

## Thermo-oxidative stability of waterborne polyurethanes with catalysts of different selectivity evaluated by non-isothermal thermogravimetry

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*Abstract:* Thermogravimetry was used for the evaluation of the thermo-oxidative stability of waterborne polyurethanes (wbPUR) containing catalysts of different selectivity. From Arrhenius plots, activation energies of between 50 and 120 kJ mol<sup>-1</sup> for wbPUR were determined, depending on the temperature interval, selectivity of the catalyst and degree of degradation. Waterborne polyurethanes without catalyst showed lower thermal stability than waterborne polyurethanes with catalysts of different selectivity. Non-isothermal thermogravimetry indicated the presence of different degradation processes and enabled the kinetics parameters at higher degrees of degradation to be evaluated.

*Keywords:* waterborne polyurethanes, thermo-oxidation, thermogravimetry, thermal stability, activation energy.

### INTRODUCTION

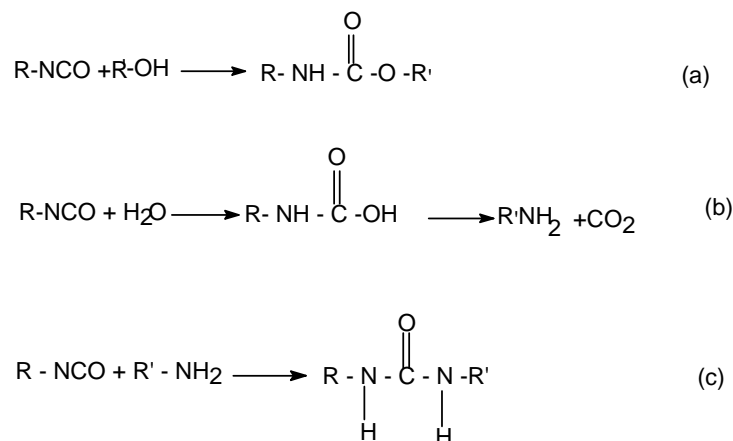
Two-pack paint systems are used in various segments of the industrial coatings market. The performance of these systems is, in general, surprisingly good. Gloss, appearance, chemical resistance and mechanical properties are on the level of solvent-borne products. However, the application window of these water-borne, two-pack polyurethanes is rather small and this impedes the breakthrough of this technology in some segments of the industrial coatings market. It is, for example, difficult to obtain a high layer thickness without surface defects with these two-pack systems.<sup>1</sup>

The main aspect in the development of waterborne polyurethanes is at first to find methods for preventing undesired secondary reactions with water and achieving the best crosslinking. One novel approach to control the water side reaction is the use of catalysts which selectively catalyze the isocyanate–polyol reaction and not the isocyanate–water reaction (Scheme 1). This reaction is reduced to a minimum by use of non-tin catalysts.<sup>2</sup>

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Scheme 1. Isocyanate reactions with alcohol (a) and with H<sub>2</sub>O (b,c).

The reactions of isocyanate, especially aliphatic isocyanate, with hydroxyl or water are relatively slow at ambient temperature in the absence of a catalyst. Organo-metallic compounds or tertiary amines are normally required to catalyze the crosslinking of isocyanate with hydroxyl groups for ambient cure applications.<sup>2,3</sup>

Blank<sup>3</sup> examined the selectivity of various compounds to model compounds. Butyl isocyanate and 2-ethyl-1-hexanol were selected as model compounds because of their similarities with aliphatic polyisocyanates and hydroxyl resins, as well as because of the simplicity of their FTIR spectra. The relative selectivity (*S*), which can be obtained from Eq. (1), was measured as the urethane IR peak area (*P*<sub>urethane</sub>)/urea IR peak area (*P*<sub>urea</sub>) ratio:

$$S = P_{\text{urethane}}/P_{\text{urea}} \quad (1)$$

After integration of the characteristic absorption maxima of urethane and urea, the relative selectivity was calculated.

