Full Paper

Thermal Stability of Aqueous Polyurethanes Depending on the Applied Catalysts

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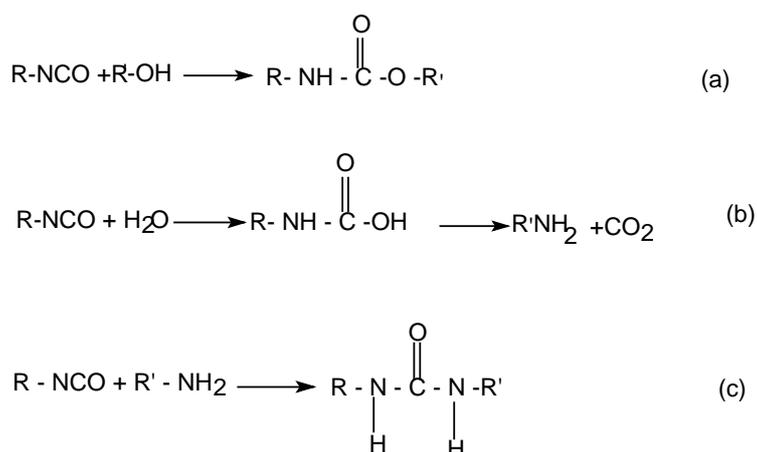ukilaki@eunet.yu

Abstract: The thermal stability of aqueous polyurethanes has been measured applying the thermogravimetric analysis. The aqueous polyurethanes (aqPUR) with catalysts of different selectivity have been studied by use of the dynamic method. To obtain degradations of 0.025, 0.05, and 0.10, employing the dynamic method, the heating rates of 0.5, 1, 2, 5, and 10 °C min^{-1} have been used in the range of 30-500 ºC. Using the more selective catalysts in the aqueous polyurethanes, the total resulting time of the decompositon has been on the increase at all degrees of the degradation and at the particular starting temperature. This paper shows that the dynamic method based on the thermogravimetric analysis can be used to assess the thermal stability of the aqueous polyurethanes using the catalysts of different selectivity.

Keywords: aqueous polyurethanes, catalysts, thermal degradation, thermogravimetric analysis.

Introduction

Two-component paint systems are used in various segments of the industrial coatings market. The performances of these systems are, in general, surprisingly good. The gloss, looks, chemical resistance and mechanical properties have the standard of solvent based products. However, the application of these aqueous two-component polyurethanes is rather less intense and it prevents the breakthrough of this technology into the market of the industrial coatings. It is, for instance, difficult to obtain greater layer thickness without surface defects using these two-component systems [1]. Likewise, the procedure itself of obtaining the polyols is rather essential and is reflected on characteristics of the obtained film [2,3].

The main objective in the development of the aqueous polyurethanes is, in the first place, to find methods for preventing the undesired secondary reactions with water and achieving the best crosslinking. This reaction is reduced to a minimum by use of the non-tin catalysts [4]. One novel approach to control the water side reaction is the use of catalysts that selectively catalyze the isocyanate-polyol reaction but not the isocyanate-water reaction as shown in the following reactions (Sheme 1).

$$R\text{-}NCO + R\text{-}OH \longrightarrow R\text{-}NH\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}O\text{-}R' \qquad (a)$$

$$R\text{-}NCO + H_2O \longrightarrow R\text{-}NH\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OH \longrightarrow R'NH_2 + CO_2 \qquad (b)$$

$$R\text{-}NCO + R'\text{-}NH_2 \longrightarrow R\text{-}\underset{\underset{H}{|}}{N}\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}\underset{\underset{H}{|}}{N}\text{-}R' \qquad (c)$$

Sheme 1. Isocyanate reactions with alcohol (a) and with water (b,c).

The reactions of isocyanates, especially the aliphatic isocyanates, with the hydroxyl group or water are relatively slow at the ambient temperature in the absence of a catalyst. Organo metallic compounds or tertiary amines are normally needed to catalyze the crosslinking of the isocyanates with the hydroxyl groups in the ambient conditions [4,5].

