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CORRELATION OF REACTION KINETIC PARAMETERS IN TWO COMPONENT POLYURETHANE SYSTEMS

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Abstract. *Two component polyurethane systems are the new materials that have ever growing application in everyday practice, mainly in the dye industry, and the corrosion protection. The advantages of these systems are in lower content of the organic solvents, with the same level of the film properties. From the research and developing view, one must have the information's about the mechanism of final structure formation and their properties. Correlation between the final film structure and their kinetic parameters, could lead to the formation process optimization. Goal of presented research was to find time event sequence during two-component polyurethane water film formation. Experiments were designed in that way that each event, which takes place during film formation process, could be identified and quantified. All the factors, which have influence on the identified event, were also investigated, as well as their influence on final film properties. Film formation mechanism is presented in the form of the time event sequence which identified the process interactions such as: particle coalescence, izocyanates-hydroxyl group and water reactions water evaporation and organic solvent evaporation. For two-component water systems, viscosity changes is not a valuable measure of system changes, so reologic methods could not be used for this research. For measuring macro kinetic parameters (activation energy and reaction order), we used differential scanning calorimetric (DSC). Mechanical properties, hardness, were measured in order to correlate the structure with the mechanical properties. All obtained results were used for defining the time event sequence of two-component water polyurethane film formation.*

Key words: *DSC method, two-component system, kinetic of reaction, organic solvent, polyurethane coatings, water system*

INTRODUCTION

Two component polyurethane systems with the organic solvents and water are the newly developed systems for different applications in the field of material protection. System with water have minimum amount of organic solvents, with almost the same functional properties as former systems with the organic solvents. Water induced polyurethane film (WIPF) could full field the highest functional demands such as: atmospheric influent resistant, abrasion resistant elasticity and adhesion. WIPF systems have ever increasing demands for various application's, over past years. This fact is due to the increasing ecological protection demands, and due to increasing WIPF quality. Research in the field of water two component epoxy polyurethane films shows that these systems could be used in very severe and complex environments.

This paper presents the thermal analysis of water and organic solvent polyurethane films. The research goal was to analyze the kinetic parameters of reaction: activation energy and reaction order, using differential scanning calorimetric DSC methodology. This method is more practical and precise then standard DTA method, for quantitative enthalpy evaluation. Calibration factors are not sensitive to the temperature changes, so areas under the min/max peaks are directly proportional to the enthalpy changes. /4/. Gradient dH/dt directly proportional to the reaction rate $d\alpha/dt$ so there is possibility of obtaining reaction kinetics parameters acquiring:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H} \left(\frac{dH}{dt} \right) \quad (1)$$

Total reaction heat ΔH is

$$\Delta H = \int \frac{dH}{dt} dt \quad (2)$$

and the partial reaction heat, which generate from the some moment t , is related to the conversion degree α , as $\alpha = H / \Delta H$.

According to literature data, there are several methods [9,10,11] for calculating apparent kinetic parameters, from DSC data: Crane-Ellestein, Kissinger, Freeman Carroll and others.

a) Kissinger method

Starting from
$$\frac{d\alpha}{dT} = \frac{A}{\phi} \cdot e^{-\frac{E}{RT}} (1-\alpha)^n \quad (3)$$

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\phi} \cdot \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT \quad (4)$$

and

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{A \cdot R}{\phi \cdot E} \cdot \frac{-E}{RT} \quad (5)$$

Kissinger [9] had suggested several approaches for appear kinetic parameter calculations, from DSC data:

$$\ln\left(\frac{\phi}{T_m^2}\right) = \ln\left(\frac{A}{RT}\right) - \frac{E}{R} \cdot \frac{1}{T_m} \quad \text{for } n = 1 \quad (6)$$

$$n(1 - \alpha_m)^{n-1} \approx 1 + (n-1) \cdot \frac{2RT_m}{E} \quad \text{for } n \neq 0 \text{ and } n \neq 1 \quad (7)$$

$$n = 1,26 \cdot S^{1/2} \quad (8)$$

where T_m temperature of max/min peaks of DSC curve, α_m is conversion degree to temperature T_m , S is the form factor which presents the absolute value of the gradients of DSC curves in the points of min/max. For the reaction order different than 1 parameters are calculated from [9]:

$$\ln\left(\frac{\phi}{T_m^2}\right) = \ln\left(\frac{C_0^{n-1} \cdot A \cdot R}{E}\right) - \frac{E}{R} \cdot \frac{1}{T_m} \quad \text{for } n > 0 \text{ and } n \neq 1 \quad (9)$$

which state that activation energy could be calculated from $\ln(\phi/T_m^2)$ as the relation $1/T_m$ without interfering the values of n .

