-1-ol (Merck)) under reflux according to the following reaction:



Benzene (Alkaloid) was used as an inert solvent. The reaction was catalyzed by concentrated sulfuric acid (Lachema), and the evolved water was removed from the system using a Dean–Stark apparatus. After the usual work-up procedure (washing with 10% NaOH aqueous solution to remove the catalyst, unreacted itaconic acid, and half ester, washing with water to neutralize, drying with anhydrous CaCl_2 (Kemika), and removing benzene), the crude diester was fractionally distilled under vacuum.

DiBI was polymerized in bulk at 60 °C for 60 min in an ampule sealed under high vacuum. Azobisisobutyronitrile (AIBN) (Aldrich) at a concentration of 0.5 mol % was used as the initiator. After cooling, the formed poly(diisobutyl itaconate) (PDiBI) was precipitated from the reaction mixture by pouring into methanol (Zorka) containing 5% water. The obtained polymer (a white powder) was purified by two further precipitations from an acetone (Zorka-Pharma) solution using the same precipitant. Finally, PDiBI was dried to constant mass in a vacuum oven at room temperature.

The molar mass of PDiBI was determined by GPC analysis using a Varian 9010 system with five columns and a type RI-4 differential refractometer. Tetrahydrofuran (Merck) at a flow rate of 1 mL/min was used as the solvent. The molar mass was determined using narrow molar mass distribution polystyrene standards for calibration.

Thermogravimetry was performed using a Perkin–Elmer TGS-2 apparatus connected to a first-derivative accessory

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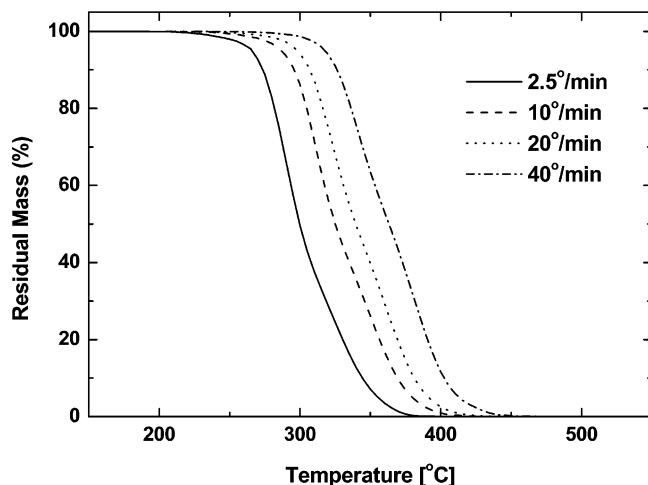


Figure 1. TG curves of PDiBI recorded at 2.5, 10, 20, and 40 °C/min in a dynamic nitrogen atmosphere (25 mL/min). Sample mass is ~2.5 mg

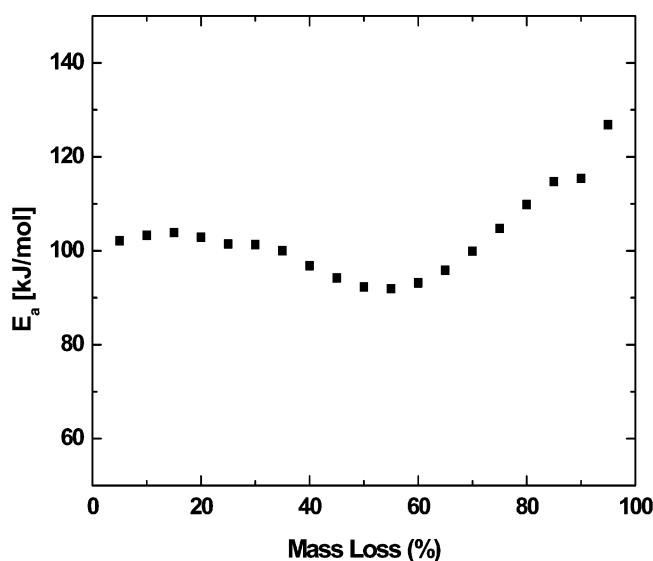


Figure 2. Apparent activation of mass loss (E_a) calculated from the curves presented in Figure 1 using the Flynn–Wall method as a function of mass loss (conversion)

FDA-1 for the simultaneous recording of thermogravimetric (TG) curves and differential TG (DTG) curves.

