

# Thermooxidative Stability of Different Polyurethanes Evaluated by Isothermal and Dynamic Methods

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**ABSTRACT:** Two methods for the evaluation of resistance to the thermooxidation of different classes of polyurethane films (PURs) throughout thermogravimetric analyses were used. Normal and waterborne polyurethanes were characterized using either isothermal or dynamic heating. In the isothermal method, the times required to reach degradations of 0.025, 0.05, and 0.10 were determined at several temperatures in the interval of 190–250 °C. In the dynamic method, heating rates of 0.5, 1, 2, 5, and 10 °C/min were used in the range of 30–500 °C, and degradations of 0.025, 0.05, 0.10, 0.20, and 0.40 were considered. From the Arrhenius plots, activation energies were evaluated ranging between 130 and 230 kJ/mol for normal PURs and between 80 and 170 kJ/mol for waterborne PURs depending on the method, temperature interval, and degree of degradation. Advantages and disadvantages of the two methods were compared. The isothermal method requires a preliminary test, and it was more useful for degradation studies up to 0.05. The dynamic method offered evidence for the presence of different degradation processes, and it was more suitable for the evaluation of kinetics parameters at higher degrees of degradation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1216–1225, 2001

**Key words:** polyurethanes; waterborne polyurethanes; thermooxidation; thermal stability; activation energy

## INTRODUCTION

Several thermogravimetric methods have been used to study the thermal stability of polymeric materials both in oxidative and nonoxidative conditions. The evaluation of the kinetics parameters can be derived from isothermal and dynamic data, as reported/shown by various researchers.<sup>1–10</sup> The choice of testing method can affect the results, and quite large differences can be found as a result of the different analytical approaches that treat the thermal-degradation data, even for simple polymers. For instance, in

the case of the nonoxidative degradation of polyethylene, the dynamic method recently proposed by Park et al.<sup>11</sup> gave apparent activation energies and overall reaction orders rather dissimilar from those reported in the literature for similar material;<sup>12–16</sup> the researchers also comment that the values calculated according to the previous methods were significantly different from each other.

The prediction of the lifetime service of polymeric materials under accelerated degradation conditions using thermogravimetric analysis (TGA) has been reviewed by Flynn.<sup>17</sup> From the kinetics of degradation, activation energy can be calculated from an Arrhenius correlation,<sup>6,9–10,17–19</sup> and this parameter can be useful for predicting material stability; for instance, the 5% weight loss is a reasonable criterion for defining the life-

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time of the material at service temperatures. Similarly, an activation energy can be also evaluated after dynamic experiments at different heating rates, and various percentages of degradation can be considered. In the case of polyurethane materials only the initial weight loss (up to 10, and in some cases 40) can be used to calculate apparent activation energies<sup>6,20</sup> because at higher degradation percentages, the reaction becomes too complex to evaluate the kinetics parameters, and the interpretation is not easy. In fact, the mechanism of polyurethane degradation is very complicated, involving the disruption of the urethane bond at about 210 °C with the formation of isocyanate and alcohol groups<sup>20</sup> as confirmed by spectroscopic analysis. The thermal degradation of polyurethane materials has been examined by several researchers.<sup>8,21–23</sup> In particular, the composition of polyurethane, that is, the type of isocyanate/polyol and the chain extender or crosslinker, was found to directly influence the thermal stability,<sup>9–10,24–27</sup> and in some cases the degradation curves were proposed as «fingerprint» to identify commercial polyurethanes.<sup>28–30</sup>

In a previous article, the different thermal stabilities of polyether- and polyester-based polyurethanes were measured using the criterion of the required time to reach 5% weight loss during the isothermal experiments.<sup>10</sup>

The objective of the present article is to evaluate the resistance to thermooxidation of different classes of normal and waterborne polyurethane films (PURs) by means of two different methods based on TGA, that is, an isothermal and a dynamic method.

## KINETIC ANALYSIS

The thermooxidation experiments are generally described by the percentage of weight loss,  $W_{\%}$ , and the degree of degradation,  $\alpha$ , defined as

$$W_{\%} = 100 \times (w_0 - w)/w_0 \quad (1a)$$

$$\alpha = (w_0 - w)/w_0 \quad (1b)$$

where  $w_0$  and  $w$  are the initial and the actual weight of the sample, respectively.