b) Freeman-Carroll method

Conversion degree relation developed by Freeman-Carroll /10/:

$$\frac{\Delta \ln \frac{d\alpha}{dt}}{\Delta \ln(1-\alpha)} = -\frac{E}{R} \cdot \frac{\Delta \frac{1}{T}}{\Delta \ln(1-\alpha)} + n \quad (10)$$

was used for kinetic analysis of DSC data. This linear relation presents the energy activation energy E_a as gradient.

c) Method Crane Ellerstein-a

Starting from Arrhenius relation for the apparent reaction rate, $K(t)$ /12/

$$K = A \cdot e^{-\frac{E}{RT}} \quad (11)$$

where A is apparent pre exponential factor and E activation energy and they are not dependent on the conversion degree α , R is the universal gas constant. Using:

$$\frac{d\alpha}{dt} = K_{(T)} \cdot (1-\alpha)^n \quad (12)$$

$$\frac{d\alpha}{dT} = \frac{1}{\phi} \cdot K_{(T)} \cdot (1-\alpha)^n \quad (13)$$

and including relations (1) i (2) Crane /11/ for DSC constant scanning rate $\phi = dT/dt$:

$$\frac{dH}{dT} = A \cdot \left(\frac{\Delta H}{\phi}\right) \cdot \exp\left(-\frac{E}{R \cdot T}\right) \cdot (1-\alpha)^n \quad (14)$$

Differentiate relation (14) by T relation for calculation of kinetic parameters:

$$\left[\frac{\frac{d^2H}{dT^2}}{\frac{dH}{dT}} \right] \cdot T^2 = \left[\frac{E}{R} - \frac{n \cdot T^2}{(1-\alpha)\Delta H} \cdot \left(\frac{\Delta H}{dT} \right) \right] \quad (15)$$

Gradient dH/dt could be converted for constant scanning rate ϕ to:

$$h = \frac{dH}{dT} = \frac{dH}{\phi \cdot dt} \quad (16)$$

Area r under DSC curve is the unconverted functional groups:

$$r = (\Delta H - H) = ((1 - \alpha)) \cdot \Delta H \quad (17)$$

EXPERIMENTAL PART

Method

Perkin Elmer Model 4 apparatus obtained DSC data. For each sample four measurements were carried out, and mean values are present. Mean masses of samples are presented in Table 1.

Table 1. Mean weight of used samples

Sample name	Mean mass (g)
PU-1	0.346
PU-2	0.353
PU-3	0.352
PU-4	0.351
PU-5	0.353
PU-6	0.353

Samples were analyzed in closed Al-containers with the hole on the top for gas release. Reference sample was Al-container with the air. Experiments were carried out in temperature range from 50°–350°K with sensitivity less than 1 mJ. Scanning rate was 0.25°C/min. Experimental model samples were made from the compounds made by the leading world chemical manufacturers shown in Table 2.

Table 2. Used compounds for the model systems

Sample	Description	Manufacturer
Poliol 5766	Acryl resin with OH groups	Vianova Resins AG Austria
Poliol 120	Alkyds resin modified with acrylate OH groups	Vianova Resins AG Austria
Poliizocijanat 75	Aliphatic polyisocyanate with higher molecular mass and biuretic groups	BAYER AG Germany
Polidisperzija 8833	Acrylic water dispersion with OH groups	BASF AG Germany
Polidisperzija 8845	Acrylic water dispersion with OH groups	BASF AG Germany
Poliizocijanat 8963	Modified polyisocyanate on HDI basis	BASF AG Germany

Composition of two component polyurethane model systems used in experiments is present in Table 3.

Table 3. Compound composition used for model experimental systems (%)

Components	PU1	PU2	PU3	PU4	PU5	PU6
Poliol 57	140	140	–	–	–	–
Poliol 120	–	–	140	140	–	–
Poliizocijanat 75	40	40	40	40	–	–
Polidisperzija 8833	–	–	–	–	179.2	–
Polidisperzija 8845	–	–	–	–	–	175.49
Poliizocijanat 8963	–	–	–	–	10	10
TEA	–	–	–	–	1.8	1.8
Coalescent	–	–	–	–	10.8	14
Foam removal compound	–	–	–	–	1.2	1.2
Organic solvent	60	–	60	–	–	–

RESULT AND DISCUSSION

For easier understanding of obtained DSC data, standard DSC curve is shown on Figure 1, with characteristic maximums (peaks) marked.

