Thermal Degradation of Biomedical Polyurethanes—A Kinetic Study Using High-Resolution Thermogravimetry

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ABSTRACT: The kinetics of thermal degradation of polyurethanes (PUR) has been studied by means of high-resolution and constant heating rate thermogravimetry (TG), under nitrogen and synthetic air atmospheres. The high-resolution TG provided a way to increase resolution with decreasing the time of data acquisition. In this mode, the heating rate is dynamically varied to maximize resolution. A method to calculate the kinetic parameters from this technique was used. The TG curves showed two or three decomposition steps, depending on the atmosphere employed. The parameters calculated for the PUR decomposition were the activation energy, reaction order, and preexponential factor. A method to estimate the polymer lifetime was also used. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 910–919, 2001

Key words: polyurethane; kinetics; high-resolution thermogravimetry

INTRODUCTION

Polyurethanes (PUR) are a broad class of polymers that have urethane groups [—OC(=O)NH—] in their main chain, and that find many useful applications.[1] The most common procedure of PUR synthesis is the polyaddition of an organic isocyanate, and a polyol, and sometimes a low molecular weight diol or diamine. The use of different reactants is responsible for a great variety of characteristics of PUR, allowing tailor-made uses of them. Some PUR are blood compatible, and this characteristic, together with the good mechanical resistance, have been allowed their usage as biomedical materials.[2] A peculiar characteristic of PUR is the existence of two distinct segments in its structure: a rigid one, which contains all the structures related to the isocyanate and the diol or diamine; and a soft one, which contains all the structures related to the polyol.

The thermal stability of PUR was studied extensively, because of their widespread applications. Generally, PUR is thermally stable up to 250°C, and their stability is related with the kind of isocyanate and polyol used.[3]

The thermal degradation investigation of polymers allows determination of the proper conditions for manipulating and processing them, and for obtaining high-performance products that are stable and free of undesirable by-products. If not processed properly, the PUR can generate toxic products to the human body, which is very critical in biomedical applications. Besides that, TG provides a method for accelerating the lifetime testing of polymers so that short-term experiments can be used to predict in-use lifetime.

Until recently, the thermal degradation had been studied only by means of constant heating rate or isothermal thermogravimetry (TG) techniques.[4] The last one is often a long-time experiment. The former is faster to run, but to obtain
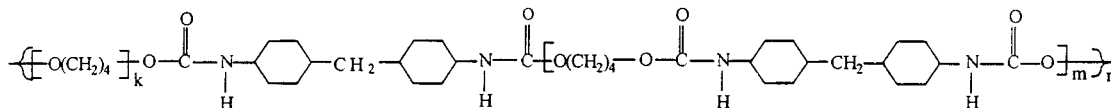

Figure 1 Proposed structure of PUR Tecoflex (*k, m,* and *n* are different for each kind of sample).

good resolution data, the heating rate has to be lowered, increasing the time of data acquisition. Nowadays, however, the use of high-resolution TG to evaluate the thermal degradation of compounds and their kinetics, has been improved the relationship time-resolution. The high-resolution TG, introduced by TA Instruments, is a technique that provides a way to increase resolution, with decreasing the time required for experiments.

There are only a few studies using the high-resolution TG to study the thermal degradation of polymers. Gill et al.[5] showed a number of possible applications of this technique, including the degradation study of ethylene-vinyl acetate (EVA) copolymer with different contents of vinyl acetate, the separation of different components in a polymer fiber blended with a natural one, and the polytetrafluoroethylene (PTFE) decomposition. Salin and Seferis[4] proposed a methodology to ob-

tain kinetic parameters from variable heating rate data (high-resolution); they studied the two decomposition steps of EVA copolymer, and the decomposition of the poly(ether ether ketone) (PEEK) resin. Gradwell et al.[6] showed that the thermal degradation of the polyurethane/poly-(ethyl methacrylate) interpenetrating polymer networks were best understood by using the dynamic rate technique (high-resolution). Li studied the kinetics of thermal degradation of cellulose esters,[7] poly(2,6-dimethyl-1,4-phenylene oxide),[8] and poly(4-methyl-1-pentene).[9] Li et al.[10] also studied the kinetics of thermal degradation of Kevlar fiber.

