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Scientific paper
UDC:

Reticulation of aqueous polyurethane systems

The DSC method has been employed to monitor the kinetics of reticulation of aqueous polyurethane systems without catalysts, and with the commercial catalyst of zirconium (CAT®XC-6212) and the highly selective manganese catalyst, the complex Mn (III)-diacetylacetonemaleinate (MAM).

Among the polyol components, the acrylic emulsions were used for reticulation in this research, and as suitable reticulation agents the water emulsible aliphatic polyisocyanates based on hexamethylendoisocyanate with the different contents of NCO-groups were employed. On the basis of DSC analysis, applying the methods of Kissinger, Freeman-Carroll and Crane-Ellerstein the pseudo kinetic parameters of the reticulation reaction of aqueous systems were determined.

The temperature range of the examination was from 50^0C to 450^0C with the heat rate of $0.5^0C/min$.

The reduction of the activation energy and the increase of the standard deviation indicate the catalytic action of the selective catalysts of zirconium and manganese. The impact of the catalysts on the reduction of the activation energy is the strongest when using the catalysts of manganese and applying all the three afore-said methods. The least aberrations among the stated methods in defining the kinetic parameters were obtained by using the manganese catalyst.

Key words: *aqueous polyurethanes, selective catalyst, differential scanning calorimetry, pseudo activation energy.*

1. INTRODUCTION

The kinetics of reticulation with the two-component polyurethane systems can be observed through the conversion degree of the functional groups over a certain time period. The physical and chemical methods are applied to quantify the kinetic parameters of the reaction, as well as the structural modifications in the analyzed system. The physical methods of the analysis are usually more suitable than the chemical ones and are based on measuring some physical property of the reaction mixture that is altered during the reaction.

The calorimetry gives the quantitative data on the development of the chemical reaction, but without the possibility to make the difference between the main reactions from the side ones.

The thermogravimetric method [1,2] is based on measuring the mass loss in the form of volatile products, at the controlled temperature regime or isothermally. If the volatile products occur during the chemical reaction, the thermogravimetric method can be applied to perform kinetic analysis of the chemical reaction and to determine the kinetic parameters.

The differential scanning calorimetry (DSC) is one of the thermoanalytical methods used to measure the difference of the inlet heat into the analyzed sample and the referent substance in the temperature function, when the sample and the referent substance are exposed to the controlled temperature program. This thermoanalytical method has been developed as a better quantitative modification of the differential thermal analysis (DTA). In the last twenty or so years the DSC has put out of use the DTA because with the DSC the calibrating factors do not change along with the temperature, so the surface of the thermogram below the maximum and the minimum is directly proportional to the temperature change.

The following methods for determining the kinetic parameters of the simple chemical reactions are applied: Freeman-Carroll [2-4] method, Crane-Ellerstein [5] method and Kissinger[6] method.

The situation is very much complicated if it is not the case of the simple chemical reaction. While the physical transformation advances, the other physical changes cannot start. The sample of the material stays at the constant temperature until the physical transformation ends completely. However, the chemical reactions can go on simultaneously at different rates and at different reaction temperatures. This will complicate the DSC curve very much and require considerably complex mathematics.

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Sandu and Sing [7] have studied this problem and formulated the equations using which the pseudo kinetic parameters for the complex reactions can be obtained, but only if the orders of the simple chemical reactions are units. The most significant assumption they make in this matter is that the system consists of the two homogenous reactions of the first order, and that the entire DSC signal is the result of the both processes.

Another possibility, that Sandu and Sing [7] anticipate, to obtain the pseudo kinetic parameters from the complex DSC curve, makes it possible to divide the complex curve ito two simple ones, and then to analyse each "simple" curve using some of the previous methods that have been worked out for such simple reactions.

The main aspect in the development of the aqueous PUR is in the first place to find methods for preventing the 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. This reaction is reduced to a minimum by use of the non-tin catalysts[8].

The relative selectivity (S), was measured as the urethane IR peak area ($P_{urethan}$)/ urea IR peak area (P_{urea}) ratio, by the method at Werner Blank [8].

The complex of Mn(III)-diacetylacetonatomaleate with various ligands based on the acetylacetonate and maleic acid that was used in the experiment in our researches showed the high selectivity for the isocyanate-hydroxyl reaction [9,10].