Results and Discussion

The yield of polymer under the given polymerization conditions was 0.9%. Such a low conversion ensures a linear polymer necessary for thermogravimetric analysis where structural “impurities” can greatly affect the results. The weight-average molar mass of the examined PDiBI was 1.03×10^5 g/mol with a molar mass distribution of 1.48. A molar mass in this range is typical for poly(dialkyl itaconates) prepared in bulk at this temperature. The relatively narrow molar mass distribution is also typical because of the high degree of chain transfer to monomer, which occurs during the polymerization of dialkyl esters of itaconic acid.⁹

The obtained TG curves of PDiBI obtained at heating rates of 2.5, 10, 20, and 40 °C/min are shown in Figure 1.

When the curves shown in Figure 1 are used as the basis for the determination of the apparent E_a as a function of conversion (i.e., mass loss) using the Flynn–Wall method, the results shown in Figure 2 are obtained.

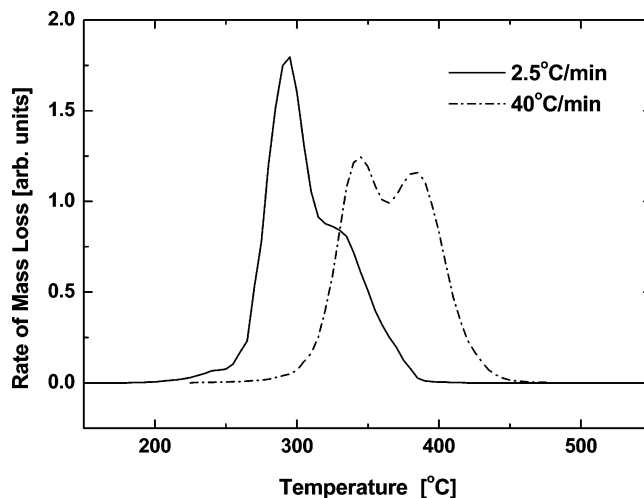


Figure 3. DTG curves of PDiBI recorded at 2.5 and 40 °C/min. Other details are the same as in Figure 1

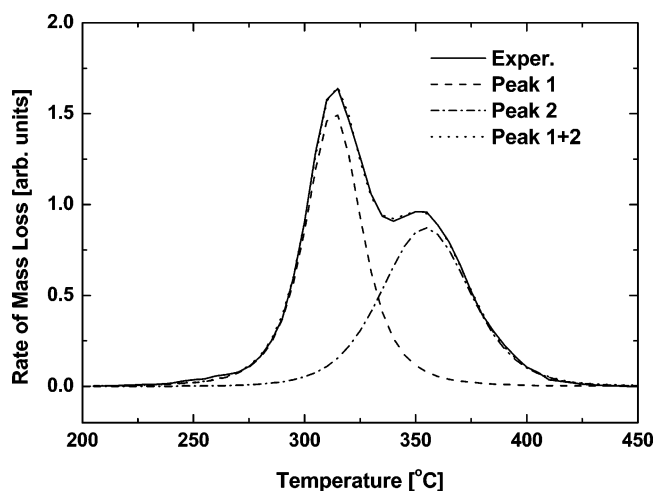


Figure 4. Deconvolution of the DTG peak recorded at a heating rate of 10 °C/min into its two constituent peaks

From Figure 2, it may be seen that the E_a value is approximately constant over the relatively short range from 0 to 20 % mass loss after which it decreases, reaching a minimum at about 50 % mass before increasing steadily during further degradation. It should be noted that this minimum in the E_a versus mass-loss graph corresponds to a slight change in the slope of the TG curves (especially in the curve recorded at a heating rate of 2.5 °C/min).

These changes in slope manifest themselves much more clearly in the corresponding DTG curves, as may be seen in Figure 3, which shows the DTG curves recorded at heating rates of 2.5 and 40 °C/min. The other two DTG curves recorded at heating rates of 10 and 20 °C/min are not included for the sake of clarity, but they are both intermediate between the curves recorded at the slowest and fastest heating rates.

It may be seen from Figure 3 that the polymer degrades by two main processes corresponding to a peak and a shoulder on the DTG peak recorded at the slower heating rate. At the faster heating rate, however, the size of the first peak is reduced, and the shoulder develops into a second peak. The peaks at the higher heating rate (40 °C/min) are not as sharp as the one at the lower rate (2.5 °C/min). Such behavior has been predicted by Flynn¹⁰ when discussing two reactions in relatively even competition. The lower activation energy reaction is expected to dominate the kinetics at slow heating rates, and the higher