In the researches of Werner Blank [4,5], the selectivity of various compounds compared to model compounds has been examined. Butyl isocyanate and 2-ethyl-1-hexanol have been selected as model compounds due to their similarity to the aliphatic polyisocyanates and the hydroxyl resins as well as because of the simplicity of their FTIR spectra.

The relative selectivity (S), can be obtained by the method of Werner Blank [5], from the Equation 1, by measuring the ratio of the urethane IR peak area ($P_{urethan}$) and the urea IR peak area (P_{urea}):

$$S = \frac{P_{urethan}}{P_{urea}} \qquad (1)$$

Upon the integration of the characteristic absorption maximums of the urethane and the urea, the relative selectivity has been calculated.

The complex of Mn(III)-diacetylacetonatomaleate with various ligands based on the acetylacetonate and the maleic acid, used in some of the experiments [6,7], has showed a high selectivity for the isocyanate-hydroxyl reaction (Figure1).

Different thermogravimetric methods can be used to study the thermal stability of polymeric materials both in oxidative and nonoxidative conditions. The evaluation of the kinetic parameters can be derived from the isothermal and dynamic data, as reported by various researchers [8-18].

The thermal stability of the aqueous polyurethanes measured by using the dynamic method of the thermogravimetric analysis has been studied by Fambi and Pegoretti [19]. They have studied the thermal stability of polyurethanes based on a solvent and on an aqueous base in the process of which the polyester and the polyether components without the catalysts have been used as polyol components.
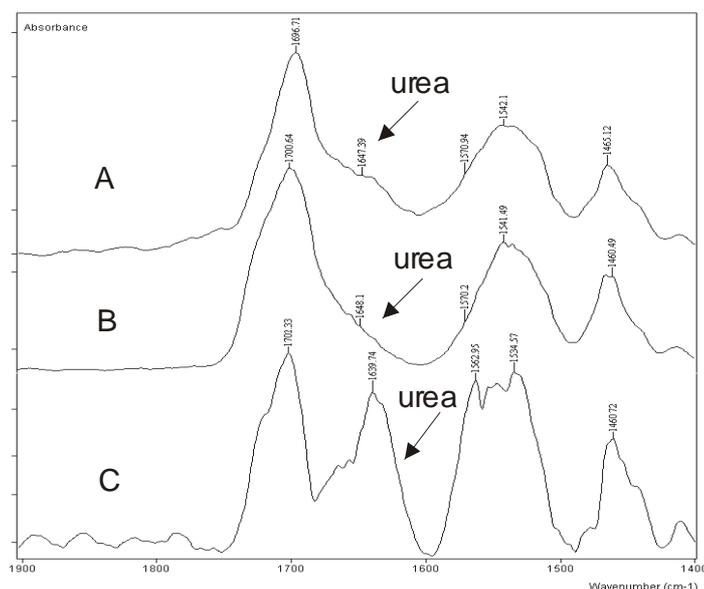

Figure 1. The comparative FTIR spectrum of the catalyzed model system NCO/OH/H_2O =1.0/1.0/2.0 with: A)- the catalyst of zirconium K-KAT$^{®}$XC-6212 (King industries, Norwalk-USA);
    B)- the complex of Mn(III)-diacetylacetonatomaleate; C)- Co-octoat.

The objective of the this paper is to evaluate the thermal stability of the aqueous polyurethanes (aqPUR) by means of the dynamic method based on the TGA, applying employing the polyol components based on different acrylic copolymers and the catalysts of different selectivity.