In the isothermal method the time,  $t_{\alpha}$ , required to reach a certain percentage of degradation,  $\alpha$ , is determined at several temperatures. The resulting experimental data usually fit quite well with

the Arrhenius plot that can be constructed according to

$$\log t_{\alpha} = \log A_{\text{ISO}} + E_{\text{act-ISO}}/2.303RT \quad (2)$$

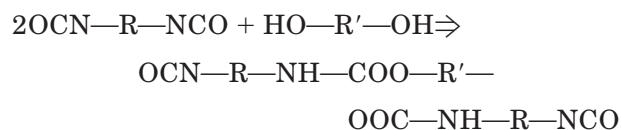
where  $A_{\text{ISO}}$  is the pre-exponential factor,  $E_{\text{act-ISO}}$  is the activation energy,  $R$  is the gas constant, and  $T$  is the absolute temperature. In the dynamic method, derived from Ozawa<sup>15</sup> and Flynn,<sup>16</sup> several heating rates,  $\beta$ , are used that are related to the temperature at which a definite percentage of weight loss occurs, according to

$$\log \beta = \log A_{\text{DYN}} - E_{\text{act-DYN}}/2.303RT_{\alpha} \quad (3)$$

where  $A_{\text{DYN}}$  is the pre-exponential factor,  $E_{\text{act-DYN}}$  is the activation energy, and  $T_{\alpha}$  is the absolute temperature at which the degree of degradation  $\alpha$  is reached. Both procedures can be used to calculate an activation energy; however, the pre-exponential factor has a different meaning. The  $A_{\text{ISO}}$  constant encompasses steric and entropic effects and formally represents the time  $t_{\alpha}$  required to reach a certain degree of degradation at infinite temperature; the higher its value, the higher the resistance to thermooxidation.<sup>10</sup> On the other hand,  $A_{\text{DYN}}$  formally represents the heating rate  $\beta$  at which a certain percentage of weight loss occurs at infinite temperature; the lower its value, the higher the material stability. The kinetics of the thermooxidation process depend on both activation energy and the pre-exponential factor.

## EXPERIMENTAL

Normal and waterborne polyurethanes (see Table I) were synthesized by Morton International S.p.A (Mozzate, Como, Italy) from both polyester and polyether diols via prepolymer. In the first stage, the prepolymer was prepared by the reaction of a molar excess of a diisocyanate with a diol having a molar mass of 2000. With a molar ratio of 2/1, the reaction is the following:



Moreover, in the case of waterborne polyurethanes, a diol with a hydrophylic group was also used.

**Table I** Composition of Normal and Waterborne Polyurethanes Synthesized from Diphenylmethane-4,4'-diisocyanate (MDI) or Isophoronediiisocyanate (IPDI)

Name	Polyol	Isocyanate	Film Thickness (mm)
polyester-urethanes			
PU-PBAc	Polybutylene adipate	MDI + polymeric MDI	0.70
wbPU-PCL	Polycaprolactone	IPDI	0.06
polyether-urethanes			
PU-PPG	Polypropylene oxide	MDI	1.21
wbPU-PPG	Polypropylene oxide	IPDI	0.04
wbPU-PTMEG	Polytetramethylene oxide	IPDI	0.03

In the second stage, a chain extender was used to complete the reaction for obtaining a polymer of suitable molar mass.<sup>31,32</sup>

Normal PURs were prepared from diphenylmethane-4,4'-diisocyanate (MDI) and polybutylene adipate (PU-PBAc) or polypropylene oxide diol (PU-PPG). After addition of an aliphatic diamine as a chain extender, polymer films were cast from the reaction mixture with a solvent-free technology based on dioctylphthalate.

Waterborne PUR prepolymers<sup>33</sup> were obtained from isophoronediiisocyanate (IPDI), dimethylolpropanoic acid containing the hydrophylic group and polycaprolactone (wbPU-PCL), or polypropylene oxide diol (wbPU-PPG) or polytetramethyleneoxide (wbPU-PTMG). The neutralized prepolymer was dissolved in aqueous solution and then extended with amine; after casting at room temperature the polymer films were dried at 120 °C up to 10 min.

Normal and waterborne PURs were finally stored at room temperature and used without any drying treatment.

TGA was performed on about 20 mg of polymer using a Mettler TG50 thermobalance with an air flow of 200 mL/min both in isothermal and dynamic heating. Isothermal experiments were carried out at several temperatures in the range of 190–250 °C up to degradations of 0.025, 0.05, and 0.10. In the case of the dynamic method, heating rates of 0.5, 1, 2, 5, and 10 °C/min were used in the range of 30–500 °C, and degradations up to 0.025, 0.05, 0.10, 0.20, and 0.40 were investigated.