Complexes of Mn(III)-diacetylacetonatomaleate with various ligands based on acetylacetonate and maleic acid showed high selectivity for the isocyanate-hydroxyl reaction.<sup>4,5</sup>

Several thermogravimetry methods have been used to study the thermal stability of polymeric materials both under oxidative and non-oxidative conditions. Kinetics parameters can be derived from isothermal and dynamic data, as reported by various researchers.<sup>6-12</sup>

The prediction of the lifetime service of polymeric materials under accelerated degradation conditions using thermogravimetry (TG) was reviewed by Flynn.<sup>13</sup> From the kinetics of degradation, the activation energy can be calculated from an Arrhenius correlation,<sup>8,10,11,13,14</sup> and this parameter can be useful for predicting the stability of a material. Also, the 5 % weight loss is a reasonable criterion for defining the lifetime of a material at service temperatures. Similarly, the acti-

vation energy can also be evaluated from dynamic experiments at different heating rates, whereby various percents 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 the apparent activation energies<sup>11,20</sup> because the reaction becomes too complex at higher percents of degradation 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>14</sup> as was confirmed by spectroscopic analysis. The thermal degradation of polyurethane materials has been examined by several researchers.<sup>15,17</sup> In particular, the composition of polyurethane, *i.e.*, the type of isocyanate/polyol and the chain extender or crosslinker, was found to directly influence the thermal stability<sup>11,12,18,19</sup> and, in some cases, degradation curves have been proposed as “fingerprints” to identify commercial polyurethanes.<sup>20</sup>

The objective of the present study was to evaluate the resistance to thermo-oxidation of different classes of waterborne polyurethanes (wbPUR) by thermogravimetry, using catalysts of different selectivity.

#### Kinetic Analysis

The thermoxidation experiments are generally described by the percentage of weight loss,  $W\%$ , and the degree of degradation,  $\alpha$ , defined as

$$W\% = 100(w_0 - w)/w_0 \quad (2a)$$

$$\alpha = (w_0 - w)/w_0 \quad (2b)$$

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

In the dynamic method,<sup>14</sup> several heating rates,  $\beta$ , are used which are related to the temperature at which a definite percent 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,  $E_{\text{act-DYN}}$  the activation energy and  $T_\alpha$  the absolute temperature at which the degree of degradation  $\alpha$  is attained. The value of  $A_{\text{DYN}}$  formally represents the heating rate  $\beta$  at which a certain percent of weight loss occurs at infinite temperature; the lower its value, the higher the stability of the material. The kinetics of the thermo-oxidation process depends on both activation energy and the pre-exponential factor.

#### EXPERIMENTAL

The polyols and polyisocyanates employed in this study were commercial materials which were used without further purification. The two polyol components with a hydroxyl number above 130 used in this study were: an acrylic dispersion in a water-butanol mixture, (Macrynal VSM 2521 w/42 WAB, Solutia Austria GmbH) and an acrylic resin as a water dispersion (Macrynal VSM 6299 w/42 WA, Solutia Austria GmbH). The content of dry matter in both these dispersions was 42 %.

As suitable hardeners for these dispersions, aliphatic polyfunctional isocyanates based on hexamethylene diisocyanates were employed, *i.e.*, Bayhydur VP LS 2319 (18.2 % NCO), Bayhydur VP

LS 2336 (16.2 % NCO), Bayhydur VP LS 2150 (13.4 % NCO) and Desmodur 3600 (23 % NCO), purchased from Bayer AG Germany. All the applied hardeners were without an organic solvent (100 %), except Bayhydur VP LS 2150 (70 %).

The Zirconium catalyst (ZrCAT) was a proprietary zirconium tetra-dionato complex 21 in a reactive diluent with a metal content of 0.4 %.

The manganese catalyst, the complex Mn(III)-diacetylacetonatomaleate, has shown unusually high selectivity for the isocyanate–polyol reaction in comparison with commercially available zirconium catalyst 4.5. The manganese catalyst (MnCAT) was in a reactive diluent with a metal content of 0.4 %.

Catalyst concentrations of 2 % and 4 %, relating to the coating hardener, were added to component B.

The Tables I and II show the composition of the employed components.