The thermoxidation experiments are generally determined by the percentage of weight loss, $W_\%$, and the degree of degradation, α, defined as:

$$W_\% = 100 \times (w_o - w)/\, w \qquad (2a)$$

$$\alpha = (w_o - w)/\, w_o \qquad (2b)$$

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

Several heating rates, β, have been used in the dynamic method [20,21] to obtain the temperature at which the defined percentage of weight loss occurs, according to the following equation:

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

where A_{DYN} is the pre-exponential factor, $E_{act\text{-}DYN}$ is the activation energy and T_α is the absolute temperature at which the degree of degradation, α, is reached.

Experimental

The polyols and polyisocyanates, being the commercial materials, have been used during the study without further purification. The two polyol components, with the hydroxyl number above 130, have been employed in this experiment and they are: the acrylic dispersion in the mixture water/butyl alcohol (Macrynal VSM 2521 w/42 WAB, Solutia Austria GmbH) and also the acrylic resin as the water dispersion (Macrynal VSM 6299 w/42 WA, Solutia Austria GmbH). Macrynal VSM 6299 is a pure acrylic copolymer and Macrynal VSM 2521 is the acrylic copolymer modified by fatty acids. The content of dry matter has been 42% in these dispersions.

Being suitable hardeners for these dispersions, the aliphatic polyfunctional isocyanates based on hexamethylen diisocyanates have been employed and they are as follows: Bayhydur VP LS 2319 (18.2% NCO), Bayhydur VP LS 2336 (16.2% NCO), Bayhydur VP LS 2150 (13.4% NCO) as well as Desmodur 3600 (23% NCO), purchased from Bayer AG Germany. All the applied hardeners have been without the organic solvents (100%), except for Bayhydur VP LS 2150 (70%).

The zirconium catalyst (ZrCAT) is a proprietary zirconium tetra-dionato complex [22] in the reactive solvent with a metal content of 0.4%.

The manganese catalyst, the complex of Mn(III)-diacetylacetonatomaleate, has shown the unusually high selectivity for the isocyanate-polyol reaction in comparison with the commercially available zirconium catalyst [8,9]. The manganese catalyst (MnCAT) has been used in the reactive diluent with the metal content of 0.4%.

The catalyst, concentrated 2% and 4% relating to the coating hardness, has been added to the B component . The Table 1 and Table 2 show the composition of the employed components.

Table 1. The composition of the two-component aqueous polyurethane sample (aqPUR1) based on the polyol component 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, weight %			
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, relative to 2 % (4%) resin solids	no catalyst	0.65 (1.30)	-
Mn catalyst, relative to 2 % (4%) resin solids	no catalyst	-	0.65 (1.30)
Total components mass	100.00	100.6	100.6

Table 2. The composition of the two-component aqueous polyurethane (aqPUR2) sample based on the polyol component 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, relative to 2 % (4%) resin solids	no catalyst	0.8 (1.60)	-
Mn catalyst, relative to 2 % (4%) resin solids	no catalyst	-	0.8 (1.60)
Total	99.5	100.3	100.3

The thermograms have been recorded on the instrument DSC 4 from Perkin-Elmer. The samples have been prepared with the organic solvents and water, and therefore the laced up aluminium ampoules with a lid gap for gases release have been used, the sample weight being 360 mg.

In order to examine the the degradations of 0.025, 0.05 and 0.10, the heating rates of 0.5, 1, 2, 5 and 10 ℃ min^{-1}, ranged 30-500 ℃, have been employed during the dynamic method.

The instrument has the autocalibration and the linear regulation of a settled temperature gradient.

Results and Discussion

Table 3 and Table 4 sum up the experimental data of the thermal analysis of the different aqueous polyurethanes without the catalysts and with the catalysts of different selectivity measured by the dynamic method.

Table 3. The obtained temperatures of the sample aqPUR1, with the different concentrations of the catalysts, at the degradations of 0.025, 0.05 and 0.10 in the function of the different heating rates.