## RESULTS AND DISCUSSION

Tables II and III summarize the experimental data of the thermooxidation of the different polyurethanes measured by the isothermal and dy-

**Table II** Times at Which Degradations of 0.025, 0.05, and 0.10 Occurred during Isothermal Heating as Function of the Different Temperatures

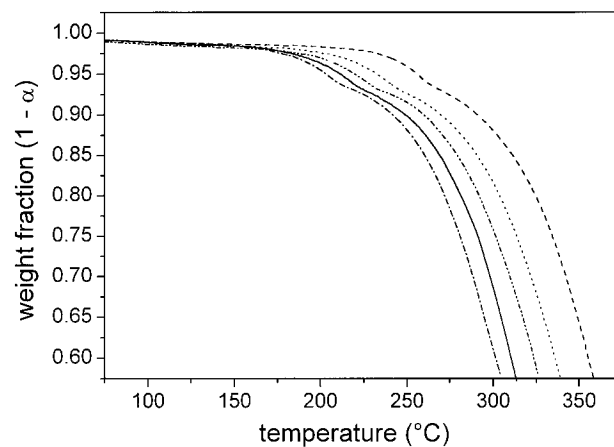
Temperature (°C)	$\alpha$ Degradation	PU-PBAc (min)	PU-PPG (min)	wbPU-PCL (min)	wbPU-PPG (min)	wbPU-PTMG (min)
190	0.025	552	407	26	60	28
	0.05	>2000	742	98	294	96
	0.10	>2000	1288	632	819	278
210	0.025	199	81	7	10	6
	0.05	703	172	28	66	27
	0.10	>1000	266	149	213	133
230	0.025	50	25	5	3	3
	0.05	214	37	15	8	9
	0.10	757	62	52	49	48
250	0.025	10	8	2	2	2
	0.05	46	14	5	5	4
	0.10	166	26	11	20	14

**Table III** Temperatures at Which Degradations of 0.025, 0.05, 0.10, and 0.20 Occurred during Dynamic Heating as Function of the Different Heating Rates

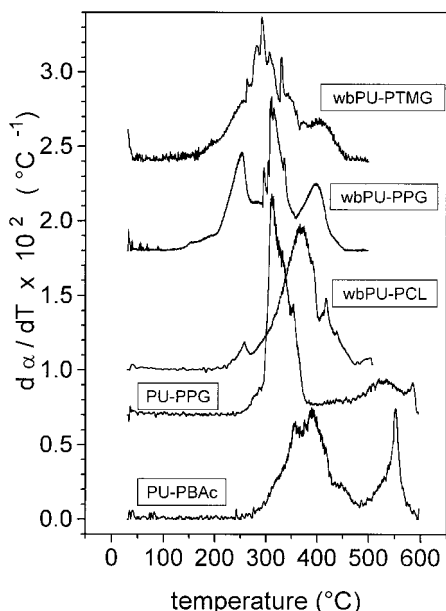
$\beta$ Heating Rate (°C/min)	$\alpha$ Degradation	PU-PBAc (°C)	PU-PPG (°C)	WbPU-PCL (°C)	wbPU-PPG (°C)	wbPU-PTMG (°C)
0.5	0.025	195	224	163	161	157
	0.05	245	240	202	190	190
	0.10	272	256	241	223	226
	0.20	299	264	272	245	265
1	0.025	234	232	183	159	175
	0.05	268	241	210	194	210
	0.10	290	251	250	232	246
	0.20	315	265	280	258	279
2	0.025	251	240	188	187	195
	0.05	282	253	219	218	224
	0.10	302	263	257	241	257
	0.20	326	280	292	284	287
5	0.025	267	257	204	199	195
	0.05	295	272	233	247	236
	0.10	318	290	270	270	278
	0.20	342	299	304	295	313
10	0.025	279	269	233	217	216
	0.05	304	288	256	252	257
	0.10	326	303	291	283	301
	0.20	351	311	325	303	337

dynamic methods. The results are compared and related to the structure of PUR, the testing method and degree of degradation. From isothermal degradation, it is immediately evident that all the waterborne polyurethanes require a considerable lower time to reach a fixed grade of degradation. This lower thermal stability is also confirmed by dynamic experiments in which wbPURs reach  $\alpha = 0.1$  at lower temperatures. In particular, among the waterborne polyurethanes, wbPU-PCL was the most prone to degradation in the isothermal experiments, but it seemed to be more stable during dynamic degradation. This effect can be explained by taking into account that during dynamic heating, both water and other volatile species were removed at a relative low temperature, and, hence, above 175 °C the polymer can be considered dried. On the other hand, during isothermal experiments the sample was directly inserted in the oven chamber at the testing temperature (190–250 °C) so some residual water could be involved in the thermal reactions of the ester bonds that are very sensitive to hydrothermal degradation. For instance, PBAc specimens stored at room conditions and heated to 250 °C lost 5% of their initial weight in 46 min, whereas dried material required 150 min, as previously reported.<sup>10</sup>