TABLE I. Composition of the two-component waterborne polyurethane (wbPUR1) based on the polyol Macrynal VSM 6299 w/42 WA (coating hardness 32.5 %)

Component A / weight %	Control	ZrCAT	MnCAT
Polyol VSM 6299	44.1	44.1	44.1
Water	41.2	41.2	41.2
Component B / wt. %			
Bayhydur VP LS 2319	5.88	5.88	5.88
Dezmodur N 3600	5.88	5.88	5.88
Methoxypropyl acetate	2.94	2.94	2.94
Zr Catalyst, 2 % (4%) on resin solids	No catalyst	0.65 (1.30)	–
Mn Catalyst, 2 % (4%) on resin solids	No catalyst	–	0.65 (1.30)
Total	100.00	100.6	100.6

TABLE II. Composition of the two-component waterborne polyurethane (wbPUR2) based on the polyol Macrynal VSM 2521 w/42 WAB (coating hardness 40.2 %)

Component A / weight %	Control	ZrCAT	MnCAT
Polyol VSM 2521	56.2	56.2	56.2
Water	22.6	22.6	22.6
Component B / weight %			
Bayhydur VP LS 2336	9.8	9.8	9.8
Bayhydur VP LS 2150 BA	9.8	9.8	9.8
Methoxypropyl acetate	1.1	1.1	1.1
Zr Catalyst, 2 % (4%) on resin solids	No catalyst	0.8 (1.60)	–
Mn Catalyst, 2 % (4%) on resin solids	No catalyst	–	0.8 (1.60)
Total	99.5	100.3	100.3

The waterborne polyurethanes were finally stored at room temperature and used without any drying treatment. The films were, however, dried for 4 – 8 h.

The thermograms were recorded on a Perkin–Elmer DSC 4 instrument. The samples were prepared using aluminum pans with cover gap for the passage of gas. The sample weight was 360 mg. In the case of the dynamic method, heating rates of 0.5, 1, 2, 5, and 10 °C min<sup>-1</sup> were employed in the range of 30 – 500 °C, and degradations up to 0.025, 0.05, and 0.10 were investigated. The instrument had an autocalibration and linear regulation of the chosen temperature gradient.

## RESULTS AND DISCUSSION

Tables III and IV summarize the experimental data of the thermo-oxidation of the different waterborne polyurethanes measured by dynamic methods.

TABLE III. Temperatures at which degradations of 0.025, 0.05 and 0.10 occurred during dynamic heating at different heating rates

$\beta$ Heating Rate $^{\circ}\text{C min}^{-1}$	$\alpha$ Degradation	wbPUR1- Control $^{\circ}\text{C}$	wbPUR1- ZrCAT 2 %, $^{\circ}\text{C}$	wbPUR1- MnCAT 2 %, $^{\circ}\text{C}$	wbPUR1- ZrCAT 4 %, $^{\circ}\text{C}$	wbPUR1- MnCAT 4 %, $^{\circ}\text{C}$
0.5	0.025	127	139	153	150	164
	0.05	163	173	188	185	200
	0.10	181	190	205	202	217
1	0.025	131	144	157	155	168
	0.05	175	186	199	198	211
	0.10	181	192	205	204	217
2	0.025	143	154	169	166	180
	0.05	178	188	203	199	214
	0.10	192	201	216	213	228
5	0.025	174	184	199	195	210
	0.05	221	228	245	240	257
	0.10	248	254	271	266	283
10	0.025	181	191	205	202	217
	0.05	265	271	287	283	300
	0.10	277	282	299	294	312

TABLE IV. Temperatures at which degradations of 0.025, 0.05 and 0.10 occurred during dynamic heating at different heating rates

$\beta$ Heating Rate $^{\circ}\text{C min}^{-1}$	$\alpha$ Degradation	wbPUR1- Control $^{\circ}\text{C}$	wbPUR2- ZrCAT 2 %, $^{\circ}\text{C}$	wbPUR2- MnCAT 2 %, $^{\circ}\text{C}$	wbPUR2- ZrCAT 4 %, $^{\circ}\text{C}$	wbPUR2- MnCAT 4 %, $^{\circ}\text{C}$
0.5	0.025	141	153	176	164	178
	0.05	178	188	203	199	214
	0.10	190	199	214	211	226
1	0.025	150	161	179	173	190
	0.05	181	190	210	202	222
	0.10	203	211	232	223	244
2	0.025	165	176	190	187	201
	0.05	215	223	239	235	251
	0.10	220	228	244	240	256