In this work, the thermal degradation of three different PUR mainly used in biomedical applications was studied using the Salin and Seferis's method,[4] which is based on Kissinger's method.[11] The basic equation is:
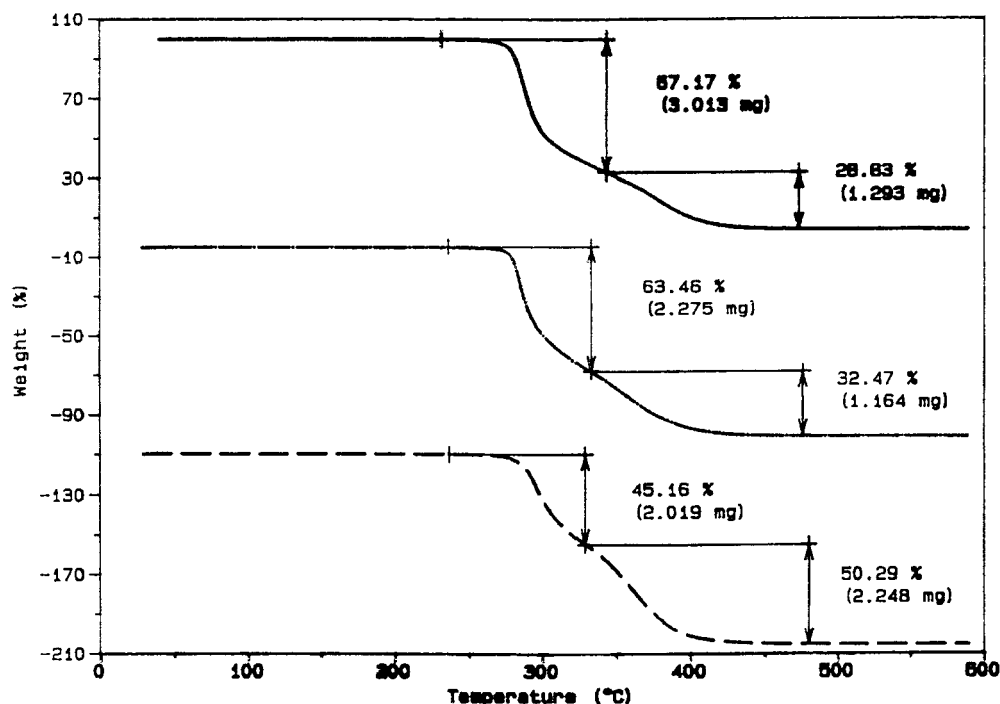

Figure 2 TG curves of PUR 60 D (solid line), PUR 93 A (dash-dotted line), and PUR 80 A (dashed line), at 20°C · min^{-1}, resolution 4, under nitrogen atmosphere.
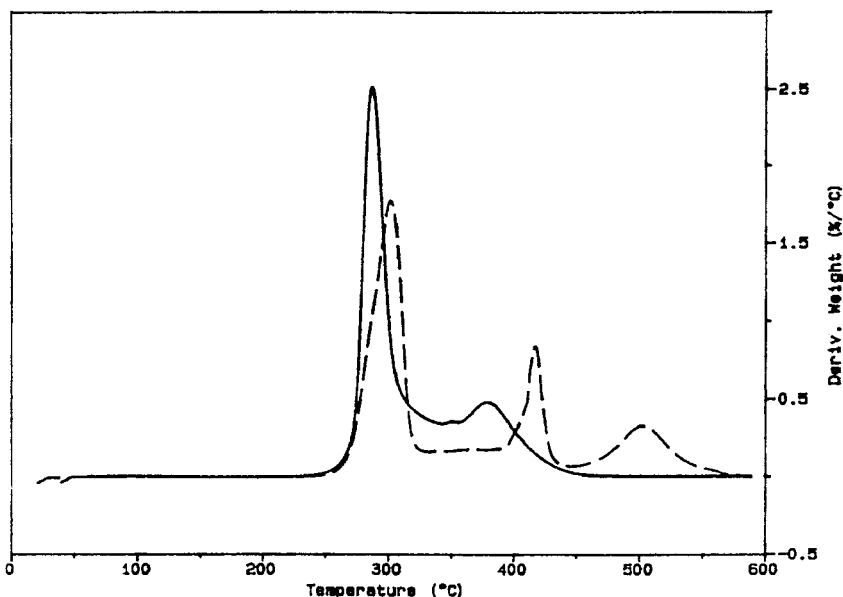
Figure 3   DTG curves for PUR 60 D ($20°C \cdot \min^{-1}$, resolution 4), under nitrogen (solid line) and synthetic air atmosphere (dashed line).