The isothermal method requires a preliminary test to determine an appropriate range of temperature to study. It can easily provide information in a relatively short time, and it can be used to study kinetic data of the various degradation stages after selection of the proper temperature range. A convenient temperature range was approximately chosen as the interval in which the



**Figure 1** Weight fraction ( $1 - \alpha$ ) of wbPU-PCL versus temperature during dynamic thermooxidation at heating rates of 0.5 (---), 1 (—), 2 (— · — · —), 5 (····), and 10 °C/min (— —).



**Figure 2** Derivative curve of the degree of degradation after thermogravimetric analysis performed at a heating rate of 10 °C/min. The curves of PU-PPG, wbPU-PCL, wbPU-PPG, and wbPU-PTMG are shifted upward by  $0.7 \times 10^2$ ,  $1.0 \times 10^2$ ,  $1.8 \times 10^2$ , and  $2.4 \times 10^2$  °C<sup>-1</sup>, respectively.

corresponding degradation reached about 2.5–5% ( $\alpha = 0.025$ – $0.05$ ) during dynamic thermooxidation at 10 °C/min. In previous work<sup>10</sup> the interval of 250–300 °C was selected for PU-PPG and PU-PBAC, and degradations up to 5% of weight loss ( $\alpha = 0.05$ ) were examined. As a result of the fact that waterborne polyurethanes were more prone to degradation, in the present work, the selected temperature range was lowered to 190–250 °C for both PUR types. On the other hand, the dynamic method did not require any preliminary test, and

in about 20 h all the measurements were performed for each material. During dynamic thermooxidation, it was also possible to detect the presence of different degradation stages as shown in the case of wbPU-PCL in Figure 1. The change of the slope in the interval 200–250 is due to a change in mechanism and confirms the different activation energy measured at degradations of 0.05, 0.10, and 0.20. Below 100 °C a weight loss of about 1%, as a result of the evaporation of equilibrium moisture or other volatile products, was observed. The derivative curve of the degree of degradation,  $d\alpha/dT$ , can readily distinguish a single degradation process, as shown in Figure 2 in the case of film heated at 10 °C/min. This function represents the degradation rate of the material in those particular experimental conditions, and the main data are summarized in Table IV. The onset temperature, evaluated in the initial part of the derivative curve, revealed that waterborne PURs started to degrade at lower temperatures (130–224 °C) with respect to normal PURs (250–285 °C). Moreover, polyester-based polymer showed a higher onset temperature than the corresponding polyether-based ones, confirming a higher thermal stability. Also, the position of the main peak, which is related to the maximum of degradation rate, confirms the same tendency. Polyester-based polymers showed the highest temperatures (389 and 366 °C) with respect to polyether-based PURs. In particular, both normal and waterborne PURs based on PPG showed the same position of the main peak at 310 °C. According to the maximum of the peak, polyester-based polyurethane (PU-PBAC) has the lowest rate of decomposition  $d\alpha/dT$ , ( $0.75 \times 10^2$  °C<sup>-1</sup>), whereas polyether-based polymers (PU-PPG) exhibited the highest degradation rate ( $1.5 \times 10^2$  °C<sup>-1</sup>), and water-

**Table IV** Data Evaluated from the Derivative of the Degree of Degradation during Dynamic Heating Performed at 10°C/min

	$T_{\text{onset}}$ (°C)	Low-Temperature Peak		Main Peak		High-Temperature Peak	
		$T$ (°C)	$d\alpha/dT \times 100$ (°C <sup>-1</sup> )	$T$ (°C)	$d\alpha/dT \times 100$ (°C <sup>-1</sup> )	$T$ (°C)	$d\alpha/dT \times 100$ (°C <sup>-1</sup> )
PU-PBAC	284	—	—	389	0.75	552	0.73
PU-PPG	252	—	—	311	1.48	533	0.23
wbPU-PCL	224	257	0.19	366	0.97	417	0.47
wbPU-PPG	129	251	0.66	310	1.03	396	0.45
wbPU-PTMG	154	256	0.41	291	0.97	403	0.28



borne polyurethanes showed an almost constant value of about  $1.00 \times 10^2 \text{ }^\circ\text{C}^{-1}$ . The presence of more peaks in the  $da/dT$  curve attests to the various steps of degradation. Two peaks for normal PURs and three peaks for waterborne PURs were distinguished. In this latter case, the secondary peak at low temperature, exhibited in the range of 250–260  $^\circ\text{C}$  from waterborne PURs only, is attributable to the degradation of lateral groups. On the other hand, the main peak is related to thermooxidation of the main polymer backbone, whereas the secondary peak at high temperature corresponds to the degradation of the final 20% of residual material (degree of degradation from 0.8 to 1).