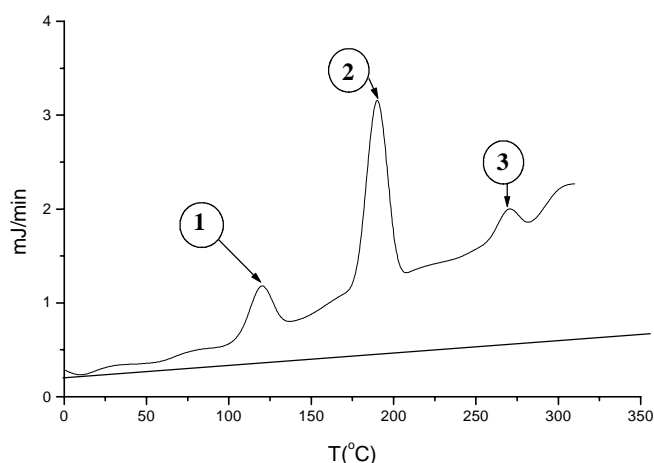


Fig. 1. Standard DSC curve obtained for used model two component polyurethane systems

All model systems have characteristic transformation reaction around 100°C for systems with organic solvents and around 150°C for water model system. peak 1, Figure 1. This maximum (peak), transformation, could be explained as the solvent evaporation. Organic solvents have lower boiling point in the system, while water system have the higher boiling point. This is the first important step during film formation.

The next important step is reaction of polyisocyanate and starting the formation and bonding of final film structure. Transformation (maximum 2, Figure 1.) occurs between 180-200°C in all experimental model systems, which is due to bonding and polyurethane

film formation, which is done over $-NCO$ groups. This reaction is followed by the "disappearance" of isocyanate from the system and reaction with the polyole. Conversion degree of polyisocyanate determines the final mechanical quality of formed films.