$$\ln(q/T^2) = (-E_a/R)(1/T) + \ln[(AR/E_a)$$
$$\times n(1 - \alpha)^{n-1}] \quad (1)$$

where q is the heating rate at the maximum weight loss rate, T the temperature at this point, E_a the activation energy, R the gas constant, A the Arrhenius' preexponential factor, n the reaction order, and α the conversion degree. A plot of $\ln(q/T^2)$ vs. $1/T$ produces a straight line, which slope is $-E_a/R$. If the reaction order is unknown, it can be calculated from:

$$n = (d\alpha/dT)^{-1}(E_a/qR)\exp(b)\exp(-E_a/RT)(1 - \alpha) \quad (2)$$

where $(d\alpha/dT)$ is the maximum weight loss as a function of temperature, and b is the intercept of (1).

Another way of performing the calculations was based on the onset temperature, developed by Dobkowski and Rudnik.[12] This method allows the evaluation of polymer lifetime, with the approach that at the initial conditions there are no weight loss ($\alpha = 0$) and the reaction order is unity ($n = 1$), and according to eq. (1):

$$\ln(q_i/T_i^2) = (-E_i/R)(1/T_i) + \ln(A_iR/E_i) \quad (3)$$

where the subindex i is referred to the initial conditions. The polymer lifetime (t) is given by:

$$t = (1/A_i)\exp(E_i/RT) \quad (4)$$

where T is the temperature of interest. A plot of ln t vs. $1/T$ produces a straight line, and usually this graph is used to calculate the polymer lifetime at a given temperature.

Although the existence of several methods and ways of calculating the kinetic parameters, there is a controversy in the current literature about the meaning of these parameters.[13,14] Some authors claim that these parameters do not have any physical significance, being only mathematical entities. However, some authors claim a physical meaning to these parameters. Redfern[13] defined E_a as the average energy obtained from the vibration of a molecule in the lattice, which could, at a certain temperature, provide sufficient energy at a particular point for the reaction to start. Denq et al.[14] defined the reaction order n, for polymers, as follows: a zero-order reaction ($n = 0$) would reflect the scission of the ending mer from the polymer chain (depolymerization), small molecule scission from a side chain, or cyclization; a first-order reaction ($n = 1$) would reflect intramolecular transfer and random scission of the main chain; and a second-order reaction ($n = 2$), the weight loss related to two random polymer segments colliding simultaneously, such as intermolecular transfer and scission.

Table I   Experimental Conditions and Kinetic Parameters Calculated Using Salin and Seferis's Method, for the First Step of Decomposition in Nitrogen

Sample	q_i (°C · min^{-1})	Resolution	q (°C · min^{-1})	T (°C)	E_a (kJ · mol^{-1})	n	$\log A$
PUR 60 D	20	2	8.7	323.2	156	1.4	13.6
	20	3	2.9	306.6	156	1.0	13.3
	20	4	1.1	287.4	156	1.0	13.3
	20	5	0.30	269.3	156	0.90	13.3
PUR 60 D	10	—	10	323.8	123	1.4	10.1
	5.0	—	5.0	306.3	123	1.3	10.2
	2.0	—	2.0	284.6	123	1.3	10.2
	1.0	—	1.0	279.3	123	1.8	9.93
PUR 93 A	20	3	3.5	311.6	155	1.5	11.6
	20	4	1.0	285.2	155	0.85	11.6
	20	5	0.30	274.1	155	1.4	11.7
PUR 93 A	10	—	10	325.3	123	0.13	11.0
	5.0	—	5.0	311.6	123	0.28	10.7
	2.0	—	2.0	292.5	123	2.4	10.0
	1.0	—	1.0	277.8	123	1.1	10.3
PUR 80 A	20	2	12	330.6	151	1.7	12.5
	20	3	5.8	314.6	151	1.2	12.7
	20	4	1.6	296.1	151	2.2	12.3
	20	5	0.70	278.1	151	1.3	12.7
PUR 80 A	10	—	10	319.2	108	0.76	9.31
	5.0	—	5.0	302.6	108	0.75	9.32
	2.0	—	2.0	288.0	108	1.6	8.75
	1.0	—	1.0	264.0	108	0.90	9.18

Table II   Experimental Conditions and Kinetic Parameters Calculated Using Salin and Seferis's Method, for the Second Step of Decomposition in Nitrogen