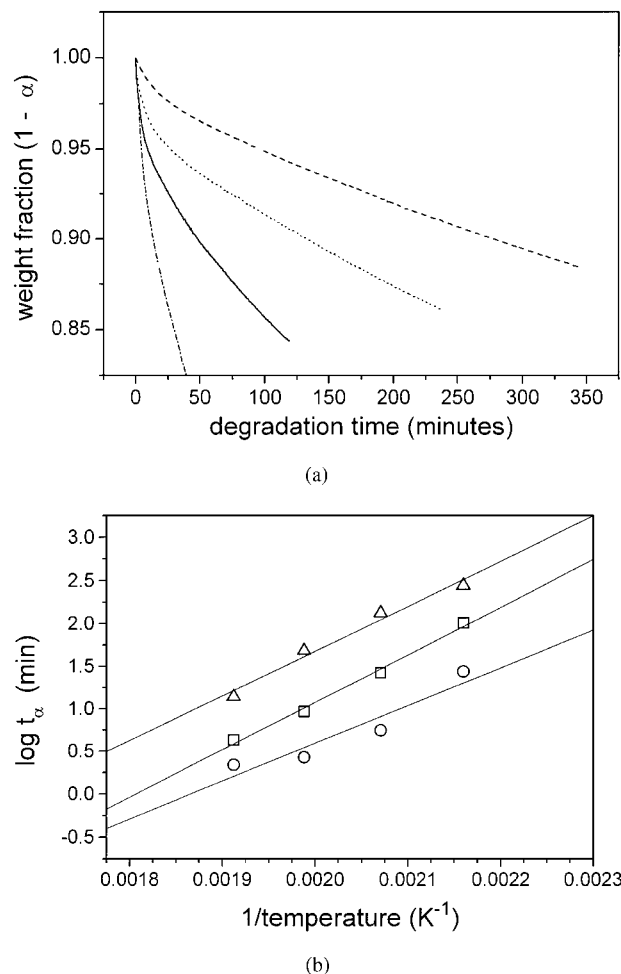
By using dynamic methods, the degradation kinetics can be studied at very high percentages of weight loss, very close to complete thermooxidation. However, these latter data are quite time-consuming, and the kinetic data could be the result of the superposition of various reaction stages. The heating rate showed its upper limit of application at about 10  $^\circ\text{C}/\text{min}$ , depending on the material stability.

To exemplify the procedure for the kinetics evaluation from the experimental data, both the isothermal and dynamic experiments are illustrated in Figures 3(a) and 4(a), respectively, in the case of a waterborne polyurethane, wbPU-PTMG. From this analysis, the time and the temperature were achieved at degradations of 0.025, 0.05, 0.10, and 0.20 (this latter degree of degradation is for the case of the dynamic method only). The correspondent Arrhenius plots were determined from eqs. (2) and (3) and are given in Figures 3(b) and 4(b), respectively.

### Activation Energy

The activation energies and their standard deviations were calculated from the slope of the best-fitting linear regression according to eqs. (2) and (3). Values in the range of 80–230 kJ/mol were found with both methods, as a function of the material, the degree of degradation, and the kinetics method.

In particular, in the initial stage of thermooxidation the activation energy ranges between 130 and 150 kJ/mol for normal PURs and 80 and 100 kJ/mol for waterborne PURs, as demonstrated in Figures 5(a,b). Moreover, polyester-based PURs (PU-PBAC and wbPU-PCL) exhibit higher values than polyether-based polymer, as expected and previously reported for similar polymers.<sup>10</sup> The