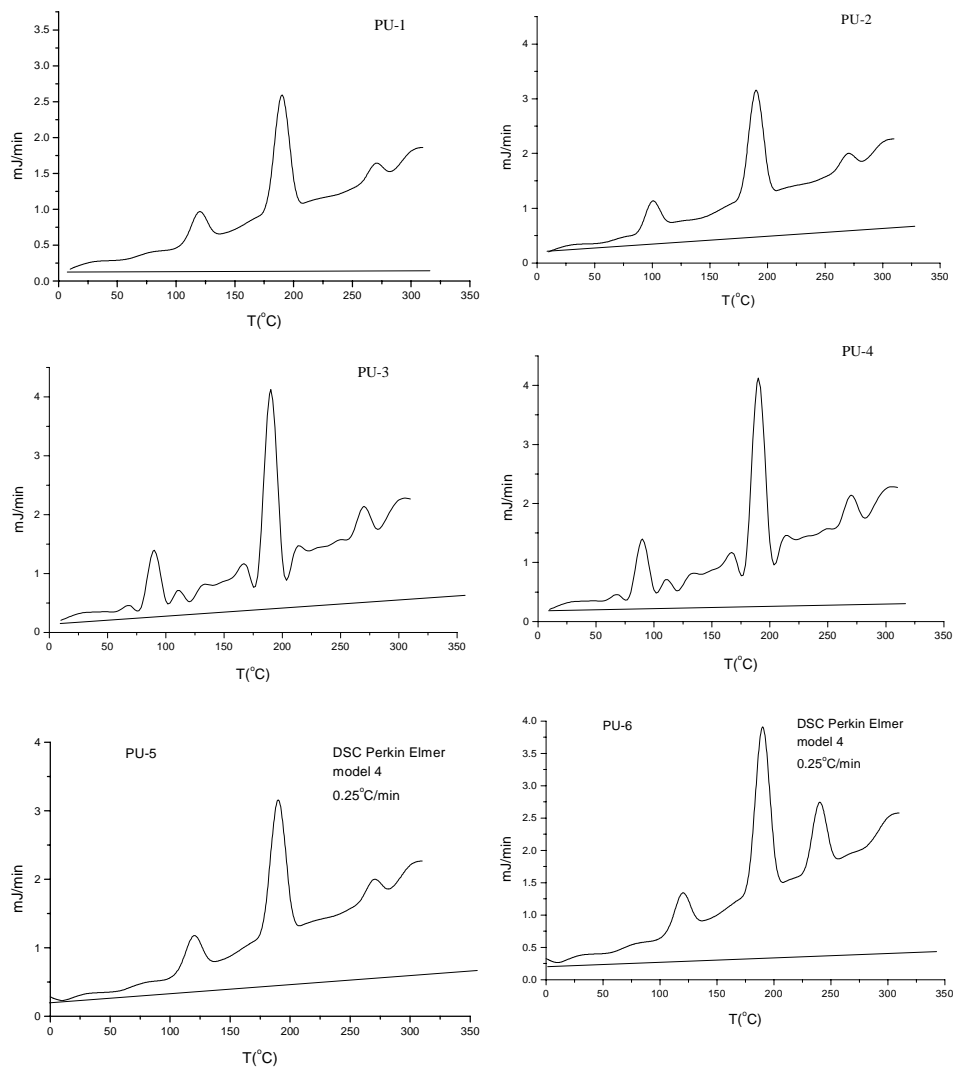


Fig. 2. Represent DSC curves for the model systems

All systems have characteristic peaks at the 250°C or higher (peak 3, Figure 1.). This transformation is due to the local system rearranging which is dependent on $-NCO$ conversion degree. Model systems with the organic solvents, have this transformations less intense than water model systems. The whole present amount of polyisocyanate must be converted in order to obtain the best film quality. In all other cases the residual polyisocyanate could cause some uncontrollable or unpredictable reactions that can have influence on final film properties.

Obtained model DSC curves are present on Figure 2. Model systems from PU-1 to PU-4 are two component systems with the organic solvents, and the PU-5-PU-6 is the systems with water.

The described models calculated using acquired DSC data activation energy. Results are present in Table 4.

Table 4. Calculated kinetic parameters obtained from DSC data

System	Kissinger		Freeman-Carrolla		Crane-Ellestein	
	Ea [kJ/mol]	n	Ea [kJ/mol]	n	Ea [kJ/mol]	n
PU-1	150.082	1.305	138.001	1.422	135.412	1.385
PU-2	148.373	1.425	141.532	1.5622	130.217	1.548
PU-3	133.376	1.334	132.986	1.2285	125.902	1.533
PU-4	128.330	1.534	133.075	1.345	143.533	1.342
PU-5	143.825	1.145	138.415	1.2256	140.030	1.230
PU-6	157.653	1.457	144.565	1.334	151.325	1.401

Calculated energy activation data were statistical analyzed in purpose to find the degree of consistency, and the results are present in Table 5.

Table 5. Statistical analysis of energy activation data

Method	Mean value Ea [kJ/mol]	Standard deviation [kJ/mol]	Variation coefficient (%)
Kissinger	140.04	10.82918	5.41459
Freeman-Carrolla	136.39	4.14776	2.07388
Crane-Ellestein	133.76	7.58379	3.79189

The highest values of activation energy are obtained by Kissinger model, and the other two models give lower but almost the same results. Figure 3 show the activation energy values distribution for two component model systems with the organic solvents.

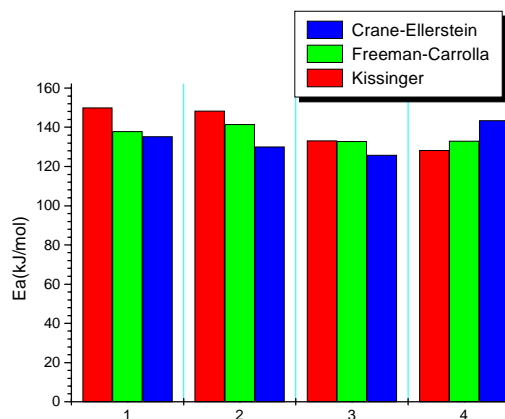


Fig. 3. Activation energy values distribution fro two-component polyurethane system with the organic solvents

Calculated values for the reaction order were statistically analyzed for the two component systems with the organic solvents, and the results are present in the Table 6.