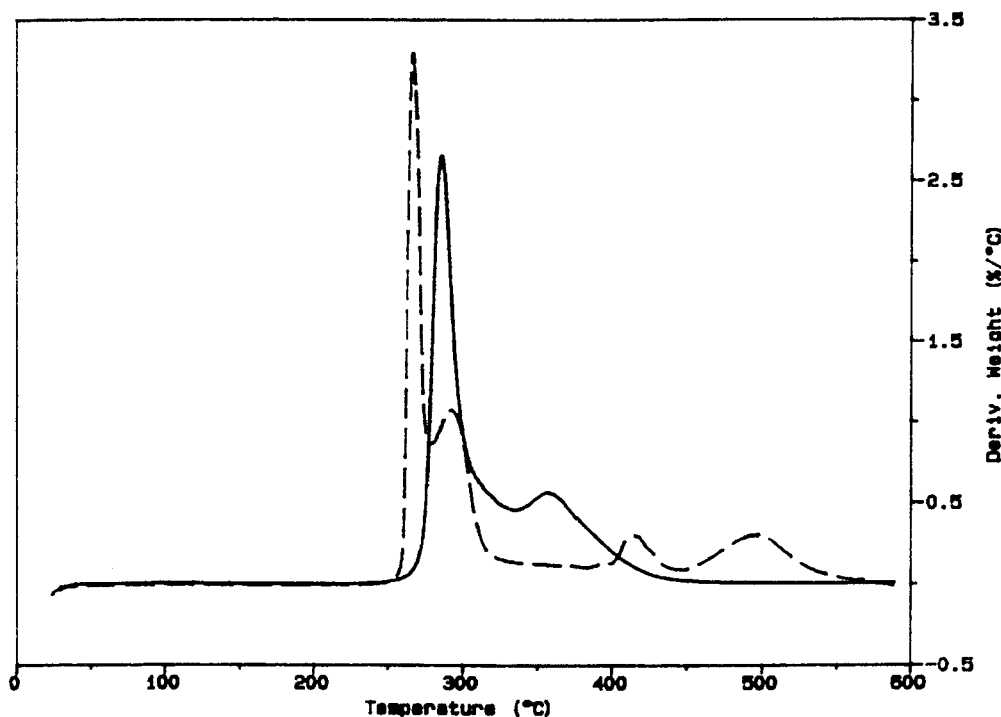| Sample	q_i (°C · min^{-1})	Resolution	q (°C · min^{-1})	T (°C)	E_a (kJ · mol^{-1})	n	$\log A$	Residue at 600°C (%)
PUR 60 D	20	2	14	400.1	198	1.3	15.4	2.15
	20	3	5.5	392.5	198	1.2	15.3	2.60
	20	4	3.6	378.9	198	1.7	15.6	3.80
	20	5	1.2	361.3	198	1.8	15.6	3.97
PUR 60 D	10	—	10	403.6	153	1.1	11.6	1.47
	5.0	—	5.0	375.8	153	1.2	11.6	4.09
	2.0	—	2.0	363.8	153	1.5	11.8	4.60
	1.0	—	1.0	349.6	153	1.6	11.8	4.61
PUR 93 A	20	3	7.3	374.3	226	2.3	6.81	3.38
	20	4	3.1	356.6	226	1.9	6.81	3.84
	20	5	1.2	350.7	226	3.6	6.85	5.03
PUR 93 A	10	—	10	385.5	174	0.14	14.1	1.90
	5.0	—	5.0	370.8	174	0.30	13.8	3.41
	2.0	—	2.0	358.9	174	0.95	13.4	3.19
	1.0	—	1.0	342.3	174	1.6	13.3	5.24
PUR 80 A	20	2	9.4	390.3	203	1.6	15.4	1.85
	20	3	4.7	370.9	203	1.2	15.7	2.43
	20	4	2.4	359.0	203	1.4	15.5	4.25
	20	5	0.82	350.1	203	2.5	15.1	6.79
PUR 80 A	10	—	10	400.7	151	0.83	11.5	1.92
	5.0	—	5.0	378.0	151	0.96	11.4	2.58
	2.0	—	2.0	359.4	151	1.3	11.2	8.09
	1.0	—	1.0	350.5	151	1.4	11.1	4.10

Figure 4   DTG curves for PUR 93 A ($20°C \cdot min^{-1}$, resolution 4), under nitrogen (solid line) and synthetic air atmosphere (dashed line).

EXPERIMENTAL

Three different samples of PUR from Thermo Electron Corp. were used in this work: Tecoflex EG 60 D (PUR 60 D), Tecoflex EG 80 A (PUR 80 A), and Tecoflex EG 93 A (PUR 93 A). All of them were made for biomedical usage.