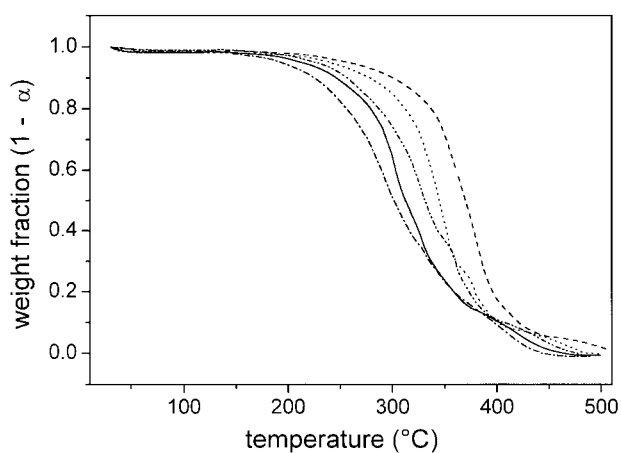


**Figure 3** (a) Isothermal thermogravimetric curves of wbPU-PTMG at 190 (---), 210 (·····), 230 (—), and 250  $^\circ\text{C}$  (- · - ·). (b) Arrhenius plot of wbPU-PTMG derived from isothermal curves at 0.025 (○), 0.05 (□), and 0.10 (△) of degradation according to eq. (2).

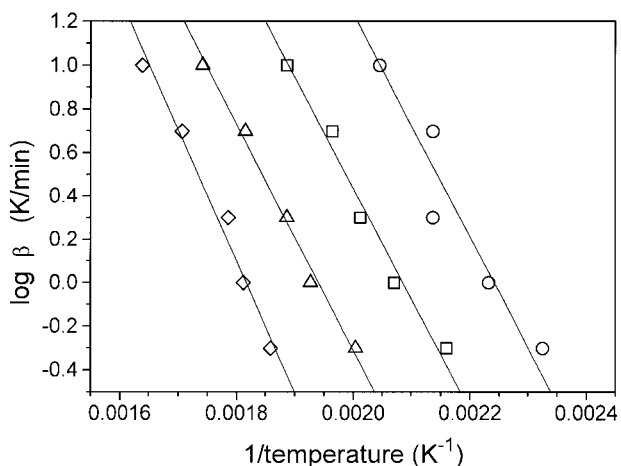
activation energies, evaluated by the isothermal method, are generally lower than those derived from the dynamic method in the case of normal PURs. These results seem to be related to the superposition of different degradation processes that occur during the dynamic thermooxidation.

Moreover, a tendency of the activation energy to increase with the degree of degradation was observed both in isothermal and dynamic methods, reaching values of 130–180 kJ/mol and 100–150 kJ/mol for normal and waterborne PURs, respectively, at  $\alpha = 0.10$ . Because of the presence of hydrophilic substituents and of lateral groups that can decompose in the range of 180–220  $^\circ\text{C}$ , the waterborne PURs resulted in less stable than normal PURs, as found in Tables II and III for

PU-PPG and wbPU-PPG, especially for degradations of 0.025 and 0.05. Hence, the variation of the apparent activation energy with the degree of degradation seems to be related to various mechanisms involved in the thermooxidation processes. The low activation energy in the first stages of degradation seems to be related to an initial step in which both the sorbed water and the degradation of lateral groups are involved. On the other hand, at  $\alpha \geq 0.1$  the higher apparent activation energy is related to the main-chain degradation. Previous analyses of isothermal thermooxidation, up to  $\alpha = 0.05$  in the range of 250–300 °C reported elsewhere,<sup>10</sup> gave activation

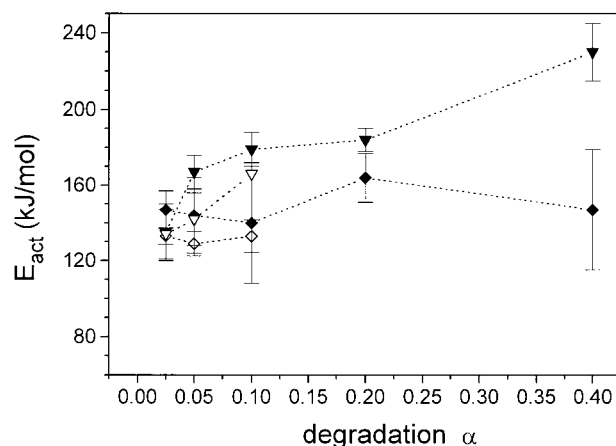


(a)

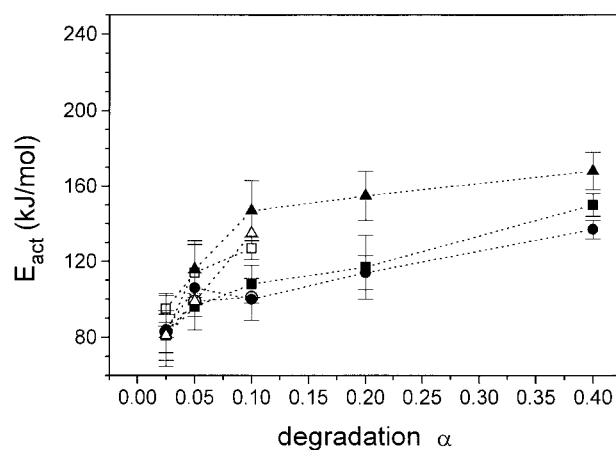


(b)