TABLE IV. Continued

$\beta$ Heating Rate $^{\circ}\text{C min}^{-1}$	$\alpha$ Degradation	wbPUR1– Control $^{\circ}\text{C}$	wbPUR2– ZrCAT 2 %, $^{\circ}\text{C}$	wbPUR2– MnCAT 2 %, $^{\circ}\text{C}$	wbPUR2– ZrCAT 4 %, $^{\circ}\text{C}$	wbPUR2– MnCAT 4 %, $^{\circ}\text{C}$
5	0.025	169	180	193	191	204
	0.05	224	232	246	244	258
	0.10	251	258	272	270	285
10	0.025	192	199	215	211	227
	0.05	273	276	294	288	307
	0.10	290	292	311	304	323

From the dynamic degradation, the lower thermal stability the two-pack the waterborne polyurethanes without catalyst is immediately evident as a fixed degree of degradation is attained at a considerable lower temperature than waterborne polyurethanes with a catalyst.

During dynamic thermo-oxidation, it was also possible to detect the presence of different stages of degradation as illustrated in Figs. 1 and 2, which show the TG curves of wbPUR1 and wbPUR2, respectively. The change in the slope in the interval 100 – 300  $^{\circ}\text{C}$  is due to a change in mechanism and confirms the different activation energy measured at degrees of degradation of 0.025, 0.05, and 0.10. Below 100  $^{\circ}\text{C}$ , a weight loss of about 1 % was observed resulting from the evaporation of equilibrium moisture or other volatile products.

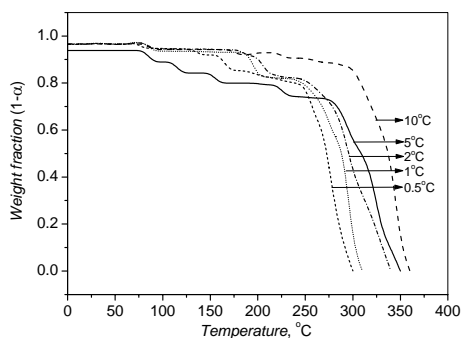


Fig. 1. Weight fraction ( $1-\alpha$ ) of wbPUR1 with MnCAT (2 %) versus temperature during dynamic thermo-oxidation at different heating rates.

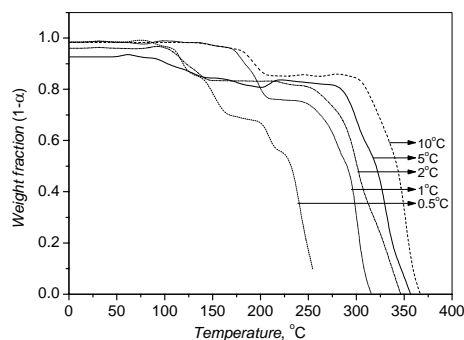


Fig. 2. Weight fraction ( $1-\alpha$ ) of wbPUR2 with MnCAT (2 %) versus temperature during dynamic thermo-oxidation at different heating rates.

From the derivative curve of the degree of degradation,  $d\alpha/dT$ , a single degradation process can readily distinguished, as shown in Figs. 3 and 4 in the case of samples heated at 10  $^{\circ}\text{C min}^{-1}$ . This curve represents the rate of degradation of the material under the particular experimental conditions. The main data are summarized in Tables V and VI.

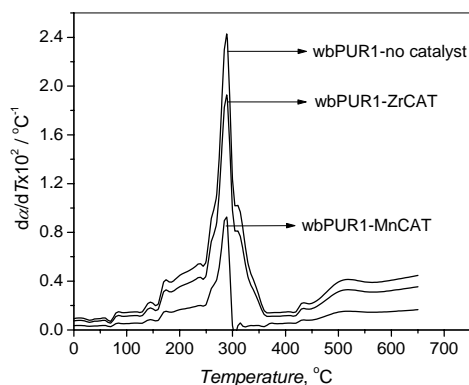


Fig. 3. Rate of mass loss of wbPUR1 with different catalysts *versus* temperature, obtained at a heating rate of 10 °C min<sup>-1</sup>.