β Heating rate, (ºC min^{-1})	α Degradation	aqPUR1-control (ºC)	aqPUR1-ZrCAT 2%(ºC)	aqPUR1-MnCAT 2% (ºC)	aqPUR1-ZrCAT 4% (ºC)	aqPUR1-MnCAT 4% (ºC)
	0.025	127	139	153	150	164
0.5	0.050	163	173	188	185	200
	0.100	181	190	205	202	217
	0.025	131	144	157	155	168
1	0.050	175	186	199	198	211
	0.100	181	192	205	204	217
	0.025	143	154	169	166	180
2	0.050	178	188	203	199	214
	0.100	192	201	216	213	228
	0.025	174	184	199	195	210
5	0.050	221	228	245	240	257
	0.100	248	254	271	266	283
	0.025	181	191	205	202	217
10	0.050	265	271	287	283	300
	0.100	277	282	299	294	312

Table 4. The obtained temperatures of the sample aqPUR2, with the different concentrations of the catalysts, at the degradations of 0.025; 0.05 and 0.10 in the function of the different heating rates.

β Heating rate, (ºC min^{-1})	α Degradation	aqPUR2-control (ºC)	aqPUR2-ZrCAT 2%(ºC)	aqPUR2-MnCAT 2% (ºC)	aqPUR2-ZrCAT 4% (ºC)	aqPUR2-MnCAT 4% (ºC)
	0.025	141	153	176	164	178
0.5	0.050	178	188	203	199	214
	0.100	190	199	214	211	226
	0.025	150	161	179	173	190
1	0.050	181	190	210	202	222
	0.100	203	211	232	223	244
	0.025	165	176	190	187	201
2	0.050	215	223	239	235	251
	0.100	220	228	244	240	256
	0.025	169	180	193	191	204
5	0.050	224	232	246	244	258
	0.100	251	258	272	270	285
	0.025	192	199	215	211	227
10	0.050	273	276	294	288	307
	0.100	290	292	311	304	323

The lower thermal stability in aqueous polyurethanes without the catalyst is immediately obvious from the dynamic degradation, requiring a lower temperature to reach the determined degree of degradation.

During the dynamic thermooxidation, it is also possible to detect the presence of different degradation stages as shown in the case of aqPUR1 and aqPUR2 in Figure 2 and Figure 3, respectively. The change of the slope in the interval 100-300 °C is due to a change in the mechanism and contributes to the different activation energy measured at the degradations of 0.025, 0.05 and 0.10. The weight loss of about 1%, observed below the temperature of 100 °C, is the result of the evaporation of the equilibrium moisture and/or other volatile products [23].
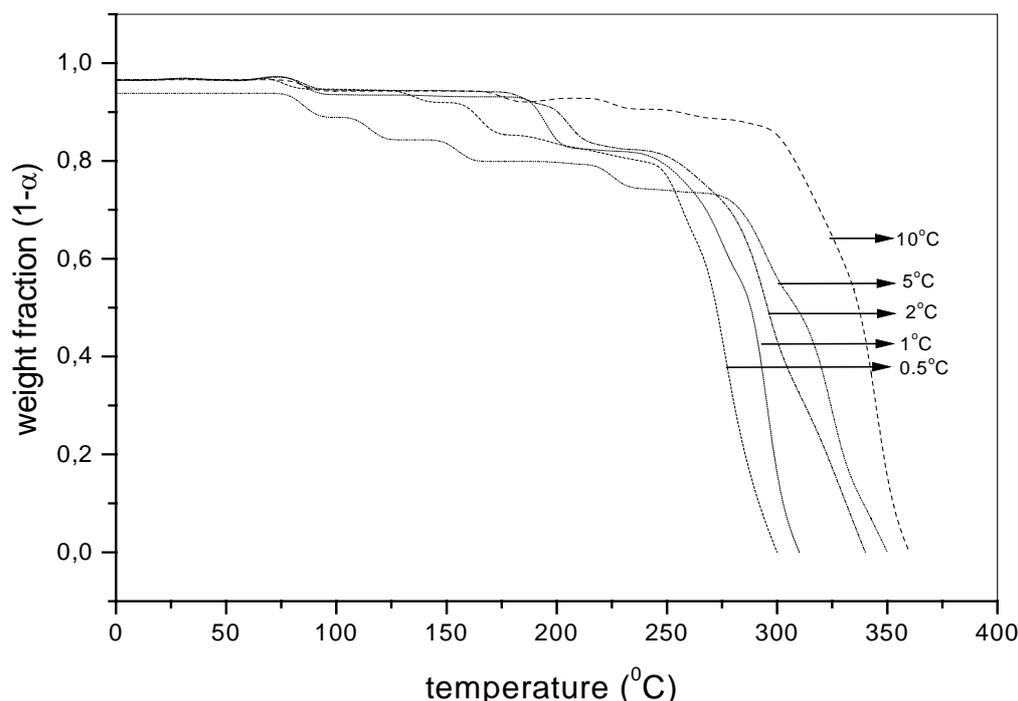