Table 6. Reaction order values statistical analysis for model systems with organic solvents

Method	Mean value n	Standard deviation	Variation coefficient
Kissinger	1.399	0.10322	0.05161
Freeman-Carrolla	1.389	0.13998	0.06999
Crane-Ellerstein	1.452	0.10387	0.05193

Highest values are calculated by the Crane-Ellstein model but all the obtain values are lower than $n = 1.5$, which is lower than literature obtained data. Calculated reaction order data are consistent with deviation less then 5%. Figure 4 presents the distribution of calculated values for the reaction order.

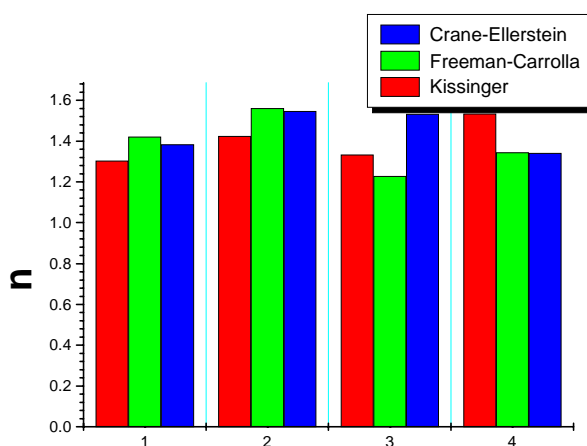


Fig. 4. Reaction order values distribution for the two component systems with the organic solvents

The same statistical analysis was done for model system with water. Results for energy activation calculation are present in the table 7.

Table 7. Basic statistical analysis of energy activation values for water systems

Method	Mean value Ea [kJ/mol]	Standard deviation [kJ/mol]	Variation coefficient (%)
Kissinger	150.73	9.77787	6.914
Freeman-Carrolla	141.49	4.34871	3.075
Crane-Ellerstein	145.67	7.98677	5.6475

Results show higher values of the activation energy then model system with the organic solvents. This means that two-component polyurethane water system spend more energy for film formation the systems with organic solvents.

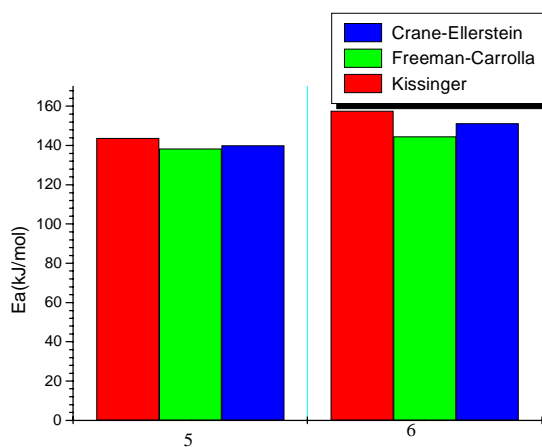


Fig. 5. Energy activation calculated values distribution for the model systems with the water

Statistical analysis of reaction order calculated data is present in Table 8. Calculated data are lower than the same data for systems with the organic solvents. Statistical analyses show the consistency of these data but have lower values than literature available.

Table 8. Statistical analysis of calculated reaction order values

Method	Mean value - n	Standard deviation	Variation coefficient
Kissinger	1.301	0.22062	0.156
Freeman-Carrolla	1.2798	0.07665	0.0542
Crane-Ellerstein	1.3155	0.12092	0.0855

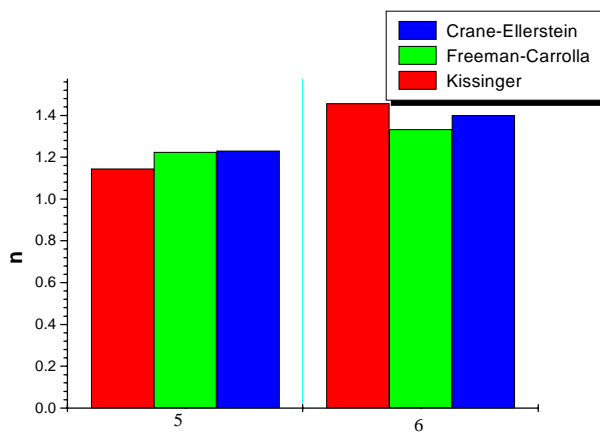


Fig. 6. Reaction order values distribution for the two component water systems.

The reason could be complex reactions that are present in the systems. On the other hand this system is not a linear one, so small changes in input parameters could lead to the unpredictable reaction paths.

CONCLUSION

Six system models were used from which for of then were with organic solvent and other two were water systems.