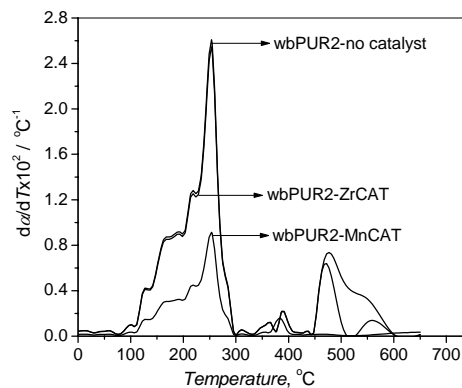


Fig. 4. Rate of mass loss of wbPUR2 with different catalysts *versus* temperature, obtained at a heating rate of 10 °C min<sup>-1</sup>.

TABLE V. Data evaluated from the DTG curves of wbPUR1 obtained at a heating rate of 10 °C min<sup>-1</sup>

	Low-temperature peak			Main Peak		High-temperature peak	
	$t_{\text{onset}}/^{\circ}\text{C}$	$t/^{\circ}\text{C}$	$\frac{d\alpha}{dt} \times 100/^{\circ}\text{C}^{-1}$	$t/^{\circ}\text{C}$	$\frac{d\alpha}{dt} \times 100/^{\circ}\text{C}^{-1}$	$t/^{\circ}\text{C}$	$\frac{d\alpha}{dt} \times 100/^{\circ}\text{C}^{-1}$
wbPUR1–Control	140.0	171.6	0.40	287.6	2.43	430.9	0.22
wbPUR1–MnCAT	144.2	172.7	0.14	288.6	0.92	433.3	0.08
wbPUR1–ZrCAT	144.4	171.6	0.33	288.6	1.92	432.3	0.17

TABLE VI. Data evaluated from the DTG curves of wbPUR2 obtained at a heating rate of 10 °C min<sup>-1</sup>

	Low-temperature peak			Main peak		High-temperature peak	
	$t_{\text{onset}}/^{\circ}\text{C}$	$t/^{\circ}\text{C}$	$\frac{d\alpha}{dt} \times 100/^{\circ}\text{C}^{-1}$	$t/^{\circ}\text{C}$	$\frac{d\alpha}{dt} \times 100/^{\circ}\text{C}^{-1}$	$t/^{\circ}\text{C}$	$\frac{d\alpha}{dt} \times 100/^{\circ}\text{C}^{-1}$
wbPUR2–Control	150.1	201.0	0.91	253.2	2.60	389.5	0.22
wbPUR2–MnCAT	160.5	198.6	0.31	253.2	0.90	383.5	0.14
wbPUR2–ZrCAT	150.5	198.6	0.88	253.2	2.54	389.5	0.21

The onset temperature, evaluated from the initial part of the derivative curve, revealed that wbPUR1 without catalyst and those with catalysts which also started to degrade at a similar temperature (140 °C) were less stable with respect to wbPUR1 with the selective catalyst (144 °C). In particular, waterborne PUR1 without catalyst and with catalysts showed the same position of the main peak at

288 °C. According to the maximum of the peak, the waterborne polyurethane (wbPUR1) with the MnCAT (4 %) catalyst had the lowest rate of decomposition  $d\alpha/dT$ , ( $0.92 \times 10^2 \text{ °C}^{-1}$ ), whereas waterborne polyurethane (wbPUR1) with ZrCAT (4 %) catalyst exhibited the highest degradation rate ( $1.92 \times 10^2 \text{ °C}^{-1}$ ), and the waterborne polyurethane (wbPUR1) without catalyst exhibited a value of about  $2.43 \times 10^2 \text{ °C}^{-1}$ . The sample wbPUR2 showed the same decreasing trend of degradation rate with the MnCAT (Fig. 4).

The presence of more than one peak in the  $d\alpha/dt$  curve attests to the various steps of degradation. For example, in the case of the oxidative degradation of a waterborne polyurethane with similar polyester–polyol components, the dynamic method proposed by Fambri *et al.*<sup>14</sup> gave three peaks.

In this case, the secondary peak at low temperatures, exhibited in the range of 170 °C for the waterborne PUR1 only, is attributable to the degradation of lateral groups. On the other hand, the main peak is related to the thermo-oxidation of the main polymer backbone, whereas the secondary peak at high temperature corresponds to the degradation of the final 20 % of the residual material (degree of degradation from 0.8 to 1). Using dynamic methods, the degradation kinetics can be studied at very high percent of weight losses, very close to complete thermo-oxidation. 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  $10 \text{ °C min}^{-1}$ , depending on the stability of the material.