The TG experiments were performed under nitrogen and also under synthetic air atmosphere at $60 \ cm^3 \cdot min^{-1}$ to the furnace and $40 \ cm^3 \cdot min^{-1}$ to the thermobalance on a Hi-Res™ TGA 2950 (TA Instruments Inc.) interfaced to the Thermal Analyst 2000 software. Sample mass was 3–5 mg. According to Salin and Seferis,[4] the best performance of Hi-Res™ TGA 2950 was fixing the initial heating rate and varying the resolution, so a set of experiments using $20°C.min^{-1}$ heating rate and resolutions from 2 to 5, sensitivity 1, from ambient temperature until 600°C, were performed to all samples. For comparison, a series of constant heating rate experiments were also carried out using 1, 2, 5, and $10°C \cdot min^{-1}$ heating rates.

RESULTS AND DISCUSSION

The proposed structure of PUR Tecoflex is shown in Figure 1. The ratio between the concentration of soft segment (k) and hard segment (m) is responsible for the mechanical properties of PUR Tecoflex. Usually, high ratios mean more flexible PUR. It is known that the ratio (k/m) is inversely proportional to the Shore hardness of PUR. For the three samples studied, the ratio (k/m) increases in the following order: PUR 60D < PUR 93 A < PUR 80 A.

The TG curves of PUR usually show a two-step decomposition under nitrogen atmosphere.[1,3,6,15–18] The first step can be split in two, depending on the resolution employed in the experiment (or the heating rate), as stated by Petrovic et al.[3] Figure 2 shows the TG curves of the three PUR studied. The DTG curves (derivative of the TG curve as function of temperature) under nitrogen and synthetic air for PUR 60 D, 93 A, and 80 A samples are shown in Figures 3, 4, and 5, respectively. The kinetic parameters calculated for the first and second step of decomposition in nitrogen, using the Salin and Seferis's method, are illustrated in Tables I and II, respectively.

As expected, the increasing of resolution produced a decrease in the temperature at the maximum of weight loss rate; this effect was observed in both high-resolution and constant heating rate experiments. Although the activation energy should be independent on the heating rate, it was
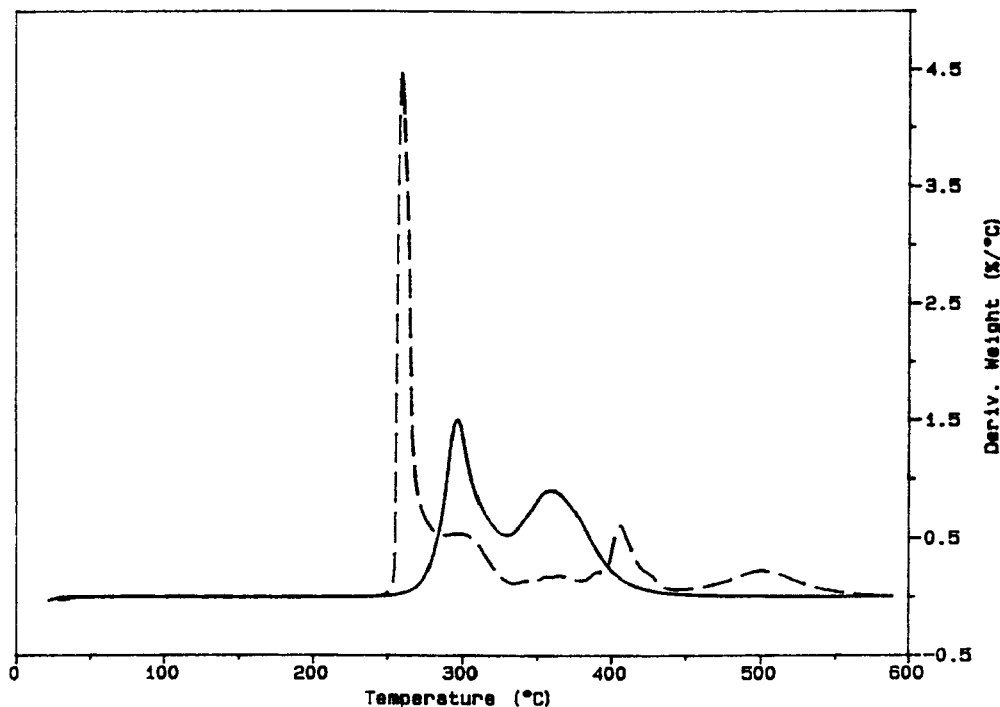
Figure 5   DTG curves for PUR 80 A ($20°C \cdot min^{-1}$, resolution 4), under nitrogen (solid line) and synthetic air atmosphere (dashed line).

observed that in the high-resolution experiments the activation energies were always higher than those in the constant heating rate experiments. The resolution 2 for the sample PUR 93 A did not give a resolved two-step decomposition, so this curve was neglected in the calculations.