The DSC method has been employed to monitor the kinetics of reticulation of the two representative samples of aqPUR1 and aqPUR2, without the catalysts and with the commercial catalyst of zirconium (CAT®XC-6212) and the highly selective manganic catalyst, the complex Mn (III)- diacetylacetone-maleinate (MAM).

2. EXPERIMENTAL

The polyols and polyisocyanates used during the study are the commercial materials and were used without further purification.

The two polyol components with the hydroxyl number above 130 used in this experiment are: acrylic dispersion in the mixture water/butyl alcohol, (Macrynal VSM 2521 w/42 WAB, Solutia Austria GmbH) and also the acrylic resin as water dispersion (Macrynal VSM 6299 w/42 WA, Solutia Austria GmbH). The contents of dry matter with these dispersions are 42%.

As the 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 used reticulation agents are 100% without the organic solvents except for Bayhydur VP LS 2150 that is 70% in butylacetate.

The zirconium catalyst (ZrCAT) is a proprietary zirconium tetra-dionato complex[10] in a reactive diluent with a metal content of 0.4%.

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

The catalyst concentrated 2% relating to the coating hardness has been added to the component B.

Table 1 - Two-component aqueous polyurethane (aqPUR1) composition 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, 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 2 % on resin solids	no catalyst	0.65	-
Mn catalyst 2 % on resin solids	no catalyst	-	0.65
Total	100.00	100.6	100.6

The samples were with the organic solvents and water, and so the laced up aluminium ampules with the opening on the lid to release the gases were used. The referent vessel was made of aluminium.

The temperature range of the analyses was from 50-450^{0}C. In order to record the modifications in the samples in the examined temperature measuring range adequately, the heating rate of 0.5^{0}C/min was employed. The sample weight was 360 mg.

Table 2 - Two-component aqueous polyurethane (aqPUR2) composition 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 % on resin solids	no catalyst	0.8	-
Mn catalyst 2 % on resin solids	no catalyst	-	0.8
Total	99.5	100.3	100.3

The instrument has the autocalibration and the linear program package for the realization of the programed temperature gradient.

3. RESULTS AND DISCUSSION

The analysis of the DSC curve of the aqueous two-component polyurethane systems (Fig. 1) shows that the systems (aqPUR 1) have the characteristic reactions of transformation at about 100°C that suits the evaporation of the solvent from the system[12].

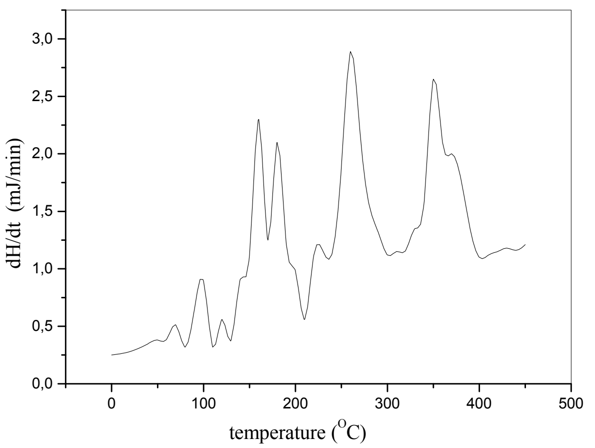

Fig. 1 - DSC curve of the aqPUR 1 simple, no catalyst

The second key moment taking place in the system is the full reaction of polyisocyanates, the beginning of forming the side bonds or final formation of films structure. The transformation that happens at the temperature of 120-300°C suits the reticulation reaction and the formation of polyurethane films, that is, the disappearance of the NCO - groups.

The third key moment in the system is the degradation of the polymer film with the peaks above 300°C.

The effect of the catalyst, with the sample aqPUR1, reflects in moving the DSC peaks toward the lower temperature values (Fig.2 and Fig.3).