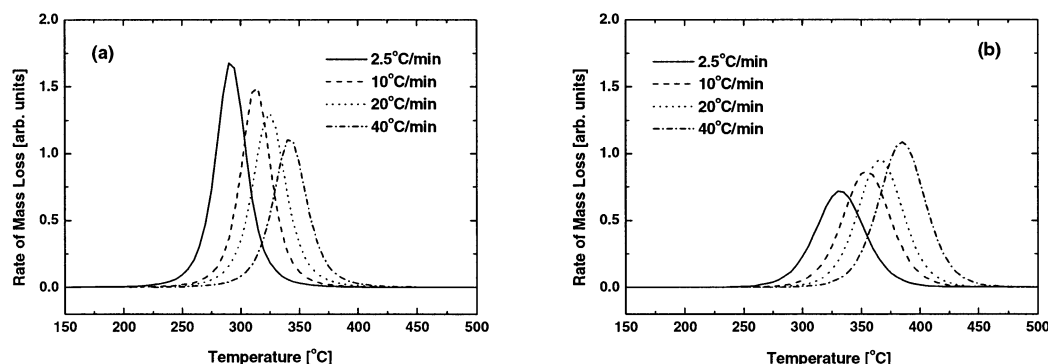


Figure 5. (a) First set of DTG peaks and (b) second set of DTG peaks obtained by the deconvolution of the DTG curves recorded at heating rates of 2.5, 10, 20, and 40 °C/min

activation energy reaction will take over at fast rates and high temperatures.

From previous work,¹¹ it is known that depolymerization is the main degradation mode of PDiBI, the monomer being the major volatile product of degradation. Depolymerization is initiated by end-chain and main-chain scission. As with all poly-(dialkyl itaconates), PDiBI has a large degree of chain-end unsaturation resulting from chain transfer to monomer during its polymerization.⁹ Thus, the first DTG peak originates from depolymerization initiated by the scission of the C–C bond in the position β to the unsaturated chain ends, and the second DTG peak originates from depolymerization initiated by random main-chain scission. No elimination reactions take place according to the mechanism proposed by Grassie¹² because there is only one β -hydrogen atom in the alkyl substituent.

DTG curves are quantitative (i.e., the area under a DTG curve is directly proportional to the mass of polymer lost). The areas under the DTG curves shown in Figure 3 were normalized to account for the different masses of polymer taken for degradation. Not only the total area under a DTG curve but also the areas under the individual peaks are quantitative, representing the amount of polymer degrading by each mechanism. Hence, it was decided to deconvolute the DTG curves recorded at the four heating rates. For this purpose, a noncommercial PC program was employed.¹³ This program allowed Gaussian or Lorentzian fitting of the individual peaks. It was found that both peaks were best fitted using a Lorentzian function. The percentage error of the fitted to experimental curves was less than 2.5%. An example of such a fitting is shown in Figure 4 for a heating rate of 10 °C/min.

It may be seen from Figure 4 that the fitting procedure was excellent and that the degradation proceeds by two processes—the first, end-chain-initiated depolymerization exemplified by a relatively sharp peak (peak 1) and the second, depolymerization initiated by random main-chain scission by a broader peak (peak 2).

The deconvoluted DTG curves recorded at the four heating rates are shown in Figure 5a and b for the first and second peaks, respectively. It may be seen clearly from Figure 5 that the relative degrees of degradation by both mechanisms change with heating rate. The amount of degradation proceeding by the second mechanism increases steadily with heating rate at the expense of that proceeding by the first.

The DTG curves of the individual peaks were then integrated, and the Flynn–Wall method was applied to the thus-formed TG curves of the individual processes. An example of a reconstructed TG curve is shown in Figure 6 for a heating rate of 10 °C/min.

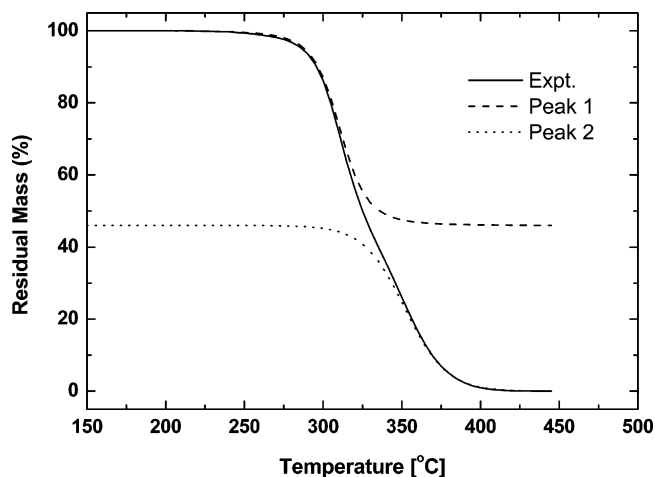


Figure 6. Reintegration of the deconvoluted DTG peaks obtained from DTG recorded at a heating rate of 10 °C/min and the corresponding experimental TG curve.