Figure 2. The weight fraction (1-α) of the sample aqPUR1 with the MnCAT (2%) depending on the temperature during the dynamic thermooxidation at different heating rates.

The total experimental time periods required to collect the TGA data during the kinetic analyses of the aqueous polyurethanes without the catalysts and with the catalysts of different selectivity have been compared by means of the dynamic method [19]. Table 5 and Table 6 show the decompositon time of the dynamic experiments at which the degradations of 0.025, 0.05 and 0.10 have occurred.

The overall time of the decompositon for the dynamic experiments, t_{dyn}, for each degradation degree can be evaluated from the data presented in Table 3 and Table 4, taking into consideration the temperature at which a certain degradation, T_r, occurs, the heating rate, r (°C min^{-1}) and the starting temperature, T_s (30 or 100 °C), according to the following equation:

$$t_{dyn} = \sum_{r=0.5}^{10} \frac{(T_r - T_s)}{r}$$ (4)

For instance, in the case of the sample aqPUR1, the control test (no catalyst) of the degradation of 0.025 at the heating rate of 0.5 °C min^{-1} has been obtained at the temperature of 127 °C, taking into account the various heating rates, the total resulting time being 395.4 min.

By using the catalyst MnCAT (2% and 4%), which is more selective than the ZrCAT, the total resulting time of the decompositon has increased at all degradation degrees as shown in Table 5 and Table 6.

Likewise, the use of the more selective manganese catalyst with the sample aqPUR2 has resulted in obtaining the similar increase of the total resulting decomposition time. The relatively shorter total resulting time of the decomposition that has occurred with the sample aqPUR1 in relation to the aqPUR2 sample shows that the sample aqPUR1 is less thermally stable.
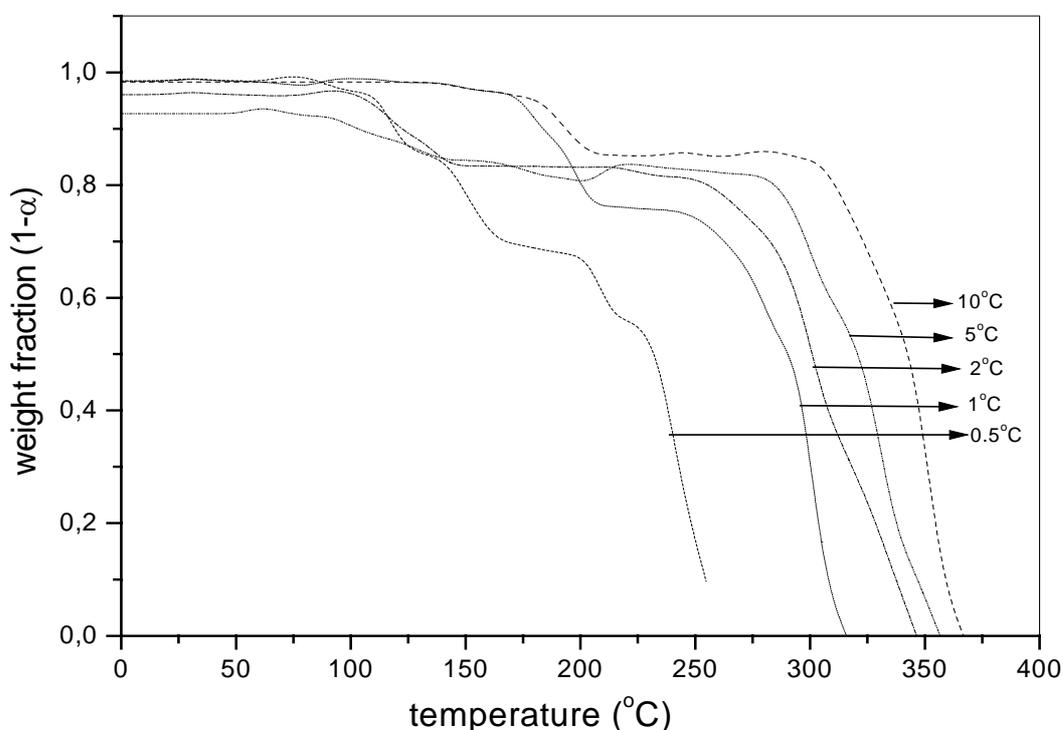