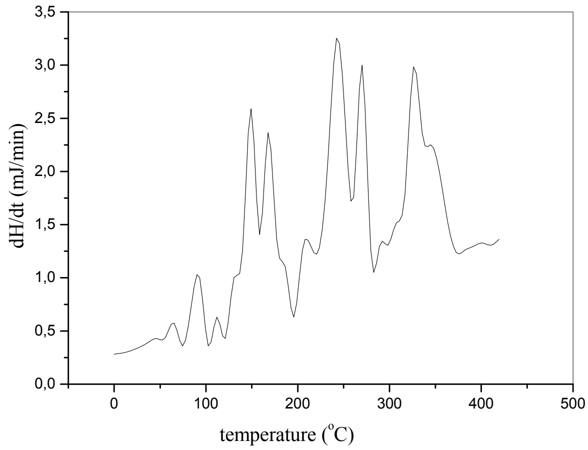

Fig. 2 - DSC curve of the aqPUR 1 sample, with the catalyst ZrCAT, (2 % relating to the coating hardness)

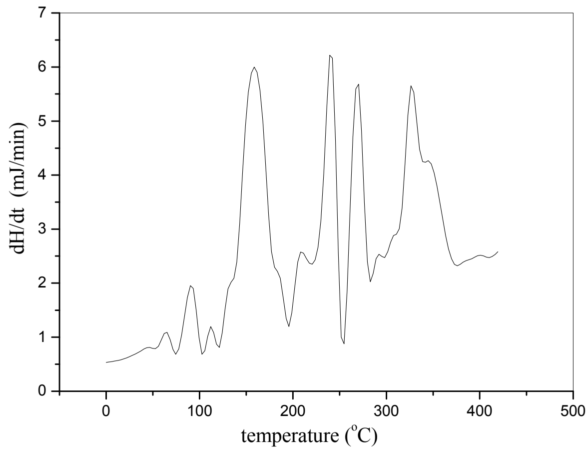

Fig. 3 - DSC curve of the aqPUR 1 sample, with the catalyst MnCAT, (2 % relating to the coating hardness)

The additional peak at about 260 °C points to the reaction of the catalyst with the polyol component. The catalytic action of manganese takes place in the same temperature range, and it is indicated by the same peak values with the catalyst CAT®XC-6212 and the catalyst Mn (III) – diacetylacetonemaleinate.

The union of the two peaks at about 150 ^{o}C, with the manganese catalyst (Fig.3), point to the different mechanism of the catalyst effect.

With the sample aqPUR2, the reaction of reticulation has a somewhat more pronounced maximum at 120 ^{o}C that indicates a different reticulation mechanism, which is attributed to the structure of the polyol component that presents the acrylic copolymer modified by the fatty acids (Fig.4).

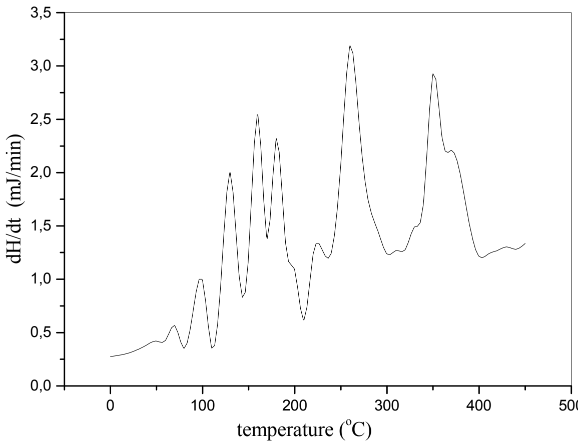

Fig. 4 - DSC curve of the aqPUR 2 simple, no catalyst

The use of the catalyst with this sample, too, leads to the movement of the DSC peaks toward the lower temperatures (Fig.5 and Fig.6).

On the basis of the DSC measurings, and according to the models of Kissinger [6], Freeman-Carroll [2,4] and Crane-Ellerstein [5], the activation energy values of the reticulation reaction and the standard deviations of the samples aqPUR1 and aqPUR2 (Tables 3 and 4) have been calculated.

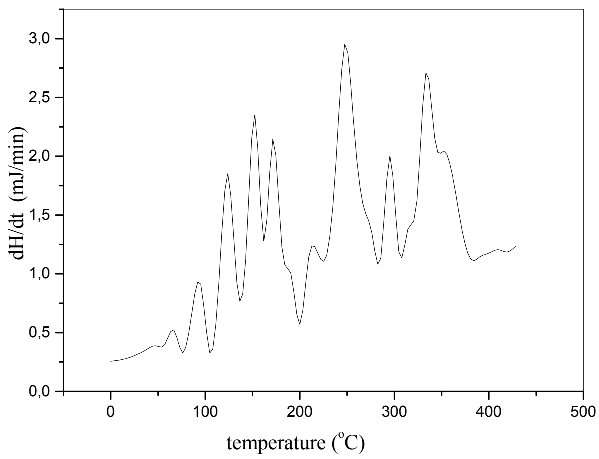

Fig. 5 - DSC curve of the aqPUR 2 simple, with the catalyst ZrCAT,(2 % relating to the coating hardness)