The procedure for the evaluation of the kinetics from the experimental data from dynamic experiments is exemplified in Figs. 1 and 2 for the waterborne polyurethanes wbPUR1 and wbPUR2, respectively. From this analysis, the temperatures were achieved at degradations of 0.025, 0.05, and 0.10. The correspondent Arrhenius plots were determined from Eq. (3) and are given in Figs. 5a and b, respectively.

#### *Activation energy*

The activation energies and their standard deviations were calculated from the slope of the best-fitting linear regression according to Eq. (3). Values in the range of 53 – 120  $\text{kJ mol}^{-1}$  were found for both samples, as a function of the material, the degree and of the degradation.

In particular, in the initial stage of thermo-oxidation, the activation energy ranged between 53 and 86  $\text{kJ mol}^{-1}$  for wbPUR1 and between 64 and 120  $\text{kJ mol}^{-1}$  for wbPUR2, as shown in Figs. 6a and b. Both samples showed the tendency of increased activation energy for all degree of degradation on addition of the more selective catalyst. Then the values of the activation energy of 53 – 62  $\text{kJ mol}^{-1}$  and 64 – 78  $\text{kJ mol}^{-1}$  for wbPUR1 and wbPUR2, respectively, at  $\alpha = 0.10$  were found.



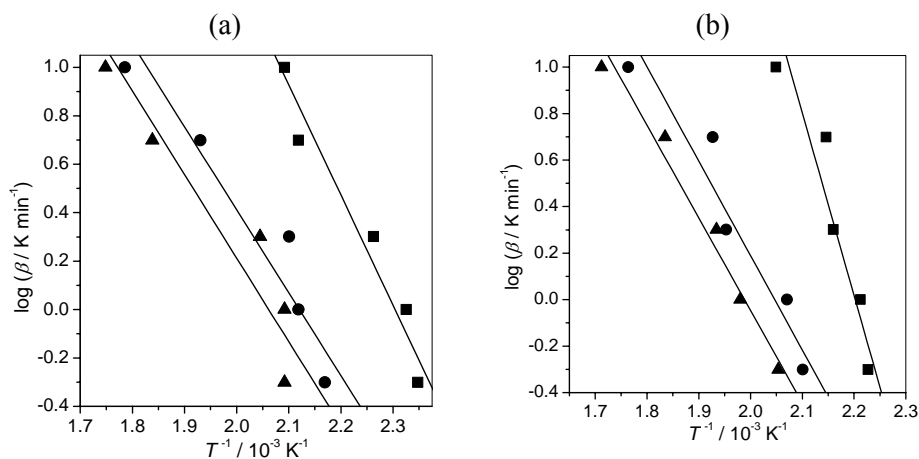


Fig. 5. (a) Arrhenius plot of wbPUR1 with catalyst MnCAT (2 %) derived from dynamic curves at 0.025 (■), 0.05 (●), and 0.10 (▲) of degradation according to Eq. (3). (b) Arrhenius plot of wbPUR2 with catalyst MnCAT (2 %) derived from dynamic curves at 0.025 (■), 0.05 (●), and 0.10 (▲) of degradation according to Eq. (3).