After analyses finds disappearing of NCO groups and formation of new amid groups. DSC analyses were used to calculate the activation energy and reaction order. Obtained values for activation energy are in good agreement with the literature published values, but calculated values for reaction order are lower.

According to obtained results suggest that the film properties are dependent on the conditions in which there form.

In water system influence have the classification of polymer network done by water molecules as well as indirect reaction of water with polyizocianate functional groups. As the consequence of that films formed in water system have lower values of hardness.

For all systems we can conclude that the solvent disappearance from the systems lead to the increase of molecular mixture density which on the other hand increase the number of reactant contact in time and formation of new polymer systems.

Two component water polyurethane films are the new system with increase usage in various areas of material protection, which is the reason of it ecological properties, lower solvent content and the comparable properties with the systems of organic solvent.

REFERENCES

1. H.Kittel *Lehrbuch der Lacke und Beschichtungen* Verlag W-A Calomb, Berlin-Ober-schwandorf (1973), 534-556
2. Ljiljana Rašković, *Osnovi polimernog inženjerstva*, Tehnološki fakultet Leskovac, Leskovac (1995), 72
3. L.Kahl, M. Bock, *Waterborne Two-Component PU Clear Coats for Automotive Coatings: Development of Raw Materials and Mixing Technology*, Proc. Third Nurnburg Congress, Nurnburg, Germany, March (1995), 13-15
4. A. Bittner P Liegler, *Waterborne Two-Pack Polyurethane Coatings for industrial Applications*, Proc. Third Nurnburg Congress, Nurnburg, Germany, March (1995), 13-15
5. B.P.Jacobs and C.P.Yu, *Journal of Coatings Technology*, Vol.65.N^o882(1993),45
6. D.I.Fischer, *Aqueous 2-Pack-PUR-Systems based on OH-functional Dispersions and Polyisoxyanates*, Technical seminar II, BASF AG, Ludwigschafen(1997)
7. J.C.Padget, *Journal of Coatings Tehnology*, Vol.66,N^o839(1994), 89-105
8. C.A.Hawkins,A.C.Scheppard, T.G.Wood, *Progress in Organic Coastings* 32 (1997), 253-261
9. Kissinger H.E., *Anal.Chem* 29(1957) 1702
10. Freeman S.E., Carwell D., *J.Phys Chem.*, 62 (1958) 394
11. Crane L.W., Dynes P.J., Kaelbe D.H., *Polymer Letters* 11 (1973) 533
12. Nikolić Lj., *Optimizacija uslova reakcije umrežavanja lak filmova termoreaktivnih polimera*, magistarski rad TF Leskovac 1995

KORELACIJA KINETIČKIH PARAMETARA U REAKCIJAMA DVOKOMPONENTNIH POLIURETANSKIH SISTEMA U ORGANSKIM RASTVARAČIMA I SA VODOM

Suzana Perošević, Ljiljana Rašković,

Dvokomponentni vodeni poliuretanski premazi predstavljaju nove sisteme, koji se koriste za različite aplikacije u oblasti površinske zaštite. Manji sadržaj isparljivih organskih rastvarača, uz očuvanje kvaliteta funkcionalnih svojstava koje imaju sistemi sa organskim rastvaračima, predstavlja njihovu komparativnu prednost. pri primeni dvokomponentnih poliuretanskih sistema, reakcija stvaranja filмова je veoma brza pa je neophodno reaktante mešati neposredno pre primene, jer bi u suprotnom dolazilo do preranog geliranja sistema. Osnov za razvoj dvokomponentnih poliuretanskih sistema organskih prevlaka sa visokim radnim svojstvima, predstavlja visoka reaktivnost izocijanatne grupe, koja lako reaguje sa poliolima i formira stabilnu poliuretansku strukturu. Tokom istraživanja, za ispitivanje mikrokinetičkih parametara (energije aktivacije i rada reakcije), korišćena je metoda diferencijalne skening kalometrije (DSC). Diferencijalna skanirajuća kalorimetrija je termoanalitička metoda koja se bazira na merenju razlike sadržaja toplote u uzorku i referenci u funkciji temperature, kada se uzorak i referenca izlože kontrolisanom temperaturnom programu.

Ključne reči: DSC metoda, dvokomponentni sistemi, kinetika reakcije, organski rastvarači, poliuretanski premazi, vodeni sistemi