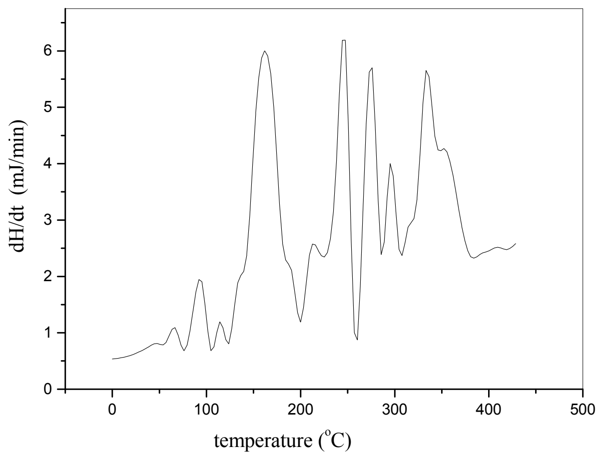

Fig.6 - DSC curve of the aqPUR 2 sample, with the catalyst MnCAT, (2 % relating to the coating hardness)

Table 3 - Pseudo kinetic parameters for the DSC curves of the aqPUR1 sample obtained by the methods that use only one curve

Sample	Kissinger method		Freeman-Carrolla method		Crane-Ellerstein method	
	Mean value E_a(kJ/mol)	Standard deviation (kJ/mol)	Mean value E_a(kJ/mol)	Standard deviation (kJ/mol)	Mean value E_a(kJ/mol)	Standard deviation (kJ/mol)
aqPUR1 control	158.22	8.25	138.36	6.21	140.36	5.32
aqPUR1 ZrCAT, 2%	156.72	21.56	148.79	22.15	128.15	38.21
aqPUR1 MnCAT, 2%	147.14	12.44	129.46	17.32	130.82	18.56

Table 4 - Pseudo kinetic parameters for the DSC curves of the aqPUR2 sample obtained by the methods that use only one curve

Sample	Kissinger method		Freeman-Carrolla method		Crane-Ellerstein method	
	Mean value E_a(kJ/mol)	Standard deviation (kJ/mol)	Mean value E_a(kJ/mol)	Standard deviation (kJ/mol)	Mean value E_a(kJ/mol)	Standard deviation (kJ/mol)
aqPUR2 control	166.32	2.36	158.12	4.25	136.52	7.14
aqPUR2 ZrCAT, 2%	158.17	31.25	150.32	28.56	129.43	24.36
aqPUR2 MnCAT, 2%	153.79	32.25	142.56	21.24	129.35	25.36

The greatest reduction of the activation energy has been achieved by the use of the manganese catalyst, as it has turned out in all the cases of calculation applying different methods.

The reduction of the activation energy and the increase of the standard deviation indicate the catalytic action of zirconium and manganese. The higher values of the standard deviation in relation to the non-catalyzed system of the samples aqPUR1 and aqPUR2, using the more selective catalysts, point to the occurrence of the secondary reactions in the system and thereby also to the greater aberrations from the mean value of the calculated activation energy.

The action of the catalyst in the reduction of the activation energy with the sample aqPUR1 is the most intensive when the manganese catalyst is used (Table 5), according to all the applied methods (7%, 6.4%, 6.7%), while it has been noted that the use of the zirconium catalyst leads to the greater reduction only if the Crane-Ellerstein method is applied (8.5%).

The action of the catalyst in the reduction of the activation energy with the sample aqPUR2, as well, is the greatest when using the manganese catalyst (Table 5), according to all the applied methods (8.2%, 9.8%, 5.0%). When the zirconium catalyst is used, the greatest reduction of the activation energy of the reticulation reaction with all the three methods does not surpass 5.4%.