The average reaction order is in the range between 1 and 2 for the first step of decomposition, and between 1 and 3 for the second step. Kutty et al.,[16] Corrêa et al.,[17] and Suhara et al.[18] had shown that, in the initial conditions of degradation, this kind of reaction is first order. The calculated reaction order does not present a constant value. This fact could be related to the complex mechanism of thermal decomposition.

It was also observed that the decreasing of heating rate is responsible to a slight increasing of the content of the final residue at 600°C.

According to infrared (IR) and Raman spectra of these samples,[19] the ratio between the relative intensity of the bands of the functional groups pertaining to the soft segment and to the hard segment agree with the ratio between the soft and the hard segment observed in Shore hardness. In the literature,[3,15] it is proposed that the first step of PUR decomposition under nitrogen is related to the degradation of the hard segment, and the

second (and further) step(s) would be associated to the decomposition of the soft segment. Under nitrogen atmosphere, as shown in Figure 2, it is observed that the conversion degree for the first step is high in PUR 60 D (67%), followed by PUR 93 A (63%), and PUR 80 A (45%). This order agrees with the Shore hardness scale, and IR and Raman data,[19] concerning the contents of soft segment related to the hard one.

Petrovic et al. [3] showed that a high ratio between soft and hard segments implies in a higher thermal stability of PUR. From the TG curves under nitrogen, the decomposition temperature at the maximum weight loss rate in the first step usually follows the order: T (PUR 60 D) < T (PUR 93 A) < T (PUR 80 A) for high-resolution experiments, and T (PUR 60 D) < T (PUR 80 A) < T (PUR 93 A) for constant heating rate experiments. The thermal stability of PUR in the high-resolution experiments obeys the same relation between the soft and hard segments observed by Petrovic et al.,[3] Shore hardness data, and IR and Raman spectral data.[19]

For the second step, usually, T (PUR 80A) < T (PUR 93 A) < T (PUR 60 D) for high-resolution, and T (PUR 93 A) < T (PUR 80 A) < T (PUR 60 D) for constant heating rate experiments, that is the

Table III   Experimental Conditions and Kinetic Parameters Calculated Using Salin and Seferis's Method, for the First Step of Decomposition in Synthetic Air

Sample	q_i (°C · min^{-1})	Resolution	q (°C · min^{-1})	T (°C)	E_a (kJ · mol^{-1})	n	log A
PUR 60 D	20	2	8.4	339.3	132	1.6	10.5
	20	3	3.4	324.7	132	1.5	10.5
	20	4	1.4	302.1	132	1.3	10.6
	20	5	0.49	284.3	132	1.7	10.5
PUR 60 D	10	—	10	342.7	123	2.0	9.75
	5.0	—	5.0	326.2	123	2.0	9.75
	2.0	—	2.0	309.1	123	2.7	9.60
	1.0	—	1.0	291.8	123	2.5	9.64
PUR 93 A	20	2	9.6	333.2	158	3.5	12.9
	20	3	4.7	315.9	158	3.2	12.9
	20	4	0.61	267.0	158	0.43	13.8
	20	5	0.030	251.5	158	2.6	13.0
PUR 93 A	10	—	10	324.0	108	2.0	8.62
	5.0	—	5.0	319.9	108	3.0	8.44
	2.0	—	2.0	297.8	108	3.4	8.39
	1.0	—	1.0	275.1	108	3.0	8.45
PUR 80 A	20	2	9.4	280.1	391	10	36.1
	20	3	2.8	270.6	391	4.2	36.5
	20	4	0.41	260.3	391	2.4	36.8
	20	5	0.020	243.0	391	1.8	36.9
PUR 80 A	10	—	10	274.9	65	1.5	5.31
	5.0	—	5.0	266.0	65	3.4	4.96
	2.0	—	2.0	231.1	65	2.0	5.19
	1.0	—	1.0	210.7	65	0.93	5.52

inverse order observed in the first step. According to Shore hardness and vibrational spectral data, the thermal stability would be T (PUR 80A) < T (PUR 93 A) < T (PUR 60 D), the same order presented in high-resolution experiments. The second step of decomposition can also be related to the volatilization of residues previously formed.[3,15]

The main difference between the two sets of experiments, constant heating rate, and high-resolution, is that in the former the relationship among heating rate, time and temperature is linear, while in the later it is nonlinear. This experimental difference may affect the mechanism of reaction(s) and, consequently, the calculated kinetic parameters.