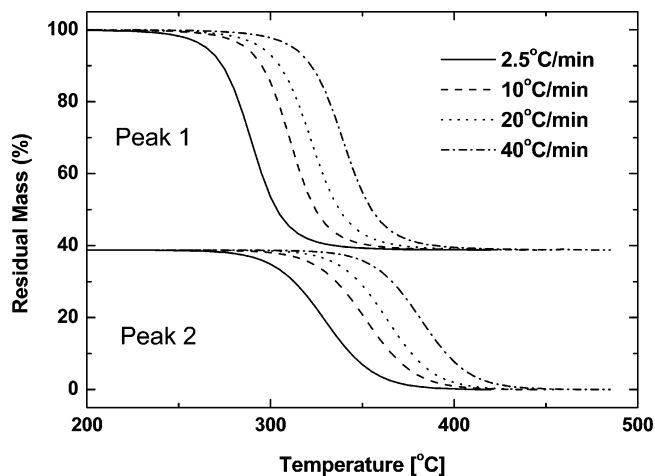


Figure 7. Sets of reintegrated DTG peaks corresponding to the first and second degradation processes.

For the sake of clarity and to show how the calculated TG curves correspond to the experimental TG curve in regions where there is little or no overlap, the start of the second peak was offset by the final mass loss of the first peak.

For each heating rate, similar diagrams were constructed, but the amount of polymer degrading by each mechanism was normalized to the corresponding values obtained at a heating rate of 2.5 °C/min. This normalization did not affect further calculations because the TG curves are just either expanded or

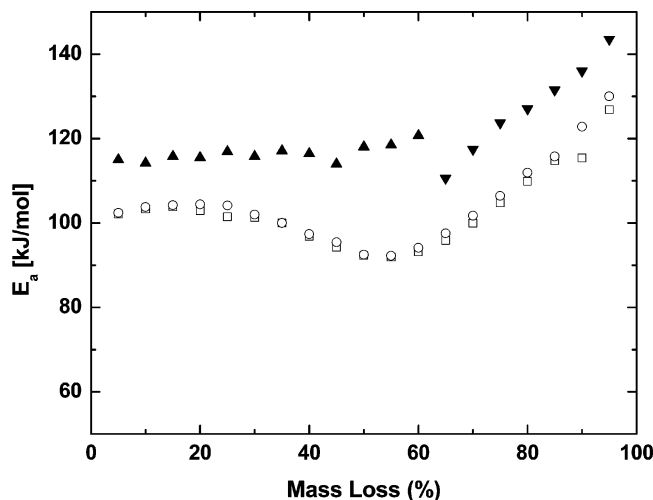


Figure 8. Apparent activation energies of mass loss calculated from the TG curves corresponding to the separated DTG curves (first DTG peak, ▲; second DTG peak, ▼), together with the values calculated from the experimental TG curves (□) and the curves corresponding to the sum of the individual peaks (○).

contracted in this manner. The resulting sets of reconstructed TG curves are shown in Figure 7.

The reconstructed TG curves shown in Figure 7 were then used to calculate the activation energies of the two degradation processes in the usual manner. The results of these calculations are shown in Figure 8, using the residual mass values shown in Figure 7 as the basis for the mass-loss values shown in Figure 8. Also shown in Figure 8 for comparison are the degradation activation energy values calculated from the experimental TG curves and TG curves reconstructed from the sum of the DTG curves of peaks 1 and 2.

It may be seen from Figure 8 that there is no minimum in the values of the activation process when the reconstructed TG peaks of the individual processes are used as the basis for the calculations of the E_a values. This minimum arises solely because of the overlap of the two degradation processes. In addition, the values calculated for the first process are approximately constant and amount to 116.5 ± 1.9 kJ/mol. This value is about 14 kJ/mol higher than the values calculated from the experimental TG curves at the very beginning of the degradation when there is minimal overlap of the two processes. The E_a values of the second process increase linearly with conversion, as is to be expected in the latter stages of thermal

degradation when the residue becomes increasingly carbonaceous. These values are also approximately 14 kJ/mol higher than those calculated from the experimental TG curves. Finally, the extremely good correlation between the E_a values obtained from the TG curves reconstructed from the sum of the individual peaks and those obtained using the experimental TG curves shows that the differences noted above are genuine.

Conclusions

We believe that we have shown that by separating the thermal degradation processes by the deconvolution of DTG curves obtained at different heating rates one of the major problems encountered when using the Flynn–Wall method of determining apparent activation energies of mass loss can be overcome. This method eliminates anomalies resulting from the influence of a subsequent degradation process on the determination of activation energies from nonisothermal thermogravimetry and so leads to more reliable values.

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Note Added after ASAP Posting. This article was posted ASAP on the Web on 5/30/2003. A change was made in the first paragraph of the Results and Discussion section. The correct version was posted on 6/13/2003.

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