Table 5 - The action of the ZrCAT and MnCAT catalysts in the reduction of the activation energy of the reticulation reaction of aqPUR1 i aqPUR2

Method	Catalyst action $E_{a\text{-no cat.}}$-$E_{a\text{-with cat.}}$/$E_{a\text{-no cat.}}$(%)			
	aqPUR 1		aqPUR 2	
	ZrCAT, 2%	MnCAT,2%	ZrCAT,2%	MnCAT, 2%
Kissinger	1.0	7,0	5.0	8,2
Freeman-Carrolla	0.0	6,4	5.1	9,8
Crane-Ellerstein	8.5	6,7	5.4	5,0

5. CONCLUSIONS

On the basis of the DSC analysis, applying the methods of Kissinger[6], Freeman-Carroll[2,5] and Crane-Ellerstein[5], the pseudo kinetic parameters of the reticulation reaction of the analyzed aqueous two-component polyurethane systems, without the catalysts, and with the highly selective catalysts of zirconium and manganese, have been determined.

The reduction of the activation energy and the increase of the standard deviation indicate the catalytic action of the selective catalysts of zirconium and manganese.

The action of the catalyst in the reduction of the activation energy is the most intensive with the catalyst of manganese in relation to the zirconium catalyst, when all the three methods of calculating with the analyzed samples are applied. The smallest aberrations among the above-mentioned methods in determining the kinetic parameters have been obtained with the manganese catalyst.

REFERENCES

[1] V. L. Zvetkov. *Polymer*, 43 (2002) 1979.

[2] Lj. Raskovic, Osnovi polimernog inzenjerstva, Tehnoloski fakultet, Leskovac, 1995.

[3] P.D. Sheetz. *J.Appl.Polymer Sci*, 9 (1965) 3759.

[4] V.Schlichenmaier, G.Widmann, *Thermochim.Acta*, 21 (1977) 39.

[5] L.W.Crane, P.J.Dynes, D.H.Kaelble, *Polymer Letters*, 11 (1973) 533

[6] H.E.Kissinger, *J.Res.Nat.Bur.Standards*, 57 (1956) 217

[7] C.Sandu, R.Sing, *Thermochim. Acta,* 159 (1990) 267

[8] W. J. Blank, Z.A. He, Ed T. Hessell, *Progress in Organic Coatings*, 35 (1999) 19.

[9] J.Stamenković, S.Cakić, G.Nikolić, *Hemijska industrija*, 57 (2003) 559.

[10] J. Stamenković, S.Cakić, S. Konstantinović, S.Stoilković, *Facta Universitatis*, Series Working and Living Environmental Protection, 2 (2003) 235.

[11] K-KAT® XC-6212 a product of King Industries Inc. Norwalk, CT 06852, USA, *US patent* 5, 846, 897

[12] J.Opfermann, Journal of Thermal Analysis and Calorimetry, 60 (2000) 641

REZIME

PROCES UMREŽAVANJA VODENIH POLIURETANSKIH SISTEMA

DSC metodom praćena je kinetika umrežavanja vodenih poliuretankih sistema, bez katalizatora, sa komercijalnim katalizatorom cirkonijuma (KAT®XC-6212) i visokoselektivnim manganovim katalizatorom, kompleksom Mn(III) - diacetilacetonatomaleinatom (MAM).

U ovom radu za umrežavanje od poliolnih komponenti korišćene su akrilne emulzije a kao pogodni umreživači koričćeni su vodoemulgujući alifatični poliizocijanati na bazi heksametilendiizocijanata sa različitim sadržajem NCO-grupa. Na osnovu DSC-analize, metodama Kissinger-a, Freeman-Carrolla-a i Crane-Ellerstein-a, određeni su prividni kinetički parametri reakcije umrežavanja vodenih sistema.

Temperaturni opseg ispitivanja koričćen je od 50 do 450°C sa brzinom grejanja od 0.5°C/min.

Smanjenje energije aktivacije i povećanje standardne devijacije ukazuju na katalitičko dejstvo selektivnih katalizatora cirkonijuma i mangana. Učešće katalizatora u smanjenju energije aktivacije je najveće kod katalizatora mangana, korišćenjem sve tri bbbmetode izračunavanja kod ispitivanih uzoraka u odnosu na cirkonijumov katalizator. Najmanja odsupanja između pomenutih metoda u određvanju kinetičkih parametara dobijena su korišćenjem manganovog katalizatora.

Key words: *vodeni poliuretani, selektivna kataliza, diferencijalna skening kalorimetrija, energija aktivacije.*