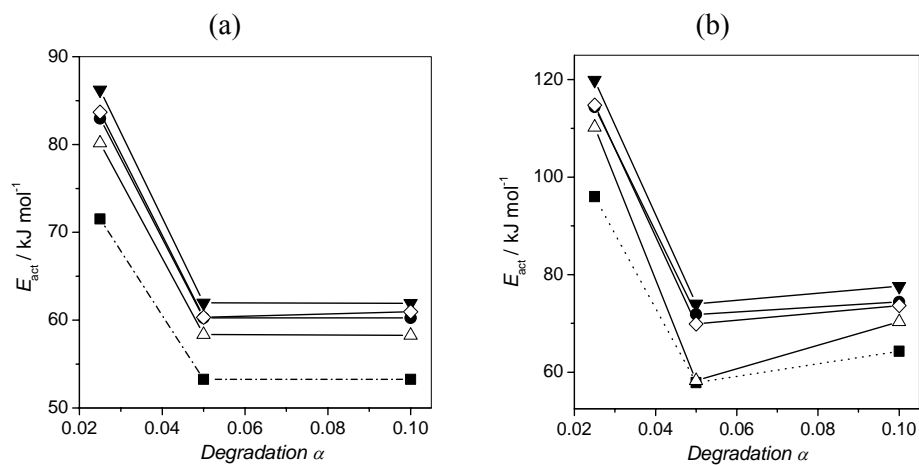


Fig. 6. (a) Activation energies evaluated at various percents of degradation of wbPUR1, without catalyst (■), wbPUR1 with catalyst ZrCAT (2 %) (Δ), wbPUR1 with catalyst ZrCAT (4 %) (◇), wbPUR1 with catalyst MnCAT (2 %) (●), wbPUR1 with catalyst MnCAT (4 %) (▼). (b) Activation energies evaluated at various percents of degradation of wbPUR2, without catalyst (■), wbPUR2 with catalyst ZrCAT (2 %) (Δ), wbPUR2 with catalyst ZrCAT (4 %) (◇), wbPUR2 with catalyst MnCAT (2 %) (●), wbPUR2 with catalyst MnCAT (4 %) (▼).

### Pre-exponential factors

The pre-exponential factors could provide information on intrinsic thermal stability because they formally describe the behavior at infinite temperature. The

higher is the tendency to thermal oxidize at infinite temperature, the higher is the dynamic pre-exponential factor. As indicated in Table VII, the dynamic pre-exponential factors tend to decrease with increasing degree of degradation.

TABLE VII. Pre-exponential factors calculated from the Arrhenius plot obtained from dynamic thermogravimetry for different degrees of degradation

	$\log A_{\text{DYN}}$			
	$\alpha$	0.025	0.05	0.10
wbPUR1–Control	9.16	6.24	6.06	
wbPUR1–MnCAT (2 %)	9.98	6.69	6.69	
wbPUR1–ZrCAT (2 %)	9.96	6.68	6.49	
wbPUR1–MnCAT (4 %)	10.13	6.72	6.53	
wbPUR1–ZrCAT (4 %)	10.14	6.75	6.62	
wbPUR2–Control	11.84	6.59	7.03	
wbPUR2–MnCAT (2 %)	13.29	7.70	7.73	
wbPUR2–ZrCAT (2 %)	13.24	6.48	7.56	
wbPUR2–MnCAT (4 %)	13.59	7.75	7.87	
wbPUR2–ZrCAT (4 %)	13.44	7.57	7.73	

Moreover, the pre-exponential factors evaluated by dynamic methods predict that wbPUR1 has a greater thermal stability than wbPUR2.

Hence, the activation energy is a more useful parameter for comparing the thermal stability of materials and is the dominant factor with respect to the pre-exponential factor.

Also results of the K $\ddot{o}$ nnig hardness<sup>5</sup> and of the activation energy show that the wbPUR2 sample was more stable than wbPUR1.

The more selective catalyst favors the reaction between isocyanate and the polyol component. This increased the percent of urethanic bonds and degree of hardness in the films formed from two-component, waterborne polyurethane lacquers. The polyol Macrynal VSM 2521, based on the single step synthesis route, is superior in pot-life and hardness relating to the polyol Macrynal VSM 6299 based on multistep synthesis route.<sup>22</sup>

The obtained results show that the performances of the two component waterborne polyurethane coatings depend on the polymer structure of the polyols as well as of the selectivity of the employed catalyst.<sup>23,24</sup>

The addition of the selective catalyst and favoring the isocyanate–polyol reaction contribute to obtaining the greater hardness of the formed films, also showed higher thermo-oxidative stability.

#### *Data – collection times*

The total experimental times required to collect the TG data during the kinetics analysis of the degradation were compared by the dynamic method.

Tables VIII and IX show the times during the dynamic experiments at which degradations of 0.025, 0.05, and 0.10 had occurred; from each series, the activation energies and the pre-exponential factors were calculated using Eq. (3).