Under synthetic air atmosphere, the decomposition of PUR occurred in three steps. In some cases, the first step appear split in two (e.g., Figs. 4 and 5), and in this case it was considered as only one step. The data of the first, second, and third steps of decomposition are shown in Tables III, IV, and V, respectively, using the Salin and Seferis's method.

In the same way as in the nitrogen atmosphere experiments, the increasing of resolution pro-

duced a decrease in the temperature at the maximum of weight loss rate; the same effect was observed in high-resolution and constant heating rate experiments. It was also observed that in the high-resolution experiments the activation energies were usually higher than those in the constant heating rate experiments, except in the third step, where an inversion in the samples PUR 60 D and 93 A occurred.

The values of reaction order in the air experiments also do not present a constant value, and are more dispersed than the ones in nitrogen atmosphere, possibly indicating that the mechanism of decomposition is more complex than in nitrogen.

For the first step of decomposition in air T (PUR 80 A) < T (PUR 93 A) < T (PUR 60 D), for high-resolution and also for constant heating rate experiments. This order is the reversal of that observed for the first step in nitrogen for high-resolution experiments. The values of activation energy and temperatures of decomposition observed for the first step in both atmospheres were near the same, except for PUR 80 A samples, which values were dispersed, due to a possibly change in the reaction mechanism. In this step

Table IV Experimental Conditions and Kinetic Parameters Calculated Using Salin and Seferis's Method, for the Second Step of Decomposition in Synthetic Air

Sample	q_i (°C · min^{-1})	Resolution	q (°C · min^{-1})	T (°C)	E_a (kJ · mol^{-1})	n	log A
PUR 60 D	20	2	15	432.6	286	2.5	20.4
	20	3	6.1	427.9	286	2.9	20.3
	20	4	2.0	416.7	286	3.6	20.2
	20	5	1.0	398.8	286	0.68	20.9
PUR 60 D	10	—	10	429.3	275	4.0	19.8
	5.0	—	5.0	414.1	275	1.9	20.1
	2.0	—	2.0	403.5	275	1.9	20.1
	1.0	—	1.0	398.8	275	2.8	19.9
PUR 93 A	20	2	13	432.2	222	3.6	19.0
	20	3	9.0	434.1	222	4.5	18.9
	20	4	4.5	417.0	222	4.1	19.0
	20	5	1.3	397.8	222	2.5	19.2
PUR 93 A	10	—	10	435.2	165	1.9	11.4
	5.0	—	5.0	423.0	165	1.7	11.5
	2.0	—	2.0	404.4	165	1.5	11.5
	1.0	—	1.0	384.8	165	1.6	11.5
PUR 80 A	20	2	15	426.1	351	0	32.9
	20	3	7.3	417.3	351	3.4	26.0
	20	4	3.2	409.9	351	4.4	25.9
	20	5	1.3	399.3	351	4.9	25.9
PUR 80 A	10	—	10	429.6	183	2.2	13.0
	5.0	—	5.0	408.8	183	1.4	13.2
	2.0	—	2.0	390.8	183	1.5	13.1
	1.0	—	1.0	387.1	183	3.2	12.8

the higher thermal stability is related to the higher content of hard segment in the samples.

In Table I, the average reaction order in nitrogen in the first step is 1, which validates the use of the second method to perform the calculations of polymer lifetime, developed by Dobkowski and Rudnik. Under air atmosphere, the reaction order is quite different from 1, but in a way of comparing the results, the method was applied to these experiments also. The parameters calculated by means of Dobkowski and Rudnik's[12] method and the polymer lifetime are shown in Tables VI and VII, respectively. It is important to note that this calculation can only be made with constant heating rate experiments.

From Table VII, we noticed that the longer lifetime of PUR under nitrogen atmosphere is PUR 93 A, followed by PUR 80 A, and PUR 60 D. Under air atmosphere, the thermal stability is in the reversal order. These results are related to the thermal stability observed in constant heating rate experiments (Salin and Seferis's method), even when we are comparing

two different parameters: the onset temperature, and the temperature at the maximum weight loss rate.