**Figure 4** (a) Dynamic thermogravimetric curves of wbPU-PTMG at heating rates of 0.5 (— · — · —), 1 (—), 2 (— · — · —), 5 (· · · · ·), and 10 °C/min (— —). (b) Arrhenius plot of wbPU-PTMG derived from dynamic curves at 0.025 (○), 0.05 (□), 0.10 (△), and 0.20 (◇) of degradation according to eq. (3).



(a)



(b)

**Figure 5** (a) Activation energies evaluated at various percentages of degradation for normal PURs, that is, PU-PBAc (▽ and ▼) and PU-PPG (◇ and ◆), after isothermal (empty symbols) and dynamic (full symbols) thermooxidation methods, respectively. (b) Activation energies evaluated at various percentages of degradation for waterborne PURs, that is, wbPU-PCL (△ and ▲), wbPU-PPG (□ and ■), and wbPU-PTMG (○ and ●), after isothermal (empty symbols) and dynamic (full symbols) thermooxidation methods, respectively.

energies of 196 kJ/mol for PU-PBAc and 145 kJ/mol for PU-PPG and are slightly higher than those evaluated in a range of lower temperatures 190–250 °C (142 and 129 kJ/mol, respectively). These results appeared to be dependent on various factors and are not surprising. For instance, similar and in some cases wider variations of the activation energy for thermal degradation of MDI and PTMO-based PURs with minima and maxima were reported by Fambri et al.<sup>10</sup> to range between 50 and 250 kJ/mol as a function of condition and the degradation degree.

### Pre-exponential Factors

The pre-exponential factors could provide information on the intrinsic thermal stability because they formally describe the behavior at infinite temperature. Isothermal ( $A_{\text{ISO}}$ ) and dynamic ( $A_{\text{DYN}}$ ) pre-exponential factors have an opposite meaning because of the inverse position of time in  $\log(\text{time}_\alpha)$  and  $\log(\beta)$ , the first member of eqs. (2) and (3), respectively. The higher the tendency to thermal oxidate at infinite temperature, the lower the isothermal pre-exponential factor and the higher the dynamic pre-exponential factor. As indicated in Table V, the isothermal pre-exponential factors tend to decrease with the degree of degradation, whereas the dynamic pre-exponential factor increases.

Moreover, both the pre-exponential factors evaluated in the isothermal and the dynamic methods predict that PU-PPG has a tendency to be more thermally stable than PU-PBAC and to have similarly normal PURs with respect to wbPURs. However, experimental data show that polyether-based polyurethanes are generally less stable than polyester-based polyurethanes. Hence, the activation energy is the more useful parameter for comparing the thermal stability of materials and the dominant factor with respect to the pre-exponential one.

### Data-Collection Times

The total experimental times required to collect the TGA data during the degradation kinetics analysis were compared by the two different methods. Table VI shows the times for isothermal and dynamic experiments at which degradations of 0.025, 0.05, and 0.10 occurred; from each series, the activation energies and the pre-exponential factors were calculated using eq. (2) or (3). The total times for isothermal experiments,  $t_{\text{iso}}$ , for each degree of degradation according to eq. (4) derive from the sum of the required times,  $t_i$  (at 190, 210, 230, and 250 °C) (see Table II)

$$t_{\text{iso}} = \sum_{i=190}^{250} t_i \quad (4)$$

On the other hand, the time required to collect dynamic data,  $t_{\text{dyn}}$ , for each degradation degree can be evaluated from the data reported in Table III, taking into consideration the temperature at which a certain degradation occurred,  $T_r$ , the

Table V Pre-Exponential Factors Calculated from the Arrhenius Plot with Isothermal and Dynamic Methods at Different Degrees of Degradation