Figure 3. The weight fraction (1-α) of the sample aqPUR2 with the MnCAT (2%) depending on the temperature during the dynamic thermooxidation, at different heating rates.

Table 5. The total time of the decomposition required to calculate the thermal stability of the sample aqPUR1 at various degrees of the degradation.

Method	α Degradation	aqPUR1-control (min)	aqPUR1-ZrCAT 2% (min)	aqPUR1-MnCAT 2% (min)	aqPUR1-ZrCAT 4% (min)	aqPUR1-MnCAT 4% (min)
Dynamic method, from 30 ℃	0.025	395.4	440.9	493.8	483.2	535.7
	0.050	546.7	584.7	640.2	629.8	685.4
	0.100	602.3	637.5	693.1	683.1	738.8
Dynamic method, from 100 ℃	0.025	129.4	174.9	227.8	217.2	269.7
	0.050	280.7	318.7	374.2	363.8	419.4
	0.100	336.3	371.5	427.1	417.1	472.8

Table 6. The total time of the decomposition required to calculate the thermal stability of the sample aqPUR2 at various degrees of the degradation.

Method	α Degradation	aqPUR2-control (min)	aqPUR2-ZrCAT 2% (min)	aqPUR2-MnCAT 2% (min)	aqPUR2-ZrCAT 4% (min)	aqPUR2-MnCAT 4% (min)
Dynamic method, from 30 ℃	0.025	453.5	496.9	572.1	539.8	596.0
	0.050	602.6	637.5	700.1	681.1	743.8
	0.100	658.2	689.8	753.5	735.4	799.3
Dynamic method, from 100 ℃	0.025	187.5	230.9	306.1	273.8	330.0
	0.050	336.6	371.5	434.1	415.1	477.8
	0.100	392.2	423.8	487.5	469.4	533.3

Conclusion

The thermogravimetric dynamic method has been used to study the thermal stability of the aqueous polyurethane materials. Different degradation stages can be observed by using the derivative of the degree of degradation after the dynamic experiments.

The relatively shorter total resulting time of the decompositon with the sample aqPUR1 than with the sample aqPUR2 indicates that the sample aqPUR1 has the lesser thermal stability.

The aqueous polyurethanes (aqPUR2) based on the polyol Macrynal 2521 component, with the more selective catalyst (MnCAT), demonstrate the higher thermal stability than the aqueous polyurethanes (aqPUR1) based on the polyol Macrynal 6299 component, also with the more selective catalyst (MnCAT).

Acknowledgements

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