We should stress that the extrapolation of time–temperature plot may be critical, because the decomposition mechanism involved is very complex in the PUR, as stated by Petrovic et al.[3] and Grassie et al.[15]

CONCLUSIONS

In the high-resolution TG experiments under nitrogen atmosphere, the thermal stability observed is in accordance with Shore hardness data, and IR and Raman spectral data.[19] Besides that, the high-resolution TG has some advantages compared to constant heating rate TG: the time of data acquisition is shorter; the derivative of TG curve (DTG) is more defined, allowing more precision in determining some parameters, such as temperature and weight loss rate.

Table V   Experimental Conditions and Kinetic Parameters Calculated Using Salin and Seferis's Method, for the Third Step of Decomposition in Synthetic Air

Sample	q_i (°C · min^{-1})	Resolution	q (°C · min^{-1})	T (°C)	E_a (kJ · mol^{-1})	n	$\log A$	Residue at 600°C (%)
PUR 60 D	20	2	17	540.8	157	2.2	9.70	2.63
	20	3	11	530.4	157	2.2	9.70	1.63
	20	4	4.5	502.5	157	1.7	9.81	1.56
	20	5	1.4	468.2	157	1.6	9.85	3.04
PUR 60 D	10	—	10	511.6	175	2.7	10.7	2.54
	5.0	—	5.0	500.2	175	3.0	10.6	1.21
	2.0	—	2.0	471.5	175	2.6	10.7	3.22
	1.0	—	1.0	456.1	175	2.4	10.8	3.62
PUR 93 A	20	2	17	535.8	136	1.7	8.07	1.78
	20	3	11	529.7	136	2.0	8.00	1.71
	20	4	4.7	495.9	136	1.7	8.08	4.61
	20	5	1.5	459.4	136	1.7	8.09	2.12
PUR 93 A	10	—	10	513.7	139	2.4	8.21	4.50
	5.0	—	5.0	499.1	139	2.4	8.21	1.67
	2.0	—	2.0	468.1	139	2.2	8.24	3.43
	1.0	—	1.0	444.2	139	1.7	8.36	6.78
PUR 80 A	20	2	17	533.6	145	2.1	8.91	1.42
	20	3	12	522.2	145	2.0	8.93	1.17
	20	4	5.5	499.7	145	2.0	8.94	1.98
	20	5	2.0	466.3	145	1.7	9.01	2.51
PUR 80 A	10	—	10	509.4	128	1.8	7.65	1.86
	5.0	—	5.0	487.5	128	2.0	7.61	1.81
	2.0	—	2.0	463.9	128	2.2	7.58	1.67
	1.0	—	1.0	433.0	128	1.7	7.70	5.79

In the experiments carried out under nitrogen atmosphere for the three PUR samples, the values of activation energy for each step present compatible data, considering the particular experimental method. However, under air atmosphere, the values of activation energy present results with a great dispersion, even considering the same experimental method, that could reflect the complex mechanism of decomposition in presence of oxygen.

When comparing both methods (Salin and Seferis's and Dobkowski and Rudnik's methods), the later is easier to use than the former. However, the later method has some limitations, like the extrapolation of the time–temperature plot; this could be critical in the evaluation of polymer lifetime, and it ignores the decomposition in the initial stages, it has the approach that the reaction order is always 1 (exactly), and the use of the onset temperature in the calculations is more susceptible to changes with the experimental conditions than the temperature at the maximum of decomposition.

It would be also interesting to evaluate the biodegradation of the biomedical PUR.

Table VI   Kinetic Parameters Calculated from Dobkowski and Rudnik's Method

Sample	E_i (N$_2$) (kJ · mol^{-1})	E_i (Air) (kJ · mol^{-1})	$\log A_i$ (N$_2$)	$\log A_i$ (Air)
PUR 60 D	113	124	10.0	10.8
PUR 80 A	128	95.0	11.7	9.11
PUR 93 A	177	62.3	16.2	4.96

Table VII   Polymer Lifetime Calculated from Dobkowski and Rudnick Method (a: year; d: day)

Temperature (°C)	Lifetime (PUR 60 D)		Lifetime (PUR 80 A)		Lifetime (PUR 93 A)	
	N_2	Air	N_2	Air	N_2	Air
25	10^4 a	10^5 a	10^5 a	60 a	10^9 a	2 a
40	10^3 a	10^4 a	10^4 a	10 a	10^8 a	1 a
100	1 a	8 a	4 a	10 d	10^7 a	2 d
150	6 d	26 d	10 d	10^2 min	1 a	10^2 min

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