TABLE VIII. Total time required to attain various degrees of degradation during the dynamic thermo-oxidation of wbPUR1

Method	$\alpha$ Degradation	wbPUR1– Control/min	wbPUR1– ZrCAT 2 %/min	wbPUR1– MnCAT 2 %/min	wbPUR1– ZrCAT 4 %/min	wbPUR1– MnCAT 4 %/min
Dynamic from 30 °C	0.025	395.4	440.9	493.8	483.2	535.7
	0.05	546.7	584.7	640.2	629.8	685.4
	0.10	602.3	637.5	693.1	683.1	738.8
Dynamic from 100 °C	0.025	129.4	174.9	227.8	217.2	269.7
	0.05	280.7	318.7	374.2	363.8	419.4
	0.10	336.3	371.5	427.1	417.1	472.8

The total times for dynamic experiments,  $\tau_{dyn}$ , for each degradation degree can be evaluated from the data reported in Tables III and IV, taking into consideration the temperature at which a certain degradation occurred,  $t_r$ , the heating rate,  $r$  ( $^{\circ}\text{C min}^{-1}$ ), and the starting temperature,  $t_s$  (30 or 100  $^{\circ}\text{C}$ ), according to

$$\tau_{dyn} = \sum_{r=0.5}^{10} \frac{(t_r - t_s)}{r} \quad (4)$$

TABLE IX. Total time required to attain various degrees of degradation during the dynamic thermo-oxidation of wbPUR2

Method	$\alpha$ Degradation	wbPUR1– Control/min	wbPUR2– ZrCAT 2 %/min	wbPUR2– MnCAT 2 %/min	wbPUR2– ZrCAT 4 %/min	wbPUR2– MnCAT 4 %/min
Dynamic from 30 °C	0.025	453.5	496.9	572.1	539.8	596.0
	0.05	602.6	637.5	700.1	681.1	743.8
	0.10	658.2	689.8	753.5	735.4	799.3
Dynamic from 100 °C	0.025	187.5	230.9	306.1	273.8	330.0
	0.05	336.6	371.5	434.1	415.1	477.8
	0.10	392.2	423.8	487.5	469.4	533.3

For example, in the case of wbPUR1 – control (without catalyst), a degradation of 0.025 at 0.5  $^{\circ}\text{C min}^{-1}$  was reached at a temperature of 140  $^{\circ}\text{C}$ , taking into consideration the contributions of the various heating rates, the resulting total time was 395.4 min.

When MnCAT (2 % and 4 %) as more selective catalyst was used, the resulting total time was longer for all degrees of degradation.

Also, in case of the sample wbPUR2, a similar increase of the resulting total time was observed. This fact shows that the wbPUR1 sample was thermally less stable than the sample wbPUR2.

#### CONCLUSIONS

Dynamic thermogravimetry was used to study the thermal stability of waterborne polyurethane materials. 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 thermo-oxidation of the material. Different degradation stages could be observed using the derivative of the degree of degradation after dynamic experiments. According to the dynamic method, the activation energy was more useful to assess the thermal stability than the pre-exponential factor.

The waterborne polyurethanes (wbPUR2) based on polyol Macrynal 2521 component with the more selective catalyst (MnCAT) showed higher thermal stability and higher activation energies than the waterborne polyurethane (wbPUR1) based on polyol Macrynal 6299 component also with the more selective catalyst (MnCAT).

#### ИЗВОД

#### ТЕРМООКСИДАТИВНА СТАБИЛНОСТ ВОДЕНИХ ПОЛИУРЕТАНА ИЗРАЧУНАТА ПОМОЋУ ДИНАМИЧКЕ МЕТОДЕ КОРИШЋЕЊЕМ КАТАЛИЗАТОРА РАЗЛИЧИТЕ СЕЛЕКТИВНОСТИ

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За израчунавање отпорности према термооксидацији водених полиуретана коришћена је термогравиметријска анализа. Водени полиуретани (wbPUR) са катализаторима различите селективности били су окарактерисани методом динамичког загревања. У динамичкој методи, биле су коришћене брзине загревања од 0,5; 1; 2; 5; и 10 °C min<sup>-1</sup> у опсегу од 30 – 500 °C при чему су разматране деградације од 0,025; 0,05; и 0,10. Из Аренијусових графика, израчунате активационе енергије за водене полиуретане кретале су се између 50 и 120 kJ mol<sup>-1</sup> зависно од температурног интервала, селективности катализатора и степена деградације. Водени полиуретани без катализатора су показали нижу термичку стабилност од водених полиуретана са катализаторима различите селективности. Приказана динамичка метода указује на присуство различитих деградационих процеса, и она је погодна за израчунавање кинетичких параметара код високих степена деградације.

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