$\alpha =$	Log $A_{\text{ISO}}$				Log $A_{\text{DYN}}$				
	0.025	0.05	0.10		0.025	0.05	0.10	0.20	0.40
PU-PBAC	-12.3 ± 1.4	-12.5 ± 1.4	-14.4		13.3 ± 1.5	16.1 ± 0.9	16.6 ± 0.8	16.4 ± 0.6	19.3 ± 1.2
PU-PPG	-12.4 ± 0.5	-11.8 ± 0.7	-11.9 ± 0.9		14.5 ± 2.9	14.5 ± 1.6	14.8 ± 2.3	13.0 ± 0.8	10.6 ± 1.8
wbPU-PCL	-7.9 ± 1.4	-9.2 ± 0.9	-12.4 ± 1.8		9.6 ± 1.2	12.6 ± 1.3	14.7 ± 1.6	14.6 ± 1.2	15.0 ± 0.9
wbPU-PPG	-8.9 ± 0.7	-10.6 ± 1.8	-11.4 ± 0.7		9.7 ± 1.5	10.5 ± 0.8	11.1 ± 1.6	11.5 ± 1.6	13.2 ± 0.4
wbPU-PTMG	-8.3 ± 2.1	-10.1 ± 0.7	-8.8 ± 1.1		8.3 ± 2.1	10.4 ± 0.9	10.0 ± 0.5	10.8 ± 0.9	12.3 ± 0.4



**Table VI Total Time Required to Collect Isothermal and Dynamic Data for the Evaluation of Thermooxidative Degradation of PURs and wbPURs at Various Degrees of Degradation**

Method	$\alpha$ Degradation	PU-PBAc (min)	PU-PPG (min)	wbPU-PCL (min)	wbPU-PPG (min)	wbPU-PTMG (min)
Isothermal	0.025	811	522	40	75	39
	0.05	>2000	964	146	373	136
	0.10	>3000	1642	844	1101	473
Dynamic from 30°C	0.025	793	764	549	522	533
	0.05	902	817	679	644	661
	0.10	985	869	825	767	798
Dynamic from 100°C	0.025	527	498	287	256	267
	0.05	636	551	416	378	395
	0.10	719	603	564	501	532

heating rate,  $r$  (°C/min), and the starting temperature,  $T_s$  (30 or 100 °C), according to

$$t_{\text{dyn}} \sum_{r=0.5}^{10} \frac{(T_r - T_s)}{r} \quad (5)$$

For instance, in the case of PU-PPG, the degradation of 0.025 at 0.5 °C/min has been reached at the temperature of 216 °C, corresponding to 388 min; taking into consideration the contributions of the various heating rates, the resulting total time was 764 min. Up to 0.05 of degradation, the isothermal method appeared less time-consuming than the dynamic method for PU-PPG and for all the waterborne PURs. On the contrary, in the case of the more thermally stable PU-PBAc, or for higher degrees of degradation, the dynamic method was less time-consuming. In particular, at the lowest temperature, 190 °C, for normal PURs, a degradation of 0.10 could not be achieved even after 1000 min; in this particular case, a more appropriate temperature interval should be set, for instance, 250–300 °C. The relative shorter time of isothermal experiments in the case of waterborne PURs that is about one order of magnitude lower than the correspondent dynamic time (normal PURs showed isothermal and dynamic times of the same order of magnitude), has to be attributed to some residual water that at high temperatures increases degradation in the isothermal mode. On the other hand, in the dynamic mode the residual water can be removed at a lower temperature, before degradation of the polymer.

## CONCLUSIONS

Thermogravimetric isothermal and dynamic methods were used to study the thermal stability

of normal and waterborne polyurethane materials. Each method showed advantages and disadvantages. The dynamic method is quite time-consuming especially for degradations up to 0.05, but it allows the examination of the highest percentage of weight loss until almost complete thermooxidation of the material. On the other hand, a preliminary test is required in the case of isothermal analysis, that is, a dynamic scan, for the evaluation of the most convenient range of temperature. For degradations higher than 0.05, the isothermal method generally requires more time than the dynamic method. Too high a temperature, for studying a low degree of degradation in the isothermal mode, requires low degradation times, and the errors can be quite high.

Dynamic and isothermal data were fit with an Arrhenius-type correlation, and, at any given degree of degradation, the activation energy calculated with the dynamic method is generally higher than that evaluated by the isothermal method and increases with the degree of degradation. Different degradation stages can be observed by using the derivative of the degree of degradation after dynamic experiments. According to both methods, the activation energy was the predominant factor with respect to the pre-exponential factor to assess the thermal stability. As expected, polyester-based PURs showed a higher thermal stability and higher activation energies than the polyether-based PURs. Also, waterborne polyurethanes showed lower thermal stability than normal polymers.

In conclusion, kinetics results can depend on the thermooxidation method, that is, isothermal or dynamic, and the corresponding conditions. Hence, it is recommended that the calculated degradation parameters (activation energy, pre-exponential factor) should always be associated with

the experimental conditions (range of temperature or heating rate, degree of degradation).

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